

# Heterogeneous Photocatalysis with Transition Metal Modified Layered Titanates for Solar Hydrogen Production

Von der Fakultät für Mathematik und Naturwissenschaften der Carl von Ossietzky Universität Oldenburg zur Erlangung des Grades und Titels

Doktor der Naturwissenschaften

-Dr. rer. nat.-

angenommene

Dissertation

von

Herrn

M.Sc. Martin Pilarski geb. am 18.06.1987 in Tarnowitz, Polen

Die vorliegende Arbeit wurde in der Zeit von Oktober 2012 bis Dezember 2013 am Lehrstuhl für Technische Chemie der Ruhr-Universität Bochum sowie von Januar 2014 bis Juni 2016 am Lehrstuhl für Technische Chemie der Carl von Ossietzky Universität Oldenburg unter der Leitung von Herrn Prof. Dr. Michael Wark angefertigt.

Erstgutachter:	Prof. Dr. Michael Wark
Zweitgutachterin:	Prof. Dr. Katharina Al-Shamery
Promotionsausschuss:	Apl. Prof. Dr. Axel Brehm

Tag der Disputation:05.09.2016

# Danksagung

An dieser Stelle möchte ich mich bei all denen bedanken, die mit ihrer Hilfe und Unterstützung zum Gelingen dieser Doktorarbeit beigetragen haben.

Mein besonderer Dank gilt Herrn Prof. Dr. Michael Wark für die Betreuung meiner Doktorarbeit in den vergangenen Jahren und die Möglichkeit diese Arbeit an seinem Lehrstuhl anzufertigen. Insbesondere bedanke ich mich für das entgegengebrachte Vertrauen diese Arbeit frei mit eigenen Ideen und Konzepten zu gestalten und diese mit mir stets kritisch zu diskutieren.

Dr. Dereje Hailu Taffa danke ich für die Einführung in den Bereich der Photoelektrochemie und für sämtliche Hilfestellungen bei der Durchführung der (photo)-elektrochemischen Messungen und bei der Herstellung von Photoelektroden. Außerdem bedanke mich für die vielen hilfreichen Anmerkungen und Diskussionen, welche die Entwicklung dieser Arbeit begleitet haben und zu ihrer Vollendung beitrugen.

Ein großes Dankeschön geht an alle Mitarbeiter des Lehrstuhls für Technische Chemie für die freundliche Arbeitsatmosphäre und entgegengebrachte Hilfe bei sämtlichen Problemen, die während dieser Arbeit auftraten. Dr. Christian Dunkel danke ich für die Durchführung der REM-Messungen, Florian Meyer und Janine Leppin für die TG-Messungen am EWE-Forschungszentrum für Energietechnologie Next Energy, sowie Bernd Werner und Rainer Bölts für ihre Hilfe beim Aufbau meines Teststands.

Prof. Dr. Jürgen Parisi danke ich für die freie Nutzung des Röntgendiffraktometers am Lehrstuhl für Energie- und Halbleiterforschung am Institut für Physik, sowie Ulf Mikolajczak und Dr. Martin Knipper für die technische Einweisung.

Dr. Erhard Rhiel und Ute Friedrich danke ich für die Aufnahme sämtlicher TEM-Bilder und der Durchführung der EDX-Messungen.

Bei Dr. Silvia Gross bedanke ich mich für die Durchführung und Auswertung aller XPS-Messungen an der Fakultät für Chemie der Universität Padua.

Dr. Bernhard Schnetger danke ich für die Röntgenfluoreszenzmessungen im Institut für Chemie und Biologie des Meeres.

Für das erste Jahr meiner Promotion am Lehrstuhl für Technische Chemie der Ruhr-Universität Bochum danke ich allen Mitarbeiter für die kurze aber schöne Zeit. Dr. Thomas Reinecke danke ich für sämtliche XRD-Messungen in dieser Zeit und für die Unterweisung in die Röntgendiffraktometrie. Dr. Roland Marschall danke ich für die hilfreichen Denkanstöße und Diskussionen in den Anfängen meiner Doktorarbeit.

Besonders möchte ich meiner Familie und meinen Freunden danken, die mich während des Studiums und der Promotion unterstützt haben. Allen voran danke ich meiner Mutter Margarethe und meinem Bruder Damian, die mir den nötigen Rückhalt vor allem in schwierigen Zeiten gegeben haben und mich motivierten nie aufzugeben. Tausend Dank, dass ihr stets für mich da seid und ich mich immer auf euch verlassen kann.

# Kurzzusammenfassung

Diese Arbeit berichtet über die Synthese des geschichteten Cäsium Titanates Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> und der Anwendung in der photokatalytischen Wasserstofferzeugung. Zunächst erfolgte die Herstellung von reinem Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> durch eine alternative Sol-Gel-Syntheseroute, die im Gegensatz zur klassischen Festphasensynthese, die Herstellung oxidischer Halbleiter bei geringeren Temperaturen und kürzeren Reaktionszeiten ermöglicht. Des Weiteren stand die Modifizierung der Photokatalysatoroberfläche durch die Abscheidung metallischer Nanopartikel, welche als Co-Katalysatoren agieren und zu einer Aktivitätssteigerung führen, sowie deren Einfluss auf die Umsetzung verschiedenster Ausgangsmaterialien im Vordergrund. Neben den üblichen Edelmetall Co-Katalysatoren Rh, Au und Pt wurde Cu als günstigere Alternative in der photokatalytischen Wasserstoffherstellung untersucht. Als Ausgangsmaterialien wurde neben Methanol und Ethanol auch Glycerol, was als Nebenprodukt der Biodieselherstellung leicht verfügbar ist, in der photokatalytischen Umsetzung zu Wasserstoff untersucht.

Metallische Cu und Au Nanopartikel verfügen über besondere optische Eigenschaften, die eine Untersuchung der abgeschiedenen Co-Katalysatoren während des photokatalytischen Prozesses ermöglichen. Die Untersuchung der in-situ Bildung des aktiven Co-Katalysators erfolgt über die Beobachtung des sich entwickelnden Signals der Oberflächenplasmonen. Somit konnten neue Einblicke über den laufenden Prozess gewonnen werden.

 $Cs_{0.68}Ti_{1.83}O_4$  weist mit einer Bandlücke von 3.4 eV ausschließlich UV-Aktivität auf. Allerdings ermöglicht die Defektstruktur von  $Cs_{0.68}Ti_{1.83}O_4$  einen leichteren Einbau von Fremdionen in das Kristallgitter, solange die Fremdionen einen ähnlichen Ionenradius zu Ti<sup>4+</sup> aufweisen, um eine Verkleinerung der Bandlücke herbeizuführen. Der Ioneneinbau ins Kristallgitter von  $Cs_{0.68}Ti_{1.83}O_4$  erfolgt durch die alternative Sol-Gel-Syntheseroute, die eine homogene Verteilung der Fremdionen gewährleistet. Als Fremdionen wurden  $Cu^{2+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$  und  $Mn^{3+}$ ins Kristallgitter von  $Cs_{0.68}Ti_{1.83}O_4$  eingebaut. Nach ersten Aktivitätstests durchgeführte Bandlückenuntersuchungen zeigten, dass der Bandlückenverkleinerungseffekt der eingebauten Fremdionen nach der Exposition mit dem Reaktionsmedium verloren gegangen ist. Des Weiteren weist fremdionenmodifiziertes  $Cs_{0.68}Ti_{1.83}O_4$  eine deutliche Abnahme der photokatalytischen Aktivität gegenüber reinem  $Cs_{0.68}Ti_{1.83}O_4$  auf.

Abschließend wurden  $Cs_{0.68}Ti_{1.83}O_4$  und Cu modifiziertes  $Cs_{0.68}Ti_{1.83}O_4$  als Photoelektrodenmaterial untersucht. Zum einen wurden Photoströme unter Bestrahlung mit UV- und sichtbarem Licht durchgeführt und zum anderen wurden elektrochemische Messungen zur Ermittlung der elektronischen Bandstruktur vorgenommen.

## Abstract

This thesis reports on the synthesis of the layered cesium titanate  $Cs_{0.68}Ti_{1.83}O_4$  and its utilization in the photocatalytic hydrogen production. Initially, the production of pristine  $Cs_{0.68}Ti_{1.83}O_4$  was carried out via an alternative sol-gel synthesis route, which enables the synthesis of oxidic semiconductors at lower temperatures and shorter reaction times in contrast to the classic solid state reaction. Furthermore, the modification of the photocatalyst surface via the deposition of metallic nanoparticles, which act as so called co-catalysts and lead to an activity increase, as well as their influence in the conversion of different feedstocks was a main aspect of this thesis. Beside of the common noble metal co-catalysts Rh, Au and Pt, Cu was investigated in the photocatalytic hydrogen production as an earth abundant alternative. Beside methanol and ethanol, glycerol was investigated as a feedstock in the photocatalytic conversion to hydrogen, due to the readily availability as a byproduct of the biodiesel production.

Metallic Cu and Au nanoparticles exhibit special optical properties, which enable the investigation of the deposited co-catalyst during the photocatalytic process. The investigation of the in-situ formation of the active co-catalyst is carried out by the observation of the developing surface plasmon signal. Hence, new insights about the running process could be obtained.

 $Cs_{0.68}Ti_{1.83}O_4$  exhibits a band gap of 3.4 eV and therefore exclusively active under UV-light. However, the defect structure of  $Cs_{0.68}Ti_{1.83}O_4$  enables a simple incorporation of foreign ions in its crystal lattice as long as the foreign ion exhibits a similar ionic radius to  $Ti^{4+}$  in order to induce a band gap decrease. The ion incorporation into the lattice of  $Cs_{0.68}Ti_{1.83}O_4$  is carried out via the alternative sol-gel synthesis route, in order to ensure a homogeneous distribution of the foreign ions.  $Cu^{2+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$  and  $Mn^{3+}$  were incorporated into the crystal lattice of  $Cs_{0.68}Ti_{1.83}O_4$ . Band gap investigations which were performed after the initial activity tests reveal that the band gap decreasing effect of the incorporated foreign ions is lost after an exposition in the reaction medium. Furthermore,  $Cs_{0.68}Ti_{1.83}O_4$  modified with foreign ions show a significant decrease of the photocatalytic activity compared to pristine  $Cs_{0.68}Ti_{1.83}O_4$ .

Finally,  $Cs_{0.68}Ti_{1.83}O_4$  and Cu modified  $Cs_{0.68}Ti_{1.83}O_4$  were investigated as photoelectrode materials. Photocurrents under UV- and visible light irradiation were performed as well as electrochemical measurements were made for the determination of the electronic band structure.

### **Table of Contents**

1 Introduction	1
2 Objective	5
3 Fundamentals	9
3.1 Electronic and Optical Properties of Semiconductors	9
3.1.1 Electronic Properties of Solids	
3.1.2 Optical Properties of Semiconductors	
3.2 Heterogeneous Photocatalysis on Semiconductors	16
3.2.1 Photocatalytic Hydrogen Production	
3.2.2 Role of Co-Catalysts on Semiconductor Surfaces	
3.2.3 Sacrificial Agents in Heterogeneous Photocatalysis	
3.3 Band gap Engineering by Ion Doping	
3.4 Coupled Semiconductors: Photocatalyst Composites	
3.5 Photocatalytic Semiconductors	
3.5.1 Layered Titanates	
3.6 Synthesis Methods	
3.7 Fundamentals of Photoelectrochemistry	
4 Experimental	
4.1 Preparation of Mixed Metal Oxides	
4.1.1 Sol-gel process	
4.1.2 Wet Impregnation	
4.1.3 Photodeposition of noble and non-noble metals	
4.2 Characterization Methods	41
4.2.1 X-ray diffraction	
4.2.2 UV-Vis spectroscopy in diffuse reflectance	
4.2.3 Localized surface plasmon resonance	
4.2.4 Thermogravimetric analysis	
4.2.5 Electron microscopy	
4.2.6 X-ray photoelectron spectroscopy	
4.3 Photoelectrochemical Analysis	
4.3.1 Doctor Blading	

	4.3.2 Capacitance Measurement for flat band determination	53
	4.3.3 Photocurrent measurement	54
	4.4 Setups for Photocatalytic H <sub>2</sub> and O <sub>2</sub> Production	55
	4.5 Photocatalytic H <sub>2</sub> production via sacrificial agent reformation	59
5	Results & Discussion	63
	5.1 Unmodified Layered Cesium Titanate	63
	5.1.1 Synthesis and Characterization	63
	5.1.2 Photocatalytic H <sub>2</sub> Production - Investigations of Extrinsic Factors	69
	5.1.3 Photocatalytic H <sub>2</sub> Production on Noble Metal Co-catalysts	82
	5.1.4 Copper as an Earth-abundant Co-Catalyst in Photocatalytic H <sub>2</sub> Production	90
	5.1.5 M/Cr <sub>2</sub> O <sub>3</sub> (M: Rh, Cu) Core/Shell Co-Catalyst for Overall Water Splitting	96
	5.1.6 Summary	98
	5.2 Copper and Gold modification of Layered Cesium Titanate by Wet Impregnation	101
	5.2.1 Synthesis and Characterization of Copper modified Cs <sub>0.68</sub> Ti <sub>1.83</sub> O <sub>4</sub>	101
	5.2.2 Photocatalytic H <sub>2</sub> Production with $Cs_{0.68}Ti_{1.83}O_4/Cu$ prepared by Wet Impregnation	105
	5.2.3 Copper Impregnation on Stabilized Cs <sub>0.68</sub> Ti <sub>1.83</sub> O <sub>4</sub>	115
	5.2.4 Gold Impregnation on Stabilized Cs <sub>0.68</sub> Ti <sub>1.83</sub> O <sub>4</sub>	123
	5.2.5 Summary	133
	5.3 Copper modification of Layered Cesium Titanate by Sol-Gel Process	137
	5.3.1 Synthesis and Characterization	137
	5.3.2 Photocatalytic H <sub>2</sub> Production and In-Situ SPR Tracking	140
	5.3.3 Post Characterization	145
	5.3.4 Summary	153
	5.4 Chromium, Iron and Manganese Doped Layered Cesium Titanate	157
	5.4.1 Synthesis and Characterization	158
	5.4.2 Photocatalytic $H_2$ Production with Cr, Fe and Mn Doped $Cs_{0.68}Ti_{1.83}O_4$	163
	5.4.3 Post Characterization	165
	5.4.4 Summary	168
	5.5 Photoelectrochemical Investigations on Layered Cesium Titanates	171
	5.5.1 Photoelectrode Preparation	171
	5.5.2 Capacitance Measurements	174
	5.5.3 Photocurrent Measurements	178
	5.5.4 Summary	181
6	Conclusion	183

7 Outlook	
8 References	
9 Appendix	
9.1 Additional Information to Chapter 4.1	201
9.2 Additional Information to Chapter 4.4	
9.3 Additional Information to Chapter 5.1	207
9.4 Additional Information to Chapter 5.2	212
9.5 Additional Information to Chapter 5.3	216
9.6 Additional Information to Chapter 5.4	226
9.7 Additional Information to Chapter 5.5	227
10 Curriculum Vitae	

# Symbols

Symbol	Notation	Unit
А	(absorption) constant	-
С	capacitance	[F]
d	material thickness	[m]
d	lattice plane distance	[nm]
Е	energy	[eV]
E <sub>CB</sub>	energy of conduction band	[eV]
E <sub>VB</sub>	energy of valence band	[eV]
$\mathrm{E_{g}}$	band gap energy	[eV]
$\mathrm{E}_\mathrm{F}$	Fermi level energy	[eV]
${}^{*}\mathrm{E}_{\mathrm{Fn}}$	quasi Fermi level of electrons	[eV]
${}^{*}\mathrm{E}_{\mathrm{Fh}}$	quasi Fermi level of holes	[eV]
E <sub>kin</sub>	kinetic energy	[J]
$E_{bind}$	binding energy	[eV]
E <sub>P</sub>	energy of electron momentum	[eV]
exp	exponential function	-
F	Faraday constant	[C/mol]
$f_{FD}(E)$	Fermi-Dirac distribution	-
$F(\mathbf{R}_{\infty})$	Kubelka-Munk function	-
h	Plank constant	$[J \cdot s]$
ħ	$h/2\pi$	$[J \cdot s]$
$I_0$	incident light	-
Ι	transmitted light	-
Κ	(diffraction) constant	-
Κ	absorption coefficient of $F(R_{\infty})$	-
k	Boltzmann constant	[J/K]
L	average particle size	[nm]
m <sub>eff</sub>	effective mass	[kg]
$N_D$	doping degree	-
n	order of diffraction	-
n	order of electron transition	-
q	electron charge	[C]

Symbol	Notation	Unit
R	reflectance	-
$\mathbf{R}_{\infty}$	reflectance at infinite film thickness	-
S	scattering coefficient of $F(R_{\infty})$	-
Т	temperature	[K]
V	volume	[mL]
V	voltage	[V]
Z(E)	density of states function	-
Greek Symbol	Notation	Unit
α	absorption coefficient	-
β	full width at half maximum	[°]
$\Delta G$	change in free Gibbs energy	[kJ/mol]
$\Delta_{ m oct}$	energy of octahedral splitting	[eV]
3	relative permittivity	[F/m]
$\epsilon_0$	permittivity of free space	[F/m]
θ	diffraction angle	[°]
λ	wavelength	[nm]
$\widetilde{\mu}_{e}$	electrochemical potential of electrons	[J/mol]
ν	frequency	[Hz]
Φ	work function	[eV]
χ	electron affinity	[kJ/mol]
eΨ	electrostatic potential	[V]

## Abbreviations

Abbreviation	Notation
СВ	Conduction Band
CLV	Chopped Light Voltammetry
СТО	Cesium Titanium Oxide
CVD	Chemical Vapor Deposition
DTG	Derivative of Thermo Gravimetric Analysis
DOS	Density Of States
FTO	Fluorine doped Tin Oxide
GC	Gas Chromatograph
HAADF	High Angle Annular Dark Field
HR	High Resolution
НОМО	Highest Occupied Molecular Orbital
ICTAC	International Confederation for Thermal Analysis and Calorimetry
IUPAC	International Union of Pure and Applied Chemistry
LSPR	Localized Surface Plasmon Resonance
LUMO	Lowest Unoccupied Molecular Orbital
Μ	Metal
MFC	Mass Flow Controller
NHE	Normal Hydrogen Electrode
PD	Photo Deposition
PVD	Physical Vapor Deposition
QE	Quantum Efficiency
SC	<b>S</b> emiconductor
SEM	Scanning Electron Microscopy
SMR	Steam Methane Reforming
SMSI	Strong Metal-Support Interaction
SPR	Surface Plasmon Resonance
SSR	Solid State Reaction
STEM	Scanning Transmission Electron Microscopy
STH	Solar To Hydrogen
TEM	Transmission Electron Microscopy
TGA	Thermo Gravimetric Analysis

Abbreviation	Notation
UV/Vis	Ultra Violet/Visible
VB	Valence Band
WI	Wet Impregnation
XPS	X-ray Photoelectron Spectroscopy
XFA	X-ray Fluorescence Analysis
XRD	X-ray Diffraction

#### **1** Introduction

The growing energy demand in the 21<sup>st</sup> century, due to the rapid rise of emerging economies such as India<sup>[1-4]</sup>, China<sup>[3-6]</sup> and Brazil<sup>[4-5, 7-9]</sup>, requires the exploitation of new energy sources. Nevertheless, the global energy supply is mainly ensured by fossil fuels, like crude oil, coal and natural gas, while crude oil still holds the greatest significance.<sup>[4, 10]</sup> The combustion of these fossil fuels causes a tremendous emission of the greenhouse gas CO<sub>2</sub>, which is partly responsible for global warming. For example, the worldwide energy consumption in 2013 has reached  $533 \cdot 10^{18}$  J with a corresponding rate of 16.9 TW and an associated CO<sub>2</sub> emission of 36 Gt (36 billion tones), according to the British Petroleum statistical review of world energy of 2014.<sup>[11-12]</sup> Referred to 2013, the global primary energy consumption increased only by 0.9%.<sup>[4, 11]</sup> But an increased fossil fuel consumption rate and CO<sub>2</sub> emission of 27.6 TW and more than 40.3 Gt, respectively, are predicted for 2050.<sup>[13]</sup> To counteract this development, the prospective usage of renewable energies and sustainable resources is inevitable. Several renewable energies provide a great utilization potential like biomass (5 - 7 TW), underground heat (10 TW), ocean/tide/current (2 TW), wind (2 - 4 TW) and the most abundant energy source sunlight with an exceeding energy potential of 36.000 TW on land.<sup>[13-14]</sup>

Solar energy is mainly harvested and converted into electric energy by photovoltaic<sup>[15-16]</sup> with photoelectrochemical<sup>[17]</sup> or silica based solar cells.<sup>[12]</sup> But these technologies still suffer from high fabrication costs, insufficient light absorption, low power density and inconvenient transportation.<sup>[12]</sup> The incident sunlight has to be converted and stored in a more practical form to ensure an effective usage. One of these forms is, e.g. hydrogen (H<sub>2</sub>), because of its high energy content of 436 kJ/mol stored in the H-H bond.<sup>[18]</sup> H<sub>2</sub> can be afterwards oxidized in a fuel cell to electric energy with water as the resulting reaction product.<sup>[19]</sup> Nowadays, industrial scale H<sub>2</sub> production is mainly accomplished by steam methane reforming (SMR), the water-gas-shift reaction (Eq.1.1 and 1.2)<sup>[20]</sup>,

$$CH_4 + H_2O \rightarrow 3 H_2 + CO; \Delta G^0 = 142 \text{ kJ mol}^{-1}$$
 (1.1)

$$CO + H_2O \rightarrow H_2 + CO_2; \Delta G^0 = -29 \text{ kJ mol}^{-1}$$
(1.2)

partial oxidation<sup>[21]</sup> of natural gas and heavy hydrocarbons and coal gasification<sup>[22]</sup>. Disadvantageous of the SMR is the large and positive change in the Gibbs free energy, which requires high temperatures even in the presence of a heterogeneous catalyst and the coupled production of CO and CO<sub>2</sub>.<sup>[18]</sup> In detail, the SMR and the connected water-gas-shift reaction produce 5 kg CO<sub>2</sub> per metric kilo of H<sub>2</sub>.<sup>[23]</sup> Therefore, large scale H<sub>2</sub> production via SMR cannot be seen as an ecological foundation of a H<sub>2</sub> based energy system. Alternative H<sub>2</sub>

production by direct water electrolysis<sup>[24]</sup> is also unsuitable from the economic point of view, because of high energy costs. In contrast, the consumed energy for the electrolysis process has to be produced from renewable energies for a neutral CO<sub>2</sub> balance. Despite of the future utilization of H<sub>2</sub> as fuel, the general demand for H<sub>2</sub> will also grow in the next decade,<sup>[25]</sup> because nowadays H<sub>2</sub> is primarily used as a component of syngas for the production of ammonia and methanol as well as a feedstock in the Fischer-Tropsch process.<sup>[26-27]</sup> The second largest amount of H<sub>2</sub> is consumed by refineries mainly for the removal of sulfur from gasoline and the conversion of heavy hydrocarbons into gasoline and diesel fuel by hydrocracking.<sup>[13, 27]</sup>

A simple and direct  $H_2$  production driven by solar light has to be established in order to handle the predicted growing demand. One promising solution is the usage of photoactive semiconductor nanoparticles as photocatalysts for overall water splitting (Eq. 1.3).<sup>[19]</sup>

$$H_2O \rightarrow \frac{1}{2} O_2 + H_2; \Delta G^0 = 237 \text{ kJ mol}^{-1}$$
 (1.3)

Since the pioneer work of Boddy<sup>[28]</sup>, Fujishima and Honda<sup>[29]</sup> in 1968 and 1972 respectively, on photoelectrochemical electrodes for O<sub>2</sub> and H<sub>2</sub> production, around 130 photocatalytic active semiconductor materials were discovered.<sup>[30]</sup> Among this amount of semiconductors, titanium dioxide (TiO<sub>2</sub>) represents the best investigated photocatalysts in the world.<sup>[31]</sup> Transition metal oxides are commonly used as photocatalysts, but these material class suffers from large band gaps (> 3.0 eV) and for this reason only active under irradiation with ultra violet (UV) light. Unfortunately, the solar light spectrum on earth surface contains only 5% UV light.<sup>[26, 30]</sup> According to Bahnemann et. al.<sup>[13]</sup> a maximum solar to H<sub>2</sub> (STH) conversion efficiency of 48% can be achieved by considering the usable light spectrum between 280 -1000 nm as well as a photocatalyst with a band gap energy of 1.23 eV, if all absorbed photons are converted into H<sub>2</sub> or in other words, a quantum efficiency (QE) of 100% is present. Energy excess, exceeding 1.23 eV, are exclusively transformed into heat and not reused for H<sub>2</sub> formation. Realistically, a STH conversion efficiency of 10% by a QE of 50% under visible light irradiation is sufficient enough for an industrial usage of photocatalysts for solar H<sub>2</sub> production.<sup>[13]</sup> For this reason, a band gap reduction into the visible light region for an effective utilization of the incident sunlight is needed. Beside the band gap size, also the band alignment is a crucial factor to run the overall water splitting reaction.<sup>[32]</sup> The ideal photocatalyst for visible water splitting has not been developed yet. Beside the development of visible light active photocatalysts, other practical problems are still evident and require

further developments, like an efficient large scale  $H_2/O_2$  gas separation and a cost effective and simple  $H_2$  storage technique.<sup>[33]</sup>

Layered titanates, a TiO<sub>2</sub> related material class, provide an appropriate band alignment for overall water splitting, ideal conditions for subsequent band gap modifications as well as an adequate photocatalytic activity for H<sub>2</sub> production.<sup>[34-37]</sup> Among the great variety of layered titanate materials, the layered cesium titanate represents one promising semiconductor material for further modifications of the electronic structure due to its beneficial structural conditions.<sup>[37-40]</sup> According to its chemical structure  $Cs_{0.68}Ti_{1.83}\square_{0.17}O_4$  ( $\square$  = vacancy)<sup>[41]</sup> and open layered crystal structure, the cesium titanate provide an ideal foundation for anion<sup>[42]</sup> and cation<sup>[43]</sup> doping. Especially,  $Cs_{0.68}Ti_{1.83}\square_{0.17}O_4$  enables a homogeneous distribution of the inserted doping agent throughout the bulk structure, which results in a complete shift of the absorption edge into the visible light region. Contrary, cationic and anionic doped TiO<sub>2</sub> experiences defined absorption shoulders in the visible light region and therefore suffer from minor visible light activity. Anion and cation doping of layered cesium titanate were intensively investigated mainly in regard of visible light activity in different degradation reactions.<sup>[36, 44-45]</sup> Contrary, the usage of layered cesium titanates in H<sub>2</sub> production is less investigated and requires further developments.<sup>[35]</sup>

#### **2** Objective

The present research study gives an overview and new insights about the photocatalytic activity of transition metal modified layered cesium titanates in respect of their capabilities for photocatalytic  $H_2$  production. For the development, improvement and understanding of a catalytic or to be more precise of a photocatalytic system, a general three steps cycle has to be followed, as illustrated in figure 1.



Figure 1: Catalyst development scheme in regard of photocatalyst studies.

Starting with the catalyst preparation, which influences the intrinsic factors of the photocatalyst material, like crystal phases<sup>[31]</sup>, crystallite size<sup>[46]</sup> and shape, doping degree<sup>[47]</sup>, amount of impurities and defects<sup>[48]</sup>, exposed crystal facets<sup>[49]</sup> and associated surface states. A complete characterization of the synthesized photocatalyst is inevitable to clarify the catalyst properties and constitution for later understanding of the catalytic activity. Several characterization methods are used for the investigation of structural, electronic and optical properties of photocatalysts as X-ray diffraction, UV/Vis- and X-ray photoelectron spectroscopy, as well as different physisorption and chemisorption techniques and photoelectrochemical methods. After a complete characterization, the activity evaluation, e.g. for H<sub>2</sub> and/or O<sub>2</sub> evolution can be seen as the end of the photocatalyst development cycle. The activity evaluation enables the investigation of extrinsic factors like pH, sacrificial agent concentration, catalyst amount, temperature and light intensity, which also influence the photocatalyst precursor. The real acting photocatalyst is formed during the evaluation test in regard of co-catalyst deposition/activation and potential structural changes. Therefore an in-

operando characterization of the respective photocatalyst system is required. For this reason, a subsequent characterization of the used photocatalyst is needed for the interpretation of the performed evaluation tests and for a potential modification of the photocatalyst synthesis. All investigations towards transition metal modified and unmodified layered cesium titanates were performed according to the presented catalyst development scheme.

The unmodified cesium titanate  $C_{s_{0.68}}T_{i_{1.83}}\square_{0.17}O_4$  serves as a foundation for the investigation of the ideal preparation conditions and as a standard material for the study of extrinsic factors on the photocatalytic activity. A sol-gel process, related to the Pechini method<sup>[51-53]</sup>, is used for the synthesis of modified and non-modified layered cesium titanates. This sol-gel approach enables, especially for the preparation of metal modified cesium titanates, an improved distribution of the doping ions in the photocatalyst bulk structure. Furthermore, the chosen preparation method allows the synthesis of mixed metal oxides at more moderate conditions compared to the classic solid state reaction<sup>[54-55]</sup>, which requires high temperatures and long reaction times. Noble metals are commonly deposited on the photocatalyst surface to act as electron traps, in order to decrease the electron/hole pair recombination rate.<sup>[56-57]</sup> The photodeposition technique is the standard method for the deposition of metal nanoparticles on photocatalyst surfaces.<sup>[58-59]</sup> Three selected noble metal, platinum (Pt)<sup>[59-60]</sup>, gold (Au)<sup>[57, 59, 61-</sup> <sup>62]</sup> and rhodium (Rh)<sup>[59, 63-64]</sup> are used as known co-catalysts for the enhancement of the photocatalytic activity in H<sub>2</sub> production. But, the utilization of noble metals as H<sub>2</sub> evolution co-catalysts is not cost effective and requires a cheap and abundant alternative. Copper (Cu) resembles an alternative co-catalyst material for H<sub>2</sub> production.<sup>[65-67]</sup> The photocatalytic potential of Cu nanoparticles as a co-catalyst material is studied in regard of different deposition methods for the unmodified  $Cs_{0.68}Ti_{1.83}\square_{0.17}O_4$ .

The majority of mixed metal oxide photocatalysts are not capable to run the overall water splitting reaction (Eq. 1.3).<sup>[30]</sup> For this reason, the usage of so called sacrificial agents is necessary, in order to block one half reaction for H<sub>2</sub> or O<sub>2</sub> formation.<sup>[68-69]</sup> The effect of selected sacrificial agents on the H<sub>2</sub> evolution activity has to be investigated for each co-catalyst on  $Cs_{0.68}Ti_{1.83}\square_{0.17}O_4$ , to receive new insights about new sustainable feedstocks and photocatalyst systems. Cu and Au possess unique optical properties, which enable a direct observation of the co-catalyst formation under photocatalytic conditions.<sup>[62, 70-72]</sup> The co-catalyst formation can be traced down by the observation of their respective localized surface plasmon resonance (*LSPR*) signal. The development of co-catalyst LSPR signals in terms of intensity, shape and signal shift relative to the expected position based on literature data can

be related to the observed photocatalytic activity and provide new information about the working photocatalyst/co-catalyst system.<sup>[73]</sup>

Different non-noble and noble transition metals are used as doping agents for band gap reduction for visible light absorption of the bulk material<sup>[74-75]</sup> and, as already mentioned, as co-catalysts on the photocatalyst surface to improve the photocatalytic activity. The band gap reduction is accomplished by the insertion of specific transition metal cations like Cu<sup>2+[76-77]</sup>, Fe<sup>3+[78-79]</sup>, Cr<sup>3+[44, 80]</sup> and Mn<sup>3+[81-82]</sup> into the host matrix of the layered cesium titanate, creating additional donor and acceptor states in the electronic band structure. The crystallographic B-site defects (Ti position) of Cs<sub>0.68</sub>Ti<sub>1.83</sub> $\square_{0.17}$ O<sub>4</sub> may promote the incorporation of the stated metal ions into the crystal lattice forming the respective metal oxide within the titanate sheets.<sup>[54]</sup> Effects of metal cation doping on Cs<sub>0.68</sub>Ti<sub>1.83</sub> $\square_{0.17}$ O<sub>4</sub> were investigated in literature in terms of crystal structure transformation<sup>[83]</sup>, degradation reactions under visible light irradiation<sup>[79]</sup> or lithium storage<sup>[84]</sup> but poorly for photocatalytic H<sub>2</sub> production.

The superior goal of this thesis is the development of a highly active H<sub>2</sub> evolution photocatalyst by the utilization of alternative co-catalyst materials and sacrificial agents as H<sub>2</sub> feedstocks. A detailed characterization of the photocatalyst material during each preparation steps should give a direct view on different states of the photocatalyst material and provides a greater overview on the photocatalytic activity. Cu and Au modified  $Cs_{0.68}Ti_{1.83}\square_{0.17}O_4$  are used as model photocatalyst for the observation of the operating photocatalyst by in-situ tracking of their respective LSPR signal. The development of the LSPR signal as well as the signal shape and intensity provide new insights about the operating photocatalyst under experimental conditions. Furthermore, the effects of doping cations on the photocatalytic activity of  $Cs_{0.68}Ti_{1.83-(x/2)}M_x\square_{0.17}O_4$  ( $M^{n+} = Cu^{2+}$ ) and  $Cs_{0.68}Ti_{1.83-(x-3/4)}M_x\square_{0.17}O_4$  ( $M^{n+} = Fe^{3+}$ ,  $Cr^{3+}$  and  $Mn^{3+}$ ), assuming an exclusive incorporation on the crystallographic B-site without vacancy occupation, in H<sub>2</sub> production are also investigated.

Beside of the evaluation of the photocatalytic activity in  $H_2$  production, the photoelectrochemical potential of stoichiometric doped cesium titanates and unmodified  $Cs_{0.68}Ti_{1.83}\square_{0.17}O_4$  are analyzed as immobilized powder photocatalysts on electric conductive glass substrates, like fluorine doped tin oxide (FTO). The preparation of photoactive electrodes from a solid material is realized by the conventional doctor blading technique.<sup>[85-86]</sup> A suspension consisting of the powder photocatalysts and a solvent are spread on a substrate to produce a compact photocatalyst film. Photocurrent measurements are used for the

quantification of the photoelectrochemical activity of the produced photoelectrodes. Photoelectrodes are additionally used for the investigation of the electronic band structure of layered cesium titanates.

#### **3** Fundamentals

#### **3.1 Electronic and Optical Properties of Semiconductors**

The electronic and optical properties of a conductive, semiconductive or nonconductive material are mainly subjected by its individual band structure. Semiconductors represent a median material class between conductors and insulators in regard of electronic conductivity. Extrinsic factors like temperature or radiation influence the intrinsic electronic conductivity of these materials. Semiconductors at absolute zero (T = 0 K) are not conductive like insulators.<sup>[87]</sup> Thermally induced energy increases the conductivity of semiconductors up to a certain range because of excited electrons into the conduction band becoming the majority charge carrier. Contrary, conductors experienced a decrease in conductivity with increasing temperature while insulators are unaffected by temperature changes. Radiation with light of an appropriate wavelength causes a different behavior of the mentioned material classes to the extent that some insulator can be conductive under illumination by overcoming a discrete energy barrier.<sup>[13]</sup> To explain the difference in behavior, the band theory of solids and Fermi Dirac distribution has to be acquired.<sup>[88]</sup>

#### **3.1.1 Electronic Properties of Solids**

The "electronic band structure" or "energy band model" serves as a quantum mechanical description of electronic energy states in an ideal crystal system. The energy band model is roughly defined by two energy bands, the valence and conductions band, which are separated by an energy barrier called band gap  $(E_g)$ .<sup>[89]</sup> The valence band (VB) is described as the highest occupied band while the conduction band (CB) is defined as the lowest unoccupied band in a solid material at T = 0 K.<sup>[87]</sup> The specific size of the band gap is the crucial dimension for the differentiation between conductors, semiconductors and insulators.<sup>[88, 90]</sup>

To understand the band formation, a one-dimensional chain of atoms with a single valence electron on a discrete energy state is assumed.<sup>[89]</sup> According to the molecular orbital theory the short distance between two atoms leads to the formation of a bonding and antibonding molecular orbital by the hybridization of two atomic orbitals. A molecule chain, consisting of three atoms, forms a bonding, antibonding and an additional non-bonding orbital in between, while a four atomic molecule chain build up four molecular orbitals and so on. All contributed electrons in these molecules are distributed in regard of the Pauli Exclusion principle.<sup>[91]</sup> In general, a defined number of atomic orbitals from an equivalent number of molecular orbitals results in a narrowing of the discrete energy states. In a solid, these energy states are no longer



distinguishable due to the high number of hybridized atomic orbitals, forming a continuum of energy states or bands (Figure 2a).<sup>[87]</sup>

Figure 2: a) Formation of molecular orbitals,<sup>[87]</sup> b) Schematic band structures of conductors, semiconductors and nonconductors.<sup>[92]</sup>

The formed band structure, in detail the band occupation, the overlap and the band distance define conductors, semiconductors and nonconductors (Figure 2b). Fully occupied bands as well as empty bands do not contribute in the charge carrier transport because of the inability of energy absorption. In order to establish conductivity, an energy difference in the valence band electrons is required to enable charge mobility.<sup>[87]</sup> Metals are excellent conductors because of the overlapping bands and hence of a partly occupied valance and conduction band, which enables a charge carrier transport. Due to the overlapping energy bands, metals literally do not possess a band gap. Semiconductors and insulators show a different band structure. Valence and conduction band are strictly separated from each other by an energy gap ( $E_{\alpha}$ ). By definition, semiconducting materials exhibit band gap energies between 0.1 eV -4.0 eV, divided in thermal semiconductors  $(0.1 \text{ eV} < E_g < 1.0 \text{ eV})$  and photoactive semiconductors (1.0 eV <  $E_g$  < 4.0 eV).<sup>[93]</sup> Materials with band gaps larger than 4.0 eV are categorized as insulators. In semiconductors and insulators, the electrons are located in the valence band, while the conduction band stays empty. Without external energy input for electron excitation, semiconductive materials are nonconductive due to the lack of mobile charge carriers.<sup>[87]</sup> Electron excitation can be realized by the induction of thermal or photo energy, which defines the difference between a thermal and a photoactive semiconductor as well.

The thermal behavior of metals and semiconductors is explained by the Fermi Dirac distribution (Eq. 3.1) and the density of states (DOS) theory.<sup>[87-89]</sup> The Fermi Dirac distribution resembles the Boltzmann distribution, which puts the Pauli exclusion principle into consideration.<sup>[87]</sup> In a metal at T = 0 K half of the contributed molecular orbitals are occupied by electrons. In this case, the Fermi level (E<sub>F</sub>) is equal to the edge of the highest occupied molecular orbital (HOMO). The lowest unoccupied molecular orbital (LUMO) is directly located on the edge of the Fermi level. A temperature increase leads to an electron excitation into the LUMO energy states. In detail, the Fermi Dirac distribution describes the temperature dependence of the orbital population in a solid material.<sup>[87, 91, 94]</sup>

$$f_{FD}(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}$$
(3.1)

According to equation 3.1, the probability of orbital occupation increases with increasing temperature. Nevertheless, metallic conductors experience a decrease in conductivity due to a higher probability of electron to atom collision, which effectively reduces the single electron mobility.<sup>[87]</sup> Semiconductors show an opposite thermal behavior compared to metals. A temperature increase equivalent to Eg is necessary for an excitation of valence band electrons into the empty conduction band, creating a positively charged vacant site, a so called hole, in the valence band.<sup>[95]</sup> Both charge carriers are mobile in the respective band and provide the foundation for electrical conductivity. A linear temperature increase leads to a corresponding rise in the conduction band occupation (Eq. 3.1) and, in case of a semiconducting material, to an increased conductivity.<sup>[94]</sup> Semiconductors with large Eg require larger energy contents for an electron excitation, coming to the extent that an electron excitation cannot be realized. Materials with large Eg (> 4.0 eV) are considered as insulators or nonconductors because of their inability of electron excitation. Nevertheless, to receive the orbital population, the electron DOS has to be considered. The DOS function (Eq. 3.2) describes the available energy states per given energy or frequency interval. The effective electron population in the conduction band is given by the product of  $f_{FD}(E)$  and Z(E).<sup>[89]</sup>

$$Z(E) = \frac{V}{4\pi^2} \left(\frac{2 m_{eff}}{\hbar^2}\right)^{3/2} \sqrt{E}$$
(3.2)

Beside the differentiation between thermal and photoactive semiconductors, the Fermi level position additionally classifies semiconductors into intrinsic and extrinsic semiconductors (Figure 3).<sup>[96]</sup> The Fermi level of an intrinsic semiconductor is located midway between the valence and conduction band. Pure semiconductors, which consist of a single element like

silicon and germanium or of an ideal single crystal compound, are intrinsic semiconductors.<sup>[87]</sup> The insertion of foreign elements into the crystal structure of a semiconductor shifts the position of the Fermi level near to the valence or conduction band edge and generates an extrinsic semiconductor. These extrinsic semiconductors are further divided in p-type and n-type semiconductors. The process of impurity state creation by the incorporation of foreign atoms is called doping.<sup>[87, 93]</sup>



Figure 3: Band structure of a) Intrinsic and b) Extrinsic (n and p-type) semiconductor.<sup>[89, 96]</sup>

A semiconductor doped with acceptor atoms, atoms with less electrons than the host material, like indium doped silicon is classified as a p-type semiconductor.<sup>[87, 97]</sup> The created empty acceptor energy states are located near the upper edge of the valence band.<sup>[89]</sup> Electrons are easily transferred to the acceptor atoms, increasing the number of positively charged holes in the valence band. In case of p-type semiconductors, holes are considered as the majority charge carriers. Furthermore, the Fermi level is shifted to lower energies and is located between the valence band and the acceptor states.<sup>[89]</sup> Also un-doped semiconductors with deficit cation stoichiometry show p-type semiconduction.<sup>[96, 98]</sup> Analogous, the insertion of donor impurity atoms, atoms with more electrons than the host material, into a semiconductor crystal structure like arsenic or phosphor doped silicon are categorized as n-type semiconductors.<sup>[87, 96-97]</sup> The occupied donor states are located below the conduction band edge, which enable an easy donation of impurity state electrons into the conduction band. By increasing the density of negative charges in the conduction band, electrons are the majority charge carries in an n-type semiconductor. The Fermi level itself is shifted to higher energies and is positioned between the donor energy states and conduction band edge.<sup>[89]</sup> Beside doped semiconducting materials, also compound semiconductors with a defect crystal structure caused by stoichiometric deviation experience n-type semiconduction.<sup>[99]</sup> Semiconductive

materials with an oxygen vacant crystal structure like in case of well investigated  $TiO_2$  are known n-type semiconductors. The oxygen vacancies are compensated by the formation of an equivalent amount of  $Ti^{3+}$  ions, which act as electron donors.<sup>[96-97, 100]</sup>

For the determination of the electron energy in a solid material the concept of vacuum level has to be introduced. The vacuum level acts as a reference value for the electron energy and is considered as zero (Figure 4). The electrochemical potential of excited valence band electrons in a semiconductor will be stated as  $\tilde{\mu}_e$ . Thermodynamically, the Fermi level  $E_F$  can be literally considered as the electrochemical potential of the semiconductor electrons itself. On the other hand, statistically the probability of an energy level occupation by an excited electron is 0.5 on the Fermi level energy state. The work function  $\Phi_{SC}$  describes the work which is needed to move an electron from the bulk to a distance x on the surface where the classical image force potential is negligible. This requirement can be achieved at a distance of  $10^{-4}$  cm. The electron affinity  $\chi_{SC}$  is a crucial factor for the estimation of band bending which happens at the interface of two materials.  $\chi_{SC}$  is specified as the difference of the lower conduction band edge energy and the outer electrostatic potential e $\Psi$  of the semiconductor surface.<sup>[96]</sup>



Figure 4: Electronic energy band diagram of a semiconductor.<sup>[96]</sup>

#### 3.1.2 Optical Properties of Semiconductors

Semiconductors with band gap energies larger than 1.0 eV are typed as photo active because thermally induce energy is not sufficient enough for an electron excitation. Nevertheless, the valence and conduction band separation lays the foundation for the ability of light absorption of semiconductive materials. When a semiconductor is irradiated with light of wavelengths equal or larger than the band gap energy, the absorbed photon causes an electron excitation into the conduction band.<sup>[100]</sup> The electron transition from the valence band maximum to the conduction band minimum depends on the position of the valence band peak and conduction band valley in the k-space forcing two different types of excitation, a direct and indirect transition.<sup>[101]</sup> The k-space is defined as a Cartesian coordinate system of energy and momentum. In case of a parallel band orientation, the upcoming electron excitation provoked by photon absorption is stated as a direct valence to conduction band transition. Contrary, for indirect transition a change in energy as well as in momentum is needed (Figure 5b). The additional change in momentum is achieved by the absorption or emission of a phonon, a quasiparticle caused by crystal lattice vibrations.<sup>[102]</sup>



Figure 5: a) Direct and b) Indirect electron transition in a semiconductor.<sup>[101-102]</sup>

Therefore, an indirect transition is considered as a two-step process, which is less probable than a direct one and leads to a lower absorption coefficient  $\alpha$ .<sup>[102]</sup> The absorption coefficient  $\alpha$  is easily obtained, accessible through product of the logarithm of the inverse transmittance and inverse sample thickness *d* (Eq. 3.3).<sup>[101]</sup>

$$\alpha = \ln \frac{I_0}{I} \cdot \frac{1}{d}$$
(3.3)

With the knowledge of the absorption coefficient  $\alpha$ , the band gap energy can be determined through equation 3.4:

$$\alpha = A \frac{\left(hv - E_g\right)^n}{hv}$$
(3.4)

The exponent *n* of equation 3.4 defines the type of optical transition with four different values of 0.5, 1.5, 2 and 3 for allowed direct, forbidden direct, allowed indirect and forbidden indirect transition, respectively.<sup>[102]</sup> For band gap determination, only the allowed and allowed indirect transition are of practical interest. Unfortunately, the absorption spectrum of a solid material is hardly available due to the undefined sample thickness.<sup>[102]</sup> Several models like the Kubelka-Munk function or Tauc plot were developed for band gap estimation from diffuse reflectance spectra of a semiconductor powder.<sup>[96]</sup> The band gap estimation by Kubelka-Munk theory and Tauc plot model are explained in detail in chapter 4.2.2.

Beside direct and indirect transition, a variety of electron transitions exist, which are illustrated in figure 6. By the introduction of the exact energy amount equivalent to  $E_g$ , a simple band to band transition occurs (Figure 6a). Electrons excited to higher conduction band levels due to a higher energy input fall down to the lower conduction band edge within 1 - 0.1 ps followed by heat emission (Figure 6b). Impurity states caused by doping enable an electron transition from and to unionized donor and acceptor states (Figure 6c and d). Intraband transitions (Figure 6e) typically take place at low energy contents and are mostly observed in metals, which already possess a partly filled conduction band. An exciton is defined as the quasi-particle of electron/hole pair bound by coulomb attraction and is further distinguished between Mott-Wannier and Frenkel excitons,<sup>[15]</sup> which are not discussed here. The exciton energy state is located near the conduction band minimum (Figure 6f) and can be thermally separated into a single electron and hole.<sup>[102]</sup>



Figure 6: Additional electron transitions in a photoactive semiconductor.<sup>[102]</sup>

#### 3.2 Heterogeneous Photocatalysis on Semiconductors

Photocatalysis is defined, according to IUPAC (*International Union of Pure and Applied Chemistry*) as the change in the rate of a chemical reaction or its initiation under the action of ultraviolet, visible or infrared radiation in the presence of a substance, the photocatalyst that absorbs light and is involved in the chemical transformation of the reaction partners.<sup>[103]</sup> In case of the heterogeneous photocatalysis, the chemical reaction is performed by a photoactive semiconductor, which acts as the mentioned photocatalyst. The fundamental steps of a photocatalytic reaction on semiconductor particles are schematically illustrated in figure 7a.<sup>[104]</sup>



**Figure 7:** a) Single steps of heterogeneous photocatalysis (adapted from Hoffmann et. al.<sup>[104]</sup> and Park el. al<sup>[105]</sup>), b) Recombination possibilities after excitation (adapted from Beranek et. al.<sup>[102]</sup>).

Each step is numerically listed with the respective time scale, basing on charge carrier transportation processes in  $TiO_2^{[104]}$ , starting with 1) Absorption of light with energy equal or larger than  $E_g$ , followed by electron/hole pair generation (about 200 fs)<sup>[106]</sup>. 2) Migration of mobile charge carriers from the bulk to the photocatalyst surface. Electrons and holes are trapped on reaction sites on the photocatalyst surface (10-100 ns for holes; about 100 ps for electrons). 3) Electrons are transferred to an adsorbed acceptor species (very slow, ms-range) while 4) Holes are transferred to an adsorbed donor species (about 100 ns).<sup>[104]</sup> Step 3) and 4) are almost simultaneous processes and represent the reduction and oxidation reaction on a semiconductor surface followed by the desorption of the reaction products. In case of a photocatalyst, the Fermi level principle cannot be used anymore because the Fermi level theory is only valid at thermodynamic equilibrium and fails for an explanation of the electron and hole densities under illumination.<sup>[99]</sup> In detail, under irradiation electron and hole densities cannot be described by the same Fermi level but by individual *quasi*-Fermi levels for

electrons (\* $E_{Fn}$ ) and holes (\* $E_{Fp}$ ), which are located in the vicinity of the conduction and valence band edge, respectively.<sup>[99]</sup> In an n-type or p-type semiconductor the majority charge carrier density does not change significantly under illumination. Therefore, the electron and hole *quasi*-Fermi levels are nearly at the same energy state as the Fermi level of an n-type and p-type semiconductor at equilibrium. Primarily, the concept of *quasi*-Fermi levels enables the description of the minority charge carrier density in the respective semiconductor type.<sup>[99]</sup>

The reduction by an excited electron (step 3) only occurs when the redox potential of the adsorbed species is more positive than  $*E_{Fn}$ . Contrary, holes migrate to redox potentials, which posses a more negative potential than  $*E_{Fp}$  (step 4). In conclusion, for the performance of a photocatalytic reaction the enclosure of the redox potentials of a specific reaction by the valence and conduction band of the photocatalyst is required (Figure 8).<sup>[107]</sup>



**Figure 8:** Band alignment and redox potential positions for the performance of a photocatalytic reaction (adapted from Hoffman et. al<sup>[104]</sup>. and Domen et. al.<sup>[107]</sup>).

The photocatalytic activity of a semiconductor is mainly limited by the number of electrons and holes on the photocatalyst surface. On the other hand, the number of charge carriers is limited by the recombination rate of the electron/hole pairs. After energy absorption and excitation into the conduction band, an electron can directly relax back into the valence band followed by heat emission (Figure 7b, step 5). The recombination process can also result in the emission of photons (Figure 7b, step 6). However radiative recombination of electron/hole pairs is fairly negligible for bulk photocatalysts. Recombination mainly occurs on so called trap states (Figure 7b, step 7), which are evidently present in a non-ideal crystal. Crystal defects as well as grain boundaries are typical trap states in a non-doped semiconductor. The time scale of recombination effects is not well defined for bulk photocatalysts and may vary between 10 - 100 ns, depending on the photocatalyst crystallinity.<sup>[104]</sup> Doping with foreign atoms creates additional trap states in the band structure and therefore increases the

probability for electron/hole pair recombination. Also increased charge carrier mobility by increased temperature or longer migrations paths caused by bigger particle sizes usually tend to higher recombination rates.<sup>[47, 102]</sup>

Photocatalytic reactions are divided in so called downhill and uphill reactions. The classification into the mentioned reaction groups depends on the change of the free Gibbs energy ( $\Delta G$ ) of the desired reaction. Photocatalytically driven degradation reactions often experience a negative change in  $\Delta G$  and hence are considered as downhill reactions, while the photon energy is only needed to overcome the activation energy. This reaction proceeds irreversible.<sup>[108]</sup> Energy storage reactions for the conversion of photon energy in chemical energy like the overall water splitting reaction are uphill reactions due to their positive change in  $\Delta G$ . Contrary, uphill reactions proceed reversible, due to the reactive reaction products.<sup>[108]</sup>

#### 3.2.1 Photocatalytic Hydrogen Production

Photocatalytic water splitting (Eq. 3.5 - 3.7)<sup>[13]</sup> for the production of solar H<sub>2</sub> is one main topic in the research field of heterogeneous photocatalysis beside the photocatalytic degradation of organic pollutants. As already mentioned, overall water splitting with a positive change in  $\Delta G^0$  of 237 kJ/mol is classified as an uphill reaction.<sup>[108]</sup> According to the potential positions for H<sub>2</sub> formation (H<sup>+</sup>/H<sub>2</sub> 0.0 V vs. NHE pH = 0) and water oxidation for O<sub>2</sub> production (O<sub>2</sub>/H<sub>2</sub>O 1.23 V vs. NHE pH = 0), a theoretical band gap of only 1.23 eV (1100 nm) is needed to run the overall water splitting reaction.<sup>[26]</sup> Nevertheless, the stated energy barrier describes only the thermodynamic boundary for the formation of H<sub>2</sub> and O<sub>2</sub>. Due to kinetic inhibitions like overpotenial phenomena and charge carrier mobility limitations, the water splitting reaction demands a larger spatial separation of the VB and CB from the respective redox potential.<sup>[106]</sup> Semiconductors with band gaps between 2.0 – 2.2 eV should be ideally used to overcome the kinetic barriers.<sup>[23]</sup>

$$H_2O + 2h^+ \rightarrow 2H^+ + \frac{1}{2}O_2$$
 (3.5)

$$2 \operatorname{H}^{+} + 2 \operatorname{e}^{-} \to \operatorname{H}_{2} \tag{3.6}$$

$$H_2O \rightarrow \frac{1}{2}O_2 + H_2$$
 (3.7)

Several semiconductors posses an adequate band alignment and band gaps for photocatalytic water splitting, as seen in figure 9.



**Figure 9:** Band alignment of different a) n-type and b) p-type semiconductors illustrated against the normal hydrogen electrode with respective  $H^+/H_2$  and  $H_2O/O_2$  redox potential.<sup>[98]</sup>

In spite of the apparently ideal electronic conditions for the formation of  $H_2$  and  $O_2$  from water, the known semiconductors to be capable to perform the overall water splitting reaction are extremely rare.<sup>[30]</sup> For example, CdS exhibits an appropriate band alignment for overall water splitting as well as a sufficient band gap energy for visible light absorption, as seen in figure 9a. Although CdS is not capable to perform the water splitting reaction and is further subjected to photocorrosion induced by VB holes forming elemental sulfur from the S<sup>2-</sup> anion.<sup>[26]</sup> Most semiconductors suffer from the inability of O<sub>2</sub> formation because the oxidation of water to form a single O<sub>2</sub> molecule requires the transfer of four electrons, which is hardly accomplished by the majority of semiconductor materials.<sup>[107]</sup> H<sub>2</sub> formation only requires a transfer of two electrons and therefore it is easier to perform. The usage of sacrificial agents for the investigation of each half-reaction of the overall water splitting reaction as well as their promotion by co-catalysts are common techniques to shift the reaction equilibrium towards the respective half-reaction.<sup>[26, 109-110]</sup>

#### 3.2.2 Role of Co-Catalysts on Semiconductor Surfaces

Metallic or metal oxidic co-catalysts are generally used for the enhancement of the charge carrier separation in a semiconductive material. The functionality of a co-catalyst for electron/hole pair separation can be explained by the formed junction between metal and semiconductor. The Schottky junction and the Ohmic contact describe two different states of a metal/semiconductor contact.<sup>[111]</sup> For the formation of a Schottky junction, a separated metal and n-type semiconductor has to be considered in the first place; charge neutrality of each component is assumed. Additionally, a specific alignment of the respective work functions and Fermi levels has to be fulfilled for a Schottky junction. The work function of the metal component  $\Phi_M$  in order to form a Schottky junction has to be larger than the semiconductor work function  $\Phi_{SC}$ , while the semiconductor (n-type) Fermi level  $E_{F(SC)}$  is located at a higher energy state than the Fermi level of the metal  $E_{F(M)}$  (Figure 10a).<sup>[111-112]</sup>

The semiconductor/metal contact causes an electron transfer from the semiconductor VB to the metal for charge equalization, leading to the equilibration of the involved Fermi levels. In the process of Fermi level equilibration,  $E_{F(M)}$  is shifted to a higher energy state. Upon the electron transfer, the semiconductor side exhibits an accumulation of positive charges, while an excess of electrons on the metal site is available.<sup>[101]</sup> Due to the charge induction on the semiconductor/metal interface, the VB and CB of the semiconductor are shifted upwards (band bending), forming a Schottky junction (Figure 10b). The resulting potential barrier of the band bending is described as the difference of  $\Phi_M$  and  $\chi_{SC}$ .<sup>[111]</sup> Band banding enables an easy electron migration from the semiconductor to the metal side, forming a so called depletion zone. This depletion zone induces a higher potential energy for excited electrons in the CB and promotes the electron transfer to the metal side. Minority charge carriers do not contribute in the charge carriers transport process in a Schottky junction.<sup>[101]</sup>

The Ohmic contact requires an opposite alignment of the respective work functions and Fermi levels.  $E_{F(M)}$  is located on a slightly higher energy state than  $E_{F(SC)}$ , while  $\Phi_{SC}$  is insignificantly bigger than  $\Phi_M$  (Figure 11a).<sup>[112]</sup> In contact,  $E_{F(M)}$  is shifted downwards as part of the Fermi level equilibration and electrons are transferred from the metal to the semiconductor side (Figure 11b).<sup>[112]</sup> The VB and CB of the semiconductor are shifted downwards and due to the electron excess on the semiconductor side a so called accumulation zone is formed and consequently an Ohmic contact is established.<sup>[101, 111]</sup>


**Figure 10:** Electronic structure of an n-type semiconductor and a metal a) before and b) after contact forming a Schottky junction (adapted from Fu et. al.<sup>[113]</sup> and Yan et. al.<sup>[112]</sup>.).



**Figure 11:** Electronic structure of an n-type semiconductor and a metal a) before and b) after contact forming an Ohmic contact (adapted from Yan et. al.<sup>[112]</sup>).<sup>[111]</sup>

Band alignment and work function difference for the formation of an Ohmic contact or Schottky junction in a p-type semiconductor are summarized in table 2.1.<sup>[114]</sup> Due to the low difference in work functions the Ohmic contact behaves like an Ohmic resistor and therefore allows a linear transition of charge carrier, contrary to a Schottky junction.<sup>[101]</sup> For this reason, the formation of an Ohmic contact is unfavorable in the application of heterogeneous photocatalysis. On the other hand, the Schottky junction enables the trapping of excited electrons on the metal side, promoting the reduction of an acceptor species.

Semiconductor	Fermi level alignment	Work function	Contact typ
n-type	$E_{F(SC)} > E_{F(M)}$	$\Phi_{\rm SC} < \Phi_{\rm M}$	Schottky
	$E_{F(SC)} < E_{F(M)}$	$\Phi_{\rm SC} > \Phi_{\rm M}$	Ohmic
p-type	$E_{F(SC)} > E_{F(M)}$	$\Phi_{\rm SC} < \Phi_{\rm M}$	Ohmic
	$E_{F(SC)} < E_{F(M)}$	$\Phi_{\rm SC} > \Phi_{\rm M}$	Schottky

 Table 2.1: Summary of metal/semiconductor contacts.

The difference in work function has a significant influence on the photocatalytic activity of a semiconductive material decorated with metal particles as co-catalysts. In general, large  $\Phi_M$ provide higher Schottky junctions and are more effective in electron trapping.<sup>[19]</sup> Photocatalytic performance tests revealed that noble metals like Pt, Au and Rh show higher activities in e.g. H<sub>2</sub> production due to their high work function values than earth abundant metals. More noble metals provide higher activities than less noble metals as in the stated order Pt > Au > Rh, basing on their respective work function.<sup>[115]</sup> Beside noble metal cocatalysts for H<sub>2</sub> evolution also metal oxides like IrO<sub>2</sub>, RuO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub> are well-known cocatalysts for O<sub>2</sub> evolution.<sup>[64, 67, 116]</sup> An ideal co-catalyst for the overall water splitting reaction should promote the formation of H<sub>2</sub> and O<sub>2</sub> and inhibit the backward reaction to H<sub>2</sub>O. The most prominent co-catalyst system for assisting water splitting are Rh<sub>2-v</sub>Cr<sub>v</sub>O<sub>3</sub> and the core/shell structured Rh/Cr<sub>2</sub>O<sub>3</sub> developed by Domen et al.<sup>[64]</sup> The efficiency of the Rh/Cr<sub>2</sub>O<sub>3</sub> co-catalyst mainly bases on the inhibited back reaction to  $H_2O$ . Rh is capped by a 2 nm thick Cr<sub>2</sub>O<sub>3</sub> passivation layer, which blocks the re-adsorption of O<sub>2</sub> on Rh, while showing a selective permittivity to protons and gaseous H<sub>2</sub>. Electrochemical analysis revealed that the selective permittivity of this passivation layer originates from a hydrated chromia layer of the form  $CrO_{(1.5-m)}(OH)_{2m} \cdot x H_2O$ .<sup>[106]</sup> Therefore,  $Cr_2O_3$  effectively prevents the reaction of H<sub>2</sub> and O<sub>2</sub> to H<sub>2</sub>O. In spite of the high activity of noble metals, this material class is too rare and expensive to be utilized as co-catalysts for large scale H<sub>2</sub> production. Earth abundant cocatalyst material like Co, Cu and Ni/NiO<sub>x</sub>, NiO<sub>x</sub> acts as a hole trap and not as a passivation layer, provide a cost effective alternative to noble metal co-catalysts.<sup>[106, 110, 117-118]</sup> Cu and Ni are also well-known H<sub>2</sub> evolution co-catalysts, while Co in form of Co-phosphate (CoPi)<sup>[118]</sup> is commonly used as an O2 evolution co-catalyst. Experimental results showed that nanoscaled metal co-catalyst particles of Cu and Ni lead to a high photocatalytic performance, which is comparable to noble metal particles. Nevertheless, to keep up with the performance of noble metal co-catalysts, higher loadings of the earth abundant metal are required. In spite

of the mentioned drawbacks, non-noble metals are three orders of magnitude cheaper than Pt and due to this circumstance more practicable for large scale application.<sup>[110]</sup>

## 3.2.3 Sacrificial Agents in Heterogeneous Photocatalysis

To get a complete overview of the reductive and oxidative capabilities of a photocatalyst in a specific redox reaction, the respective half reaction has to be blocked by the usage of a so called sacrificial agent.<sup>[119]</sup> To block one half reaction, the redox potential of the sacrificial agent has to exhibit a higher potential, in order to block e.g. H<sub>2</sub> formation or a lower potential to block e.g. O<sub>2</sub> formation (Figure 12).<sup>[32]</sup> Sacrificial agents are divided in inorganic and organic inhibitors.<sup>[13]</sup> The electrochemical redox potential position, relative to the photocatalyst band structure, of a sacrificial agent determines its functionality to act as an electron donor or electron acceptor. In detail, electron donating compounds are oxidized by holes, which are "refilled" in the process (Figure 12a). On the other hand, photo excited electrons are consumed by electron acceptor sacrificial agents, which are reduced during the scavenging process (Figure 12b).<sup>[26]</sup> The scavenging of one charge carrier leads to a reduced recombination rate and in conclusion to a higher quantum yield of the opposite electric charge and to an increased activity. The photocatalytic activity in the investigated half reaction is therefore subjected to the presence of the sacrificial agent. For this reason, the maintaining of a constant concentration of the sacrificial agent is crucial for a stable photocatalytic performance.<sup>[13]</sup>



**Figure 12:** Scavenging of a) holes by donor species and b) electrons by acceptor species (adapted from Cheng et. al.<sup>[19]</sup>).

The overall water splitting reaction for the production of clean solar  $H_2$  is mainly limited by the formation of  $O_2$ , which requires the transfer of four electrons. To inhibit the oxidation of

 $H_2O$  to  $O_2$ , organic compounds like alcohols, organic acids or hydrocarbons are used as electron donors for hole scavenging.<sup>[57, 61]</sup> Methanol is commonly used as a sacrificial agent for hole scavenging in the mean of photocatalytic  $H_2$  production.<sup>[69]</sup> The total oxidation of methanol to  $CO_2$  and water is not straight forward. The photocatalytic decomposition of methanol is a three step process with three corresponding intermediate products.<sup>[109]</sup> Each step results in the formation of one  $H_2$  molecule. In conclusion, the conversion of one methanol molecule results in the formation of three molecules of  $H_2$ . The proposed decomposition mechanism by Kawai et al.<sup>[120]</sup> (Eq. 3.8 - 3.11) reveals that the reforming of methanol is thermodynamically more favored, due to the formation of  $CO_2$  which represents a thermodynamic minimum, than the direct formation of  $H_2$  and  $O_2$  from  $H_2O$ .

$$CH_{3}OH (l) \xrightarrow{hv, TiO_{2}} HCHO (g) + H_{2} (g) \Delta G^{0} = 64.1 \text{ kJ mol}^{-1}$$
(3.8)

HCHO (g) + H<sub>2</sub>O (l) 
$$\xrightarrow{\text{hv, IIO}_2}$$
 HCOOH (l) + H<sub>2</sub> (g)  $\Delta G^0 = 47.8 \text{ kJ mol}^{-1}$  (3.9)

HCOOH (1) 
$$\xrightarrow{\text{hv,TiO}_2} \text{CO}_2(g) + \text{H}_2(g) \ \Delta \text{G}^0 = -95.8 \text{ kJ mol}^{-1}$$
 (3.10)

CH<sub>3</sub>OH (l) + H<sub>2</sub>O (l) 
$$\xrightarrow{hv, TiO_2}$$
 CO<sub>2</sub> (g) + 3 H<sub>2</sub> (g)  $\Delta G^0 = 16.1 \text{ kJ mol}^{-1}$  (3.11)

Methanol can be directly oxidized by VB holes or in an indirect way via interfacially formed hydroxyl radicals. Hydroxyl radicals are formed in two different ways: (1) By the trapping of holes by surface exposed OH-groups or (2) By direct oxidation of water. Direct or indirect methanol decomposition is determined by the dominant species adsorbed on the photocatalyst surface.<sup>[109]</sup> Experimental results by Wang et al.<sup>[121]</sup> revealed that a specific ratio between water and methanol has to be established to perform a direct or indirect methanol oxidation. A water/methanol ratio of around 300 leads to an indirect decomposition of methanol via hydroxyl radicals because of the low methanol concentration and the resulting H<sub>2</sub>O dominating surface species. Ratios lower than the stated value show that the predominant oxidation mechanism is processed by VB holes. The oxidation via hydroxyl radicals starts with the abstraction of a hydrogen atom on the C-H bond, creating a <sup>•</sup>CH<sub>2</sub>OH radical species. Under aerobic condition, formaldehyde is formed as the first stable intermediate product according to equation 3.8. In the absence of  $O_2$ , formaldehyde is formed by the injection of the free electron of <sup>•</sup>CH<sub>2</sub>OH into the CB.<sup>[13]</sup> In other words, the photo induced formation of formaldehyde causes an implementation of a second electron into the CB and therefore to an improved rate in H<sub>2</sub> production. This process is known as "photocurrent doubling".<sup>[122]</sup> These additional electrons are mainly trapped, in case of TiO<sub>2</sub>, by Ti<sup>4+</sup> site in the form of Ti<sup>3+</sup>, causing a blue discoloration of the photocatalyst suspension.<sup>[123]</sup> In the presence of a cocatalyst forming a Schottky junction with the photocatalyst, the formation of Ti<sup>3+</sup> sites is

hindered due to the electron trapping ability of the co-catalyst. Therefore, electron trapping co-catalysts act as active reaction sites for proton reduction and accordingly for  $H_2$  formation. Proton reduction on e.g. TiO<sub>2</sub> and Pt as co-catalyst is described by the Volmer reaction (Eq. 3.12-3.13) and two possible pathways given by the Heyrowsky (Eq. 3.14) and Tafel (Eq. 3.15) reaction.<sup>[13]</sup> A clear preference to one of the possible pathways is not known.

$$H_{ads}^{+} + e^{-}(Pt^{0}) \rightarrow H_{ads}^{\bullet}(Pt^{0})$$
(3.12)

$$H_2O_{ads} + e^{-}(Pt^0) \rightarrow H^{\bullet}_{ads}(Pt^0) + OH^{-}$$
(3.13)

$$H^{\bullet}_{ads}(Pt^{0}) + e^{-}(Pt^{0}) + H^{+}_{ads}(Pt^{0}) \rightarrow H_{2}(g)$$
(3.14)

$$H^{\bullet}_{ads}(Pt^{0}) + H^{\bullet}_{ads}(Pt^{0}) \to H_{2}(g)$$
(3.15)

The mentioned methanol oxidation mechanisms were investigated on  $TiO_2$  or  $TiO_2/Pt$  and cannot be used as a formalism for the description of methanol decomposition reactions on other photocatalyst materials due to their difference in surface states and adsorption capabilities. Despite of the effective photocatalytic conversion of methanol to H<sub>2</sub>, the utilization of methanol as a sacrificial agent is from the environmental and economic point of view inconvenient, because of its toxicity and high production costs. An appropriate sacrificial agent should be non-toxic in the mean of environmental issues as well as for the photocatalytic system, cheap, sustainable and should provide high conversion rates for H<sub>2</sub> production.

Inorganic sacrificial agents like sulfides (S<sup>2</sup>) or sulfites (SO<sub>3</sub><sup>2-</sup>) are also used as hole scavengers to support the photocatalytic formation of H<sub>2</sub>.<sup>[124]</sup> But inorganic sacrificial agents are rather used as electron acceptors for photocatalytic H<sub>2</sub>O oxidation to form O<sub>2</sub>. Silver cations Ag<sup>+</sup> are the most prominent used electron acceptor for the investigation of the O<sub>2</sub> formation capabilities of a photocatalyst.<sup>[26]</sup> The reduction of Ag<sup>+</sup> during the electron scavenging process leads to the deposition of metallic Ag nanoparticles on the photocatalyst surface, which can also act as an electron trapping co-catalyst Therefore, the usage of Ag<sup>+</sup> as an electron scavenger leads to a significant change in the chemical and/or photochemical properties of a photocatalytic system. Instead of using Ag<sup>+</sup>, the formation of O<sub>2</sub> can be observed in the presence of ferric ions Fe<sup>3+</sup> or iodate ions IO<sub>3</sub><sup>-</sup>, too.<sup>[107]</sup> These sacrificial agents are reduced to Fe<sup>2+</sup> and  $\Gamma$  respectively. But the IO<sub>3</sub><sup>-</sup> anion decomposes under irradiation with UV light while the decomposition products counter react with H<sub>2</sub>O, therefore IO<sub>3</sub><sup>-</sup> has to be constantly refreshed during the test procedure.<sup>[125]</sup> Also the reduced Fe<sup>2+</sup> ion can be re-oxidized by VB holes to Fe<sup>3+</sup>. For this reason, ferric ions are used as so called redox transfer mediators in a Z-scheme photocatalytic system.<sup>[19]</sup>

## 3.3 Band gap Engineering by Ion Doping

Transition metal oxides, which are frequently used as photocatalysts, possess usually band gap energies larger than 3.0 eV and are therefore exclusively active under UV light irradiation.<sup>[30]</sup> Unfortunately, the incident solar spectrum on earth surface contains only 5% UV light.<sup>[126]</sup> For a more effective utilization of the incoming solar energy for photocatalytic applications, the band gap energy of a metal oxide photocatalyst has to be reduced in a range of  $2.0 \le E_g \le 3.0$  eV for visible light absorption. Several methods like anion- and cation doping, formation of semiconductor composites respectively coupling of different semiconductor materials, dye sensitization as well as noble metal sensitization are common methods for band gap reduction or for visible light harvesting.<sup>[127]</sup> Noble metal sensitization resembles a special case of visible light active photocatalysts and is not discussed in this thesis.<sup>[128]</sup> Direct band gap engineering is mainly realized by anion- and cation doping and enables a controllable band gap modification.

Anion doping is executed through the incorporation of main-group elements like boron, carbon, fluorine, nitrogen or sulfur into the crystal lattice of a semiconductor material.<sup>[129]</sup> The inserted foreign ions substitute lattice oxygen sites and crystal vacancies in the metal oxide structure.<sup>[130]</sup> The hybridization of the O 2p orbitals of the metal oxide and the respective 2p orbitals of the incorporated doping element leads to an upwards shift of the VB edge to a higher energy state or to a more negative potential respectively and consequently to a reduced band gap.<sup>[131]</sup> The CB is unaffected by anion doping. Nitrogen doping is the most prominent technique for anion doping. During the nitrogen doping process under ammonia atmosphere, one oxygen anion  $(O^{2-})$  is substituted by one nitrogen anion  $(N^{3-})$ . The substitution of  $O^{2-}$  by N<sup>3-</sup> leads to an increased formation of crystal defects to maintain charge neutrality.<sup>[126]</sup> Unfortunately, crystal defects act as recombination centers for excited electron/hole pairs and lead to a decreased photocatalytic performance. A thermal aftertreatment under O2 atmosphere or an additional co-doping, e.g. with fluorine is inevitable to decrease the number of crystal defects and to maintain the activity level of the un-doped photocatalyst.<sup>[49]</sup> An inhomogeneous distribution of the doping element induces selective absorption region throughout the photocatalyst material, reduces the light absorption capabilities and influences the charge carrier mobility due to the created trap states. An open layered crystal structure supports a homogeneous distribution of the doping agent, e.g. ammonia gas can easily invade the bulk structure and results in a complete shift of the absorption edge into the visible light region.<sup>[126, 132]</sup> Adverse knock-on effect of anion doping is the loss of certain oxidation

capabilities compared to the corresponding un-doped photocatalyst due to the VB shift to a more negative potential (Figure 13a).



**Figure 13:** Schematic electronic band structure of  $TiO_2$  after a) nitrogen doping (adapted from Liu et. al.<sup>[133]</sup>) and b) after doping with  $M^{n+}$  cations (adapted from Merka et. al.<sup>[134]</sup>).

The creation of impurity states in the band gap of a semiconductor can also be realized by the incorporation of metal cations instead of non-metal anions. The choice of an appropriate doping cation depends on the ionic diameter of the semiconductor host cation, e.g. Ti<sup>4+</sup> for TiO2<sup>[135]</sup>. Metal ions from 3d transition metals like chromium, manganese, iron, cobalt, niobium and copper are commonly used as doping agents for TiO<sub>2</sub> due to their analogous ionic diameter to Ti<sup>4+</sup>.<sup>[44, 136-141]</sup> Unlike to non-metal anion doping, which causes an upwards shift of the VB due to the hybridization of the involved 2p orbitals, metal cation doping of a metal oxide semiconductor can form electron donor and acceptor impurity states in the semiconductor band gap. To serve as an electron donor or acceptor depends on the energetic position and electronic configuration of the octahedral splitting ( $\Delta_{oct}$ ) of the respective MO<sub>6</sub> octahedron (M = transition metal) in the crystal lattice of the metal oxide semiconductor (Figure 13b).<sup>[134]</sup> Umebayashi et. al.<sup>[142]</sup> investigated the electronic structure of transition metal doped TiO<sub>2</sub> by ab initio band calculations and revealed that cation doping creates an occupied level either in the band gap, in the vicinity of the VB, or in the VB itself due to the  $t_{2g}$  energy state of the doping agent.<sup>[19]</sup> The electron transfer from the occupied  $t_{2g}$  level, which is located in the band gap and is acting as an electron donor, into the CB mainly contributes to the reduced band gap energy, while the eg level, located below the CB, mainly serves as an electron acceptor and contributes to a lowered excitation energy if the  $t_{2g}$  level is energetically located in the VB. Because of their specific  $\Delta_{oct}$  in the TiO<sub>2</sub> lattice, metal cations like Fe<sup>3+</sup> and

 $Mn^{3+}$  acts simultaneously as electron donors as well as electron acceptors. In detail, these metal cations are capable of an energetic separation or trapping of electrons and holes.<sup>[134]</sup> For example, the trapping of an electron and hole by Fe<sup>3+</sup> results in a oxidation state change to Fe<sup>2+</sup> and Fe<sup>4+</sup>, respectively. Fe<sup>2+</sup> and Fe<sup>4+</sup> are relatively unstable oxidation states compared to Fe<sup>3+</sup>, according to the crystal flied theory, and therefore these localized charge carriers are easily transferred to adsorbed surface species to restore the half-filled electronic configuration of Fe<sup>3+,[143]</sup> The stated electronic alignment of the t<sub>2g</sub> and e<sub>g</sub> levels in the TiO<sub>2</sub> lattice effectively decreases the recombination rate of electron/hole pairs. Metal cation doping is mainly executed by solid state reaction, sol-gel process, hydrothermal synthesis, impregnation or precipitation. To ensure an effective incorporation and homogeneous distribution of the metal cation in the semiconductor crystal lattice, aqueous synthesis methods as the sol-gel process and hydrothermal synthesis should be utilized.<sup>[96]</sup>

However, the doping process is a complex procedure of additional factors beside the delectronic configuration, energy level position and chosen synthesis method. Also the doping concentration and the doping element distribution must be put into consideration. High doping concentrations and an inhomogeneous distribution of metal cations have adverse effects like the formation of recombination centers, decreased mobility and lifetime of minority charge carriers and lead in conclusion to a reduced photocatalytic activity. The adjustment of the ideal doping element concentration is essential to establish a balance between a high photocatalytic performance and band gap reduction for visible light absorption.<sup>[47]</sup>

# 3.4 Coupled Semiconductors: Photocatalyst Composites

To overcome the major drawbacks of crystal defect and impurity state formation by metal and non-metal doping, the association of two or more semiconductor materials represents an alternative strategy to increase the photoresponse of a photocatalytic system and to improve the electron/hole separation.<sup>[97]</sup> The association of multiply semiconductors is classified in coupled and capped semiconductors.<sup>[96]</sup> The following explanations are related to coupled semiconductor systems while capped systems are bide outside. Coupled semiconductors are further subdivided in three different types which are illustrated for a two semiconductor system in figure 14.<sup>[98]</sup>

A type I heterojunction is formed by the coupling of a narrow band gap semiconductor, stated as semiconductor A and a wide band gap semiconductor, entitled with B. The VB and CB edges of semiconductor A in a type I photocatalyst composite are located in the forbidden zone of semiconductor B. In detail, CB and VB of semiconductor A are positioned at lower and higher energy, respectively, compared to the CB and VB of semiconductor B. If a sufficient contact between these semiconductors is established, the formed heterojunction leads to a transfer of photogenerated electrons and holes in semiconductor B to the CB and VB of semiconductor A. In conclusion, all produced charge carriers are accumulated on semiconductor A and recombine. An effective electron/hole pair separation is not given in a type I composite. An efficient charge carrier separation is present in a band alignment as shown for a type II photocatalyst composite. Photoexcited electrons in semiconductor B are transferred from CB(B) to CB(A) while the analogous holes are "trapped" in the VB(B). On the other hand, generated holes in the VB(A) are transferred to the VB(B) while electrons in CB(A) are unable to move to CB(B). If the mechanism of charge carrier transport bases on a direct injection into the opposite band because of the beneficial band positions or on the band bending at the interface inducing an internal electric field is still not clarified.<sup>[98]</sup> Nevertheless, such band alignment enables a spatial separation of electron/hole pairs in both participating semiconductors. For visible light utilization, in case of a type II composite, semiconductor B should provide a narrow band gap to be activated by light with higher wavelengths. A type III semiconductor composite can be seen as an extreme case of type II, while the VB(B) edge is located above the CB(A) edge. Such band alignments are called broken-gap situations and prevent an efficient electron/hole pair separation.<sup>[98, 133]</sup>



Figure 14: Three types of coupled semiconductors (adapted from Marshall et. al.<sup>[98]</sup>).

In photocatalysis only type II semiconductor composites are of practical interest due to their charge carrier separation ability. Prominent examples for type II composites are CdS/TiO<sub>2</sub><sup>[97]</sup> and ZnS/ZnO<sup>[144]</sup> as well as mutiphase composites like  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub><sup>[145]</sup> and anatase/rutile (TiO<sub>2</sub>), which is known as P25<sup>[146]</sup>.

## 3.5 Photocatalytic Semiconductors

Binary d-transition metal oxides like TiO<sub>2</sub>, ZnO, WO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> resemble the most prominent photocatalysts for photocatalytic water splitting and photocatalytic degradation of organic pollutants.<sup>[96, 147-150]</sup> Since the discovery of its photocatalytic abilities by Fujishima and Honda in 1972,<sup>[29]</sup> TiO<sub>2</sub> is evidently the most investigated and used photocatalyst due to its non-toxicity, insolubility in water, low costs, stability against photocorrosion and high photocatalytic activity under UV light irradiation. ZnO is the second most researched photocatalyst next to TiO<sub>2</sub> and has similar physical and chemical properties.<sup>[96]</sup> Photocorrosion and instability in acidic media are the major drawbacks of ZnO. WO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> are known visible light active photocatalysts, which are mainly used for photocatalytic degradation reactions and O<sub>2</sub> formation.<sup>[148-150]</sup> Beside the stated metal oxides, also other metal chalcogenides are used as photocatalysts. Metal sulfides are also well investigated photoactive semiconductors due to their reduced band gap compared to their oxidic counterpart, e.g.  $CdS^{[151]}$  and  $MoS_2^{[152]}$ . Despite of the ability of visible light harvesting, CdS and other metal sulfides suffer from photocorrosion and consequently from a time depended decrease of their photocatalytic performance lifetime.<sup>[96, 143]</sup> Photocorrosion in case of CdS originates from a self-oxidation of the  $S^{2-}$  anion induced by photogenerated holes, caused by a disadvantageous band alignment (CB: -0.75 V vs. NHE; VB: 1.75 V vs. NHE) towards the (S<sup>2-</sup>/S) redox potential (-0.45 V vs NHE).<sup>[13]</sup> The structural variety of ternary metal oxides like ferrites, niobates, tantalates and titanates provide a great potential in the modification of their electronic and optical properties.<sup>[19]</sup> For example niobates, tantalates and titanates possess a layered perovskite structure, which can be modified by anion and cation doping as mentioned in the previous chapter 3.3. Furthermore, SrTiO<sub>3</sub> and KTaO<sub>3</sub> are known photocatalysts for overall water splitting.<sup>[30, 117]</sup> Ouaternary photocatalysts are mainly accessible through the sulfonation or nitration of ternary metal oxides or the formation of mixed metal oxides.<sup>[96]</sup>

# **3.5.1 Layered Titanates**

Layered titanates with perovskite<sup>[153]</sup> and lepidocrocite ( $\gamma$ -FeOOH)<sup>[54]</sup> type structure are of great interest due to their attractive applications in photocatalysis<sup>[42]</sup>, photoelectrochemistry<sup>[15]</sup> and lithium storage<sup>[84]</sup>. Perovskite type layered titanates with chemical formula, e.g. ALa<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> (A = Ca, Sr, Ba) or La<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> are known photocatalysts for photocatalytic water splitting.<sup>[153]</sup> The structural stability of perovskite type layered titanates enables a great variation of its chemical composition, e.g. through the insertion of different transition metal ions.<sup>[44, 154]</sup> Lepidocrocite type layered titanates show also great structural stability to

accommodate 3d transition metal ions by the substitution of titanium sites or anion doping by oxygen substitution.<sup>[42, 83]</sup> This material class comprise a large class of isomorphous compounds with the general composition  $A_x Ti_{2-v} M_v O_4$ , with x = 0.7, 0.75, 0.8 for A = K, Cs or Rb and where M represents vacancy sites or Li, Mg, Zn, Cu, Co, Ni, Sc, Al, Fe(II), Fe(III), Mn(III).<sup>[54]</sup> Structurally, lepidocrocite layered titanates consist of two-dimensional corrugated single titanium oxide sheets, which are built up by edge and corner shared  $TiO_6$  octahedra.<sup>[155]</sup> The titanium oxide sheets are spatially separated by alkali ions, which compensate the negative charge of vacancy sites and transition metal modified or unmodified titanium oxide layers.<sup>[38]</sup> Furthermore, layered titanates are ideal raw materials for the synthesis of titanium oxide nanosheets.<sup>[156]</sup> Practically, the interlayer alkali ions are exchanged by protons in acidic media.<sup>[55]</sup> Afterwards the proton exchanged layered titanate is exfoliated by bulky organic bases like tetrabutylammonium hydroxide through the induction of shear forces.<sup>[132]</sup> The resulting nanosheets have notable two-dimensional abilities and anisotropic properties, representing ideal building block units for the construction of artificial nanostructures with controllable functionalities, e.g. through the sequential electrostatic deposition of single titanate nanosheets from a colloidal suspension on top of a conductive substrate.<sup>[156]</sup> Delaminated titanate nanosheets show also improved photocatalytic activities, which can be mainly referred to the increased surface area compared to the respective bulk material.<sup>[151]</sup> Contrary, the single nanosheets suffer from larger band gap energies due to the effecting quantum confinement effect which arises from the reduced orbital overlap induced by the exfoliation process.<sup>[156]</sup> Despite of the nanosheet formation, the interlayer alkali ions can be exchanged by a variety of inorganic or organic cations, in terms of the utilization of visible light by band gap reduction.<sup>[39, 79]</sup> In addition to the modification probabilities of this material class, photocatalysts with a layered structure have also shorter diffusion pathways for photogenerated charge carriers and show an improved electron/hole pair separation compared to bulk photocatalysts.<sup>[156]</sup> The separated charge carriers are isolated on their respective reduction and oxidation centers on the surface and/or the edges of the titanate nanosheets. Adsorbed species, which diffuse into the interlayer like H<sub>2</sub>O or small organic compounds, react with the isolated charge carriers.

Among the layered titanate compounds, the cesium titanate  $Cs_{0.68}Ti_{1.83}\square_{0.17}O_4$  ( $\square$  = vacancy) (Figure 15a) has to be specially mentioned. Due to its unique interlayer chemistry caused by the bulky  $Cs^+$ , the layered cesium titanate is often used as a starting material for the mentioned titanate nanosheet synthesis.<sup>[155]</sup> But  $Cs_{0.68}Ti_{1.83}\square_{0.17}O_4$  also attracts attentions because of its photocatalytic activity in the degradation of organic pollutants and the

modification probabilities.<sup>[35, 43]</sup> Cs<sub>0.68</sub>Ti<sub>1.83</sub> $\Box_{0.17}O_4$  crystallizes in an orthorombic unit cell with lepidocrocite ( $\gamma$ -FeOOH) type structure and *Immm* symmetry, with cell dimensions of a = 3.83 Å, b = 17.0 Å and c = 2.96 Å.<sup>[38, 83]</sup> Ti sites are surrounded by O1 (four-coordinated O atom) and O2 (two-coordinated O atom) atomic planes, forming a corrugated TiO<sub>6</sub> octahedral layer (Figure 15b).<sup>[38]</sup>



**Figure 15:** a) Polyhedral representation of the crystal structure of  $Cs_{0.68}Ti_{1.83}O_4$  viewed along the c-axis of the orthorhombic unit cell and b) atom coordination in the layered cesium titanate.<sup>[38]</sup>

According to the single crystal refinement by Gray et. al.<sup>[157]</sup> of  $Cs_{0.68}Ti_{1.83}\square_{0.17}O_4$ , the layered cesium titanate contains disordered titanium vacancies throughout the corrugated titanate sheets, which are separated by Cs<sup>+</sup>. These titanium vacancies form the basis for further cation modifications of the crystal structure and thus of the electronic and optical properties of the layered cesium titanate. Several transition metal cations with a similar ionic diameter like Ti<sup>4+</sup>, can be incorporated into the titanium vacancies, e.g. for band gap reduction The theoretical amount of 0.17 stoichiometric equivalents of vacancies limits the doping content of the metal cation. Higher doping concentrations may cause the formation of transition metal oxide cluster of the respective doping agent. Beside of cation incorporation into the titanium vacancies, the open layered structure of  $Cs_{0.68}Ti_{1.83}\square_{0.17}O_4$  offers also good conditions for nitrogen incorporation via ammonia gas.<sup>[132]</sup> The bulky Cs<sup>+</sup> enables an easy infiltration of the bulk structure by the ammonia gas and provides a homogeneous distribution of nitrogen throughout the material. Experimental results from Liu et. al.<sup>[42]</sup> showed a complete shift of the absorption edge into the visible light region by nitrogen doping to an extent from 3.6 eV of un-doped Cs<sub>0.68</sub>Ti<sub>1.83</sub>□<sub>0.17</sub>O<sub>4</sub> down to 2.73 eV. But, depending on the chosen synthesis

method, synthesis conditions and element composition, the interlayer spacing varies between 1.5 - 1.85 nm,<sup>[41, 151, 158]</sup> which probably influences the diffusion length of the doping agent gas into the bulk structure. Nevertheless, the complex variations of possible doping compositions open a multitude of different applications for  $Cs_{0.68}Ti_{1.83}\square_{0.17}O_4$  beside photocatalysis, e.g. nanostructured solar cells, photoelectrochemistry and lithium storage.

# 3.6 Synthesis Methods

The chosen synthesis method has a decisive influence on the subsequent photocatalyst morphology and consequently a major effect on the photocatalytic activity of the semiconductor material.<sup>[43, 80, 159-160]</sup> The photocatalytic activity is mainly attributable to the crystallinity, particle size and particle shape of the semiconductor powder. Low crystallinity implies a high degree of crystal defects, which are acting as recombination centers for electron/hole pairs and therefore responsible for a lowered photocatalytic activity.<sup>[26]</sup> Particle size and shape have a direct effect on the photocatalyst surface area and diffusion paths for photogenerated charge carriers. Large photocatalyst particles provide smaller surface areas and longer diffusion lengths, which increases the probability of electron/hole pairs to be trapped on crystal defects or grain boundaries. The particle shape controls the exposition of crystal facets on the outer particle surface.<sup>[49, 161]</sup> In conclusion, an ideal morphology for a photocatalytic material should include small, but highly crystalline particles, for high surface areas and low degree of crystal defects, with exposed active crystal facets. The classic solid state reaction (SSR) is commonly used for the synthesis of highly crystalline photocatalysts.<sup>[162]</sup> Due to the slow diffusion rate of solid materials, the SSR requires high calcination temperatures and long reaction times to overcome these limiting factors and to ensure a complete conversion of participating reactants. The required reaction conditions for the SSR generally lead to the formation of large particles and therefore to low surface areas.<sup>[54]</sup> Hydrothermal or solvothermal synthesis and sol-gel processes enable the production of small and highly crystalline photocatalyst particle at mild reaction conditions.<sup>[41, 163]</sup> Specially, the sol-gel process is of high practical interest due to its adjustable reaction parameters like the nature of precursors, reactant concentrations, pH value, reaction temperature and time, gel aging temperature and time and the addition of organic additives.<sup>[96]</sup> The advantage of the sol-gel process is the homogeneous distribution of metal ions at molecular scale. For this reason, the sol-gel method represents a promising synthesis technique for the production of metal and non-metal doped photocatalysts. Beside the mentioned synthesis methods also the sonochemical<sup>[164-165]</sup> and microwave method<sup>[85, 166]</sup> as well as the chemical and physical vapor deposition (CVD and PVD)<sup>[159, 167]</sup> and the electrochemical deposition<sup>[160, 168]</sup> are known synthesis techniques for the production of semiconductor nanoparticles.

## 3.7 Fundamentals of Photoelectrochemistry

Photoelectrochemistry is a related research field to heterogeneous photocatalysis and electrochemistry and deals with the interaction of light with photoactive electrodes. Since the discovery of the Becquerel effect, which resembles the first photoelectrochemical experiment performed by Henri Becquerel in 1839<sup>[169]</sup> and the followed works in the middle of the 20<sup>th</sup> century by Brattain and Garret<sup>[170]</sup> and Boddy<sup>[28]</sup>, photoelectrochemistry became one promising application for solar energy conversion. Photoelectrochemical measurements are generally performed in a three electrode system consisting of a working, reference and counter electrode (Figure 16).<sup>[101]</sup> The working electrode is made of a photocatalyst, which has been immobilized on an electric conductive glass or metal substrate. A reference electrode is characterized by a constant equilibrium potential, which can be reproducibly adjusted and serves as a reference value for performed measurements. The counter electrode is mainly a noble metal like platinum and acts as an electron acceptor. All three participating electrodes are arranged in an electrolyte solution.<sup>[99]</sup>



Figure 16: Flow chart of a three electrode photoelectrochemical cell (adapted from Beranek et. al.<sup>[102]</sup>).

The model of Gerischer has to be considered for the explanation of the semiconductor/electrolyte interface.<sup>[102, 169]</sup> This model allows the description of the reduction and oxidation species of a redox system by occupied and unoccupied energy states

(Figure 17a).<sup>[99]</sup> When a semiconductor is brought in contact with an electrolyte, the thermodynamic equilibrium on both sides of the interface has to be established.<sup>[99]</sup> In detail, the Fermi level of e.g. an n-type semiconductor is adjusted to the electrolyte Fermi level, which is described by the electrolyte redox potential. In the course of Fermi level equilibration, electrons from the semiconductor side are transferred to the electrolyte, which causes a depletion of majority charge carriers in the semiconductor. The equilibration process causes an excess of negative charges in the electrolyte and an increased number of positive charges in the semiconductor.<sup>[169]</sup> After equilibration where no net charge flow occurs anymore, a further electron transfer to the electrolyte is suppressed and a so called space charge layer is formed (Figure 17b).<sup>[101]</sup>



Figure 17: Schematic energy model of the n-type/electrolyte interface a) before and b) after the establishment of equilibrium.<sup>[99]</sup>

Due to the new charge distribution in the equilibrated semiconductor/electrolyte interface, the band structure is bended upwards for an n-type semiconductor or bended downwards for a p-type semiconductor.<sup>[171]</sup> The height of the band bending can be seen as the energy difference between the CB edges in the bulk and at the surface of the semiconductor and is related to the potential drop in the space charge layer.<sup>[101]</sup> Furthermore, an additional charged layer is present in the electrolyte adjacent to the semiconductor interface and is known as Helmholtz

layer. The presence of the Helmholtz layer markedly affects the band bending of the semiconductor, which is in contact with the electrolyte and causes an additional potential drop. <sup>[169]</sup> The effect of the Helmholtz layer is similar to the previously discussed Schottky junction (Chapter 3.2.2), where the potential barrier and band bending are strongly influenced by the presence of semiconductor surface states.<sup>[169]</sup>

The conditions in a photoeletrochemical cell enable a detailed characterization of the (photo)electronic properties of a semiconductor material. For example, the determination of the flatband position can be realized via capacitance measurements by the compensation of the band bending by an applied voltage or the quantification of photoactivity is performed by incident photon-to-current efficiency (*IPCE*) measurements.<sup>[122]</sup>

# **4** Experimental

The following chapter presents a detailed overview of the utilized synthesis methods for photocatalyst preparation and provides a theoretical background of the used characterization methods. A description of the photocatalysis and photoelectrochemical setups and the respective experimental procedure is given at the end of this chapter.

## 4.1 Preparation of Mixed Metal Oxides

Unmodified and transition metal modified layered cesium titanates were synthesized by an aqueous Pechini sol-gel process.<sup>[53]</sup> The photocatalysts, obtained from the sol-gel process, are formally seen as a support material for the deposition of noble and non-noble metals. The metal deposition on top of the photocatalyst surface is executed by two different methods, via i) wet impregnation and ii) photodeposition. All preparation methods, except the photodeposition technique, provide only photocatalyst precursors, which have to be activated under experimental conditions.

## 4.1.1 Sol-gel process

For the preparation of each mixed metal oxide, a ratio of 1 : 1.05 : 1.5 was adjusted between metal cations to ethylendiaminetetraacidic acid (EDTA) and citric acid mono hydrate.<sup>[52]</sup> The used quantities for the synthesis of unmodified  $Cs_{0.68}Ti_{1.83}O_4$  are exemplary summarized in table 4.1. All additional synthesis approaches for the preparation of the corresponding transition metal modified layered cesium titanates are summarized in the appendix in table A1-A11.

	molar mass /	density /	mass /	volume /	molar amount /
	(g/mol)	$(g/cm^3)$	g	mL	mmol
CsNO <sub>3</sub>	194.91	3.7	1.36		7
Ti(O-nBu) <sub>4</sub>	340.32	0.99	6.47	6.53	19
EDTA	292.25	0.86	7.98		27.3
$C_6H_8O_7\cdot H_2O$	210.14	1.67	8.2		39
Cs <sub>0.68</sub> Ti <sub>1.83</sub> O <sub>4</sub>	242		2.35		9.7

**Table 4.1:** Synthesis of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> by sol-gel process.

The cesium precursor amount was kept constant at 7 mmol for each synthesis approach. Basing on the stoichiometric formula of the layered cesium titanate and relative to the fixed cesium content, a 3% excess of the titanium precursor was used in order to prevent the formation of undesired cesium titanate compounds and hence to achieve full phase purity. All precursor solutions, containing the respective metal cation, were freshly prepared for each synthesis. Solid precursors were stored dry in sealed vessels in order to prevent any moisture contamination. The liquid titanium precursor was stored dry at low temperatures to inhibit a hydrolysis reaction, which causes the formation of TiO<sub>2</sub>. A schematic representation of the single synthesis steps are illustrated in figure 18.



Figure 18: Synthesis scheme of sol-gel process (adapted from Schwertmann et. al..<sup>[90]</sup>)

The complexing agents EDTA and citric acid mono hydrate were dissolved in a basic mixture of deionized water and ammonia hydroxide solution, containing 580 mL water and 18.5 mL 33% ammonia hydroxide solution. Afterwards, the pH-value of the complexing agent containing solution was re-adjusted down to pH = 5 with 7.5 mL of 65% nitric acid (HNO<sub>3</sub>). The complexing agents stayed in solution. A low pH-value was necessary to inhibit an early precipitation of the metal cation precursors in form of their respective metal hydroxides. A fixed amount of cesium nitrate (CsNO<sub>3</sub>) was dissolved in 50 mL of water. In case of transition metal modified cesium titanate, the respective metal nitrate salt was dissolved in 50 mL water in a separate vessel. Titanium(IV)-n-butoxide (Ti(O-nBu)<sub>4</sub>), which was utilized as a titanium source, was also separately dissolved in 240 mL of absolute ethanol in a sealed PET bottle and stirred for 0.5 h to ensure a complete dissolution of the respective metal nitrate solution into the solvent. After the insertion of the dissolved CsNO<sub>3</sub> and the respective metal nitrate solution into the

complexing agent solution, Ti(O-nBu)<sub>4</sub> was slowly added to the mixture. The clear solution was evaporated at 100 °C down to a total volume of 25 mL, resulting in a yellow gel in case of the unmodified cesium titanate. The gel color can differ, depending on the additionally inserted transition metal cation. The residual gel was transferred into a ceramic basin and annealed at 450 °C in a heating mantle. The annealing process led to the decomposition of the complexing agents and the respective metal precursor anion, forming a carbon contaminated solid photocatalyst precursor. The amorphous photocatalyst precursor was calcined in a furnace under atmospheric conditions for 10 h in a temperature range between 500 - 800 °C with a heating rate of 1 K/min and a subsequent cooling rate of -2 K/min in order to decompose all carbon contamination and to receive a crystalline photocatalyst material.

### 4.1.2 Wet Impregnation

Wet impregnation is generally used in the preparation of heterogeneous catalysts, in terms of metal precursor deposition on a support material with a high inner surface area. This preparation method enables a simple deposition of different transition metals even at high concentrations on a support. For the impregnation process, a metal salt, containing the metal cation and an easy decomposable anion, will be dissolved in an aqueous medium with a total volume corresponding to the pore volume of the mesoporous support. The support will be imbued with the metal salt solution, that all pores are completely filled with the metal precursor. A subsequent drying step, in order of solvent evaporation, can affect the metal distribution on the support. Further calcination of the dried catalyst precursor is required for the decomposition of the metal salt anion, which implies the formation of the corresponding metal or metal oxide. A drawback of the wet impregnation method is an inhomogeneous distribution of the deposited metal on the support surface, caused by different surface states, which guide a preferential deposition.<sup>[172-173]</sup>

The wet impregnation method was used for the deposition of a co-catalyst precursor on the surface of  $Cs_{0.68}Ti_{1.83}O_4$ . Photocatalyst materials synthesized by an aqueous Pechini sol-gel process (Chapter 4.1.1) do not possess any ordered or disordered mesoporous structure and therefore exhibit no inner surface area. The solvent content was fixed to a volume of 3 mL to ensure a complete moistening of  $Cs_{0.68}Ti_{1.83}O_4$  with the dissolved metal salt. The adjusted solvent volume is also required to ensure a complete dissolving of the metal salt in a defined concentration range. The wet impregnation process scheme is presented in figure 19.

For each wet impregnation approach, 550 mg of unmodified  $Cs_{0.68}Ti_{1.83}O_4$ , calcined in a temperature range of 600 – 800 °C, were transferred in a 100 mL flask. A defined amount of  $CuSO_4 \cdot 5 H_2O$  or  $HAuCl_4 \cdot 3 H_2O$  were dissolved in 3 mL of deionized water and afterwards slowly dropped on the  $Cs_{0.68}Ti_{1.83}O_4$  powder. For a homogeneous distribution of the used metal salt, the moistened photocatalyst was rotated for 30 min in a water bath tempered at 40 °C. Water evaporation was executed in a rotating evaporator at a bath temperature of 40 °C and a pressure of 70 mbar. The received photocatalyst precursor was dried in a drying chamber at 100 °C for 24 h, in order to remove residual water. The dried photocatalyst precursor was transferred in a crucible and calcined in a furnace under atmospheric conditions at 450 °C for 2 h,<sup>[174]</sup> with an applied heating and cooling rate of 5 K/min and –5 K/min, respectively.



Figure 19: Process scheme for wet impregnation.

#### 4.1.3 Photodeposition of noble and non-noble metals

The photodeposition technique represents the standard method in heterogeneous photocatalysis for the formation of metal nanoparticles on the photocatalyst surface. Formation of metal nanoparticles via photodeposition requires a specific band alignment of the semiconductor material towards the redox potential of the respective metal or metal oxide. The respective redox couple has to be located in the forbidden zone of the semiconductor to fulfill the thermodynamic condition for photodeposition. During the photocatalytic process (Chapter 3.2), photoexcited electrons are trapped at the respective M<sup>x+</sup>/M redox potential, reducing the metal cation into its metallic state.<sup>[58]</sup> Therefore the photodeposition method is considered as an in-situ deposition technique. The formed Schottky contact, due to the

semiconductor/metal contact, leads to a transfer of photoexcited electrons from the semiconductor CB to the metal side of the junction. Deposited metal nanoparticles act as electron acceptors and can be considered as new reaction sites for a photocatalytic reduction reaction. In other words, the in-situ photoreduction of metal cation by photoexcited electrons has the advantage that the co-catalyst particles are directly placed on active reaction sides of the photocatalyst surface.<sup>[59]</sup> The photodeposition technique is known to create a homogeneous particle distribution as well as for the formation of metal particles in nanometer scale. A schematic overview of the photodeposition process is shown in figure 20.



Figure 20: Process scheme for photodeposition.

A detailed description of a generally performed photodeposition process is given in chapter 4.4.1.

#### 4.2 Characterization Methods

Different characterization methods were utilized for the determination of the photocatalyst status before and after photocatalytic H<sub>2</sub> production. Crystal phase analysis was performed by X-ray diffraction, while UV/Vis-spectroscopy in diffuse reflectance was used for the determination of the optical band gap of the probed photocatalysts and for the detection of the localized surface plasmon resonance of copper and gold co-catalyst particle. Thermogravimetric measurements were performed to clarify the calcination temperature range of different photocatalyst precursors. The photocatalyst morphology as well as the photocatalyst particle shape were investigated by scanning and transmission electron microscopy. X-ray photoelectron spectroscopy was utilized for the identification of the chemical state of selected transition metal modified cesium titanates.

#### 4.2.1 X-ray diffraction

X-ray diffraction (XRD) is the standard method for the analysis of ordered structures. In heterogeneous (photo)-catalysis, XRD is mainly used for the identification of the actual (photo)-catalyst phase composition and also for the estimation of particle sizes. The creation of monochromatic X-radiation is accomplished by an X-ray tube, where electrons are emitted by a cathode and afterwards accelerated in anode direction. The cathode consists of a tungsten filament, while the anode is made out of copper. The generated X-rays arise from two different processes. Initially, the accelerated electrons are slowed down by the anode material, resulting in the emission of a continuous background spectrum, which is known as Bremsstrahlung. Secondary, electrons from the inner K-shell of the anode material are removed, caused by the high energy cathode electron bombardment, and refilled with electrons from the outer L-shell. In the course of this process, X-ray photons are emitted, which are superimposed upon the background spectrum. A copper anode creates monochromatic X-rays (Cu-K<sub>a</sub>) with a wavelength of 0.154 nm and a corresponding energy of 8.04 keV.<sup>[175]</sup>



**Figure 21:** a) X-rays scattered on a periodic lattice and interfere constructively in directions given by Bragg's law. b) Calculation of lattice plane spacing d by Bragg's law. c) Diffraction on a polycrystalline powder. d) Measuring geometry scheme.<sup>[175]</sup>

The incident monochromatic radiation is elastically scattered by atoms in a periodic lattice with a specific plane distance d (Figure 21). If the scattered emergent beams are oscillating in phase, constructive interference takes place. In detail, if the distance between two diffracted beams correspond to the wavelength  $\lambda$  or a multiple wavelength and constructive interference

happens, Bragg's law (Eq. 4.1) is fulfilled.<sup>[93]</sup> The constant n is the integer and is stated as the reflection order, while  $\theta$  describes the angle between the incoming X-rays and the normal to the reflecting lattice plane. The detection of constructive interfered beams is accomplished in Bragg-Brentano geometry, where the detector unit is placed in a 2 $\theta$  angle relative to the measured angle.<sup>[93]</sup>

$$\mathbf{n} \cdot \boldsymbol{\lambda} = 2\mathbf{d} \cdot \sin\theta; \, \mathbf{n} = 1, \, 2, \, \dots \tag{4.1}$$

In a sample with appropriate long-range order, i.e. sufficiently large particles (40 - 50 nm), a characteristic diffraction pattern with defined and sharp reflexes is obtained. However, small particles and disordered crystal lattices lead to reflex broadening and limit the analytic capabilities of the XRD. Nevertheless, the reflex broadening gives information about the (photo)-catalyst particle sizes, which can be extracted by the Scherrer equation<sup>[175]</sup> (Eq. 4.2).

$$L = \frac{K\lambda}{\beta\cos\theta}$$
(4.2)

The Scherrer equation describes the average particle size L as a function of the full reflex width at half maximum  $\beta$ . The constant K is a particle shape form factor, ranging between 0.8 - 1.

X-ray powder diffraction was performed on a PANalytical X Pert Pro diffractometer in a 20 range of  $5 - 80^{\circ}$  in Bragg-Bentano geometry ( $\theta$ - $\theta$  scan) with Cu K<sub>a</sub> radiation ( $\lambda = 0.154$  nm) at room temperature. A step size of  $0.013^{\circ}$  with an actual collection time of 198.7 seconds per measuring step was chosen for data collection. Soller slits of 0.04 rad were applied in order to reduce scattered radiation. Nickel filters were used to cut off the Cu K<sub>β</sub> radiation. A PIXcel PW3018/00 detector with a 14 x 14 mm beryllium window was applied to count the diffracted radiation. Diffraction patterns shown in chapter 5.3 were measured on a PANalytical Empyrean diffractometer under the stated conditions.

### 4.2.2 UV-Vis spectroscopy in diffuse reflectance

UV-Vis spectroscopy is generally used in the concentration quantification of diluted aqueous media by utilizing the Lambert-Beer law. For the investigation of solids by optical spectrometric methods the usage of the diffuse reflectance mode is required. In the reflectance spectroscopy the reflectivity of the sample is used as a benchmark instead of the transmission or absorption factor. The reflectivity itself indicates the ratio of reflected to incident light intensity. A distinction is made between directional and diffuse reflection. In diffuse reflection the reflected light is distributed evenly in all directions regardless of the irradiation

conditions, and thus represents the technique for studying matt and rough surfaces of powders and solids. In this technique, a part of the radiation is mirrored at the surface irregularities (total reflection) and reflected while the other part penetrates into deeper layers, where it is partly absorbed and again scattered back to the surface. This type of reflection is called diffuse reflectance and is summarized in the Kubelka-Munk theory (Eq. 4.3).<sup>[176]</sup>

In the Kubelka-Munk theory, optical properties of a solid are described by the absorption and scattering coefficient K and S, respectively. The basis of this theory is a one-dimensional model, where a differentially thin layer dx is considered in the interior of the sample. Furthermore, the influence of the incident and reflected rays is considered in the Kubelka-Munk theory.<sup>[177]</sup>

$$F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} = \frac{K}{S}$$
 (4.3)

Conditions of the Kubelka-Munk function are the low absorption capacity of the investigated material and an infinite optical layer thickness  $R_{\infty}$ . However,  $R_{\infty}$  cannot be practically measured. For this reason a relative unit according to equation 4.4 is introduced.

$$\mathbf{R}_{\infty}' = \frac{\phi_{\text{refl. sample}}}{\phi_{\text{refl. white standard}}}$$
(4.4)

A so called white standard is used as a reference value for the measured sample reflectance. A white standard is characterized by a low absorption capacity and serves as a background spectrum. The band gap energy ( $E_g$ ). can be extracted from the Kubelka-Munk function.  $E_g$  is proportional to the absorption coefficient  $\alpha$  nearby the absorption edge, while the reciprocal absorption coefficient  $\alpha$  is proportional to the Kubelka-Munk function. This empirical relation is stated as Tauc-Plot (Eq. 4.5).<sup>[178-179]</sup>

$$(F(R_{\infty}) \cdot hv)^{1/n} \propto \text{const.} (hv - E_g)$$
(4.5)

The factor n is adjusted for allowed indirect (n = 2) or direct  $(n = \frac{1}{2})$  semiconductor. E<sub>g</sub> is directly achieved by an extrapolation of the absorption edge towards the abscissa. The resulting intersection determines E<sub>g</sub>.

Diffuse reflectance spectroscopy was performed on a Varian Cary 400 UV-Vis spectrometer with an applied integrating sphere. The diffuse reflectance spectra were recorded in a wavelength range of 200 - 800 nm with a step width of 1 nm in reflectance mode. In order to fulfill the Kubelka-Munk theory and equation 4.4, magnesium oxide powder (MgO) was used as white standard for all performed diffuse reflectance measurements.

### 4.2.3 Localized surface plasmon resonance

Surface plasmon resonance (SPR) describes the collective oscillation of surface electrons of a conductive material induced by light irradiation. The frequency of incident photons has to match with the natural frequency of the surface electrons, which are adjacent oscillating against the restoring force of the positive nuclei.<sup>[73]</sup> Nevertheless, due to the difference in phase velocity between surface electrons and incident light, frequency matching photons are not capable to force a SPR. The incident photon beam has to be an evanescent wave, a wave with exclusively imaginary momentum, to excite a SPR, due to the evanescent wave nature of surface plasmons.<sup>[177]</sup> SPR is mainly utilized in sensor technology in terms of deposition analysis on surfaces of metallic substrates like gold and silver and metal nanoparticles.<sup>[71, 180]</sup> Investigation of SPR of metallic nanoparticles describes a special case.

When light impinges upon a metal nanoparticle with a diameter smaller than the wavelength of the incident light, a collective oscillation of the surface electrons is caused at a frequency known as localized surface plasmon resonance (LSPR).<sup>[181]</sup> Due to the localization of the SPR on the nanoparticle, LSPR experiences considerably shorter field decay length (5 - 6 nm) over SPR (100 nm). This circumstance makes LSPR less sensitive for solution fluctuations and additionally more sensitive for surface changes, due to enhanced far-field scattering.<sup>[181]</sup> The particle size, shape and support material affects the actual LSPR frequency and enables a tuning of the respective light absorption abilities.<sup>[73, 182]</sup> Beside the application in sensor techniques, SPR is also used in surface-enhanced Raman spectroscopy, solar cells and in heterogeneous photocatalysis.<sup>[73, 128, 183]</sup> The usage of LSPR active metal nanoparticles in photocatalysis serves for the enhancement of visible light activity. Analogous to dye sensitization, an excited plasmonic metal nanoparticle injects electrons into the semiconductor conduction band.<sup>[17, 184]</sup> The charge transfer mechanism proceeds in composite photocatalysts where the plasmonic nanoparticles and semiconductor are in direct contact with each other, allowing a rapid charge transfer.<sup>[128]</sup> The stated photocatalyst composite systems can be seen as geometric analogs to standard co-catalyst/semiconductor photocatalysts.

In-situ LSPR measurements were performed on a Varian Cary 400 UV-Vis spectrometer with an applied integrating sphere in reflectance mode. In chronological intervals, 3 mL of photocatalyst suspension were removed from the respective photoreactor during a running photocatalytic experiment and transferred into a full quartz glass cuvette. The cuvette containing the photocatalyst suspension was placed in front of the sample opening of the integrating sphere. A UV-Vis powder sample holder containing MgO, which is also used as white standard material, was directly attached on the backside of the cuvette to ensure a complete backscattering of the induced light and to improve the collection of diffuse reflected light. Reflectance spectra were recorded in a spectral range of 200 - 800 nm with a step width of 1 nm. Afterwards, the photocatalyst suspension was returned to the photoreactor.

### 4.2.4 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is counted in the superordinate concept of thermal analysis, which further includes differential scanning calorimetry (DSC), thermomicroscopy and thermomechanical analysis.<sup>[185]</sup> IUPAC and ICTAC (International Confederation for Thermal Analysis and Calorimetry) define: A group of techniques in which a physical property of a substance and/or its reaction product is measured as a function of temperature while the substance is subjected to a controlled temperature program.<sup>[103]</sup> Therefore, TGA measures the mass change of a sample as a function of temperature or time, in case of isothermal measuring conditions. In order to enable an interference-free measuring of temperature depending mass change, the sample pad is connected to an automatically compensating balance in a closed furnace. The sample pad itself consists of an inert material like platinum or aluminum oxide. According to the conservation law, a mass change cannot occur in a closed thermodynamic system. A mass change can only be detected, if volatile components are produced during the thermogravimetric measurement, in case of a decomposition reaction, or a reactant can be accumulated from the environment (oxidation). In other words, when a system exchanges matter with the environment. A constant carrier gas flux has to be established in order to avoided any backreactions or reaction equilibrium of the volatile components with the measured sample. The chosen carrier gas type has a significant effect on the kinetics of the reaction. TGA measurements are generally performed in an inert gas stream, e.g. in nitrogen, but H<sub>2</sub>, O<sub>2</sub> and even vacuum are used for TGA. A standard TGA setup consists of a furnace and a balance, which both build up the so called thermobalance, a gas supply and a detection unit.<sup>[186]</sup>

TGA measurements were performed on a Perkin Elmer TGA4000 instrument. 10 - 15 mg of the powdered photocatalyst precursors were weighed in a ceramic crucible. All TGA measurements were carried out under a constant O<sub>2</sub> gas flow of 30 mL/min. The measured samples were heated up with a rate of 5 K/min in a temperature range of  $30 - 800^{\circ}$ C. Depending on the tested photocatalyst precursor, the measured temperature range was individually adjusted.

#### 4.2.5 Electron microscopy

The visualization of a (photo)-catalyst surface in order to examine the predominant surface state is a fundamental aspect of catalyst characterization. Conventional optical microscopy with visible light source only enables a resolution of around 1  $\mu$ m. In contrast, electrons have wavelengths in Angstrom scale, depending on the applied voltage, which enable the imaging of atomic details. Therefore, a microscope supported by an electron beam source (electron microscope) is able to visualize a catalyst surface with a resolution of about 0.1 nm and consequently exhibit a 10<sup>6</sup> higher magnification than visible light supported microscopes. Electron microscopy is generally used for particle size and shape determination as well as for the analysis of the chemical composition of the probed sample. Chemical analysis is generally performed by energy-dispersive X-ray (EDX) analysis. The stated sample information is extracted from different interaction types of the primary electron beam with the sample, which are illustrated in figure 22.<sup>[175, 187]</sup>



Figure 22: Interactions between primary electron beam and sample in an electron microscope.<sup>[175]</sup>

For example in transmission electron microscopy (TEM), transmitted and diffracted electrons are utilized to form a two-dimensional projection of the sample, while in scanning electron microscopy (SEM), the detection of either secondary or backscattered electrons are used for imaging. Scanning transmission electron microscopy (STEM) is a combination of SEM and TEM and is further explained in detail below.<sup>[188]</sup> Element analysis via EDX is performed by the detection of sample X-rays, which are produced as a byproduct of the primary electron beam. The three mentioned operating modes of electron microscopy are schematically illustrated in figure 23. All mentioned electron microscopy techniques require an air-free



environment of 10<sup>-6</sup> mbar or below to prevent any electron scattering and to enable an interference- free mean free path of electrons.<sup>[175]</sup>

Figure 23: Schematic set-up of an transmission, scanning and scanning transmission electron microscope. <sup>[175]</sup>

### Scanning electron microscopy

Imaging of catalyst particles by SEM is carried out by a focused electron beam which scans over the catalyst surface. The image is formed by establishing a scanning relation between object points and image points or in other words, the image detection is a function of detected secondary or backscattered electrons and the position of the primary beam. Secondary electrons originate from the sample surface and exhibit low energies (5 - 50 eV), while backscattered electrons come from the bulk structure. Back scattered electrons hold information of the sample composition, due to their deeper penetration depth. Elements with higher atomic number exhibit improved scattering abilities than low atomic number elements and therefore appear brighter in the SEM-image. Beside these material contrast factors also an instrumental contrast factor influences the image quality. Instrumental contrast is caused by the sample orientation relative to the detection unit. Sample particles, which are directly facing the detector, generate brighter images than particles orientated in the opposite direction from the detector side. SEM devices are capable to generate resolutions of about 3 - 10 nm and provide information about the topology and surface composition of the probed sample. Due to the low resolution of SEM instruments, this technique is not often used in the characterization of heterogeneous catalysts, except for length scales over 5 - 10 nm. Higher resolutions can be realized by TEM.<sup>[175, 187]</sup> However, modern SEM devises are capable of higher magnifications than 3 nm

SEM images were recorded on a Helios NanoLab 600i scanning electron microscope with a secondary electron detector at an acceleration voltage of 15 kV and a working distance of 4 mm. 1 mg of the powdered photocatalyst was distributed on an adhesive conductive carbon tape, which acts as a sample holder. Unattached photocatalyst material was removed by a low gas stream of synthetic air.

#### Transmission electron microscopy

TEM devices are instrumental analogous to conventional optical microscopes, which use electromagnetic lenses instead of optical lenses and electron rays instead of a visible light source. An electron beam emitted by an electron gun is passing through condenser lenses in order to generate parallel electron rays, which are homogeneously hitting on top of the sample surface. A two-dimensional image of the sample surface is produced due to the difference in electron attenuation caused by density and sample thickness variations over the sample. The transmitted electrons form a projection of the sample surface, which is called bright-field image. Contrary, the dark-field image is generated from diffracted electrons, which are collected off-angle related to transmitted electrons. These phenomena are known as scattering contrast. Further known contrast contributions are induced by diffraction and interference (phase contrast). Diffraction contrast is observed when a particle shows a favored orientation of exposed lattice planes for Bragg diffraction and the electron diffraction caused by these lattice planes does not contribute in the sample projection. Changes in the sample position can eliminate the diffraction contrast. Phase contrast is observed when an image contributing electron wave (transmitted electron) interferes with a diffracted electron wave. In order to avoid the presence of phase contrast, the focal width has to be varied to establish a constructive inference between diffracted and transmitted electron beam.<sup>[175, 189]</sup>

TEM instruments enable the projection of solid particles with a resolution of 0.3 nm, which resembles a magnification of  $10^6$  compared to optical microscopes. TEM operating in such resolution scale is categorized as high resolution TEM (HR-TEM) and require a very good instrumental stability, the utilization of phase contrast and a supporting imaging model.<sup>[175]</sup>

TEM, HR-TEM and STEM images were recorded on a JEOL JEM2100F transmission electron microscope. Cu and Au grids with 200 meshes were utilized as sample holders. For sample preparation, 1 mg of the powdered photocatalyst was suspended in 500  $\mu$ L of absolute

ethanol and ultrasonicficated for 30 min.  $100 \,\mu\text{L}$  of the ultrasonic treated photocatalyst suspension were further diluted in 400  $\mu$ L of absolute ethanol and again treated in an ultrasonic bath for additional 30 min. Afterwards, 5  $\mu$ L of the diluted photocatalyst suspension were dropped on a Cu or Au grid and dried for 30 min at room temperature.

## Scanning Transmission electron microscopy

According to the instrumental design of a scanning transmission electron microscope, as shown in figure 23, an STEM device uses a narrow electron beam for sample illumination while the detection unit is directly placed behind the sample stage instead of in rectangular position. Transmitted primary electrons are utilized for the visualization of the probed sample in the STEM operation mode. STEM resembles a combination of SEM, due to the used irradiation geometry, and TEM, because of the usage of transmitted primary electrons for image formation. Achieved resolutions in STEM are comparable to TEM. Related to TEM, bright field and dark field images of the sample are received by transmitted and diffracted electrons, respectively. Bright field detector is located exactly on the optical axis of the electron beam, while for the collection of diffracted electrons for dark field projection, the respective dark field detectors are concentric arranged below the sample holder. These annular dark-field (ADF) measurements are performed slightly off-angle similar to TEM. At higher off-angles, where even no Bragg diffraction can occur, the high-angle annular dark field (HAADF) detection is operating. The HAADF detection mode enables the distinguishing of different elements on the sample, by means of different signal intensities caused by the difference in atomic weights. The scattered part increases by the square of the atomic number in the HAADF operation range. Therefore, this detection mode is also stated as Z-contrast microscopy. The HAADF signal intensity depends also on the sample thickness, in case of sufficiently thin samples. STEM in HAADF mode enables the visualization of metal particle distribution on a support material; therefore STEM is an indispensable characterization method for supported catalysts.<sup>[175, 189]</sup>

# 4.2.6 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) enables the investigation of the chemical composition of surface-near regions of a solid. Surface-sensitivity is only accomplished if the responding signal originates from no more than a few atomic distances from the solid surface. Surface-near regions are defined in depth range of 0.5 - 2 nm, depending on the mean free path of element electrons. Furthermore, statements about the oxidation states of the examined

elements can be made. Generally, the photoelectron spectroscopy, which lays the theoretical foundation for XPS, Auger electron spectroscopy (AES) and ultraviolet photoelectron spectroscopy (UPS) are based on the photoelectric effect, postulated by Einstein in 1905.<sup>[175]</sup> By irradiation of a solid, electrons are excided into the vacuum level and afterwards detected by an analyzer. In the UPS, the irradiation is performed with ultraviolet light for the excitation of valence band electrons, while the X-ray irradiations is used in XPS in order to excite electrons from the core level. If a core level electron is excited into the vacuum level, the resulting gap is refilled by an electron from a higher energy level under the emission of a photon. In addition to the photon emission, the released energy can be used for secondary processes, like for the emission of fluorescence radiation or for an additional electron excitation into the vacuum level. The emission of secondary electrons, also called Auger electrons, can be especially observed for light elements and is utilized in the AES.<sup>[175]</sup> Excited electrons exhibit a characteristic binding energy, which can be determined by the measurement of the respective kinetic energy, according to equation 4.6.<sup>[190]</sup> The binding energy determination requires also the usage of monochromatic X-rays with defined energy to fulfill the conditions of equation 4.6. Commonly used X-ray sources are Mg  $K_{\alpha}$  (1253.6 eV) and Al  $K_{\alpha}$  (1486.3 eV).<sup>[175]</sup>

$$E_{kin} = h\nu - E_{bind} - \Phi_{spec}$$
(4.6)

Due to the Fermi level equilibration of the solid sample and the sample holder, which are in electric contact, the work function of the spectrometer  $\Phi_{\text{spec}}$  can be applied in equation 4.6 for binding energy determination. The spectrometer work function  $\Phi_{\text{spec}}$  is a known value, which is equal to the work function of the sample holder material. With the knowledge of the specific binding energy, the oxidation state of the considered element species can be determined. Generally, the binding energy increases with increasing oxidation state due to an increased coulomb interaction between electrons and the atomic nucleus and that the number of excited electrons is proportional to the concentration of the considered element.<sup>[190]</sup>

XPS-spectra were recorded on a Perkin-Elmer  $\Phi$  5600ci spectrometer using a standard Mg radiation (1253.6 eV) working at 250 W, to avoid signal overlaps occurring by the usage of an Al source. The working pressure was  $< 5 \cdot 10^{-8}$  Pa. The reported binding energies were corrected for charging effects. Signal scans (187.85 pass energy, 0.4 eV/step, 25 ms/step) were obtained in the respective range of Cs, Ti, Cu and O. The assignment of the signals was carried out by using values reported in the reference handbook, i.e. the NIST XPS database<sup>[191]</sup>.

### **4.3 Photoelectrochemical Analysis**

(Photo)-electrochemical analysis methods were used to determine the electronic band structure of selected photocatalysts and for photocurrent measurements. Photoelectrodes were prepared by doctor blading.

# 4.3.1 Doctor Blading

Doctor blading is a conventional printing and coating method for the deposition of pigments on a solid substrate. This coating technique is used for the preparation of photoelectrodes, consisting of an electric conductive glass substrate and a photocatalyst prepared by sol-gel process (chapter 4.1.1), which is transformed into a paste like substance. Fluorine doped tin oxide (FTO) glass was used as the electric conductive glass substrate, while unmodified and copper modified layered cesium titanates were utilized as photocatalysts.

## Paste Preparation

For paste preparation, 100 mg of a powdered photocatalyst calcined at 700 °C or 800 °C for 10 h (heating rate 5 K/min; cooling rate -5 K/min) were finely ground in an agate mortar. The grained photocatalyst powder was transferred in a sealed vessel and mixed with 500  $\mu$ L of absolute ethanol. The suspension was ultrasonicficated for 1 h to achieve a fine dispersion of the photocatalyst powder in the solvent.<sup>[192]</sup>

# Photoelectrode Preparation

Four FTO-glass plates (6 x 2 cm) were cleaned by subsequent immersion and 20 minutes of ultrasonicfication in 0.1 M HCl, 0.1 M NaOH, absolute ethanol and acetone. The FTO-glass plates were washed-up with water and dried by an air stream after each immersion step. Four plates were lined up to each other on the broad side. The conductive sides of the FTO-glass plates were exposed. The plate edges were covered with scotch tape (1 cm) to ensure an uncoated area for later contacting with a copper wire and adhesive copper tape. The exposed area is 8 cm<sup>2</sup> per plate. Afterwards, 200  $\mu$ L of the previously prepared photocatalyst paste were dropped on top of the bottom plate. The paste was immediately smeared with a continuous movement up to the top plate. The coated glass plates were dried for 1 h at 80 °C to remove any residual solvent. The dried coated glass plate were calcined for 3 h at 600 °C with a heating rate of 2 K/min and a subsequent cooling rate of -2 K/min under atmospheric conditions in order to improve the photocatalyst/FTO-glass contact. The coated and calcined

glass plates were cut in half and contacted with a 6 cm long copper wire, which was fused with an adhesive copper tape on the uncoated area, to construct the final photoelectrode  $(3 \times 2 \text{ cm})$  with a coated area of 4 cm<sup>2</sup>.

## 4.3.2 Capacitance Measurement for flat band determination

The determination of the flat band potential is essentially to characterize a photocatalyst as an n-type or p-type semiconductor and to determine the reductive and oxidative capabilities of a photocatalyst. Practically, the flat band potential is determined by the Mott-Schottky method. In a semiconductor/electrolyte interface three distinct double layers are formed. The first double layer is the semiconductor space charge layer, which is positively charged in form of ionized donors while the negative charges are located at the semiconductor surface. Second double layer is the Helmholtz double layer, which is further divided in the inner (IHP) and outer (OHP) Helmholtz plane. The IHP is located in the direction of the semiconductor space charge layer and is established through adsorbed ions on the semiconductor surface while the Gouy-Chapman layer which is an extended region where an excess of free ions is predominant. The three described double layers are considered as parallel plate capacitors connected in series.<sup>[99, 169]</sup> Each double layer contributes to the overall capacitance of the semiconductor/electrolyte interface, according to equation 4.7.<sup>[99]</sup>

$$\frac{1}{C} = \frac{1}{C_{SC}} + \frac{1}{C_{H}} + \frac{1}{C_{G}}$$
(4.7)

At high electrolyte concentrations ( $c \ge 0.1$  M) the contribution of the Gouy-Chapman layer is neglected. In a first approximation, the semiconductor/electrolyte interface state can be considered as a Schottky diode. According to the Schottky relation and the assumption of a parallel plate capacitor model (Eq. 4.8),<sup>[99]</sup> the flat band potential can be determined by a potential depended capacitance measurement.

$$\frac{1}{C_{SC}^2} = \frac{2}{\epsilon \epsilon_0 q N_D} \left( E_{appl} - E_{FB} - \frac{kT}{q} \right)$$
(4.8)

From the linear part of the constructed Mott-Schottky plot the doping density  $(N_D)$  and the flat band potential  $(E_{FB})$  can be extracted from the slope and the abscissa intercept of the extrapolation of the linear part.

The Mott-Schottky measurements were performed and recorded on a Zahner (photo)electrochemical workstation (Zahner-Elektrik GmbH & Co.KG). The prepared photoelectrodes were clamped onto a three-electrode (photo)-electrochemical cell with an Ag/AgCl (3 M NaCl) reference electrode and a platinum wire as counter electrode. A 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution was used as electrolyte. The Mott-Schottky plots were recorded in the serial mode in a range of -1.15 - 0.6 V vs. Ag/AgCl with a fixed potential amplitude of 10 mV and a step width of 0.05 V. Three different frequencies of 100 Hz, 1 kHz and 10 kHz were applied for each photoelectrode. Each measuring point resembles the mean value of five measurements.

#### 4.3.3 Photocurrent measurement

In order to understand the occurring processes during a photocurrent measurement, the Gerischer model has to be considered (Chap. 3.7). The chosen irradiation geometry depends on the identified semiconductor type, which is determined form the plot shape of a constructed Mott-Schottky plot. Generally, upon photoexcitation and generation of electron/hole pairs, the minority charge carriers move towards the semiconductor surface while the majority charge carriers are moving towards the semiconductor bulk. For a photoelectrode consisting of an n-type semiconductor, the backside illumination geometry (incident light on the transparent substrate/semiconductor interface) is chosen, because photogenerated electrons (majority charge carrier) can be directly transferred to the external circuit while holes (minority charge carrier) are accumulated on the semiconductor surface, where the electrolyte is oxidized. Electrons travel towards the counter electrode and a photocurrent is obtained. Contrary, for a p-type semiconductor photoelectrode, the front side illumination geometry (incident light on semiconductor/electrolyte interface) is applied. Front side illumination enables the instant consumption of photogenerated holes (majority charge carriers) by the electrolyte species, avoiding recombination with electrons (minority charge carriers), which are again transferred to the external circuit creating a photocurrent respond. Chopped light voltammetry (CLV) is used for the photocurrent quantification. This method employs a light source with defined wavelength, which is switched on and off in regular time intervals. A CLV experiment is performed in an alternating potential range. The resulting voltammogram contains oscillating current transients in each irradiation period. N-type semiconductors generate anodic (positive) photocurrents while for p-type semiconductors cathodic (negative) photocurrents are observed.<sup>[122]</sup>

CLV measurements were performed and recorded on a Zahner (photo)-electrochemical workstation (Zahner-Elektrik GmbH & Co.KG). The prepared photoelectrodes were clamped onto a three-electrode (photo)-electrochemical cell with an Ag/AgCl (3 M NaCl) reference

electrode and a platinum wire as counter electrode. A diode lamp with a discrete wavelength of 375 nm was used as irradiation source with an intensity of 60 W/cm<sup>2</sup>. The irradiated photoelectrode surface is  $0.785 \text{ cm}^2$ . The chopped light voltammograms were recorded in a potential range between -0.6 - 1.0 V vs. Ag/AgCl with a scanspeed of 10 mV/s and in irradiation intervals of 10 s. Each photoelectrode was tested in 0.1 M Na<sub>2</sub>SO<sub>4</sub> and a mixture of 0.1 M Na<sub>2</sub>SO<sub>4</sub>/0.1 M KI, which act as electrolyte solutions.

### 4.4 Setups for Photocatalytic H<sub>2</sub> and O<sub>2</sub> Production

Photocatalytic performance investigations were carried out in two different setups. Selected photocatalysts were studied under high energy irradiation of a mercury (Hg) midpressure immersion lamp in a 600 mL semi-batch reactor. Standard performance experiments were processed under the irradiation of a xenon (Xe) arc lamp in a 100 mL batch reactor. Irradiation with a Xe-arc lamp allows activity tests under considerably more realistic conditions than with a Hg-midpressure immersion lamp, due to the more continuous spectrum and lower UV light portion of a Xe-arc lamp. Both setups are described as followed:

### Photocatalysis Setup 1: Semi-batch reactor with Hg-midpressure immersion lamp

Photocatalytic performance tests for selected photocatalysts were executed in a self-made semi-batch reactor with a total volume of 600 mL. The setup can be divided into three parts: 1) gas supply, 2) photoreactor and 3) detection unit (Figure 24).

The gas supply provides a constant gas stream (Ar 6.0), in order to transport the evolved gas from the photoreactor to the detection unit (online mode). The constant gas stream in the online mode is adjusted by a mass flow controller (MFC) (Bronkhorst; 0 - 200 NmL/min). In the offline mode, the carrier gas stream is bypassed by a three-way-valve, in order to establish a direct connection from an additional gas cylinder (Ar 5.0), with a gas flux of 15 NmL/min adjusted by a needle valve, to the detection unit. The photoreactor itself consists of three individual parts including the photoreactor reservoir made out of borosilicate glass, the lamp cooling aggregate made out of pure quartz glass and the 700 W Hg-midpressure immersion lamp (UV-Consulting Peschl<sup>®</sup>; TQ 718) and the corresponding lamp control unit (Figure 24b). The photoreactor reservoir as well as the lamp cooling aggregate are double-walled vessels, which are cooled at 10 °C by a cryostat (LAUDA Pro line RP845).



**Figure 24:** Photocatalysis setup a) Flow chart b) Photoreactor including Hg-midpressure immersion lamp and lamp controller (adapted from Schwertmann et. al.<sup>[90]</sup>).

All three individual parts are connected to form the photoreactor. The gas inlet, in form of a perfluoroalkoxy alkane tube, is placed 1 - 2 cm underneath the bottom of the lamp cooling aggregate. The gas outlet is located at the connecting element of the photoreactor reservoir and the lamp cooling aggregate. The exiting gases are cooled to 10 °C by a reflux condenser and further transported towards the detection unit. A moisture trap filled with calcium chloride (CaCl<sub>2</sub>) is connected in between. The transported gases are analyzed by a multi component analyzer (XStream Emerson Process Management). The incoming gas stream is threefold divided to three different subgroup analyzers, in order to detect  $CO_2$ ,  $O_2$  and  $H_2$  separately.  $CO_2$  is detected by an infrared sensor in the concentration range between 0 - 5000 ppm,  $O_2$  is detected via paramagnetism senor in a range between 0 - 25 vol.-% and  $H_2$  is detected by a thermal conductivity detector in a range between 0 - 20 vol.-%.<sup>[90]</sup> The analyzed gases are afterwards transferred to the laboratory exhaust.

#### Photocatalysis Setup 2: Batch reactor with Xe-arc lamp

General photocatalytic activity tests were performed in a self-made quartz glass photoreactor with a total volume of 100 mL under irradiation of a 300 W Xe-arc lamp (LOT Oriel). Figure 25 shows a flow chart of the self constructed photocatalysis setup for photocatalytic  $H_2$ and  $O_2$  production. Again, the setup can be divided into three parts: 1) gas supply, including carrier gas line and calibration gas line, 2) photoreactor including irradiation source and 3) gas chromatograph (GC) as analyzer unit (Shimadzu GC-2014).


Figure 25: Flow chart of photocatalysis setup for standard performance tests (adapted from Merka et. al.<sup>[134]</sup>).

The gas supply is controlled by two pre-calibrated MFCs (Bronkhorst). MFC 1 (Ar 5.0; 0 – 50 NmL/min) is applied to adjust a constant carrier gas flow from the photoreactor to the GC. MFC 2 (H<sub>2</sub> | O<sub>2</sub> (5 vol.-%) / Ar (95 vol.-%); 0 - 10 NmL/min) is installed for the control of the calibration gas line. Both calibration gas mixtures H<sub>2</sub>/Ar and O<sub>2</sub>/Ar were stored in different gas cylinders and were calibrated separately. During the calibration process, the photoreactor is bypassed and therefore not considered in the GC calibration. The chosen calibration gas mixture can be further diluted by connecting the carrier gas line to the calibration gas line. Both gas streams are pre-mixed in a T-fitting before reaching the GC. During a photocatalytic  $H_2$  or  $O_2$  evolution experiment, the calibration gas line is kept close. The quartz glass photoreactor is a double-walled vessel, which is tempered to 10 °C by a cryostat (Julabo F25) to avoid any thermal effects on the tested photocatalyst. Furthermore, the photoreactor is connected to the gas supply system via two quartz glass flanges, which are clamped to the carrier gas inlet and outlet by two metal fasteners. Sealing rings placed on the flanges are pressed tied by metal fasteners to ensure a gas tight system. The photocatalyst suspension is irradiated by a 300 W Xe-arc lamp with an actual energy output of 290 W. The produced gases are transported by an Ar carrier gas flow from the photoreactor gas outlet to the GC. The photocatalysis setup with the applied flow through photoreactor and GC system enables a continuous sampling during the photocatalytic process. Quantitative analysis of the produced H<sub>2</sub> or O<sub>2</sub> gas is executed by a modified GC system for gas sampling.

An internal gas sampling program called "pre-run" controls the injection of gas samples into the GC. The four determining steps are illustrated in figure 26 and described in detail. A special valve installation consisting of a three-way valve and a 6-port valve, which are tempered at 150 °C, is utilized for sampling. The status between two sampling procedures is shown in figure 26A, representing the standard condition of the valve installation, where the sample gas inlet is directly connected to the exhaust. The GC system utilizes an internal column carrier gas (Ar 5.0) stream, which is adjusted at 10 Nml/min. By starting the pre-run procedure (Figure 26B), the three-way valve is opened towards the sample loop (500  $\mu$ L). The sample loop is filled by the Ar carrier gas flow containing the evolved gases of the photocatalytic process for a total time of four minutes. Afterwards, the three-way valve is closed in sample loop direction and is switched back to the exhaust (Figure 26C). State C maintains for 30 seconds, followed by the injection of the captured gas volume of defined pressure from the sample loop into the GC-column by switching the 6-port valve (Figure 26D).<sup>[134]</sup> One pre-run cycle is finished after 5 minutes. The GC-column (ShinCarbon ST 100/120, 2 m; Restek) is micro-packed with activated carbon and tempered at 35 °C. Gas sample analysis is executed by a thermal conductivity detector, which is ever tempered at 125 °C with a bridge current of 50 mA.



**Figure 26:** 3 way valve and 6-port valve connections during pre-run phase (adapted from Merka et. al.<sup>[134]</sup>). Red line describes the gas sample flow direction; green line describes the Ar flow direction.

Evolved H<sub>2</sub> and/or O<sub>2</sub> are analyzed in a retention time range between 0-5 minutes at the given GC-column temperature of 35 °C. H<sub>2</sub> is detected at a retention time of 1.5 min, while O<sub>2</sub> detection requires a retention time of 4 min. 30 minutes are adjusted as a time interval between each sampling step. However, a minimum sampling rate of 10 minutes per sample, including 5 minutes for the pre-run procedure and additional 5 minutes for H<sub>2</sub>/O<sub>2</sub> detection, are possible for a more detailed activity analysis. After each photocatalytic H<sub>2</sub> or O<sub>2</sub> evolution experiment, the GC-column was heated up from 35 °C to 100 °C for 2 h with a heating rate of 10 K/min, in order to remove residual moisture from column packing, which was accommodated during the measurement. After the heat treatment, the GC-column temperature was readjusted to its standard operating temperature of 35 °C by a cooling rate of -10 K/min. The heat treatment is necessary to ensure a stable separation quality of the GC-column.

### 4.5 Photocatalytic H<sub>2</sub> production via sacrificial agent reformation

## Photocatalysis Setup 1: Semi-batch reactor with Hg-midpressure immersion lamp

Photocatalytic methanol reformation was performed under UV light irradiation of a 700 W Hg-midpressure immersion lamp in a 600 mL self-made semi-batch reactor. The photocatalyst suspension consisted of 500 mg of the as-synthesized photocatalyst powder and 600 mL of an 8 vol.-% methanolic solution. To ensure a high dispersion of the powdered photocatalyst in the aqueous phase, the photocatalyst suspension was constantly stirred by a magnetic stirrer with a rotation rate of 500 rpm. In order to prevent any thermal effect on the tested photocatalyst, the suspension was cooled down to 10 °C by a cryostat. For the avoidance of external irradiation sources the photoreactor was completely shielded from the outside. In order to remove atmospheric gases from the photoreactor and pipes, the whole photocatalysis setup was purged with a maximum Ar gas flow of 200 NmL/min before starting an experiment. The cleaning procedure took about 20 - 30 minutes to complete. Afterwards a constant Ar gas flow of 50 NmL/min was adjusted. Afterwards, a zero gas calibration was performed for the gases (H<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub>) to be detected. Data points were collected every 20 seconds. Before initiating the irradiation experiment, a basic value for the gases to be detected was determined in the dark. The so called dark value was recorded for 5 minutes. The Hg-midpressure immersion lamp was activated at full power by the external lamp control unit, in order to ensure the vaporization of Hg inside the lamp. Afterwards, the lamp performance was adjusted down to 500 W.

In the stepwise photodeposition of rhodium (Rh), the water solved Rh precursor  $Na_3RhCl_6$  (1 mM) was added to the methanolic photocatalyst suspension before irradiation, to ensure a homogeneous distribution of the Rh precursor in the suspension. Each photodeposition step includes the deposition of 0.0125 wt.-% related to the used photocatalyst amount of metallic Rh. The irradiation period for a single photodeposition step was adjusted to 1 h. Between each photodeposition step, the reactor system was again purged by an Ar gas flow (200 NmL/min). The stepwise photodeposition was repeated until a constant H<sub>2</sub> rate was obtained. The final photocatalyst was recovered from the suspension by filtration and subsequent drying at room temperature.

Long term measurements were performed in periods between 5 - 10 h. The photocatalyst suspension is constantly irradiated by the Hg-midpressure lamp with a power output of 500 W during the complete measurement.

### Photocatalysis Setup 2: Batch reactor with Xe-arc lamp

For a standard photocatalytic H<sub>2</sub> evolution experiment under irradiation of a 300 W Xe-arc lamp, 75 mg of the photocatalyst powder were suspended in 75 mL of a 10 vol.-% methanolic solution, if not otherwise specified. Beside methanol also ethanol and glycerol were utilized as sacrificial agents for H<sub>2</sub> production. The concentration of the respective sacrificial agent was kept constant at 10 vol.-% in deionized water. The photocatalyst suspension was stirred by a magnetic stirrer with a rotation rate of 500 rpm and cooled down to 10 °C to prevent any thermal effects on the tested photocatalyst. The photocatalysis setup was purged by a maximum Ar gas flow of 50 NmL/min to remove residual atmospheric gases from the gas line tubing and the photoreactor. The gas line purging procedure was completed after 30 minutes. Afterwards, a blind measurement was performed to verify an air free reactor atmosphere. During irradiation of the photocatalyst suspension a constant Ar carrier gas flow of 20 NmL/min was adjusted. The photocatalyst suspension was irradiated with a 300 W Xearc lamp with an effective energy output of 290 W. Different photocatalytic performance tests were performed as stepwise photodeposition of different noble and non-noble metals on photocatalyst surfaces and long term measurements for stability studies. The executed performance tests are further described in detail.

### Stepwise photodeposition

Stepwise photodeposition of Pt, Au, Rh, Cu and Cr<sub>2</sub>O<sub>3</sub> was performed, as already mentioned, in 75 mL of a respective methanolic solution (10 vol.-% methanol) if not otherwise specified. Before the first photodeposition of the respective metal, the tested photocatalyst was irradiated for 2 h in the sacrificial agent solution in order to obtain a basic value for H<sub>2</sub> production without co-catalyst. The photodeposited amount of a chosen co-catalyst metal may vary between 0.0125 - 1 wt.-% depending on their respective influence on the photocatalytic activity. A defined volume of diluted co-catalyst precursor solutions of  $H_2PtCl_6 \cdot 6 H_2O$ ,  $HAuCl_4 \cdot 3 H_2O$ ,  $Na_3RhCl_6 \cdot 6 H_2O$ ,  $CuSO_4 \cdot 5 H_2O$  or  $K_2CrO_4$  was added to the prior irradiated photocatalyst suspension. The injection of the co-catalyst solution into the photocatalyst suspension required the opening of the photoreactor by removing the gas outlet connection from the gas outlet flange. Due to the opening of the photoreactor, the setup system had to be purged again by Ar gas flow to remove atmospheric contaminations. Each photodeposition step requires 2 h of irradiation to guarantee a complete deposition of the respective metal on the photocatalyst surface. The stepwise photodeposition was repeated until a constant H<sub>2</sub> evolution rate was obtained. The obtained photocatalyst/co-catalyst system was recovered from the suspension by filtration and subsequent drying at room temperature.

#### Long term measurement

Long term measurements were performed in order to get insight in the stability of the photocatalytic performance of the tested photocatalyst. Examined photocatalysts were precursor photocatalysts obtained from the sol-gel or wet impregnation. Also photocatalysts from the stepwise photodeposition were tested in terms of stability investigations. Long term studies utilize an irradiation period of 10 h. Photocatalysts obtained from photodeposition process experience a mass loss of around 33%. Therefore, the used photocatalyst amount for a long term study may vary between 50 - 75 mg depending on the photocatalyst material. Long term studies were performed in a sacrificial agent solution containing 10 vol.-% of methanol, ethanol or glycerol. During the irradiation period of 10 h, the external conditions were not changed. Afterwards the investigated photocatalyst was recovered from the suspension by filtration and subsequent drying at room temperature.

Selected recovered and dried photocatalysts were characterized once again for the investigation of possible changes in morphology, crystal structure, optical properties or chemical composition.

# **5 Results & Discussion**

#### 5.1 Unmodified Layered Cesium Titanate

Unmodified layered cesium titanate  $Cs_{0.68}Ti_{1.83}O_4$  was synthesized by an aqueous sol-gel process utilizing citrate acid and EDTA as complexing agents. In order to determine the optimum calcination temperature to find the most photocatalytically active version of  $Cs_{0.68}Ti_{1.83}O_4$ , the solid carbon contaminated photocatalyst precursor was annealed in a defined temperature range. The evaluation of the respective photocatalytic activity was carried out by H<sub>2</sub> evolution performance tests by the stepwise photodeposition of Rh particles as co-catalyst in methanolic solution under irradiation of a Xe-arc lamp. The differently calcined unmodified cesium titanates were characterized by XRD and UV-Vis spectroscopy in diffuse reflectance. The most active  $Cs_{0.68}Ti_{1.83}O_4$  version was further characterized by electron microscopy and utilized as a foundation for additional photocatalytic investigations in regard of co-catalyst and sacrificial agent effects on the H<sub>2</sub> production rate. Subsequent characterization of the tested photocatalysts was performed to clarify possible changes of the photocatalyst state.

## 5.1.1 Synthesis and Characterization

The utilized sol-gel process, basing on the Pechini method, provides a carbon contaminated powder precursor after gel combustion at 450 °C under atmospheric conditions. In the process of gel combustion, the respective anions of the inserted metal precursors are decomposed, leading to the assumption that only carbon contaminations are present in the photocatalyst precursor. Carbon contaminations are mainly induced by the used complexing agents EDTA and citric acid which are decomposed during the gel combustion as well. Subsequent X-ray diffraction (XRD) analysis, presented in figure 27a, reveals an amorphous structure of the powdered precursor. Therefore an additional calcination step is required to form a crystalline photocatalyst material. Thermogravimetric (TG) analysis is performed for the determination of the minimum annealing temperature for the decomposition of residual carbon contaminations as well as to determine the required temperature for the formation of an ordered crystal structure. Figure 27b presents the performed TG measurement and the corresponding DTG curve, which is extracted from the first derivative of the TG curve, of the powdered precursor of unmodified cesium titanate Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>. The TG curve shows a total mass loss of 66.7% achieved at 500 °C under O2 atmosphere. Further mass loss is not observed up to 800 °C. The corresponding DTG curve shows three decomposition steps at 72, 400 and 467 °C of the precursor contaminations. The initial mass loss starting at 72 °C and finishing at 115 °C with a loss of 5% of the starting mass is mainly related to the vaporization of H<sub>2</sub>O. A significant mass loss is observed at 400 °C followed by an additional mass loss at 467 °C with a respective weight loss down to 52% and 33.3%, respectively, of the starting mass. The signals at 400 and 467 °C indicate the presence of two different carbon or carbonate species, which make the main constituent of the precursor contamination. Qualitative analyses of the volatile decomposition products by mass spectrometry during the TG measurement are not available, which excludes a detailed characterization of the contamination species. According to the stated TG/DTG analysis, a minimum calcination temperature of 500 °C is necessary for the removal of all contaminations. The precursor material is further calcined at 500, 600, 700 and 800 °C under atmospheric conditions, while the calcination time is kept constant at 10 h.



**Figure 27:** a) XRD of the carbon contaminated powder precursor from sol-gel process for the synthesis of  $Cs_{0.68}Ti_{1.83}O_4$ , b) TG/DTG analysis of the powder precursor, c) XRDs of the  $Cs_{0.68}Ti_{1.83}O_4$  calcination series with  $Cs_{0.68}Ti_{1.83}O_4$  reference pattern and d) Tauc plots of the  $Cs_{0.68}Ti_{1.83}O_4$  calcination series with respective absorption edge linearization and band gap energies (E<sub>g</sub>).

The respective XRDs of the calcination series for the formation of  $Cs_{0.68}Ti_{1.83}O_4$  are illustrated in figure 27c along with the reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$  (ICDD 00-040-0827). All shown XRDs are normalized on the most intensive reflex of the lattice plane (130) at 27.94° 20, according to the stated reference data, for qualitative phase analysis.

The diffraction pattern of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcined at 500 °C misses the reflex of the lattice plane (020) at 10.19° 20 of a lepidocrocite layered structure. Furthermore, all visible reflexes are shifted of around  $0.3^{\circ}$  to higher 2 $\theta$  values compared to the reference patterns. According to the Bragg equation (Eq. 4.1), the observed reflex shift indicates a shorter distance between parallel lattice planes, which can be referred to a disordered and not fully evolved crystal structure. Contrary, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcined at 600 °C shows all characteristic reflexes of a lepidocrocite structure as well as narrower reflexes in the diffraction pattern than in the 500 °C material. Compared to the lower calcined Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> material, the 600 °C material experiences a reduced reflex shift to higher  $2\theta$  values of around  $0.1^{\circ}$ . With increasing calcination temperature to 700 and 800 °C, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> becomes more crystalline, which is confirmed by a reflex narrowing in the respective diffraction pattern. Reflex shifts to higher or lower 20 values are not observed for Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcined at 700 and 800 °C. The evident reflex broadening, especially for the lower calcined Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> material at 500 and 600 °C, also indicates the existence of small nanometer sized particles. Particle sizes calculations by Scherrer equation (Eq. 4.2) and used on the reflexes of (040) at 20.59° 20 and (200) at 47.71° 2θ refer to an average particle diameter of around 4.4 nm for Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcined at  $500 \,^{\circ}$ C. Due to the amorphous structure of the precursor material, which also contributes to the reflex broadening, the calculated average particle size cannot be used as an absolute value for the actual particle size. Nevertheless, a trend of increasing average particle diameters of 17, 27.4 and 43.7 nm for Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcined at 600, 700 and 800 °C, respectively, is observed. In general, higher annealing temperatures lead to the formation of larger particles. Therefore, the increase in particle size is coherent with the reflex narrowing seen in the recorded XRDs caused by the mentioned extrinsic temperature factor. The presented XRDs of the differently annealed Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> do not show any phase impurities or undesired cesium titanate compounds. Higher calcination temperatures than 800 °C lead to the formation of Cs<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub> and Cs<sub>1.1</sub>Ti<sub>8</sub>O<sub>16</sub> (Appendix), which are classified as hollandites and represent thermodynamic stable conformations of the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> target compound.

Recorded diffuse reflectance spectra of the differently calcined  $Cs_{0.68}Ti_{1.83}O_4$  are transformed into their respective Tauc plots, assuming an indirect semiconductor (Figure 27d) for band

determination.<sup>[79]</sup> Direct electron transition is mainly observed in intrinsic gap semiconductors, while a defect structure, which is present in Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>, leads to an extrinsic semiconductor and indirect electron transition. Therefore, the indirect electron transition for the Tauc plot construction for Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> can be recognized as a justified assumption. The abscissa intercepts of the absorption edge linearizations, determine the respective band gap. Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcined at 500 and 600 °C shows comparable band gap energies of 3.43 and 3.44 eV as well as similar plot shapes without additional absorption shoulders. Contrary, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> annealed at 700 and 800 °C possesses an additional absorption edge in the lower energy region at 3.0 eV, while the main absorption edges provide band gaps of 3.35 and 3.43 eV. These absorption shoulders indicate impurity states in the electronic band structure caused by an additional compound, which is not evident in the diffraction patterns of the 700 and 800 °C Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> material. According to the utilized metal precursors for the synthesis of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>, TiO<sub>2</sub> could be formed as an impurity in an undetectable amount, especially for XRD analysis, through the hydrolysis of Ti(O-nBu)<sub>4</sub>. The TiO<sub>2</sub> impurity could be present in the lower calcined Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> materials at 500 and 600 °C but in its anatase modification, which is formed at calcination temperatures lower than 600 °C. But a clear evidence of an anatase impurity in the mentioned materials is not given either by XRD or diffuse reflectance spectroscopy. At higher calcination temperatures above  $600 \,^{\circ}$ C, TiO<sub>2</sub> transforms into its thermodynamic stable rutile modification. Another assumption for the formation of rutile above 600 °C is the removal of Cs<sup>+</sup> from the interlayers, forming Cs<sub>2</sub>O, which induces the formation of rutile in order to keep the overall charge neutrality. However, the existence of Cs<sub>2</sub>O as well as of rutile cannot be verified by the recorded diffraction patterns. Rutile has a characteristic absorption edge at 3.0 eV, which is clearly visible in the Tauc plots of the 700 and 800 °C Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> material. The decreased band gap energy of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcined at 700 °C can be referred to the rutile impurity, which causes a tilting of the main absorption edge to lower energies. Nevertheless, the difference in the band gap is not significant enough to be recognized as an impact factor on the electronic band structure. The calculated band gaps of the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcination series of approximately 3.4 eV differ from the literature value of 3.6 eV<sup>[37]</sup>, which was extracted from the Kubelka-Munk function instead from a Tauc plot. The assumption of an indirect electron transition in Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> for the construction of a Tauc plot leads to a band gap decrease of 0.2 eV compared to the Kubelka-Munk function.

Characterization of the  $Cs_{0.68}Ti_{1.83}O_4$  particle morphology is carried out by scanning (SEM) and transmission electron microscopy (TEM).  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600 °C is chosen as a

reference material for particle morphology characterization due to its fully advanced crystal structure at low annealing temperature. Figure 28 shows SEM images of the 600 °C  $Cs_{0.68}Ti_{1.83}O_4$  material at two different magnifications. According to the SEM images, the solgel process produces irregularly shaped particles with ragged edges. These flake-like primary particles exhibit different particle sizes; furthermore the primary particles tend to agglomerate to bigger aggregates. The agglomeration does not follow a defined order, the primary particles do not show a preferentially stacking order either an edge or plane site orientation can be observed. Nevertheless, the single particle agglomerations are loosely bound together, which manifests in an electrostatic charging and a resulting mobility of the particle agglomerations during the SEM imaging procedure. The difference in size and shape as well as the observed agglomeration of the  $Cs_{0.68}Ti_{1.83}O_4$  primary particle hinder an estimation of a particle size distribution. The entity of the particle agglomeration appears to possess a sponge-like structure with several hollows but without an ordered mesoporosity. This circumstance induces that  $Cs_{0.68}Ti_{1.83}O_4$  annealed at 600 °C will exhibit a low surface area despite of the indicated small average particle size calculated from the respective XRD pattern.



**Figure 28:** SEM images of  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600 °C at two magnifications a) scale bar 10 µm and b) heightened section of image (a) scale bar 5 µm.

The irregularities in size and shape are referred, as already mentioned, to the utilized sol-gel process and especially to the gel combustion step, which transforms the liquid gel into a solid material. For this reason, the gel combustion can be seen as the determining particle shaping step for photocatalysts synthesized by a Pechini method like sol-gel process. The SEM technique is inefficient for the visualization of the macroscopic layered structure of  $Cs_{0.68}Ti_{1.83}O_4$ . Additional TEM measurements are performed for a detailed investigation of the stacked sheet structure of  $Cs_{0.68}Ti_{1.83}O_4$ .

Figure 29 shows TEM and high resolution TEM (HR-TEM) images of  $Cs_{0.68}Ti_{1.83}O_4$  annealed at 600 °C. The influence of the non-preferential stacking of primary particle can be directly seen in the irregular packing density distribution throughout the particle aggregates, shown in figure 29a and b. More dense packed zones in the particle aggregates appear darker than less packed areas. Furthermore, the gradations in the shading indicate a terraced type structure for the primary particle agglomerations. The recorded TEM images confirm the irregular shape of primary particles and formed agglomerations as already seen in the SEM images in figure 28. The magnifications in figure 29a and b are still not sufficient enough for the display of the layered structure. Higher magnifications in high resolution range, shown in figure 29c and 29d proclaim that the layered structure is evident in the synthesized  $Cs_{0.68}Ti_{1.83}O_4$  material.



**Figure 29:** a) and b) TEM images of  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600 °C, c) and d) HR-TEM images of the layered structure of  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600 °C with marked double layer distances of respectively 1.59 and 1.64 nm.

The titanium oxide sheets and cesium cation layers are parallel aligned in a single  $Cs_{0.68}Ti_{1.83}O_4$  primary particle. The particle stacking may create junctions between the parallel layers, which appear as diversions in a HR-TEM image. Additionally recorded HR-TEM

images of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> (600 °C) show differently oriented sets of crystalline Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> primary particles, which confirm that inside single particles a parallel alignment of layers is not broken or influenced by its surrounding environment. For the determination of the layer to layer distance, a double layer was measured tenfold perpendicular to its longitudinal side across the full length of the particle. The stated values in figure 29c and d are average values of the described measurement. The measurement of the double layer of two different primary particles but from the same Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> material revealed two different double layer distances of 1.59 and 1.64 nm. The difference in layer distance of approximately 0.05 nm and the resulting average error of about 3% referred to the stated values cannot be seen as a significant discrepancy, especially in the measured scale. The measured layer to layer distances also do not effectively differ from the literature value of a double layer size of 1.72 nm<sup>[41]</sup>. The lowered double layer distance compared to the literature value can be explained by the lowered calcination temperature of 600 °C instead of 800 °C for the literature material. Higher calcination temperatures lead to a thermal distension of the separating layers. Consequently, HR-TEM images verify the existence of the layered structure and acknowledge the capability of the used synthesis approach to produce  $Cs_{0.68}Ti_{1.83}O_4$  at lower calcination temperatures and shorter annealing times compared to the conventional solid state reaction or polymerized complex method.<sup>[41]</sup>

### 5.1.2 Photocatalytic H<sub>2</sub> Production - Investigations of Extrinsic Factors

The determination of the most active version of  $Cs_{0.68}Ti_{1.83}O_4$  is executed through their respective photocatalytic H<sub>2</sub> production performance in the presence of methanol, which acts as a sacrificial agent and Rh, which is used as a standard co-catalyst for H<sub>2</sub> evolution. Rh is deposited by a stepwise photodeposition method on the photocatalyst surface. In order to define the optimum co-catalyst loading, the Rh photodeposition is carried out in a concentration range between 0.0125 - 0.15 wt.-% in 0.0125 wt.-% steps and in respect of the inserted photocatalyst amount of 75 mg. All stated co-catalyst loadings in figure 30 as well as in all other related plots describe the theoretical deposited amount of the metallic form of the respective co-catalyst precursor and not the actual amount on the photocatalyst surface. Each photodeposition step includes a total irradiation period of 2 h by a Xe-arc lamp, to ensure a complete deposition of the injected co-catalyst content. Na<sub>3</sub>RhCl<sub>6</sub> solution (1 mM) was utilized as a precursor material for the deposition of metallic Rh. The redox potential of Rh<sup>3+</sup>/Rh, which resembles the present Rh ion in the used Rh precursor material, of +0.76 V vs NHE (pH = 0) is located in the band gap of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>, according to the stated

energy band structure published by Liu et. al.<sup>[37]</sup> Thereby,  $Cs_{0.68}Ti_{1.83}O_4$  fulfills the thermodynamic requirement for the photodeposition of Rh. The optimum co-catalyst loading is used as a benchmark for further long term measurements with  $Cs_{0.68}Ti_{1.83}O_4$ . Several extrinsic factors, which influence the photocatalytic activity of the tested photocatalyst such as light source, photocatalyst amount, temperature, type of sacrificial agent and co-catalyst material are investigated for the unmodified cesium titanate  $Cs_{0.68}Ti_{1.83}O_4$ . The effect of different sacrificial agents as well as of co-catalyst materials on the photocatalytic activity in H<sub>2</sub> production are described in detail in the subchapter 5.1.3. To ensure the reproducibility of the photocatalytic performance test results, a repetition experiment is carried out to guarantee an instrumental stability and thereby a constant quality of the measurements.



**Figure 30:** a) Sequential photodeposition of Rh on  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600 °C in 0.0125 wt.-% steps; red framed measuring points determines the optimal Rh loading range; black framed section resembles the magnified loading range in graphic b), b) Sequential photodeposition of Rh on  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600 °C in 0.003125 wt.-% steps imbedded in graphic a), c) Sequential photodeposition of Rh performed on differently calcined  $Cs_{0.68}Ti_{1.83}O_4$  and d) Reproduction experiment with  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600 °C.

calcined at 600 °C.

The stepwise photodeposition of Rh in methanolic solution on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcined at 600 °C is illustrated in figure 30a. Before the initiation of the sequential photodeposition of Rh, each Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> material is irradiated for 2 h in the water/methanol mixture, in order to receive a value of the blank Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> activity. Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcined at 600 °C shows a minor blank activity in H<sub>2</sub> production with a rate of only 2 µmol/h. After the initial irradiation interval, a color change of the photocatalyst suspension from white to blue can be observed. The given experimental conditions create a reductive environment enabling a reduction of Ti<sup>4+</sup> to Ti<sup>3+</sup>, which causes the observed blue coloring of the photocatalyst suspension. After an exposure to air and without continuous irradiation, the formed Ti<sup>3+</sup> ions are immediately reoxidized to Ti<sup>4+</sup>, which is directly reflected in the discoloring of the photocatalyst suspension. Photodeposition of initially 0.0125 wt.-% of Rh leads to a significant increase in the production of  $H_2$  to a rate of 21.7  $\mu$ mol/h. The co-catalyst photodeposition is mainly completed in the first hour of irradiation. After this second irradiation period for Rh deposition, a color change of the photocatalyst suspension cannot be observed. This circumstance leads to the assumption that Rh co-catalyst particles are formed on Ti<sup>3+</sup> sites, which are located on the surface of  $Cs_{0.68}Ti_{1.83}O_4$ . The Ti<sup>3+</sup> surface species act as effective electron traps and therefore represent also suitable reaction sites for the reduction of the Rh precursor from Rh<sup>3+</sup> to its metallic state. Two subsequent depositions of 0.0125 wt.-% of Rh to a total loading of 0.025 and 0.0375 wt.-%, lead to minor increases in the H<sub>2</sub> production rate up to 22.3 and 23.2 µmol/h, respectively. Further photodeposition steps to a final Rh loading of 0.15 wt.-% do not result in a further increased or even decreased photocatalytic activity. The observed H<sub>2</sub> evolution rate remains at a constant value of approximately 23 µmol/h over the entire loading range. Therefore, the presented Rh loading depended activity plot (figure 30a) symbolizes a saturation curve for the H<sub>2</sub> evolution capability of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>

The observed photocatalytic behavior leads to two conclusions considering the photodeposition of Rh: 1) The optimum Rh loading is achieved after three successive photodepositions of theoretically 0.0125 wt.-% of Rh(0) to a total amount of 0.0375 wt.-%, while the initial photodeposition step establishes the first significant photocatalytic activity increase and 2) Further attempts to increase the Rh loading via photodeposition are futile due to the surface saturation after three photodeposition steps. The stable H<sub>2</sub> evolution rate assumes that no additional Rh is deposited after a Rh loading of 0.0375 wt.-%. Higher deposition degrees would result in an increased or decreased H<sub>2</sub> production rate due to an increased co-catalyst particle size and in this regard to a lowered co-catalyst particle surface

area. Consequently, a Rh loading of 0.0375 wt.-% is used as a standard co-catalyst amount for a  $C_{s_{0.68}}Ti_{1.83}O_4/Rh$  photocatalyst system.

Furthermore, the initial photodeposition of 0.0125 wt.-% of Rh and the corresponding activity jump indicates that a stepwise photodeposition of smaller Rh loadings especially in the range between 0 - 0.0125 wt.-% may lead to an improved co-catalyst particle distribution and an increased H<sub>2</sub> evolution rate. For this reason, a Rh photodeposition with 0.003125 wt.-% steps is performed (Figure 30b). The first deposition of 0.003125 wt.-% of Rh leads to an activity rise to a rate of 13.1 µmol/h in H<sub>2</sub> production. Two additions of the same co-catalyst amount lead to a H<sub>2</sub> evolution rate of 16.4 µmol/h for 0.00625 wt.-% Rh and 16.6 µmol/h for 0.009375 wt.-% Rh. The observed H<sub>2</sub> rate in this low loading regime follows roughly the expected H<sub>2</sub> evolution trend predicted in figure 30a. The first two deposition steps show a far steeper increase in the H<sub>2</sub> evolution rate than in the predicted trend. Nevertheless, the third Rh photodeposition, shown as the red marked measuring point in figure 30b, has no significant effect on the photocatalytic activity, while following the predicted H<sub>2</sub> evolution trend. However, this indicates also a saturation of the photocatalyst surface and is contrary to the observed H<sub>2</sub> evolution rate after the deposition of 0.0125 wt.-% Rh (Figure 30a). The direct insertion of 0.0125 wt.-% of Rh may produce more adapted co-catalyst particles provoked by a higher Rh concentration as Rh photodeposition in a low concentration regime. Either way, lower Rh loadings do not lead to an improved photocatalytic activity but ultimately to the verification of the optimum Rh loading of 0.0375 wt.-%.

Photocatalytic H<sub>2</sub> production performance tests with Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcined in a temperature range between 500 - 800 °C are presented in figure 30c. All mentioned H<sub>2</sub> evolution rates are referred to the activity value after the deposition of 0.0375 wt.-% of Rh. The initial blank values reveal that only Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcined at 600 °C is active in photocatalytic H<sub>2</sub> production without a supporting co-catalyst. Lower and higher annealed versions of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> do not show any activity without an Rh co-catalyst surface modification. However, all differently annealed versions of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> have shown a blue coloring of the photocatalyst suspension after the first irradiation period, which indicates again the formation of Ti<sup>3+</sup> as well as the presence of defect sites, independent of the calcination temperature or rather of the degree of crystallinity. After the first deposition of 0.0125 wt.-% Rh, no color change is observed for the entire Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcination series. Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcined at 600 °C has shown the highest photocatalytic activity in the formation of H<sub>2</sub> with a rate of 20.1 µmol/h in the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcination series. Higher calcination temperatures lead to a lowered H<sub>2</sub> evolution rate, while the 700 °C material shows a minor decrease in the production rate of 18.2 µmol/h. However, the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> 800 °C material experiences the lowest activity with a rate of 4.9  $\mu$ mol/h. The lowest calcined Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> material (500 °C) shows an activity rate of 14  $\mu$ mol/h, which is located between the 600 °C and 800 °C versions of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>. According to the diffraction patterns of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> (500 °C), the respective crystal structure is not completely evolved as well as suffers from a low degree of crystallinity, which is materialized in a low reflex intensity and an extended reflex broadening compared to the higher calcined Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> versions. Calcination at 600 °C creates a Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> material with ideal bulk and surface properties for the application in photocatalytic H<sub>2</sub> production. Higher calcination temperatures of 700 and 800 °C lead to the formation of larger photocatalyst particles, basing on the calculated average particle diameters by Scherrer equation, and consequently to longer diffusions lengths and an increased recombination probability for photogenerated electron/hole pairs. However, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> annealed at 700 °C showed only minor deviations in the H<sub>2</sub> evolution rate compared to the 600 °C material despite of the increased particle diameter from 17 (600 °C) to 27.4 nm. The significant activity drop down of the 800 °C material of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> can be directly referred to the increased particle diameter of 43.7 nm. The high degree in crystallinity, which is advantages for charge carrier transport due to the lowered degree of crystal defects and corresponding trap states has no positive effect on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> (800 °C). Nevertheless, the increased particle diameter is the limiting factor for the photocatalytic H<sub>2</sub> production in case of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> synthesized by the utilized sol-gel process, excluding the 500 °C material due to its not fully developed crystal structure.

Reproduction measurements are carried out with  $Cs_{0.68}Ti_{1.83}O_4$  annealed at 600 °C in the optimal Rh loading range (Figure 30d). Rh is deposited in 0.0125 wt.-% steps via photodeposition. The H<sub>2</sub> production experiment with  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C), shown in figure 30c, is repeated two more times, in order to investigate the instrumental stability of the photocatalytic setup. To investigate possible aging effects on the photocatalyst material, the reproduction experiments are performed in two week intervals with the same  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C) batch. The three measurements show a similar trend in the photocatalytic activity in the respective photodeposition steps, despite of the differences in absolute values. Also the initial activities without Rh co-catalyst do not differ significantly from the first measurement, the following measurements lay in the standard deviation of the recorded measuring points. In conclusion, the repeated experiments with  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C) in H<sub>2</sub> production show that

the photocatalyst material does not change in the period of the performed reproduction experiment as well as that the photocatalytic setup provides an instrumental stability for meaning measurements.

## Post Characterization of the Calcination Series of Unmodified Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>

According to the photocatalyst development scheme presented in figure 1, the calcination series of  $Cs_{0.68}Ti_{1.83}O_4$ , recovered from the stepwise photodeposition of Rh for photocatalytic H<sub>2</sub> production, is characterized by XRD and diffuse reflectance spectroscopy in order to investigate possible changes in the crystal structure and optical properties. The recorded diffraction patterns as well as the corresponding Tauc plots calculated from the respective diffuse reflectance spectra of  $Cs_{0.68}Ti_{1.83}O_4$  (500 - 800 °C) are pictured in figure 31.



**Figure 31:** a) XRD pattern of  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 500 – 800 °C after stepwise photodeposition of Rh with reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$  and  $H_2Ti_2O_5 \cdot H_2O$  and b) Tauc plots of  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 500 – 800 °C after stepwise photodeposition of Rh with corresponding absorption edge linearization and band gap energy (E<sub>g</sub>).

The diffraction patterns reveal a structural change of  $Cs_{0.68}Ti_{1.83}O_4$  (500 - 800 °C) after the performed activity evaluation test in H<sub>2</sub> production (Figure 31a). Evidently, the reflexes of the lattice planes (011) and (060) at 30.7° and 30.86° 2 $\theta$ , respectively, are not available in the XRDs of  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 500 and 600 °C. While the mentioned reflexes are still observable but in decreased intensity as well as shifted to lower 2 $\theta$  values about a factor of 0.8° in the 700 °C and 0.5° in the 800 °C material of  $Cs_{0.68}Ti_{1.83}O_4$ . Additionally, the less intensive reflexes in the 2 $\theta$  range 22.5 - 25° in the as-synthesized  $Cs_{0.68}Ti_{1.83}O_4$  (500 - 800 °C) are also not detectable after a performance test cycle. Furthermore, the reflex of the lattice plane (040) at 20.4° 2 $\theta$  experience a lowered intensity and a shift to a lower 2 $\theta$  value of about

 $0.6^{\circ}$  relative to the reference patterns in the complete calcination series. Interestingly, after an executed performance test, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcined at 500 °C shows the lattice plane reflex of (020) at  $10.0^{\circ}$  20, which is missing in the corresponding as-synthesized material. The examined layered cesium titanate  $Cs_{0.68}Ti_{1.83}O_4$  is known for its cation exchanging capability in acidic media. The used water in the diluted sacrificial agent solution exhibits a pH-value of around 5 - 6 and provides enough protons for a Cs<sup>+</sup> exchange. But the high pH-value as well as the short exposition time of 8 h during the photodeposition process is not sufficient enough for a complete conversion of  $Cs_{0.68}Ti_{1.83}O_4$  to its proton exchange version  $H_{0.68}Ti_{1.83}O_4$ , identified by  $H_2Ti_2O_5 \cdot H_2O$ , which exhibits an identical crystal structure to the proton exchanged  $H_{0.68}Ti_{1.83}O_4$  (Figure 31a).<sup>[83]</sup> Additionally, the lower annealed  $Cs_{0.68}Ti_{1.83}O_4$ materials (500 - 600 °C) are stronger affected by the Cs<sup>+</sup> to proton exchange than the higher calcined materials (700 - 800 °C), recognizable by the visual reflexes of the lattice planes (011) and (060) at 30.7° and 30.86° 20, respectively. Higher calcination temperatures have a stabilizing effect on the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> crystal structure, especially on the Cs<sup>+</sup> located in the interlayer. Despite of the higher structural stability of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> (700 - 800 °C), the 600 °C material still provides the highest photocatalytic activity in H<sub>2</sub> production in the tested calcination series.

The structural change of  $C_{s_{0.68}}Ti_{1.83}O_4$  (500 - 800 °C) induced by the Cs<sup>+</sup> to proton exchange, manifests also in an increased band gap energy as shown in figure 31b. All Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> materials experience a band gap increase between a value of 0.15 - 0.2 eV, while an increasing band gap energy with increasing calcination temperature is observable. Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> (800 °C) exhibits a slightly decreased band gap compared to the 700 °C material. Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> (700 - 800 °C) still exhibits a rutile impurity in the corresponding Tauc plot, which is still not detected by XRD. But, compared to the Tauc plots of the assynthesized  $Cs_{0.68}Ti_{1.83}O_4$  (700 - 800 °C) materials (Figure 27d), the used  $Cs_{0.68}Ti_{1.83}O_4$ materials show a decreased rutile absorption band in their respective Tauc plot. The intensity decrease of the rutile band indicates a coherent lowering of the rutile content in the 700 and  $800 \,^{\circ}\text{C}$  material of  $C_{\text{S}_{0.68}}\text{Ti}_{1.83}\text{O}_4$  after the performed evaluation test. The reduced rutile content and the undetectable rutile phase in the XRD patterns implies the existence of small rutile nanoparticles, which are probably removed from the bulk material during the recovery process, especially washed out during the separation of the solid from the liquid phase. However, a certain amount of rutile remains in the used Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> (700 - 800 °C) material. The lost mass is approximately 20% in average relative to the inserted photocatalyst amount. Consequently, the as-synthesized versions of  $Cs_{0.68}Ti_{1.83}O_4$  transverse a status change during the photocatalytic process in the given aqueous system and therefore resemble a precursor material, while the real acting photocatalyst is formed in-situ.

#### Investigation of Extrinsic Factors

Extrinsic factors as light source, catalyst amount, sacrificial agent and reactor temperature are investigated for  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C). The corresponding measurements are shown in figure 32.



**Figure 32:** Sequential photodeposition of Rh on  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600 °C a) under irradiation of a Hg mid-pressure immersion lamp, b) with photocatalyst contents of 25, 50, 75 and 100 mg, c) in methanol, ethanol and glycerol and d) photocatalytic activity of  $Cs_{0.68}Ti_{1.83}O_4/Rh 0.0375$  wt.-% at 10, 20 and 30 °C.

Figure 32a shows the stepwise photodeposition of Rh on  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C) under the irradiation of a Hg mid-pressure immersion lamp, executed in the photocatalysis setup 1 as described in chapter 4.4.1. The utilized Hg light source causes a tremendous increase in the H<sub>2</sub> evolution rate compared to the Xe arc lamp irradiation (photocatalysis setup 2). The initial evolution rate of 109.8 µmol/h surpasses the final H<sub>2</sub> production rate of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> after the deposition of 0.0375 wt.-% of Rh in photocatalysis setup 2 of approximately four magnitudes.

Sequential photodeposition of 0.0125 wt.-% of Rh on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> under Hg lamp irradiation leads to H<sub>2</sub> evolution rates of 1318.4, 2820.8 and 3807.9 µmol/h in the respective Rh deposition step of 0.0125, 0.025 and 0.0375 wt.-%. The increased photocatalytic activity can be directly referred to the increased energy input from the utilized Hg midpressure immersion lamp, which exhibits higher UV light proportions than a Xe arc lamp. Additionally, Hg light irradiation leads to a changed behavior in the photodeposition of Rh. The activity evolution presented in figure 32a shows no loading plateau for the used co-catalyst, as shown in figure 30a. Instead a continues activity rise with increasing Rh loading is evident. If an improved photodeposition of Rh is on hand or a higher quantum efficiency is present due to the increased energy input, cannot be clarified because of the difference in the inserted photocatalyst amount and reactor design. Nevertheless, the executed measurement under Hg lamp irradiation describes a limit case for photocatalytic H<sub>2</sub> production under high energy input and consequently for a hypothetical maximum photocatalytic activity which can be achieved. Nevertheless, photocatalytic activities observed in experiments, which are executed under irradiation of a Hg lamp, cannot be recognized as a representation of the photocatalyst performance under realistic conditions. The use of a Xe lamp offers an activity evaluation under more realistic conditions relative to sunlight irradiation, due to the lowered UV light proportion compared to a Hg lamp.

In heterogeneous photocatalysis, the inserted amount of photocatalyst is generally orientated on the volume of the liquid phase of the heterogeneous system. For example, a total reaction volume of 100 mL requires the insertion of approximately 100 mg of the solid photocatalyst. Differences in particle size, photocatalyst density and reactor design require an adjustment of the inserted photocatalyst amount for each photocatalyst material. Therefore, recorded photocatalytic activities cannot be directly scaled up for higher photocatalyst contents because an increased amount of photocatalyst, normally larger than the correlated liquid phase volume, results in a decreased photocatalytic performance. A lowered light absorption induced by a higher reflectivity degree of the photocatalyst suspension is mainly responsible for a decreased activity at higher photocatalyst amounts in a certain reactor system. For this reason, an activity designation of a scaled up photocatalyst amount in a specified unit per gram is invalid due to the exclusion of the increased reflectance degree of the photocatalyst suspension.

The effect of the inserted amount of photocatalyst on the photocatalytic performance is investigated for four different  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C) contents, which are tested in the

stepwise photodeposition of Rh. Figure 32b shows the performed deposition experiments with 25, 50, 75 and 100 mg of  $Cs_{0.68}Ti_{1.83}O_4$ . Rh loadings were individually adjusted on the respective photocatalyst content. The performed deposition experiments show only minor deviations to each other. Blank activities differ with a standard deviation of around 1.4 µmol/h. Furthermore, the initial activities do not show a clear trend in the dependency of the inserted photocatalyst amounts. The Rh photodeposition series reveal that the chosen photocatalyst contents result in a comparable H<sub>2</sub> evolution rate as well as in the same activity development, according to the Rh loading sequence. Consequently, different photocatalyst contents do not influence the photocatalytic performance of  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C) in the tested mass regime and reactor system. In terms of possible mass loses caused by a photocatalyst recovery process, the performance plateau of  $Cs_{0.68}Ti_{1.83}O_4$  in the chosen mass range enables a subsequent investigation of a photocatalyst/co-catalyst system from a previously performed photodeposition experiment. Otherwise, the chosen photocatalyst amount nor of an increased reflectance at higher photocatalyst content.

The influence of methanol, ethanol and glycerol as sacrificial agent in the stepwise photodeposition of Rh on  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C) is illustrated in figure 32c. A constant amount of 10 vol.-% is adjusted for each utilized sacrificial agent. Rh photodeposition in methanolic solution still exhibits the highest H<sub>2</sub> evolution rate, while the photodeposition procedure executed in ethanol experiences the lowest production rate. Glycerol as a sacrificial agent in the Rh photodeposition process leads to a medium H<sub>2</sub> evolution rate compared to methanol and ethanol. Nevertheless,  $Cs_{0.68}Ti_{1.83}O_4$  shows the highest blank activity without co-catalyst of 5.8 µmol/h in a glycerol containing solution. The observed activity trend of methanol > ethanol > glycerol in H<sub>2</sub> evolution cannot be directly referred to the electrochemical redox potential for the oxidation of the respective sacrificial agent towards  $CO_2$ , which also includes the formation of H<sup>+</sup>, as stated in the equations 5.1 -5.3:<sup>[193]</sup>

$$CH_3OH + H_2O + 6 h^+ \rightarrow CO_2 + 6 H^+; 0.03 V \text{ vs. NHE}$$
 (5.1)

$$C_2H_5OH + 3 H_2O + 12 h^+ \rightarrow 2 CO_2 + 12 H^+; 0.08 V vs. NHE$$
 (5.2)

$$C_3H_8O_3 + 3 H_2O + 14 h^+ \rightarrow 3 CO_2 + 14 H^+; 0.00 V vs. NHE$$
 (5.3)

A thermodynamic examination of the sacrificial agent oxidation in regard of their respective change in Gibbs free energies of  $\Delta G^0 = -4 \text{ kJ/mol}$  (CH<sub>3</sub>OH/CO<sub>2</sub>),  $\Delta G^0 = 65 \text{ kJ/mol}$  (C<sub>2</sub>H<sub>5</sub>OH/CO<sub>2</sub>) and  $\Delta G^0 = -20 \text{ kJ/mol}$  (C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>/CO<sub>2</sub>) cannot be correlated to the observed H<sub>2</sub> evolution rates, too. Despite of the observed trend in activity, the conversion of a sacrificial

agent is a multistep process with different intermediate products, which have to be considered in the overall conversion to the final products  $H_2$  and  $CO_2$ , as shown in chapter 3.2.3 for the photocatalytic conversion of methanol. According to Halasi et. al.<sup>[194]</sup>, the photocatalytic conversion of ethanol to  $CO_2$  and  $H_2$  on TiO<sub>2</sub> includes three steps, as shown in the equations 5.4 - 5.6 :

$$C_2H_5OH \rightarrow CH_3CHO + H_2 \tag{5.4}$$

$$CH_3CHO \rightarrow CH_4 + CO$$
 (5.5)

$$\mathrm{CO} + \mathrm{H}_2\mathrm{O} \to \mathrm{H}_2 + \mathrm{CO}_2 \tag{5.6}$$

The conversion of ethanol starts with formation of acetaldehyde and  $H_2$  (Eq. 5.4) followed by methane and CO formation from acetaldehyde (Eq. 5.5) and ends with the production of  $H_2$ and CO<sub>2</sub> from CO and  $H_2O$  (Eq. 5.6). Basing on this conversion mechanism (5.4 - 5.6), photocatalytic ethanol conversion results in the formation of two molecules of  $H_2$  from one ethanol molecule. Therefore, ethanol is a less efficient  $H_2$  source compared to methanol.

On the other hand, Chong et. al.<sup>[195]</sup> investigated the photocatalytic glycerol conversion on different  $TiO_2$  facets, revealing a glycerol conversion mechanism as stated in the equations 5.7 - 5.10:

$$C_3H_8O_3 + H_2O \rightarrow CH_2OHCHO + HCOOH + 2 H_2 \text{ (prim.)}$$
 (5.7)

$$CH_3OCHO + H_2O \rightarrow HCOOH + HCHO + H_2 (sec.)$$
 (5.8)

 $\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2 \text{ (sec.)} \tag{5.9}$ 

$$C_3H_8O_3 \to C_2H_5O_2CHO + H_2 \text{ (minor)}$$
 (5.10)

The primary conversion step (Eq. 5.7) results in the formation of hydroxyacetaldehyde, formic acid and two molecules of H<sub>2</sub>. This primary process explains the nearly doubled initial H<sub>2</sub> evolution rate of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> in the conversion of glycerol compared to methanol and ethanol (Figure 32c). Hydroxyacetaldehyde is further converted to formic acid, formaldehyde and H<sub>2</sub> (Eq. 5.8), while formic acid is also further converted to CO<sub>2</sub> and H<sub>2</sub> (Eq. 5.9). Both mechanistic steps (Eq. 5.8 and 5.9) are considered as secondary processes. The selectivity towards glyceraldehyde from glycerol (Eq. 5.10) is lower than 5% and therefore considered as a minor process. By the exclusion of equation 5.10, the conversion of one glycerol molecule results in the formation of four molecules of H<sub>2</sub>. For this reason, glycerol reforming should provide the highest H<sub>2</sub> evolution rate compared to methanol and ethanol. But it has to be considered that the stated conversion mechanisms are investigated on pristine TiO<sub>2</sub>. Furthermore, the deposition of a co-catalyst material like Rh inserts new reaction sites on the photocatalyst surface, which enables also alternative conversion pathways for the used

sacrificial agent (Chapter 3.2.3). These possible pathways have to be considered in the decomposition mechanism of the sacrificial agent and cross checked in each step with the electrochemical probabilities of the used photocatalyst. On the other hand, an alternative mechanism induced by a co-catalyst may also lower the energetic barrier for  $H_2$  production.

Temperature dependency measurements are performed with pre-deposited Rh co-catalyst (0.0375 wt.-%) on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> (600 °C), shown in figure 32d. Rh particles are deposited as described in chapter 4.5 in a methanolic solution under irradiation of a Xe arc lamp. 75 mg of the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Rh photocatalyst are inserted for each experiment. The measuring time has been set for 5 h. The re-used Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Rh photocatalyst shows an increased H<sub>2</sub> evolution rate at the standard measuring temperature of 10 °C of approximately 48 µmol/h. Nevertheless, the recorded production rate of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Rh at 10 °C is used as a benchmark for the comparison with experiments, which are carried out at 20 and 30 °C. A temperature increase to 20 and 30 °C leads to a nearly linear increase in activity to a H<sub>2</sub> production rate of around 55.8 µmol/h at 20 °C and 66 µmol/h at 30 °C. The increased activity can be referred to the thermal behavior of a semiconductor as described in chapter 3.1. According to the Fermi-Dirac distribution and the density of state theory (Eq. 3.1 and 3.2), the conduction band population will increase with increasing temperature. Consequently, a rise in activity is provoked by an additional thermal energy source. But the influence of the thermal energy input on the overall activity leads to a corruption of the pure photocatalytic activity of the tested semiconductor. In order to extract the proportion of the photocatalytic activity, photocatalytic experiments have to be performed at low temperatures to minimize the thermal effect on the semiconductor. Adverse effects like an increased recombination rate of electron/hole pairs manifested in a reduce photocatalytic activity are not evident.

In summary, extrinsic factors as light source, sacrificial agent and temperature have a direct effect on the photocatalytic performance of  $Cs_{0.68}Ti_{1.83}O_4$  and enable a controllable operation of a photocatalytic reaction. An influence of the inserted photocatalyst mass on the H<sub>2</sub> evolution rate could not be observed in the probed mass range but offers the measurement of comparable results at different photocatalyst contents. The usage of a Hg lamp should be resigned due to the increased UV proportions, which lead to a more corrupted photocatalytic activity in contrast to a Xe lamp.

# Post Characterization of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>: Particle Morphology

The increased activity of re-used  $Cs_{0.68}Ti_{1.83}O_4/Rh$  (0.0375 wt.-%) in the temperature dependency experiment executed at 10 °C induces a change in the photocatalyst status in terms of particle morphology. For the particle morphology investigation, SEM images of the recovered  $Cs_{0.68}Ti_{1.83}O_4/Rh$  photocatalyst material are recorded as shown in figure 33.



**Figure 33:** SEM images of  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C) after stepwise photodeposition of Rh in methanolic solution at two magnifications a) scale bar 5 µm and b) heightened section of image (a) scale bar 2 µm.

SEM images of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Rh after the photocatalytic performance test reveal that particle agglomerations are broken down during the measurement, resulting in a more loose bulk material compared to the as-synthesized  $Cs_{0.68}Ti_{1.83}O_4$  (Figure 28). The agglomeration fragments also show the diversity of particle sizes and shapes of the primary particles caused by the utilized sol-gel process. The loose constitution of the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Rh powder also manifests in an immediate dispersion of the solid material in the liquid phase. Contrary, the as-synthesized Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> material requires a time period of around 1 h until full dispersion is achieved. The fragmentation of the particle agglomerations can be mainly referred to the acting mechanical stress caused by the utilized stirrer and the resulting turbulent mixing of the photocatalyst suspension. Furthermore, the collapse of the particle agglomerations to smaller fragments should also lead to a higher surface area compared to the as-synthesized material. Nitrogen physisorption is utilized for the quantification of the photocatalyst surface area before and after photocatalytic H<sub>2</sub> production. Surface areas calculated by the theory of Brunauer-Emmet-Teller (BET), confirm an increased surface area from 2.6 m<sup>2</sup>/g of the assynthesized Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> to 10.4 m<sup>2</sup>/g of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Rh after photocatalytic H<sub>2</sub> production. Consequently, the calculated surface areas and the photocatalyst morphology observed in SEM are internally consistent and describe the same phenomena of morphology transformation. Changes in crystal structure and optical properties in terms of light absorption capabilities of  $Cs_{0.68}Ti_{1.83}O_4$  tested in methanol, ethanol and glycerol is discussed in detail in at the end of chapter 5.1.3.

### 5.1.3 Photocatalytic H<sub>2</sub> Production on Noble Metal Co-catalysts

Investigations concerning extrinsic factors and their influence on the photocatalytic activity in H<sub>2</sub> production serve for the evaluation of appropriate operating conditions on the used photocatalysis setup 2. A photocatalyst content of 75 mg and a reactor temperature of 10 °C under irradiation of a Xe arc lamp in methanolic (10 vol.-%) solution provide a reliable measurement of the photocatalytic performance of a semiconductive material. Nevertheless, the saturation value for the Rh loading on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> cannot be transferred on other cocatalyst material and has to be adjusted individually for each co-catalyst material. Beside Rh also Au and Pt are utilized as known noble metal H<sub>2</sub> evolution co-catalysts. Photodeposition of Au and Pt on  $C_{s_{0.68}}Ti_{1.83}O_4$  (600 °C) in a loading range between 0 – 0.0375 wt.-%, adapted from the optimal Rh loading, have only a minor or no positive effect in the production of H<sub>2</sub>. Higher co-catalyst loadings are necessary in order to provoke a change in activity. Furthermore, the known performance stability of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> in the probed mass range (Figure 32b) enables a subsequent analysis of the long term stability of the prepared photocatalyst/co-catalyst system. Long term measurements are performed with recovered photocatalysts in a time range of 10 h in methanolic solution. Figure 32 presents the photodeposition of Rh, Au and Pt on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>. Respective long term experiments are imbedded in the associated photodeposition graphs for direct comparison (Figure 34a - c).

Photodeposition of Rh particles is performed up to the optimum loading of 0.0375 wt.-% in constant 0.0125 wt.-% steps. The photocatalyst system  $Cs_{0.68}Ti_{1.83}O_4/Rh$  is recovered by filtration and drying at room temperature for 24 h and afterwards re-used for the upcoming long term measurement. The photodeposition procedure leads to a H<sub>2</sub> evolution rate of around 20 µmol/h after the deposition of totally 0.0375 wt.-% of Rh. The recovered mass from  $Cs_{0.68}Ti_{1.83}O_4/Rh$  of approximately 59 mg is inserted for the long term measurement.  $Cs_{0.68}Ti_{1.83}O_4/Rh$  shows no activation period in the beginning of the long term measurement and provides a H<sub>2</sub> evolution rate of 41.1 µmol/h after 30 min of irradiation (Figure 34a). The doubling in H<sub>2</sub> production rate corresponds with the recorded activity of  $Cs_{0.68}Ti_{1.83}O_4/Rh$  as shown in figure 33d, which is referred to an increased surface area after the initial photodeposition process.  $Cs_{0.68}Ti_{1.83}O_4/Rh$  provides a stable photocatalytic performance

during the entire measuring time with a mean production rate of  $44 \,\mu$ mol/h and a corresponding standard deviation of 1.1  $\mu$ mol/h (Figure 34d).



**Figure 34:** Sequential photodeposition and corresponding long term measurement (LTM) of a) Rh, b) Au and c) Pt on  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600 °C and d) average H<sub>2</sub> evolution rates extracted from the respective co-catalyst LTM with error bars calculated from standard deviation.

Photodeposition of Au and Pt in a loading range up to 0.0375 wt.-% has no or only a minor positive impact on the photocatalytic activity of  $Cs_{0.68}Ti_{1.83}O_4$  (Appendix). Therefore, higher loadings in different deposition steps are chosen to force a rise in activity. Au photodeposition is executed in irregular loading steps up to a final loading of 1 wt.-%. The initial deposition of 0.1 wt.-% of Au, generates a minor rise in H<sub>2</sub> production to a rate of 7.5 µmol/h, starting from a blank production rate of 4.5 µmol/h. Additional depositions to Au loadings of 0.25, 0.5 and 1 wt.-% lead to H<sub>2</sub> evolution rates of 9.5, 10.6 and 10.7 µmol/h, respectively. Superficial, the deposition of Au on  $Cs_{0.68}Ti_{1.83}O_4$  have only a minor supporting effect on the photocatalytic activity. A Au photodeposition up to an extent of 1 wt.-% leads only to a nearly doubled H<sub>2</sub> production in relation to the recorded blank activity. Even higher Au loadings up to 2 wt.-% in 0.5 wt.-% steps do not lead to any further increases in the photocatalytic activity. Therefore, an optimum loading of 1 wt.-% for Au on  $Cs_{0.68}Ti_{1.83}O_4$  is determined for additional photocatalytic experiments with the  $Cs_{0.68}Ti_{1.83}O_4/Au$  photocatalyst system. The subsequent insertion of 58.6 mg of the recovered photocatalyst system  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) for the long term measurement, results in an average H<sub>2</sub> evolution rate of 22.5 µmol/h with a standard deviation of around 0.9 µmol/h (Figure 34d). Re-used  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) shows a doubling in production rate in relation to the recorded H<sub>2</sub> evolution rate after a stepwise Au photodeposition of 1 wt.-%. The activity doubling correlates with the observed activity of re-used  $Cs_{0.68}Ti_{1.83}O_4/Rh$  (Figure 34a). Despite of the low activity, the long term measurement reveals a stable production rate of  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) in the measured time scale.

Pt as co-catalyst shows an analogous behavior as Rh in the stepwise photodeposition but a lowered H<sub>2</sub> evolution rate of approximately 15 µmol/h up to a loading of 0.0375 wt.-%. According to the performed photodeposition series in figure 34b, Pt loadings are increased in order to provoke a higher H<sub>2</sub> production rate. Sequential photodeposition is executed in constant 0.1 wt.-% steps up to a loading of 0.5 wt.-% of Pt. Additional Pt depositions are carried out in 0.25 wt.-% steps. As shown in figure 34c, the performed photodeposition series with Pt on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> leads to a linear increase in photocatalytic activity in the examined loading range. Loadings above 1 wt.-% do not lead to further rises in the photocatalytic activity of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Pt. An optimum Pt loading of 1 wt.-% is adjusted for further photocatalytic measurements with the  $Cs_{0.68}Ti_{1.83}O_4/Pt$  photocatalyst system. The deposition of 0.5 wt.-% of Pt in 0.1 wt.-% steps, has a supporting effect on the photocatalytic activity of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>, which is manifested in a H<sub>2</sub> evolution rate of 22.1 µmol/h. Additional depositions of 0.75 and 1 wt.-% of Pt lead to H<sub>2</sub> production rates respectively of 24.7 and 26.6 µmol/h. A recovered photocatalyst mass from Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Pt (1 wt.-%) of 58 mg is reinserted for the associated long term measurement in methanolic solution. Re-used Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Pt (1 wt.-%) experiences the highest photocatalytic activity compared to Rh and Au modified  $Cs_{0.68}Ti_{1.83}O_4$ , with an average H<sub>2</sub> evolution rate of around 65.1 µmol/h and a standard deviation of 2.2 µmol/h (Figure 34d). Nevertheless, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Pt shows an irregular activity development during the long term experiment, which is manifested in an increased standard deviation. An activity peak of 68 µmol/h is achieved after 4 h of irradiation. Afterwards, a constantly decreasing H<sub>2</sub> production down to a rate of 61 µmol/h after 10 h is observed. The observed deactivation of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Pt cannot be fully explained. Possible structural and morphology changes may contribute in the deactivation but cannot be fully clarified. Furthermore, decomposition products from the methanol conversion

to  $H_2$ , like formaldehyde and formic acid (Chapter 3.2.3) may also have a poisoning effect on co-catalyst particles. Deactivation phenomena of co-catalyst materials in heterogeneous photocatalysis are not well researched and still lack of an intense discussion.

According to the performed long term measurements with re-used  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Rh, Au, Pt) in the photocatalytic methanol reforming reaction, a clear activity trend can be highlighted as Pt > Rh > Au (Figure 34d). The observed trend is in contrast to the expectation that an activity trend according to the respective work function in the order of Pt ( $\Phi = 5.12 - 10^{-1}$ 5.93 eV > Au ( $\Phi = 5.31 - 5.47 \text{ eV}$ ) > Rh ( $\Phi = 4.98 \text{ eV}$ ) will be present.<sup>[115]</sup> The work function is a quantity of the generated Schottky barrier in a semiconductor/metal system and specifies the electron capturing potential. Metal particles with larger work functions cause higher Schottky barriers and consequently the resulting semiconductor/metal system exhibit a higher electron capturing potential. But the consideration of the work function fails as an explanation for the observed trend and requires a more realistic; in respect of the used photocatalyst Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> related solution approach. According to Ohyama et. al.<sup>[59]</sup> the specific interaction between photocatalyst and co-catalyst is a determining factor, which influences the photocatalytic activity. In the mentioned study, the concept of strong metal – support interaction (SMSI) originated from classical heterogeneous catalysis was utilized for interpretation of the photocatalyst/co-catalyst status. Photodeposited Pt, Au and Rh on the surface of TiO<sub>2</sub> in anatase modification were utilized as model photocatalyst/co-catalyst systems. The chemical similarity between  $TiO_2$  and  $Cs_{0.68}Ti_{1.83}O_4$  enables a correlation of the discussed SMSI-effect by Ohyama et. al.<sup>[59]</sup> to the investigated  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Rh, Au, Pt) photocatalyst systems. Xe sputtering experiments showed that Pt and Rh exhibit higher M/Ti ratios than Au, concluding a stronger interaction of Pt and Rh particles with the TiO<sub>2</sub> support while Au particles were only weakly bound on TiO<sub>2</sub>. Furthermore, the experimentally detected M/Ti ratios also showed that despite of the same co-catalyst precursor concentrations; Au was inefficiently deposited on the TiO<sub>2</sub> surface, which correlates with the especially performed stepwise photodeposition experiment shown in figure 34b. In detail, a trend of M/Ti ratios of Pt > Rh > Au was discovered by Ohyama et. al.<sup>[59]</sup>, which correlates with the recorded photocatalytic activities in figure 34d. Basing on the published results from Ohyama et. al., the contemplation of the interaction between the photocatalyst material, which acts formally as a support for the co-catalyst and the used co-catalyst itself is the determining factor for the interpretation of the photocatalytic activity rather than the simple consideration of the metal co-catalyst work function.

Basing on the discovered optimum loadings for Rh, Au and Pt on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> (Figure 34), the respective  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Rh, Au, Pt) photocatalyst system is synthesized by photodeposition through the direct insertion of the optimum co-catalyst amount into a methanolic photocatalyst suspension and subsequent irradiation by a Xe arc lamp for 10 h. The recovered  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Rh, Au, Pt) photocatalysts are re-used in long term experiments for photocatalytic ethanol and glycerol reforming reactions (Appendix). Long term measurements are executed again for 10 h. Figure 35 presents the average H<sub>2</sub> evolution rates with error indicators of  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Rh, Au, Pt) in the respective reforming reaction. The shown measurement errors are calculated by the standard deviation of the respective average value determination range. Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Rh shows a stable activity in the reforming of the utilized sacrificial agents without an activation period in the beginning of the experiment. Contrary, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au experiences an activation period of approximately 2 h in the reforming of ethanol and glycerol but a stable H<sub>2</sub> evolution rate over the residual measuring time. On the other hand, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Pt shows repetitively a fluctuating production rate during the complete measuring length. Additionally, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Pt experiences a rise in activity during the reforming of glycerol and ethanol after 7 and 7.5 h of irradiation. A rate increase from 29.7 to 45.9 µmol/h in glycerol reforming and an increased H<sub>2</sub> rate from 21.9 to 33.6 µmol/h in ethanol reforming is observed. Therefore, the prior irradiation time can be stated as an activation period for Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Pt and the finally observed H<sub>2</sub> evolution rate in the reforming of ethanol and glycerol are used in the calculated average production rates in figure 35. For comparison, methanol reforming results are extracted from figure 34d and plotted again in figure 35.

According to the illustrated mean values of the H<sub>2</sub> evolution rates from the performed reforming reactions, two trends are evident in the photocatalytic activity of  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Rh, Au, Pt): 1) A general co-catalyst activity trend of Pt > Rh >Au in the reforming of methanol, ethanol and glycerol with respect to their respective optimum loading (Figure 34) and 2) A trend in the efficiency of sacrificial agent reforming. In this aspect, an efficiency trend of methanol > glycerol > ethanol is present, independent of the used co-catalyst. The trend in sacrificial agent reforming is already observed in the stepwise photodeposition of Rh on  $Cs_{0.68}Ti_{1.83}O_4$  in methanol, ethanol and glycerol containing solutions (Figure 32c). In the consideration of the present results (Figure 35), it turns out that the utilized co-catalysts Rh, Au and Pt do not provide any new pathways in the conversion of methanol, ethanol and glycerol due to the similarity in the reforming trend. The recorded H<sub>2</sub> evolution rates show that the photodeposited co-catalysts exclusively act as electron traps for proton reduction or

rather for  $H_2$  formation and that the conversion mechanisms are mainly subjected by the oxidative potential of the VB holes. The VB stays unaffected from the co-catalyst deposition.



**Figure 35:** Average H<sub>2</sub> evolution rates of  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Rh 0.0375 wt.-%, Au 1 wt.-% and Pt 1 wt.-%) with measurement error indicators of long term experiments in the photocatalytic reforming of methanol, ethanol and glycerol.

Consequently, the observed H<sub>2</sub> production rates reflect again that the photocatalytic activity of  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Rh, Au, Pt) depends on their respective SMSI effect between photoand co-catalyst. Furthermore,  $Cs_{0.68}Ti_{1.83}O_4/Rh$  shows the best ratio between co-catalyst loading and H<sub>2</sub> evolution rate of 0.0375 wt.-% and a rate of 44 µmol/h in methanol reforming, despite of  $Cs_{0.68}Ti_{1.83}O_4/Pt$  with the highest rate in methanol reforming of 68 µmol/h but with a Pt loading of 1 wt.-%.  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) shows the lowest photocatalytic activity in all performed reforming reactions.

#### Post Characterization of $Cs_{0.68}Ti_{1.83}O_4/M$ (M = Rh, Au, Pt) after Sacrificial Agent Reforming

The tested photocatalysts  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Rh, Au, Pt) are again recovered after the long term experiment in the reforming of methanol, ethanol and glycerol and characterized by XRD and diffuse reflectance spectroscopy in order to investigate possible changes in the crystal structure and optical capabilities. XRD patterns and corresponding Tauc plots of  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Rh, Au, Pt) are presented in figure 36a - f. According to the presented XRD patterns in figure 36a, c and e, the sacrificial agent reforming as well as the photodeposition of the respective co-catalyst do not lead to any further structure changes as the already discussed ones in chapter 5.1.2, and pictured in figure 31a for  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600 °C.



**Figure 36:** XRD patterns with reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$  and  $H_2Ti_2O_5 \cdot H_2O$  and corresponding Tauc plots with absorption edge linearization and band gap energy (Eg) of a) – b)  $Cs_{0.68}Ti_{1.83}O_4/Rh$ , c) – d)  $Cs_{0.68}Ti_{1.83}O_4/Au$  and e) – f)  $Cs_{0.68}Ti_{1.83}O_4/Pt$  after long term measurements in methanol, ethanol and glycerol.

Consequently, the as-synthesized  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600 °C imbued in the respective water/sacrificial agent mixture results in the same  $Cs^+$  to proton exchanged photocatalyst after the photocatalytic process. Despite of the high co-catalyst loading of 1 wt.-% in case of  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Au, Pt), no XRD patterns of metallic Au and Pt are present in the corresponding XRDs. Furthermore, the fragmentation of particle agglomerations, provoked

by the experimental environment and discussed in chapter 5.1.2, does not lead to a significant reflex broadening and cohesively also not to a decreased average particle size. In accordance with the observed band gap increase in the  $Cs_{0.68}Ti_{1.83}O_4$  calcination series after the photocatalytic process, as shown in figure 31b, an overall band gap increase is also observed for  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Rh, Au, Pt) in a range between 3.5 - 3.6 eV after long term measurements in sacrificial agent reforming. Photodepositions of Rh and Pt on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> do not have a direct effect on the optical band gap, while photodepositions of Au particle lead to an absorption shoulder in the energy range below 3.5 eV in case of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au from methanol and ethanol reforming experiment, as seen in figure 36d. The observed absorption shoulder cannot be referred to the surface plasmon resonance (SPR) signal of Au particle, which show a characteristic signal at wavelengths around 550 nm or at a corresponding energy of 2.25 eV. Due to the absence of additional byproducts or impurities in the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au XRD patterns (Figure 36c), the observed absorption shoulder cannot be referred to any contaminations in the bulk material. Otherwise, the absorption shoulder can be mainly referred to interband transitions in Au nanoparticles starting at a wavelength of 355 nm or approximately 3.5 eV.<sup>[196]</sup> Nevertheless, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au after glycerol reforming does not experience the same degree of Au interband transition as Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au after methanol and ethanol reforming. Possible explanations for the smaller interband transition of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au after glycerol reforming may be a lowered Au content after the long term residual decomposition products from experiment or glycerol reforming like hydroxyacetaldehyde, which interfere with Au particles. However, a distinct explanation of the differences in the observed Au interband transition cannot be given. Nevertheless, the visible Au SPR signal and interband transition in the diffuse reflectance spectra provides a simple evidence of Au nanoparticles on the photocatalyst surface und offers a tool for an in*situ* observation of the Au co-catalyst formation under experimental conditions.

In summary, photodepositions of noble metal co-catalysts like Rh, Au and Pt have no influence on the crystal structure of the  $Cs_{0.68}Ti_{1.83}O_4$  support material. Structural as well as morphology changes are induced by the instrumental conditions of the photocatalytic setup as the turbulent mixing of the photocatalyst suspension and the experimental environment, precisely the liquid phase consisting of water and sacrificial agent, which forces a  $Cs^+$  to proton exchange. Rh and Pt nanoparticles have also no effect on the optical properties of  $Cs_{0.68}Ti_{1.83}O_4$ , despite of Au nanoparticles, which provoke an absorption in the visible light region originated from the Au SPR.

## 5.1.4 Copper as an Earth-abundant Co-Catalyst in Photocatalytic H<sub>2</sub> Production

Noble metal co-catalysts provide high photocatalytic activities if deposited on a photocatalyst surfaces. The formed semiconductor/metal contact resulting in a Schottky junction enables an effective separation of photogenerated electron/hole pairs and leads consequently to an increased quantum efficiency. Contrary, the high costs of noble metals prevent their application in future industrial scale photocatalysis plants. For this reason, cheaper co-catalyst materials have to be discovered in order to establish a cost effective alternative to noble metals. Copper (Cu) represents one promising alternative co-catalyst material for photocatalytic H<sub>2</sub> production. Earth-abundant co-catalysts like Cu are known for a lower photocatalytic performance in a semiconductor/co-catalyst systems compared to noble metal/photocatalyst systems, due to their smaller work function, e.g. Cu of  $\Phi = 4.53 -$ 5.10 eV<sup>[115]</sup>, which results in a smaller Schottky barrier and cohesively in a less effective electron/hole pair separation. This circumstance provokes the usage of higher co-catalyst loadings for earth-abundant co-catalysts in order to achieve a comparable degree of photocatalytic performance to noble metal co-catalysts. The activity of Cu as an earthabundant co-catalyst is examined on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> in photocatalytic reforming reactions of methanol, ethanol and glycerol for H<sub>2</sub> production. Prior, an adjustment of the optimum Cu loading on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> has to be executed for further investigations in regard of sacrificial agent reforming. Cu deposition on the surface of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> is performed via photodeposition in methanolic (10 vol.-%) solution under irradiation of a Xe-arc lamp.

Initially, Cu photodeposition is executed in a low mass regime between 0 - 0.1 wt.-% in 0.0125 wt.-% steps, adapted from the stepwise photodeposition of Rh (Figure 30a). The photodeposition of Cu up to a loading of 0.1 wt.-% in 0.0125 wt.-% steps is performed in three successive deposition phases. In detail, the first phase includes the deposition of totally 0.0375 wt.-% of Cu, while the second phase includes the deposition of an amount of 0.075 wt.-% and in the third phase, the final Cu loading up to 0.1 wt.-% of Cu up to 0.1 wt.-% can be found in the appendix. Photodeposition of Cu in the mentioned low loading range up to 0.1 wt.-% does not lead to a significant increase in the H<sub>2</sub> evolution rate, as observed for Rh in the equivalent loading regime. In the first deposition phase, a maximum H<sub>2</sub> production rate of around 6.8 µmol/h with a Cu loading of 0.025 wt.-% is achieved, starting from an initial blank activity of 4.6 µmol/h. Also in the second and third deposition phase with a maximum activity of 6.4 µmol/h at 0.0625 wt.-% and 5.9 µmol/h at 0.0875 wt.-%, no appreciable rise in

activity could be observed. The successive photodeposition of Cu includes also the difficulty that the experiment has be interrupt between the individual deposition phases, which results in a decreased initial activity in the upcoming phase. This circumstance induces a deactivation of the Cu co-catalyst during the experiment interruption, despite of the inert gas atmosphere of the experimental conditions. In order to overcome the time consuming disadvantage of the stepwise photodeposition, the followed Cu photodeposition is carried out by the direct injection of the desired Cu amount to the photocatalyst suspension and an irradiation period of 10 h to guarantee a complete deposition as well as to investigate possible kinetic inhibitions of the Cu photodeposition. The photodepositions of 0.1, 0.25, 0.5, 1 and 2 wt.-% of Cu are carried out by the direct injection of the stated Cu amount to the photocatalyst suspension and subsequently irradiated for 10 h. Each photodeposition experiment in the stated loading range is performed with 75 mg of as-synthesized  $Cs_{0.68}Ti_{1.83}O_4$ , in order to prevent a total mass loss under the examined mass range (Figure 32b) and to ensure the comparability of the measurements. Figure 37a presents the average H<sub>2</sub> evolution rates of the Cu photodeposition between 0.1 - 2 wt.-% with corresponding error indicators, calculated from the standard deviation of the subject region (2 - 10 h) for average determination.



**Figure 37:** a) Average H<sub>2</sub> evolution rates of the photodeposition of 0.1, 0.25, 0.5, 1 and 2 wt.-% of Cu on  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C) with corresponding error indicators and b) Photodeposition of 2, 3, 4 and 5 wt.-% of Cu on  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C); photodeposition of 3, 4 and 5 wt.-% of Cu required 24 h of irradiation.

Cu photodeposition between 0.1 - 2 wt.-% has only a minor positive effect on the photocatalytic performance of  $Cs_{0.68}Ti_{1.83}O_4$ , with a corresponding maximum H<sub>2</sub> evolution rate of 6.6 µmol/h at 0.25 wt.-% of Cu. The observed activity decrease at Cu loadings higher than 0.25 wt.-% cannot be admitted as a reliable trend because of the recorded measuring inaccuracies, which are indexed by error bars in the respective measuring point. Measuring errors, calculated by the standard deviation of the measuring point of the respective deposition

experiment, reveal an inaccuracy between  $0.57 - 0.79 \,\mu$ mol/h and paired with the narrow activity range, it can be assumed that a constant activity is present in the range between 0.1 - 2 wt.-%. Therefore, higher Cu loadings above 2 wt.-% are necessary to enforce a significant rise in photocatalytic activity. Cu loadings of 3, 4 and 5 wt.-% are examined for Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>. The produced Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu photocatalysts, after the deposition of 2, 3 and 4 wt.-%, are recovered and re-inserting in the upcoming experiment, in order to simulate a continuous stepwise Cu photodeposition in the range between 2 - 5 wt.-%. The used Cu precursor amount is adjusted to the recovered photocatalyst mass. Figure 37b pictured the simulated stepwise Cu photodeposition on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>.

In the first attempt of Cu photodeposition of 2 and subsequently 3 wt.-%, the particular deposition phases included 10 h of irradiation. While the deposition of 2 wt.-% of Cu exhibits a comparable activity as shown in figure 37a, the followed deposition of 3 wt.-% of Cu reveals a slow start-up of the H<sub>2</sub> production. After an activation time of 4 h, a minor activity of  $3 \mu$ mol/h could be detected as well as a continuously increasing H<sub>2</sub> evolution rate during 10 h of irradiation. However, a steady state in the H<sub>2</sub> production rate could not be achieved in the estimated measuring time. Therefore in a second attempt of Cu photodeposition, the estimated irradiation time for the deposition of 3 wt.-% of Cu is extended up to 24 h in order to establish a steady state in H<sub>2</sub> production. As shown in figure 37b, a stable activity in the deposition of 3 wt.-% of Cu is achieved between 27 - 34 h or rather 17 - 24 h of the real measuring time with an average rate of 40.6 µmol/h. The recorded activity development during the 24 h continuing irradiation period shows again a slow start-up of the photocatalytic activity followed by a steady rise, ending in the steady state range. The slow photocatalyst activation probably originates from a kinetic inhibition of the Cu co-catalyst precursor reduction from Cu(II) to Cu(I)  $(Cu^{2+}/Cu^{+} + 0.16 \text{ V vs. NHE})$  and finally to metallic Cu (Cu<sup>+</sup>/Cu + 0.52 V vs. NHE).<sup>[115]</sup> The inhibition results from a re-oxidation of reduced Cu species by photoinduced holes. Especially an oxidation of Cu<sup>+</sup> to Cu<sup>2+</sup> is quite possible, due to its more negative redox potential compared to the redox couples of (Cu<sup>+</sup>/Cu) + 0.52 V vs. NHE and (Cu<sup>2+</sup>/Cu) + 0.35 V vs. NHE.<sup>[115]</sup> This effect is slowing down the formation of a critical amount of metallic Cu until the co-catalyst precursor reduction is dominant. Subsequent photodeposition of totally 4 wt.-% of Cu on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (3 wt.-%) shows a similar photocatalytic behavior as the previous deposition phase but with a shorter activation period and a lowered average H<sub>2</sub> evolution rate of 34.1 µmol/h. An additional deposition of totally 5 wt.-% of Cu on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (4 wt.-%) shows again a reduced photocatalytic activity with an average  $H_2$  rate of 25.2 µmol/h after an activation time of 7 h.
In conclusion, the sequential photodeposition of 3 wt.-% of Cu, starting from 2 wt.-% of Cu, results in the highest  $H_2$  evolution rate after an irradiation time of 24 h. Higher Cu loadings lead to a decreased photocatalytic activity, probably due to an increased Cu particle size and an associated decreased co-catalyst particles surface area. The determined optimum Cu loading of 3 wt.-% is further utilized for the investigation of the sacrificial agent reforming capabilities of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  in long term experiments for sacrificial agent reforming.

To ensure a comparability of the sacrificial agent reforming experiments, the used photocatalyst  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (3 wt.-%) is identically prepared as presented in figure 37b. In detail, initially 2 wt.-% of Cu are deposited on  $Cs_{0.68}Ti_{1.83}O_4$  afterwards recovered and reinserted for the deposition of 3 wt.-% of Cu, with irradiation periods of 10 and 24 h respectively. The final photocatalyst is again re-inserted in a reaction solution containing 10 vol.-% of methanol, ethanol and glycerol and irradiated for 24 h instead of 10 h to receive a steady state in activity. For comparison, the determined activities of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  in sacrificial agent reforming are plotted with activities of  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Rh, Au, Pt) in figure 38.



**Figure 38:** Average H<sub>2</sub> evolution rates of  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Rh 0.0375 wt.-%, Au 1 wt.-%, Pt 1 wt.-% and Cu 3 wt.-%) with measurement error indicators of long term experiments in the photocatalytic reforming of methanol, ethanol and glycerol.

 $Cs_{0.68}Ti_{1.83}O_4/Cu$  (3 wt.-%) experiences an activation period between 2 - 5 h in the performed reforming reactions, which can be mainly referred to the reduction of the Cu co-catalyst precursor. Photoinduced electrons are utilized for the Cu co-catalyst reduction process instead for H<sub>2</sub> production. Related measurements concerning long term experiments with

 $Cs_{0.68}Ti_{1.83}O_4/Cu$  can be found in the appendix.  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (3 wt.-%) exhibits an equivalent activity trend in the reforming of methanol, ethanol and glycerol as the noble metal modified  $Cs_{0.68}Ti_{1.83}O_4$ , as already stated in the order methanol > glycerol > ethanol. Interestingly,  $Cs_{0.68}Ti_{1.83}O_4/Cu$  provides a similar photocatalytic activity to  $Cs_{0.68}Ti_{1.83}O_4/Rh$  in methanol reforming with a H<sub>2</sub> evolution rate of 43.1 µmol/h, while experiences less activity in the conversion of ethanol with a rate of 15.4 µmol/h. On the other hand,  $Cs_{0.68}Ti_{1.83}O_4/Cu$  shows an improved activity in glycerol reforming compared to  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Rh, Au) with a production rate of 27.5 µmol/h but lower than  $Cs_{0.68}Ti_{1.83}O_4/Pt$ , which still provides the highest activity in all examined reforming reactions. Nevertheless, the effective conversion of methanol and glycerol by  $Cs_{0.68}Ti_{1.83}O_4/Cu$  proofs that earth-abundant co-catalyst materials provide comparable photocatalytic activities to noble metal co-catalysts but only at higher loadings.

## Post Characterization of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu after Sacrificial Agent Reforming

The simulated sequential photodeposition of Cu, as shown in figure 37b, and the associated continuous photocatalyst recovery after each individual deposition step causes an extended exposition time in methanolic solution of totally 82 h and an additional mechanical stress on the bulk material.  $Cs_{0.68}Ti_{1.83}O_4/Cu$  XRD patterns of Cu loadings of 2 - 5 wt.-% are presented in figure 39a. Due to the structural similarity of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (0.1 - 2 wt.-%) only  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2 wt.-%) is shown as a representative of the not shown diffraction patterns. Tauc plots calculated from the corresponding diffuse reflectance spectra of Cu loadings between 0.1 - 5 wt.-% are presented in figure 39b.



**Figure 39:** a) XRD patterns of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2 - 5 wt.-%) with reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$  and  $H_2Ti_2O_5 \cdot H_2O$  and b) Tauc plots of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (0.1 - 5 wt.-%) with individual absorption edge linearization and band gap energies ( $E_g$ ).

The simulated stepwise photodeposition of Cu from 2 to 5 wt.-% on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> leads to a more advanced transformation of the  $Cs_{0.68}Ti_{1.83}O_4$  crystal structure to the proton exchanged  $H_{0.68}Ti_{1.83}O_4$  version. The crystal structure transformation becomes evident by the observation of the (110) lattice plane reflex of  $H_2Ti_2O_5 \cdot H_2O$  or rather  $H_{0.68}Ti_{1.83}O_4$  at 24.4° 20, which intensifies with elongated exposition time in methanolic solution or rather with increasing Cu loading. After an exposition time of 58 h or after the deposition of 4 wt.-% of Cu, the  $H_2Ti_2O_5 \cdot H_2O$  (110) lattice plane becomes visible in the respective XRD pattern. Additionally, the intensity of the most intensive (130) reflex of  $Cs_{0.68}Ti_{1.83}O_4$  at 28.1° 20 decreases with increasing Cu loading or longer exposition time in the reaction media. The lowered photocatalytic activity at Cu loadings of 4 and 5 wt.-% as well as the constantly decreasing H<sub>2</sub> evolution rate during the individual deposition phase can originate as well from the in-situ processed crystal structure transformation caused by the Cs<sup>+</sup> to proton exchange in addition to the previously mentioned decreased Cu particle surface area. A consideration of single phenomena for the explanation of the decreased photocatalytic activity is rather inadequate. Both phenomena are occurring simultaneously in the preparation of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2 - 5 wt.-%) and provoke the observed activity decrease. Nevertheless, a photocatalytic activity examination of proton exchanged Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>, synthesized by the exposure of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> (800 °C) in 1 M HCl for 72 h shows no reduced activity in the stepwise photodeposition of Rh with a rate of 27.4 µmol/h (Appendix). But the recorded photocatalytic performance describes the activity of pure H<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>, while in case of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu the proton exchanged form can be seen as an impurity, which interferes with the host material. Therefore, the reduced activity in  $C_{s_{0.68}}Ti_{1.83}O_4/Cu$  (4 - 5 wt.-%) cannot be referred to only one of the mentioned phenomena.

Tauc plots of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (0.1 - 5 wt.-%) (Figure 39b) show a decreasing trend in band gap energy starting with a Cu loading of 0.1 wt.-% with 3.60 eV to 2 wt.-% with 3.28 eV.  $Cs_{0.68}Ti_{1.83}O_4/Cu$  with loadings higher than 2 wt.-% exhibits an increased band gap energy. Differences in band gap energies indicate an influence of the Cu co-catalyst on the optical properties of the  $Cs_{0.68}Ti_{1.83}O_4$  support material. Cu interband transitions may occur in an energy range between 2 - 5 eV but cannot be directly referred to the observed band gap decrease up to 2 wt.-% of Cu. The structural transformation of  $Cs_{0.68}Ti_{1.83}O_4$  towards the proton exchanged version  $H_{0.68}Ti_{1.83}O_4$  has probably a greater effect on the band gap energy than the Cu photodeposition itself. It can be assumed that the partial exchange of  $Cs^+$  by protons is sufficient enough for a lowering of the CB edge to lower energies while the VB edge stays unaffected, which results in a reduced band gap energy. The CB edge decrease is more likely due the high energy of Ti 3d orbitals. However, according to Liu et. al.<sup>[37]</sup> the CB of  $Cs_{0.68}Ti_{1.83}O_4$  and  $H_{0.68}Ti_{1.83}O_4$  consists exclusively of Ti 3d orbitals, while the CB and VB of  $H_{0.68}Ti_{1.83}O_4$  are located at lower energies compared to the CB and VB of  $Cs_{0.68}Ti_{1.83}O_4$ . The influence of  $Cs^+$  and protons on the respective band structure is still unclear. Nonetheless, it can be assumed that a partial  $Cs^+$  to proton exchange results in a lowered CB edge energy. Due to the more advanced  $Cs^+$  to proton exchange at Cu loadings higher than 2 wt.-% (Figure 39a), which originates from a longer exposition time in the aqueous reaction medium, the increasing band gap energies can be directly referred to an increased content of  $H_{0.68}Ti_{1.83}O_4$ , which exhibits a band gap energy of 3.47 eV.  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2 wt.-%) holds the lowest band gap but showed a similar activity to photocatalysts with lower Cu contents and even a lowered activity compared to higher Cu contents. Hence, a correlation between band gap energy and photocatalytic activity is also not present.

In summary, Cu as an earth-abundant co-catalyst provides a comparable activity to noble metal co-catalysts in the photocatalytic H<sub>2</sub> production via sacrificial agent reforming. But in order to achieve a noble metal performance degree, higher Cu loadings up to 3 wt.-% are necessary to provoke a significant increase in the H<sub>2</sub> evolution rate. Furthermore, photodeposition of 3 wt.-% of Cu on  $C_{S_{0.68}}Ti_{1.83}O_4$  requires an irradiation time of totally 34 h, which includes 10 h for the deposition of 2 wt.-% and further 24 h for the deposition of additional 1 wt.-% to receive  $C_{S_{0.68}}Ti_{1.83}O_4/Cu$  (3 wt.-%). Higher Cu loadings than 3 wt.-% lead to a decreased photocatalytic activity.  $C_{S_{0.68}}Ti_{1.83}O_4/Cu$  (3 wt.-%) shows a comparable activity in methanol, ethanol and glycerol reforming to  $C_{S_{0.68}}Ti_{1.83}O_4/Rh$  (Figure 38) with an equivalent activity trend. Post characterization of  $C_{S_{0.68}}Ti_{1.83}O_4/Cu$  after ethanol and glycerol reforming reveals the same changes in crystal structure as shown in figure 39 for a Cu loading of 3 wt.-%, while the band gap after methanol reforming (Appendix). However, the long photodeposition period for  $C_{S_{0.68}}Ti_{1.83}O_4/Cu$  (3 wt.-%) is adverse for practical usage and requires therefore an alternative preparation route.

#### 5.1.5 M/Cr<sub>2</sub>O<sub>3</sub> (M: Rh, Cu) Core/Shell Co-Catalyst for Overall Water Splitting

None prepared  $Cs_{0.68}Ti_{1.83}O_4$ :M (M = Rh, Au, Pt and Cu) photocatalysts show any activity in the overall water splitting reaction even under UV light irradiation. In order to promote the overall water splitting reaction, the known co-catalyst core/shell systems of the form Rh/Cr<sub>2</sub>O<sub>3</sub> and Cu/Cr<sub>2</sub>O<sub>3</sub> developed by Domen et. al.<sup>[64, 67]</sup> are applied on pristine  $Cs_{0.68}Ti_{1.83}O_4$ . The amorphous Cr<sub>2</sub>O<sub>3</sub> shell, covering the H<sub>2</sub> formation co-catalyst, prevents the adsorption of formed O<sub>2</sub> on the Rh or Cu co-catalyst and thereby blocks the back reaction of  $H_2$  and  $O_2$  to  $H_2O$ . The deposition of the M/Cr<sub>2</sub>O<sub>3</sub> (M = Rh, Cu) co-catalyst system is executed by photodeposition in methanolic solution (10 vol.-%). Initially, Rh or Cu is photodeposited in three sequential deposition steps. Each deposition steps includes the insertion of 0.0125 wt.-% of the respective H<sub>2</sub> formation co-catalyst, followed by the deposition of an equivalent amount of Cr<sub>2</sub>O<sub>3</sub> again in three sequential steps. Photodeposition of Rh and Cu manifests in an increased H<sub>2</sub> evolution rate, while a successful Cr<sub>2</sub>O<sub>3</sub> photodeposition on Rh or Cu results in a decreased H<sub>2</sub> production rate, due the lost active Rh or Cu surface area induced by formation of the  $Cr_2O_3$  shell. M/Cr<sub>2</sub>O<sub>3</sub> (M = Rh, Cu) is photodeposited on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> either under Xe- and Hg-lamp irradiation. The Hg-lamp is used to ensure an entire deposition of the inserted photocatalyst amount. H<sub>2</sub> evolution rates of the  $M/Cr_2O_3$  (M = Rh, Cu) photodeposition can be found in the appendix. Photodeposited M/Cr<sub>2</sub>O<sub>3</sub> (M = Rh, Cu) co-catalysts on  $Cs_{0.68}Ti_{1.83}O_4$  are recovered, dried and re-used for an overall water splitting experiment in pure water. Likewise, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> shows no activity in the overall water splitting reaction even with the assistance of the  $M/Cr_2O_3$  (M = Rh, Cu) cocatalyst system either under Xe- or Hg-lamp irradiation, concluding that Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> is not capable to perform overall water splitting. The presented results reveal also that the M/Cr<sub>2</sub>O<sub>3</sub> (M = Rh, Cu) core/shell co-catalyst is not capable to provoke the overall water splitting reaction on a random photocatalyst. Concluding,  $M/Cr_2O_3$  (M = Rh, Cu) is only an assisting co-catalyst system for a photocatalyst, which is capable to perform the over water splitting reaction in its pristine form.<sup>[64, 67]</sup>

To overcome the inability of water splitting, further attempts were performed to provoke a selective  $O_2$  formation by the deposition of the known  $O_2$  forming co-catalyst cobalt phosphate also called CoPi. Photodeposition of CoPi was executed in a 0.1 M  $K_2HPO_4/KH_2PO_4$  buffer by the insertion of  $Co(NO_3)_2 \cdot 6 H_2O$  as a Co source and 5 h of constant irradiation of a Xe-arc lamp.  $Cs_{0.68}Ti_{1.83}O_4/CoPi$  photocatalysts were recovered, dried and re-used in either pure water or in 3 mM NaIO<sub>3</sub> solution for electron scavenging to increase the number of holes for  $H_2O$  oxidation. Also with the assistance of the CoPi co-catalyst as well as in a NaIO<sub>3</sub> containing solution,  $Cs_{0.68}Ti_{1.83}O_4$  showed no activity in photocatalytic  $O_2$  formation.

#### 5.1.6 Summary

Unmodified layered cesium titanate  $Cs_{0.68}Ti_{1.83}O_4$  can be synthesized by the utilized sol-gel process (Chapter 4.1.1), basing on the Pechini method, at lower calcination temperatures and shorter calcination times compared to the conventional solid state reaction. Lower annealing temperatures lead to the formation of a photocatalyst material with smaller average particle sizes, which manifests in a distinct reflex broadening in the XRD patterns. Characteristic for the resulting photocatalyst material are irregular flake-like shaped photocatalyst particles, which tend to agglomerate to larger aggregates. Particle shaping is subjected to the gel combustion step, which generates an ash-like carbon contaminated solid precursor. Microscopic particle shape characteristics are also evident in the macroscopic bulk material constitution. Higher annealing temperatures (> 600 °C) produce more crystalline  $Cs_{0.68}Ti_{1.83}O_4$  materials, which can be quantified by the reflex narrowing in the XRD patterns. Contrary,  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 700 and 800 °C exhibit a minor rutile impurity, which is not visible in the XRD patterns. However the rutile impurity can be detected as an absorption shoulder in the respective Tauc plots.

Photocatalytic activity examination of the  $Cs_{0.68}Ti_{1.83}O_4$  calcination series is carried out in the stepwise Rh photodeposition for H<sub>2</sub> production in methanolic solution.  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600 °C shows the highest activity in methanol reforming and therefore utilized as the standard support material for co-catalyst deposition and further investigations in regard of sacrificial agent reforming. The superior activity of  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C) compared to lower and higher calcined versions originates from the compromise between a sufficient degree of crystallinity and average particle size. Extrinsic factors as light source and temperature have a positive effect on the photocatalytic performance of  $Cs_{0.68}Ti_{1.83}O_4$ . However, the increased activity can be directly referred to the additional energy input caused by the high UV proportions of the used Hg-midpressure immersion lamp and the added thermal energy by the reactor temperature control unit. This additional energy input may lead to a misguided interpretation of the photocatalytic activity and has to be suppressed in order to extract the pristine activity of a photocatalyst.

Noble metals as stated Rh, Au and Pt are used as co-catalysts to increase the photocatalytic performance of  $Cs_{0.68}Ti_{1.83}O_4$ . Initially, the optimum loading has been determined for each co-catalyst material. The loading determination is executed in a stepwise photodeposition process. Afterwards, the prepared photocatalysts  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Rh, Au, Pt) with their respective optimum co-catalyst loading are tested in a methanol reforming long term

experiment to investigate the individual photocatalytic stability. Further experiments in ethanol and glycerol reforming with  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Rh, Au, Pt) enable the extraction of two activity trends: 1) Co-catalyst trend in the order of Pt > Rh > Au, with respect to their respective optimum loading and 2) Sacrificial agent reforming efficiency trend in the order of methanol > glycerol > ethanol. The observed co-catalyst trend can be referred to the SMSI-effect between  $Cs_{0.68}Ti_{1.83}O_4$ , which acts as the support material and Rh, Au and Pt particles. The SMSI-effect was previously investigated by Ohyama et. al.<sup>[59]</sup> on TiO<sub>2</sub>/M (M = Rh, Au, Pt) photocatalysts. A clarification of the determined trend in sacrificial agent reforming by a simple examination of the respective redox potential for total oxidation is insufficient. A sacrificial agent conversion reaction is a multistep process with several intermediate products, which have to be examined in their respective redox potential for total oxidation in relation to the CB and VB of the used semiconductor. Studies towards sacrificial agent reforming mechanisms on the examined  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Rh, Au, Pt) photocatalysts can be a subject for future research, which includes the determination of all intermediate products and their effect on the photocatalyst system.

Cu is chosen as an earth-abundant co-catalyst material for photocatalytic H<sub>2</sub> production. To achieve a comparable photocatalytic activity to noble metal co-catalysts, a Cu loading of 3 wt.-% is necessary to reach a similar activity degree. The slow reduction of the Cu precursor to metallic Cu can be referred to a kinetic inhibition, induced by an oxidation of an already reduced Cu species as well as to a lowered driving force for Cu<sup>2+</sup> reduction compared to noble metal reduction, displayed by the respective redox potential for (Cu<sup>2+</sup>/Cu) of + 0.35 V vs. NHE (pH = 0). Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu shows also a similar photocatalytic activity in the reforming of ethanol and glycerol as noble metal modified Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Rh. Furthermore, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu confirms the prior stated trend in sacrificial agent reforming. The overall photocatalytic activity as shown in figure 38, leads to the conclusion that all deposited co-catalysts exclusively act as electron acceptors and reduce the recombination rate of electron/hole pairs, while the oxidation capabilities of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> VB holes stay unaffected.

Post characterizations of the used  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Rh, Au, Pt, Cu) show a change in the  $Cs_{0.68}Ti_{1.83}O_4$  crystal structure after a photocatalytic process. The observed structure change originates from a  $Cs^+$  to proton exchange in the  $Cs_{0.68}Ti_{1.83}O_4$  interlayer during the photocatalytic process and is independent of the utilized sacrificial agent. Particle aggregates are fragmented, due to the turbulent intermixing in the reactor. The aggregate fragmentation results in an increased surface area. Additionally, an increased band gap after a performed

reforming reaction is observed for  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Rh, Au, Pt, Cu), while photodeposited Au nanoparticles show a characteristic SPR signal at 2.25 eV in the Tauc plots. A direct excitation of the Au SPR in  $Cs_{0.68}Ti_{1.83}O_4/Au$  by visible light irradiation, realized by an optical GG400 cut-off filter, after the photodeposition of 1 wt.-% and 10 h of irradiation, could not be achieved.  $Cs_{0.68}Ti_{1.83}O_4/Cu$  experiences a band gap change provoked by the sequential Cu photodeposition of 2 - 5 wt.-% (Figure 37). The long exposition time in the aqueous reaction medium leads to a more advanced Cs<sup>+</sup> to proton exchange and consequently to a structural change towards  $H_{0.68}Ti_{1.83}O_4$  and also to a change towards the electronic band structure of  $H_{0.68}Ti_{1.83}O_4$ .

Additional water splitting tests performed in pure water without sacrificial agent with  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Rh, Au, Pt, Cu) with individual optimum co-catalyst loading as well as with the core/shell co-catalyst system M/Cr<sub>2</sub>O<sub>3</sub> (M = Rh, Cu) showed no photocatalytic activity. Also an irradiation with a Hg-midpressure immersion lamp could not provoke a photocatalytic response of the tested photocatalysts in the overall water splitting reaction. In conclusion,  $Cs_{0.68}Ti_{1.83}O_4$  requires a sacrificial agent for photocatalytic H<sub>2</sub> production. For this reason, the utilization of a cheap and abundant sacrificial agent, e.g. glycerol is necessary as a cost effective feedstock for photocatalytic H<sub>2</sub> production with the layered cesium titanate  $Cs_{0.68}Ti_{1.83}O_4$ .

## 5.2 Copper and Gold modification of Layered Cesium Titanate by Wet Impregnation

The photodeposition of Cu and Au on the surface of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> includes two different problems. On one hand, Cu photodeposition up to the optimum loading of 3 wt.-% requires a total process time of 34 h, excluding the recovery of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (2 wt.-%). On the other hand, the low photocatalytic performance of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au in the examined sacrificial agent reforming tests can be referred to the weak SMSI-effect between the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> support material and Au particles. To counteract these two drawbacks, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/M (M = Cu, Au) photocatalysts were prepared by the classic wet impregnation technique, known from the synthesis of conventional heterogeneous catalysts. In both preparation approaches for the synthesis of  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Cu, Au),  $Cs_{0.68}Ti_{1.83}O_4$  was utilized as the support material for Cu and Au particles. Advantageous of the wet impregnation process in case of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu is the direct deposition of the appropriate co-catalyst amount on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>, overcoming the long preparation time in photodeposition. In case of  $Cs_{0.68}Ti_{1.83}O_4/Au$ , in addition to the deposition of the desired co-catalyst content, an additional essential calcination step to decompose the co-catalyst precursor should also strengthen the interaction between the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> support and the formed Au particles to increase the photocatalytic performance.

#### 5.2.1 Synthesis and Characterization of Copper modified Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>

For the synthesis of  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Cu, Au) by wet impregnation,  $Cs_{0.68}Ti_{1.83}O_4$ prepared by sol-gel process and calcined at 600 °C for 10 h is used as the solid support material for impregnation. In the progress of activity examination, six  $Cs_{0.68}Ti_{1.83}O_4/Cu$ photocatalysts with increasing Cu loading (2 - 7 wt.-%) were prepared by wet impregnation. Each CuSO<sub>4</sub> · 5 H<sub>2</sub>O content is diluted in 3 mL of deionized water, to ensure a constant volume of the liquid phase, which is afterwards dropped on the support. After solvent evaporation, the support material imbued with the Cu precursor (CuSO<sub>4</sub> · 5 H<sub>2</sub>O) is dried at 100 °C for 24 h. According to the performed TG analysis of the dried  $Cs_{0.68}Ti_{1.83}O_4/Cu$ photocatalyst precursor (Figure 40a), the primary mass loss occurs at a temperature of 84 °C, while a second mass loss, seen as a shoulder in the DTG curve, is observed at 158 °C, probably originated from the removal of crystal water from the Cu precursor. In the examined temperature range a total mass loss of around 3.7% is recorded, as shown in figure 40a. The recorded mass loss can be referred to the removal of residual water, which was accumulated during the atmospheric exposition between the drying process and TG measurement. However, a higher mass loss of approximately 20%, in relation to the used  $Cs_{0.68}Ti_{1.83}O_4$  content, is expected for the inserted amount of the Cu precursor for a Cu loading of 5 wt.-%. Nevertheless, the usage of higher calcination temperatures (> 600 °C) is resigned in order to prevent a change in the  $Cs_{0.68}Ti_{1.83}O_4$  support status. The performed TG analysis of the dried photocatalyst precursor induces the existence of a difficult decomposable impurity compound, which was formed during the wet impregnation process. No significant mass loss can be observed at temperatures higher than 200 °C. To ensure a complete decomposition of all volatile components, a calcination temperature of 450 °C is chosen. For structural analysis of the calcined photocatalysts, XRD measurements were performed. XRD patterns of the calcined photocatalysts  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2 - 7 wt.-%) prepared via wet impregnation are presented in figure 40b, while  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) is pictured separately in figure 40c for an exemplary presentation of the qualitative analysis of the photocatalyst material.



Figure 40: a) TG/DTG analysis of the dried  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) precursor prepared by wet impregnation, b) XRD patterns of calcined  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2 - 7 wt.-%) with red boxed TiO<sub>2</sub> (anatase) (011) reflex and c) XRD pattern of calcined  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) with reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$ , TiO<sub>2</sub> (anatase) and  $Cs_2SO_4$ .

Recorded XRD patterns of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2 - 7 wt.-%) reveal an advancing structural transformation of the photocatalyst composition from  $Cs_{0.68}Ti_{1.83}O_4$  to  $Cs_2SO_4$  and  $TiO_2$  in its

anatase modification with increasing Cu content. The increasing reflex of the anatase (011) lattice plane, blue lined reflex in figure 40b, as well as the rising reflexes at 27.3° and 28.5°  $2\theta$  of Cs<sub>2</sub>SO<sub>4</sub>, green lined reflexes, can be used as indicators for a transformation degree. Nevertheless, the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> support material is not completely transformed into the two stated components even at a Cu loading of 7 wt.-%, which is proven by the less intensive but still existing (020) reflex of  $Cs_{0.68}Ti_{1.83}O_4$  at 10.2° 20, red lined reflex. All other  $Cs_{0.68}Ti_{1.83}O_4$ reflexes are overlapped by Cs<sub>2</sub>SO<sub>4</sub> and TiO<sub>2</sub> impurity reflexes. The decreasing intensity of the  $Cs_{0.68}Ti_{1.83}O_4$  (020) reflex with increasing Cu content and the observed rise of TiO<sub>2</sub> and Cs<sub>2</sub>SO<sub>4</sub> diffraction patterns indicates that the formation of both impurities are correlated to each other and originates from the used raw materials and the impregnation process itself. In detail, during the impregnation of  $Cs_{0.68}Ti_{1.83}O_4$  with diluted  $CuSO_4 \cdot 5 H_2O$ , a salt metathesis like reaction initiated by the Cu precursor, where Cs<sup>+</sup> cations are removed from the titanate interlayer and bound to the sulfate anion, forming Cs<sub>2</sub>SO<sub>4</sub>, which exhibits a melting temperature of 1019 °C and probably not decomposable in the estimated TG temperature range. Furthermore, the removal of Cs<sup>+</sup> from the crystallographic A-position leads to a collapse of the sheet-like layered structure of  $Cs_{0.68}Ti_{1.83}O_4$  and causes a restacking of the single titanate sheets. As a result of the structure reorganization, TiO<sub>2</sub> in anatase modification is formed. TiO<sub>2</sub> formation in course of the structure collapse induces that the inserted Cu cations do not replace Cs<sup>+</sup> in the interlayer structure and therefore are exclusively deposited on the outer photocatalyst surface. Nevertheless, a partial Cs<sup>+</sup> to Cu<sup>+</sup> cation exchange cannot be excluded. Consequently, all Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (2 - 7 wt.-%) photocatalysts prepared by wet impregnation consists of three components: 1)  $Cs_{0.68}Ti_{1.83}O_4/Cu$ , depending on the respective Cu loading, 2) TiO<sub>2</sub> in anatase modification and 3) Cs<sub>2</sub>SO<sub>4</sub>. A formation of metallic Cu or CuO could not be observed in the XRD patterns.

Tauc plots of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2 - 7 wt.-%) (Figure 41) show a decreasing band gap energy corresponding to the impregnated Cu amount, expect of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (4 wt.-%), which exhibits a lowered band gap compared to Cu loadings of 3 and 5 wt.-%. Interestingly, Cu contents higher than 5 wt.-% (Figure 41b) lead to a significant decrease in the band gap energy relative to lower Cu amounts, as shown in figure 41a. Aside from the band gap decreasing effect of impregnated Cu on  $Cs_{0.68}Ti_{1.83}O_4$ , an additional lowering effect in respect of the overall reflectance of the examined impregnated photocatalysts can be observed in the high energy region between 3.75 - 4.5 eV. The reflectance lowering can be observed at Cu loadings of 6 and 7 wt.-%. The decreased reflectance degree corresponds with an

increasing degree of absorption of the photocatalyst material, which also manifests in a darkening of the photocatalyst powder. However, the darkening of the photocatalyst powder indicates the presence of highly dispersed Cu<sub>x</sub>O particles throughout the photocatalyst bulk material. Furthermore, the increased absorption degree and the resulting absorption edge broadening impedes a clear approximation of the band gap energy. Absorption edge linearization is executed on the most linear part of the absorption region in order to extract a reliable band gap value. Nevertheless, the nearly black powders of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (6 and 7 wt.-%) show a broad absorption region between 2.0 - 3.5 eV, that the stated band gap energies cannot be recognized as absolute values.



**Figure 41:** Tauc Plots with corresponding absorption edge linearization and band gap energies ( $E_g$ ) of a)  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2 - 5 wt.-%) and b)  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (6 and 7 wt.-%), prepared by wet impregnation.

In regard of the complex composition of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2 - 7 wt.-%) prepared by wet impregnation, the observed band gap lowering effect cannot be directly referred to one of the participating compounds. A more realistic explanation approach would consider an interaction between all three attendant photocatalyst components, which contribute in the overall light absorption capabilities of the photocatalyst. Another possibility is the incorporation of Cu<sup>+</sup> cations into the interlayer structure of  $Cs_{0.68}Ti_{1.83}O_4$ , replacing Cs<sup>+</sup> cations which are removed from the A-position due to the  $Cs_2SO_4$  formation in order to keep the overall charge neutrality. However, the big difference in ionic radii of 260 pm for Cs<sup>+</sup> and 77 pm for sixfold coordinated Cu<sup>+</sup>, being closer to the ionic radius of Ti<sup>4+</sup> (61 pm), leads also to the assumption that Cu<sup>+</sup> or Cu<sup>2+</sup> are incorporated in the titanate sheets, replacing Ti<sup>4+</sup> ions and forming CuO<sub>6</sub>octahedrons instead of replacing Cs<sup>+</sup> in the interlayers. These circumstances would imply that a simple immersion of the solid  $Cs_{0.68}Ti_{1.83}O_4$  in a diluted metal precursor solution is sufficient enough for an infiltration of the host material by the metal cation and that the short calcination step for precursor decomposition is either sufficient for a stabilization of the metal cation in the photocatalyst bulk material. This assumption could explain the missing of Cu,  $Cu_2O$  or CuO reflexes in the XRDs but cannot be confirmed by the used characterization methods. Hence, a clear explanation of the observed band gap reduction and the presence of a  $Cu_xO$  species, which could be present as small amorphous particles, cannot be given yet.

# 5.2.2 Photocatalytic $H_2$ Production with $Cs_{0.68}Ti_{1.83}O_4/Cu$ prepared by Wet Impregnation

Samples of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2 - 7 wt.-%) prepared by wet impregnation are tested in the photocatalytic methanol reforming reaction. All experiments are carried out for 10 h under Xe-arc lamp irradiation, in order to examine the respective long term stability. Figure 42a presents the recorded photocatalytic activities of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2 - 5 wt.-%), while activities of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (6 and 7 wt.-%) are pictured separately for a better comparison.



**Figure 42:** Long term experiments in photocatalytic  $H_2$  production via methanol reforming with a)  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2 - 5 wt.-%) and b) )  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (6 and 7 wt.-%), prepared by wet impregnation.

In accordance with the stated Cu loadings, a constant increase in the H<sub>2</sub> evolution rate with increasing Cu content can be observed. While a major activity jump from a Cu loading of 2 wt.-% with an H<sub>2</sub> production rate of 10 µmol/h to 3 wt.-% with a H<sub>2</sub> production rate of around 47 µmol/h is evident and comparable to their photodeposited analogues (Figure 37b). Also from 3 to 4 wt.-% of Cu, an activity increase up to a rate of around 69 µmol/h takes place. Higher Cu loadings from 5 to 7 wt.-%, lead to a constant production rate increase of 10 µmol/h per additional 1 wt.-% up to a maximum rate of 100 µmol/h achieved by  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (7 wt.-%). Nevertheless,  $Cs_{0.68}Ti_{1.83}O_4/Cu$  with 3 - 5wt.-% loading reaches a steady state after 3 h of irradiation, while Cu loadings of 6 and 7 wt.-% experience

an activation time of 4 h. Especially in case of Cu 7 wt.-%, no steady state in the photocatalytic production of H<sub>2</sub> could be achieved during the entire measuring time, which results in a fluctuating H<sub>2</sub> evolution rate. Probably, the activation period is still proceeding and requires an extended irradiation in order to establish a stable H<sub>2</sub> evolution rate. The observed elongating activation period with increasing Cu loading can be directly referred to the reduction of the Cu co-catalyst precursor into its metallic state. Due to the complex photocatalyst composition, as shown in the XRD analysis in figure 40b and c, a prediction of the Cu co-catalyst precursor type cannot be given. Basing on the used CuSO<sub>4</sub> · 5 H<sub>2</sub>O for impregnation, which consists of Cu<sup>2+</sup> ions and the oxidative calcination atmosphere, the formation of CuO as the present Cu co-catalyst precursor can be assumed. The present results of the activity examination allow a pre-selection of the most active Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu material for further investigations in sacrificial agent reforming. Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu with a Cu loading of 5, 6 and 7 wt.-% are chosen as the three most active representatives of Cu wet impregnated photocatalysts.



**Figure 43:** Long term experiments in photocatalytic  $H_2$  production via methanol, ethanol and glycerol reforming with  $Cs_{0.68}Ti_{1.83}O_4/Cu$  in loadings of a) 5 wt.-%, b) 6 wt.-% and c) 7 wt.-%. d) maximum  $H_2$  evolution rates of performed sacrificial agent reforming experiments in a) - c).

These three photocatalysts are tested in the photocatalytic reforming of ethanol and glycerol in addition to the prior presented methanol reforming (Figure 42). For long term stability studies, the performed reforming reactions are carried out for 10 h under constant irradiation of a Xe-arc lamp. Figure 43a - c presents the recorded photocatalytic activities of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 - 7 wt.-%) in methanol, ethanol and glycerol reforming, while figure 43d illustrates the activity trend through the extraction of the maximum H<sub>2</sub> evolution rate of the respective experiment.

According to the extracted  $H_2$  production rates, as shown in figure 43d, a clear trend in the reforming of the utilized sacrificial agents can be depicted as followed glycerol > methanol > ethanol. Interestingly, this activity trend differs to the prior stated trend in sacrificial agent reforming in chapter 5.1. Recorded H<sub>2</sub> evolution rates in glycerol reforming show an increased H<sub>2</sub> evolution rate of 103.2, 105 and 101.7 µmol/h for loadings of 5, 6 and 7 wt.-% of Cu, respectively, and outruns even the photocatalytic performance of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Pt (1 wt.-%) in methanol reforming (Figure 38). Also an improved reforming efficiency of methanol and ethanol compared to photodeposited Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Pt is evident. Photocatalytic ethanol reforming again provides the lowest H<sub>2</sub> yield. However, impregnated Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (5 - 7 wt.-%) shows in each performed reforming reaction a distinct activation period between 2 - 4 h. Basing on the stated mechanisms for methanol (Eq. 3.8 -3.11)<sup>[13]</sup>, ethanol<sup>[194]</sup> (Eq. 5.4 - 5.6) and glycerol<sup>[195]</sup> (Eq. 5.7 - 5.10) reforming, which are investigated on TiO<sub>2</sub>, the observed activity trend is consistent with the theoretically possibly produced H<sub>2</sub> amount per reformed sacrificial agent molecule. Additionally, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu experiences an advancing deactivation in the glycerol reforming reaction with increasing Cu content, while the activation period become shorter with increasing Cu amounts. Therefore, the observed photocatalyst deactivation is less effective for Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (5 wt.-%). On the other hand, the photocatalytic activity of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 and 6 wt.-%) in methanol and ethanol reforming is stable after the establishment of a steady state. Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (7 wt.-%) shows a different photocatalytic behavior compared the other examined photocatalysts. In addition to the fast deactivation in glycerol reforming, an increasing activity in methanol and ethanol reforming can be observed, while at the end phase of the experiment (8 - 10 h), the H<sub>2</sub> evolution rate in methanol reforming exceeds even the decreasing H<sub>2</sub> production rate in glycerol reforming. For clarification, the shown trend in figure 43d illustrates the unique maximum activity achieved in the entire measuring time and do not include the occurring deactivation effect. The effecting photocatalyst deactivation during glycerol reforming cannot be fully explained yet, due to the complex photocatalyst composition and the variety of possible glycerol decomposition products, which could interfere within the photocatalytic process.<sup>[195, 197]</sup> The upcoming post characterization tries to provide an approach to explain the photocatalytic deactivation. However, improved efficiency of impregnated  $Cs_{0.68}Ti_{1.83}O_4/Cu$  in glycerol reforming induces a change in the oxidative capabilities of the photocatalyst system, which probably originates from either the  $Cs_2SO_4$  or  $TiO_2$  impurity or from an interaction between all three present components. The origin of the improved oxidative capabilities of impregnated  $Cs_{0.68}Ti_{1.83}O_4/Cu$  is further discussed in this chapter.

 $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) is chosen for further investigations for Cu SPR tracking in methanol, ethanol and glycerol reforming, due to its stable photocatalytic activity in each reforming reaction compared to Cu loadings of 6 and 7 wt.-%. In-situ SPR measurements should provide new insights of the Cu co-catalyst constitution and the activity difference in the reforming of the utilized sacrificial agents.

# In-situ SPR Measurements of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (5 wt.-%) in Sacrificial Agent Reforming

In-situ SPR measurements were performed in a second run of the presented sacrificial agent reforming reactions, illustrated in figure 43a, with as-synthesized  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) in fresh sacrificial agent solutions. Figure 44a and b show selected SPR spectra of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) during the reforming of methanol (a) and ethanol (b). Before experiment initialization, the photocatalyst suspension was stirred for 0.5 h in absence of any external light source, in order to receive a reference spectrum for a blank Cu SPR-value, which is displayed as 0 h.



Figure 44: Selected in-situ SPR spectra recorded during a) methanol reforming and b) ethanol reforming with  $C_{s_{0.68}}Ti_{1.83}O_4/Cu$  impregnated with 5 wt.-% of Cu.

The blank spectrum of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  in methanolic solution, as shown in figure 44a, shows no SPR signal of metallic Cu, which indicates that impregnated Cu exists in an oxidic or rather in a non-reduced state in the as-synthesized photocatalyst. After an irradiation period of 0.5 h, a fully evolved Cu SPR signal at a wavelength of 540 nm with a corresponding  $H_2$ evolution rate of around 25 µmol/h could be observed. The recorded Cu SPR shows a symmetric signal shape and experiences a narrow signal width. The signal position as well as its shape provides information about the Cu co-catalyst constitution in the impregnated Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu photocatalyst. Yamaguchi et. al.<sup>[198]</sup> examined Cu SPR signals from spherical Cu particles deposited on TiO<sub>2</sub>. Cu particles on TiO<sub>2</sub> surface show a symmetric SPR signal at a wavelength of around 600 nm. Therefore according to the mentioned study, the Cu SPR signal shape (Figure 44a) indicates the existence of spherical Cu co-catalyst particles deposited on the surface of the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> support material. The SPR signal shape and position depend mainly on three factors: 1) chemical environment, 2) metal particle crystallite form and 3) particle size.<sup>[73]</sup> The observed signal shift to a wavelength of 540 nm, may originate from the chemical environment induced by the methanolic solution or from a decreased particle size compared to the examined Cu particle in the work of Yamaguchi et. al.<sup>[198]</sup> with a particle size of 30 nm. However, a distinct estimation of the actual Cu particle size basing on the recorded Cu SPR signals cannot be given yet. Therefore, the difference in chemical environment, induced by the sacrificial agent and the photocatalyst surface, probably causes the observed SPR signal shift. Interestingly, a constant intensity decrease of the Cu SPR signal until an irradiation time of 6 h is recorded. After 8 h of illumination, the Cu SPR signal intensity stabilizes until the end of the estimated measuring time of 10 h. On the other hand, the observed development of the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu photocatalytic activity in methanol reforming (Figure 43a), does not correspond with the recorded Cu SPR signal decrease, which provides a informal reduction degree of the acting Cu co-catalyst. However, upon a closer examination of the Cu SPR spectra, a coupled decrease of the SPR signal basis at lower wavelengths can be observed. If all spectra are normalized, all Cu SPR signals would nearly lie on each other only with minor deviations. Therefore, the observed intensity drop during the in-situ measurement arises from a basis shift, potentially caused by a change of the photocatalyst bulk material, which is discussed in detail in the post characterization section of this chapter.

In-situ tracking of Cu SPR signals during the photocatalytic ethanol reforming reaction with  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%), show a different signal development as in the previously described methanol reforming. Again,  $Cs_{0.68}Ti_{1.83}O_4/Cu$  shows no Cu SPR signal in the blank

measurement, proofing an non-reduced state of the Cu co-catalyst precursor. Contrary to the immediately fully evolved Cu SPR signal during methanol reforming, SPR signals of Cu cocatalyst particles during ethanol reforming are slowly but constantly rising until 8 h of irradiation. Between 8 - 10 h of irradiation, the Cu SPR signal is stabilized. However, the Cu SPR signal itself becomes more defined with irradiation time. The constant rise of the Cu SPR signal includes also an increasing signal basis, again in contrast to the observed Cu SPR behavior in methanol reforming. The Cu SPR signal maximum is shifted to a higher wavelength of 586 nm compared to the Cu SPR in methanol reforming. The signal shift can be again referred to a changed chemical environment rather than to an increased Cu particles size, due to the equality of the utilized photocatalyst synthesis batch for methanol and ethanol reforming. The slowly increasing Cu SPR signal corresponds with the lowered photocatalytic activity of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu in ethanol reforming compared to the performed methanol reforming reaction. The Cu co-catalyst precursor is less effectively reduced in an ethanol containing solution than in a methanolic solution. These photocatalytic behaviors are in relation that the tested photocatalyst system supplied fewer electrons either for H<sub>2</sub> production or the reduction of the Cu co-catalyst precursor, caused by an ineffective ethanol oxidation, which also provokes a higher recombination rate of electron/hole pairs. Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (5 wt.-%) experiences again a different Cu co-catalyst formation in glycerol reforming compared to methanol and ethanol reforming, as presented in figure 44a and b. The formation of the active metallic Cu co-catalyst is again tracked by the observation of the Cu SPR signal. Figure 45 illustrates all recorded Cu SPR spectra of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (5 wt.-%) during photocatalytic glycerol reforming.

 $Cs_{0.68}Ti_{1.83}O_4/Cu$  shows an analogous, constantly increasing Cu SPR signal at 586 nm as in the photocatalytic reforming of ethanol. The observed Cu SPR signal becomes more defined with increasing irradiation time. After 4 h of irradiation, the Cu SPR signal is fully defined. Afterwards, between 5 - 10 h of irradiation, the Cu SPR signal fluctuates in a minor extent. Interestingly, the initial Cu co-catalyst activation period and the following stabilization of the Cu SPR signal corresponds with the photocatalytic behavior of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) in glycerol reforming, as presented in figure 43a. The recorded H<sub>2</sub> evolution rate shows also an activation period of approximately 4 h, followed by a steady state establishment. Minor fluctuations in the H<sub>2</sub> production rate during the steady state phase are reflected in the intensity deviations of the Cu SPR signals between 5 - 10 h. The accordance in the Cu SPR signal position in glycerol and ethanol containing reaction solutions lead to the assumption that both sacrificial agents establish an equivalent chemical environment for the Cu cocatalyst. Apparently an explanation of the similarity in the chemical environment provided by ethanol and glycerol cannot be given. An examination of the relative permittivity, also called dielectric constant or polarity of the utilized sacrificial agents does not provide a complementary trend to the observed Cu SPR shift. However, a simple consideration of the mentioned physical properties of pure methanol, ethanol and glycerol does not reflect the actual chemical environment in the photocatalyst suspension. The utilized sacrificial agents are diluted in water in a common ratio of 1:9, which requires an examination of the relative permittivity and polarity of the sacrificial agent/water mixtures to extract a possible trend.



**Figure 45:** Selected in-situ SPR spectra of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) during photocatalytic glycerol reforming at a) 0 - 4 h and b) 5 - 10 h of irradiation.

In summary, the in-situ tracking of the Cu SPR signal during a photocatalytic reforming reaction, enables the observation of the Cu co-catalyst formation and provides information about the co-catalyst particle shape and size. Basing on literature data<sup>[73, 198-199]</sup>, the overall symmetric and narrow signal form of the Cu SPR leads to the assumption that homogeneous spherical-like Cu particles with a uniform particle size are present after illumination in the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (5 wt.-%) photocatalyst prepared by wet impregnation. However, a direct correlation between Cu co-catalyst formation and the actual recorded H<sub>2</sub> evolution rate is not straight forward. An estimation of the photocatalytic activity development by a simple consideration of the in-situ SPR measurements is not possible, because SPR spectra of the examined co-catalyst only provide information about the co-catalyst material itself and not about the overall photocatalytic activity. Structural changes of the bulk material as well as the chemical environment, which also influence the overall photocatalytic activity, must to be considered. Nevertheless, SPR spectra provide indirectly information about the reductive

capabilities of the photocatalyst via the SPR signal development and the co-catalyst constitution.

#### Post Characterization of $Cs_{0.68}Ti_{1.83}O_4/Cu$ prepared by Wet Impregnation

The complex structure of the as-synthesized  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2 - 7 wt.-%) and the already known crystal structure change of the  $Cs_{0.68}Ti_{1.83}O_4$  support material make a further characterization of the used photocatalysts mandatory. Figure 46a shows exemplary on  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) with respective reference patterns the structural changes, which occur after photocatalytic methanol reforming with  $Cs_{0.68}Ti_{1.83}O_4/Cu$  prepared by wet impregnation. Figure 46b illustrates all recorded XRD patterns of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  with Cu loadings between 2 - 7 wt.-%.



**Figure 46:** a) XRD patterns of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) with reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$ , TiO<sub>2</sub> (anatase) and  $H_2Ti_2O_5 \cdot H_2O$ , b) XRD patterns of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2 - 7 wt.-%) with marked (011) and (130) lattice plane from TiO<sub>2</sub> and  $Cs_{0.68}Ti_{1.83}O_4$ , respectively. c) Ratio of TiO<sub>2</sub> (011) and  $Cs_{0.68}Ti_{1.83}O_4$  (130) reflex intensities plotted against the Cu loading.

Recorded XRD patterns of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2 - 7 wt.-%) reveal a significant change in the photocatalyst composition after the photocatalytic process. Primary, the  $Cs_2SO_4$  impurity,

which originates from the wet impregnation process itself and represent the dominating component in the as-synthesized material is no longer present in the XRD patterns, as shown in figure 46b. An explanation of the disappearance of the  $Cs_2SO_4$  impurity is that  $Cs_2SO_4$  can be dissolved in the diluted sacrificial agent solution and thereby washed out of the photocatalyst bulk material. The high solubility of Cs<sub>2</sub>SO<sub>4</sub> in water (182 (g/100 g H<sub>2</sub>O))<sup>[115]</sup> confirms the stated assumption. Additionally, the simple removal of the Cs<sub>2</sub>SO<sub>4</sub> impurity induces that Cs<sub>2</sub>SO<sub>4</sub> is loosely bound in the bulk material and probably does not contribute to the photocatalytic activity. Furthermore, the XRD patterns also show that  $Cs_{0.68}Ti_{1.83}O_4$  is still present in the photocatalyst material after the wet impregnation process, especially seen in the XRD patterns of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (2 - 5 wt.-%). Also the already known transformation of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> to its proton exchanged H<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> version is still evident. Additionally, an increasing TiO<sub>2</sub> (anatase) content with increasing Cu loading is also still present in the XRD patterns. Contrary to the Cs<sub>2</sub>SO<sub>4</sub> impurity, which can be easily removed, TiO<sub>2</sub> is strongly bound to the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> support material and induces a strong contact between the two semiconductors, forming a coupled semiconductor composite as described in chapter 3.4. The degree of transformation is quantified via ratio formation between the absolute intensity values of the TiO<sub>2</sub> (011) and  $Cs_{0.68}Ti_{1.83}O_4$  (130) lattice plane. Calculated intensity ratios are plotted against the respective Cu loading and presented in figure 46c. According to the plotted intensity ratios, a linear increase up to a Cu loading of 5 wt.-% is visible, while a Cu loading lower than 3 wt.-% provide a TiO<sub>2</sub>/Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> ratio lower than 1, which implies a domination of the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> support material. Higher Cu loadings imply a reversed domination of the photocatalyst bulk material towards TiO<sub>2</sub>. Cu loadings above 5 wt.-% lead to a steeper slop of the intensity ratio line, inducing a predominating  $TiO_2$  phase. This  $TiO_2$ domination is also reflected in the significant band gap reduction observed for  $C_{s_0,68}T_{i_{1,83}}O_4/Cu$  (6 and 7 wt.-%) as illustrated in figure 41b. The increased TiO<sub>2</sub>/Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> ratio leads to the assumptions that the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> support material is only present in some traces, concluding that Cu loadings above 5 wt.-% force an almost complete transformation of the  $Cs_{0.68}Ti_{1.83}O_4$  crystal structure to TiO<sub>2</sub>. Interestingly, the formed TiO<sub>2</sub> shows an improved crystallinity compared to the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> host material, visible on the high intensive and sharp TiO<sub>2</sub> reflexes in the diffraction patterns.

The structural change in the  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2 – 7 wt.-%) material manifests in an increased band gap energy. Tauc plots of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2 – 7 wt.-%) are shown in figure 47 with respective absorption edge linearization and band gap energies. Band gap energies of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2 – 5 wt.-%) are increased by a factor between 0.3 – 0.46 eV, while  $Cs_{0.68}Ti_{1.83}O_4/Cu$  experiences a band gap increase of about 0.76 and 1.06 eV for a Cu loading of 6 and 7 wt.-%, respectively, compared to the corresponding as-synthesized material. The loss of the band gap decreasing effect by the impregnated Cu precursor, lead to the assumption that the incorporated Cu oxide species is removed from the  $Cs_{0.68}Ti_{1.83}O_4$  host material and reduced either on the surface of  $Cs_{0.68}Ti_{1.83}O_4$  or TiO<sub>2</sub>. A preferential deposition of Cu on  $Cs_{0.68}Ti_{1.83}O_4$  or TiO<sub>2</sub> cannot be excluded either be proven. However, basing on the XRD patterns of the used  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2 – 7 wt.-%) photocatalysts and the resulting transformation degree towards TiO<sub>2</sub>, a deposition probability of the Cu co-catalyst either on  $Cs_{0.68}Ti_{1.83}O_4$  or TiO<sub>2</sub> can be estimated. Therefore, an increased deposition probability on TiO<sub>2</sub> is present at a  $Cs_{0.68}Ti_{1.83}O_4/TiO_2$  ratio larger than 1 or rather at Cu loadings larger than 3 wt.-%, assuming an immobile Cu co-catalyst precursor.



**Figure 47:** Tauc Plots with corresponding absorption edge linearization and band gap energies ( $E_g$ ) of a)  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2 - 5 wt.-%) and b)  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (6 and 7 wt.-%), prepared by wet impregnation after photocatalytic methanol reforming.

Furthermore, the extended band gap increase for  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (6 and 7 wt.-%) can be referred to the aspect that the Cu co-catalyst precursor cannot be incorporated in the TiO<sub>2</sub> crystal lattice as simple as in case of  $Cs_{0.68}Ti_{1.83}O_4$ . In regard to this circumstance, the observed band gap decrease in the corresponding as-synthesized material mainly originates from the deposited Cu precursor on TiO<sub>2</sub>. The renewed observation of the band gap increase after photocatalytic H<sub>2</sub> production denies the visible light application of the  $Cs_{0.68}Ti_{1.83}O_4/Cu$  photocatalysts prepared by wet impregnation.

In summary, wet impregnation of  $Cs_{0.68}Ti_{1.83}O_4$  with  $CuSO_4 \cdot 5 H_2O$  leads to the formation of  $Cs_2SO_4$  as well as to the transformation of  $Cs_{0.68}Ti_{1.83}O_4$  to  $TiO_2$  in anatase modification. The crystal structure transformation originates from the removal of  $Cs^+$  from the interlayers,

resulting in a collapsing  $Cs_{0.68}Ti_{1.83}O_4$  structure. Furthermore, the impregnation process leads also to an undefined band gap reduction, probably caused by a Cu<sup>+</sup> cation incorporation into the  $Cs_{0.68}Ti_{1.83}O_4$  interlayers or titanate sheets. The increasing photocatalytic activity with increasing Cu content cannot be exclusively referred to the increased co-catalyst amount due to the correlated TiO<sub>2</sub> formation and increasing anatase content. The prepared photocatalysts are subjected to a structural change after the photocatalytic process. The removal of Cs<sub>2</sub>SO<sub>4</sub> reveals a photocatalyst composite consisting of  $Cs_{0.68}Ti_{1.83}O_4/TiO_2$  with increasing TiO<sub>2</sub> proportions at higher Cu loadings. A general band gap increase after photocatalytic H<sub>2</sub> production probably induced by the lost Cu doping effect or caused by the removal of Cu<sup>+</sup> cations from the interlayers refuses the utilization of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  photocatalysts prepared by wet impregnation in visible light applications.

# 5.2.3 Copper Impregnation on Stabilized Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>

A major drawback of the wet impregnation process is the transformation of the  $Cs_{0.68}Ti_{1.83}O_4$ support to  $TiO_2$  in anatase modification if impregnated with a co-catalyst precursor with a cesium salt forming anion, as already stated in the previous section. In order to prevent a Cs<sup>+</sup> removal from the titanate interlayers, a stabilization of the  $Cs_{0.68}Ti_{1.83}O_4$  support material has to be executed. Higher calcination temperatures have a stabilizing effect on the overall crystal structure of  $Cs_{0.68}Ti_{1.83}O_4$ , as present in the post characterization of  $Cs_{0.68}Ti_{1.83}O_4$  in chapter 5.1.2. For this reason,  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 700 and 800 °C is used as the support material for the impregnation of 5 wt.-% of Cu.  $Cs_{0.68}Ti_{1.83}O_4$ /Cu with a loading of 5 wt.-% is chosen as a reference material to investigate the extend of  $Cs_{0.68}Ti_{1.83}O_4$  transformation and the effect on the photocatalytic activity in sacrificial agent reforming.

#### Synthesis and Characterization

Wet impregnation of Cu with an amount of 5 wt.-% in respect of the used support mass is executed on  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600, 700 and 800 °C. After solvent evaporation, the imbued photocatalyst precursor is again dried at 100 °C for 24 h and further calcined at 450 °C for 2 h under atmospheric conditions. TG analysis of the dried photocatalyst precursor (Figure 48) shows a similar mass loss as  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) on  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600 °C (Figure 40a). Two significant mass losses are observed at 68 and 159 °C as well as at 69 and 154 °C for  $Cs_{0.68}Ti_{1.83}O_4/Cu$  on  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 700 and 800 °C respectively. The initial mass loss is slightly shifted to lower temperatures compared to the Cu photocatalyst on  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C), while the second mass loss remains in an equivalent temperature range. The first mass loss is related to the vaporization of accumulated moisture caused by an atmospheric exposition after the drying process. The reduced total mass loss, shown in figure 48b, of 2.9% relative to the starting mass induces a reduced moisture accumulation of the photocatalyst bulk material. An explanation could be that the increased crystallinity caused by a calcination temperature of 800 °C blocks an invasion of the interlayers by water molecules; consequently H<sub>2</sub>O is exclusively adsorbed on the outer surface. This assumption correlates with the observed temperature shift to lower temperatures, due to the decreased energy for H<sub>2</sub>O desorption from the photocatalyst surface. While the assumed crystal water liberation stays constant in a temperature range between 154 - 159 °C.



**Figure 48:** TG/DTG analysis of the dried  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) precursor prepared by wet impregnation on a)  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 700 °C and b)  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 800 °C.

For a detailed structural analysis of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%), diffraction patterns of the dried photocatalyst precursors are recorded and plotted with the reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$ , TiO<sub>2</sub> in anatase modification and  $Cs_2SO_4$  (Figure 49). Diffraction patterns of the dried  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) precursors prepared on  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600, 700 and 800 °C show the formation of  $Cs_2SO_4$ , while the degree of  $Cs_2SO_4$  formation decreases with increasing  $Cs_{0.68}Ti_{1.83}O_4$  calcination temperature. The formation of  $Cs_2SO_4$  can be observed by the most intensive (220) reflex at 27.2° 20.  $Cs_{0.68}Ti_{1.83}O_4/Cu$  consisting of  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600 and 700 °C experiences a more distinct  $Cs_2SO_4$  formation than on  $Cs_{0.68}Ti_{1.83}O_4$  annealed at 800 °C.  $Cs_2SO_4$  in  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (800 °C) can only be recognized by minor intense reflexes. Furthermore, the formation of TiO<sub>2</sub> is not completed after the drying process, which induces the requirement of the upcoming calcination step to complete the TiO<sub>2</sub> formation, as seen figure 49b. In addition, reflexes of  $Cs_2SO_4$  become also more defined after calcination. This circumstance is clearly visible by the formation of the (220) reflex of  $Cs_2SO_4$  at around 25.3° 2 $\theta$  in the diffraction patterns of the calcined

photocatalysts, as illustrated in figure 49b. Even in  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (800 °C), both impurity compounds  $Cs_2SO_4$  and  $TiO_2$  are formed after calcination also in a comparable amount as in  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (600 and 700 °C) by considering the individual reflex ratio. However, a meaningful statement about the actual degree of  $TiO_2$  transformation can only be given after the performed photocatalytic process or rather in the absence of the  $Cs_2SO_4$  impurity. Due to its high solubility in water,  $Cs_2SO_4$  is easily washed out form the photocatalyst bulk after a photocatalytic process in an aqueous medium.



**Figure 49:** XRD pattern of a) dried and b) calcined  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) on  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600, 700 and 800 °C with reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$ , TiO<sub>2</sub> (anatase) and  $Cs_2SO_4$ .

The undeveloped  $Cs_2SO_4$  and  $TiO_2$  impurities have also a major effect on the band gap energies of dried photocatalyst precursors. Figure 50a presents the Tauc plots of the dried photocatalysts. These precursor materials exhibit larger band gap energy as the corresponding calcined material, shown in figure 50b. Increasing band gap energy with  $Cs_{0.68}Ti_{1.83}O_4$  support material annealed at higher temperature in the order of 0.5 eV per 100 °C is observed for the dried photocatalyst precursors. After calcination,  $Cs_{0.68}Ti_{1.83}O_4/Cu$  materials experience a significant band gap decrease into the visible light region, while the increasing band gap trend is continued in accordance with the  $Cs_{0.68}Ti_{1.83}O_4$  calcination temperature but not in the same extend as for the dried materials. The increasing band gap can be referred to the assumed incorporation of Cu cations into the interlayers of  $Cs_{0.68}Ti_{1.83}O_4$  causing a cation doping effect. Higher calcined  $Cs_{0.68}Ti_{1.83}O_4$  hinders the incorporation of Cu cations probably due to an improved stabilization of Cs<sup>+</sup>, which prevents an infiltration of the interlayers or rather the photocatalysts bulk. This leads to the assumption that the Cu co-catalyst precursor is mainly present on the surface of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (800 °C), resulting in a broad interband transition in the visible light region, as seen by the blue graph in figure 50b. Basing on the Tauc plots, the presence of  $Cu_2O$  or CuO in impregnated  $Cs_{0.68}Ti_{1.83}O_4/Cu$  cannot be clarified, while an infiltration of the interlayers by Cu<sup>+</sup> cations would suggest to an Cu(I) species in order to keep charge neutrality.



**Figure 50:** Tauc Plots with corresponding absorption edge linearization and band gap energies ( $E_g$ ) of a) dried and b) calcined  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) on  $Cs_{0.68}Ti_{1.83}O_4$  annealed at 600, 700 and 800 °C from wet impregnation process.

Photocatalytic  $H_2$  Production via Sacrificial Agent Reforming with  $C_{s_{0.68}}Ti_{1.83}O_4/Cu$  on stabilized  $C_{s_{0.68}}Ti_{1.83}O_4$ 

Photocatalytic performance tests in regard of  $H_2$  production are carried out in a sacrificial agent solution containing 10 vol.-% of methanol, ethanol or glycerol.  $Cs_{0.68}Ti_{1.83}O_4/Cu$  prepared on  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600, 700 and 800 °C and a Cu loading of 5 wt.-% are tested in each reforming reaction for  $H_2$  production. Figure 51 presents the average  $H_2$  evolution rates with individual error indicators. All shown values are calculated from the measured production rates in the time range between 5 -10 h.

The previously observed trend in sacrificial agent reforming efficiency in the order glycerol > methanol > ethanol is continued with  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) prepared on  $Cs_{0.68}Ti_{1.83}O_4$ calcined at 600, 700 and 800 °C. Furthermore, a decreasing reforming efficiency with increasing Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcination temperature is observed, except for Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (700 °C) in glycerol reforming which exhibits the highest H<sub>2</sub> evolution rate 108.8 µmol/h in the examined experiments. However, the activity drop of around 20% for Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (5 wt.-%) on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> (800 °C) relative to highest achieved activity, as shown in figure 51, is significant low compared to the activity drop of nearly 90% for Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> (800 °C) in relation to its 600 °C material in the stepwise photodeposition of Rh (Figure 30c). Interestingly, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (5 wt.-%) on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> (700 °C) shows the highest activity exclusively in glycerol reforming. The increased efficiency in glycerol reforming cannot be explained by the executed characterization methods and requires an extended research. The minor error bars imbedded in the respective H<sub>2</sub> evolution rate imply a stable production in the considered range for average value estimation. Each tested Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (5 wt.-%) photocatalyst requires an activation period up to 5 h in the respective reforming reaction until a steady state is established.



**Figure 51:** Average H<sub>2</sub> evolution rates of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) on  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600, 700 and 800 °C with measurement error indicators of long term experiments in the photocatalytic reforming of methanol, ethanol and glycerol.

Executed long term experiments, which are utilized for the presented average  $H_2$  evolution rates in figure 51, with  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) on differently calcined  $Cs_{0.68}Ti_{1.83}O_4$  can be found in the appendix.

### Post Characterization of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (5 wt.-%) on Stabilized Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>

In order to extract the transformation degree of  $Cs_{0.68}Ti_{1.83}O_4$  to  $TiO_2$ , diffraction patterns are recorded from the recovered  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) photocatalysts from the executed sacrificial agent reforming reaction. Again, the ration between the absolute intensity value of the most intensive (011) reflex and (130) reflex of  $TiO_2$  and  $Cs_{0.68}Ti_{1.83}O_4$ , respectively, is calculated and plotted against the  $Cs_{0.68}Ti_{1.83}O_4$  calcination temperature, as presented in figure 52. Recorded diffraction patterns of recovered  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) on differently calcined  $Cs_{0.68}Ti_{1.83}O_4$  after sacrificial agent reforming are illustrated in the appendix.

In general, each tested photocatalyst in the respective reforming reaction show a removal of the  $Cs_2SO_4$  impurity after the photocatalytic process. Calculated TiO<sub>2</sub> I(011)/Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> I(130) ratios reveal a decreasing transformation degree towards TiO<sub>2</sub> with increasing  $Cs_{0.68}Ti_{1.83}O_4$  calcination temperature in each performed photocatalytic reforming reaction.



**Figure 52:** Intensity ratios of TiO<sub>2</sub> (011) and Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> (130) reflex plotted against the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcination temperature for the respective sacrificial agent reforming reaction.

Furthermore, the tested photocatalysts  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) after the execution of the glycerol reforming reaction experience the largest TiO<sub>2</sub> I(011)/Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> I(130) ratios. The stated trend is independent of the  $Cs_{0.68}Ti_{1.83}O_4$  calcination temperature. However, this observable trend cannot be referred to the actual activity trend in sacrificial agent reforming, while the transformation degrees after methanol and ethanol reforming do not correspond with the respective photocatalytic activity, except for  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) on

 $Cs_{0.68}Ti_{1.83}O_4$  (600 °C). Despite of the irregular trend, the presented results reveal that higher calcination temperatures (> 600 °C) applied on the  $Cs_{0.68}Ti_{1.83}O_4$  support lead to a stabilized crystal structure, which inhibits a leaching of  $Cs^+$  from the interlayers as well as the associated  $Cs_2SO_4$  and  $TiO_2$  formation. However, the  $Cs^+$  leakage during the wet impregnation process cannot be fully prevented, even with the highest calcined  $Cs_{0.68}Ti_{1.83}O_4$  support material. Higher calcination temperatures cannot be applied due to an occurring structure transformation of  $Cs_{0.68}Ti_{1.83}O_4$  into thermodynamically more stable conformations. Another assumption is that the formation degree of  $Cs_2SO_4$  and  $TiO_2$  stay constant while the amount of crystalline  $Cs_{0.68}Ti_{1.83}O_4$  is increased by higher annealing temperatures, causing a reduced  $TiO_2 I(011)/Cs_{0.68}Ti_{1.83}O_4 I(130)$  ratio. Nevertheless, both assumptions are legit explanation of the occurring phenomena shown in figure 52.

Tauc plots of the recovered  $C_{s_{0.68}}Ti_{1.83}O_4/Cu$  (5 wt.-%) photocatalysts on  $C_{s_{0.68}}Ti_{1.83}O_4$ calcined between 600 - 800 °C from sacrificial agent reforming confirm the already known band gap increase after the photocatalytic process. Each photocatalyst material either after methanol, ethanol or glycerol reforming exhibits a band gap energy in a range between 3 -3.13 eV, except of  $C_{s_{0.68}}Ti_{1.83}O_4/Cu$  (5 wt.-%) on  $C_{s_{0.68}}Ti_{1.83}O_4$  (800 °C) after glycerol reforming, which holds a band gap of 2.9 eV. However, the band gap estimation in case of  $C_{s_{0.68}}Ti_{1.83}O_4/Cu$  (5 wt.-%) on  $C_{s_{0.68}}Ti_{1.83}O_4$  (800 °C) remains difficult, due the broad Cu interband transition in the visible light region. Furthermore, no consistent trend either in a defined order of the used sacrificial agents or  $C_{s_{0.68}}Ti_{1.83}O_4$  calcination temperature for the estimated band gap energies can be developed. The overall increasing band gap energy after a performed photocatalytic process still prevents the utilization of the Cu impregnated  $C_{s_{0.68}}Ti_{1.83}O_4/Cu$  (5 wt.-%) on  $C_{s_{0.68}}Ti_{1.83}O_4$  (600 - 800 °C) after sacrificial agent reforming can be found in the appendix.

In conclusion, Cu deposition on stabilized  $Cs_{0.68}Ti_{1.83}O_4$  support cannot completely prevent the formation of  $Cs_2SO_4$  and the corresponding TiO<sub>2</sub> formation. XRD analyses of the dried photocatalyst precursors reveal the common  $Cs_2SO_4$  impurity phase but no TiO<sub>2</sub> in anatase modification. The following calcination step for the decomposition of  $CuSO_4 \cdot 5 H_2O$  is essential for the formation of both impurities as seen in figure 49b. All prepared  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) photocatalysts show a comparable or even increased photocatalytic performance in the reforming of methanol, ethanol and glycerol compared to utilized noble metal co-catalysts on  $Cs_{0.68}Ti_{1.83}O_4$ . Also  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) prepared

on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> (800 °C) shows a satisfactory activity in the performed sacrificial agent reforming. Despite of the band gap decreasing effect of assumed incorporated Cu ions in the  $Cs_{0.68}Ti_{1.83}O_4$  lattice, causing a homogeneous band gap shift into the visible light region, after a photocatalytic reforming reaction the band gap is re-shifted into the UV range. Nevertheless, diffraction patterns of the recovered Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (5 wt.-%) photocatalysts reveal a similarity in the actual photocatalyst composition. After a photocatalytic process, the Cs<sub>2</sub>SO<sub>4</sub> impurity is washed out of the photocatalyst bulk material independent of the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcination temperature. This leads to a binary photocatalyst system consisting of  $Cs_{0.68}Ti_{1.83}O_4$  and  $TiO_2$  in anatase modification, forming a composite material. Basing on the published VB and CB position by Liu et. al.<sup>[37]</sup>, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> and TiO<sub>2</sub> form a type I semiconductor composite as presented in figure 14. A physical contact between the two photocatalysts is obvious because  $TiO_2$  is directly formed out of  $Cs_{0.68}Ti_{1.83}O_4$ . In addition, metallic Cu is formed during each photocatalytic reforming reaction, which is tracked by insitu SPR measurements. Basing on the recorded Cu SPR spectra, the wet impregnation process forms spherical Cu precursor particles, which are reduced by photoinduced electrons of the photocatalysts. A selective deposition of the Cu co-catalyst exclusively on one photocatalyst in the composite can be neither confirmed nor denied. Therefore, a deposition on both photocatalysts is suspected or rather assumed. Basing on the summarized results of the executed study on  $Cs_{0.68}Ti_{1.83}O_4/Cu$  prepared by wet impregnation, a scheme of the present photocatalyst composite Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/TiO<sub>2</sub> with Cu as a co-catalyst on both photocatalysts with possible charge carrier flow is postulated in figure 53.



**Figure 53:** Postulated scheme of the  $Cs_{0.68}Ti_{1.83}O_4/TiO_2$  composite with Cu as co-catalyst with an assumed charge carrier transport within the photocatalyst composite plotted against the potential scale of NHE (pH = 7).

The irradiation of the used Xe-arc lamp leads to an excitation of VB electrons into the respective CB of the participating photocatalysts in the composite. Excited electrons in the CBs are transferred to the in-situ formed metallic Cu co-catalyst. Due to the established Schottky junction, which originates from the semiconductor/metal contact, electrons react with an adsorbed electron acceptor species like H<sup>+</sup> on Cu co-catalyst particles. Remaining VB holes are oxidizing adsorbed donor species like the utilized sacrificial agents. These are common processes in single semiconductor/metal photocatalyst systems, processed in hole scavenging solutions. Additionally,  $Cs_{0.68}Ti_{1.83}O_4$  may transfer its photogenerated charge carriers to the contacted TiO<sub>2</sub>, due to the lowered and increased potential of the TiO<sub>2</sub> VB and CB. However, if an increased driving force of  $Cs_{0.68}Ti_{1.83}O_4$  CB electrons towards TiO<sub>2</sub> or the Cu co-catalyst is present cannot be proven yet. Laser flash photolysis experiments for the investigation of the electron lifetime may be insightful for the occurring charge carrier transport in the stated photocatalyst composite.

# 5.2.4 Gold Impregnation on Stabilized Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>

Photodeposited Au particles on the surface of  $Cs_{0.68}Ti_{1.83}O_4$  have only a minor supporting effect on the photocatalytic performance on the formed  $Cs_{0.68}Ti_{1.83}O_4/Au$  photocatalyst in the examined H<sub>2</sub> production tests, as shown in figure 38. The low photocatalytic activity of  $Cs_{0.68}Ti_{1.83}O_4/Au$  is referred to the weak SMSI effect between the  $Cs_{0.68}Ti_{1.83}O_4$  support and the Au particles. In order to strengthen the interaction or rather the contact between the support material and the noble metal co-catalyst, the wet impregnation process is chosen for the synthesis of  $Cs_{0.68}Ti_{1.83}O_4/Au$ . A detailed characterization after each synthesis step provides insights about the photocatalyst formation and development of the Au co-catalyst particles.  $Cs_{0.68}Ti_{1.83}O_4/Au$  is tested in the reforming of methanol, ethanol and glycerol in regard of photocatalytic H<sub>2</sub> production. In-situ SPR measurements executed on  $Cs_{0.68}Ti_{1.83}O_4/Au$  (600 °C) in the respective reforming reaction give information about the cocatalyst status during the performed photocatalytic reaction. Afterwards, the used photocatalysts are recovered and again characterized for the investigation of possible changes of the photocatalyst constitution.

#### Synthesis and Characterization

 $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600, 700 and 800 °C is utilized as the support material for the wet impregnation process. HAuCl<sub>4</sub> · 3 H<sub>2</sub>O is used as a Au source. The Au loading is fixed at 1 wt.-%, for comparison with the corresponding photodeposited photocatalyst. The solid Au

precursor is solved in water and dropped on the  $Cs_{0.68}Ti_{1.83}O_4$  (600 - 800 °C) support followed by solvent evaporation. The imbued photocatalyst precursor is again dried for 24 h at 100 °C for the removal of residual water and afterwards calcined at 450 °C for 2 h. Diffraction patterns of the dried and calcined  $Cs_{0.68}Ti_{1.83}O_4/Au$  photocatalysts with reference patterns of the present components are illustrated in figure 54a and b, respectively. The recorded diffraction patterns of the dried photocatalyst precursors show a similar structural transformation as described in the previous chapter for Cu impregnated  $Cs_{0.68}Ti_{1.83}O_4$ . The impregnation process with  $HAuCl_4 \cdot 3 H_2O$  leads to the formation of a CsCl impurity compound, clearly visible on the most intensive CsCl reflex at 30.6° 20. Again, the anion of the metal precursor compound, here Cl<sup>-</sup> infiltrates the interlayers of  $Cs_{0.68}Ti_{1.83}O_4$  and removes  $Cs^+$  from the crystallographic A-position, forming the CsCl impurity. The formation of CsCl is instantaneous and do not require an additional annealing step, as seen in figure 54a. Interestingly, the removal of  $Cs^+$  from the interlayers does not cause a formation of  $TiO_2$ either in anatase or rutile modification. Even the calcination step up to 450 °C does not provoke a  $TiO_2$  formation.



Figure 54: XRD pattern of a) dried and b) calcined  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) on  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600, 700 and 800 °C with reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$ ,  $Au_{0.919}Ti_{0.081}$  and CsCl.

125

impregnated on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>. Also the impregnation of 2 wt.-% of Cu (Figure 40b) does not provoke the formation of TiO<sub>2</sub> in anatase modification. Nevertheless, impregnated Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au experiences another impurity than TiO<sub>2</sub> after calcination, namely the alloy Au<sub>0.919</sub>Ti<sub>0.081</sub>, which is visible in the diffraction patterns of the calcined  $Cs_{0.68}Ti_{1.83}O_4/Au$ photocatalyst, as presented in figure 54b. The formation of Au<sub>0.919</sub>Ti<sub>0.081</sub> may correlate with the prevention of TiO<sub>2</sub> formation. The titanate sheets may be stabilized through the insertion of Au into the titanate lattice, preventing a collapse of the layered sheet like structure. A satisfactory explanation of the non-existing TiO<sub>2</sub> cannot be given yet. Basing on the recorded diffraction patterns of the calcined Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au photocatalysts, each photocatalyst material consists again of three different compounds: 1) Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au, 2) Au<sub>0.919</sub>Ti<sub>0.081</sub> and 3) CsCl. Furthermore, the increased annealing temperatures executed on the  $Cs_{0.68}Ti_{1.83}O_4$ support could not prevent the removal of Cs<sup>+</sup> from the interlayer structure. The calcination step for the decomposition of the Au precursor leads to an incorporation of Au into the titanate sheets, forming an Au<sub>0.919</sub>Ti<sub>0.081</sub> alloy, which indicates an increased interaction between the Au co-catalyst particles and the support material as well as proofs the estimated synthesis approach for an improved SMSI-effect.

Tauc plots, constructed from the corresponding diffuse reflectance spectra, of the dried and calcined Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au (1 wt.-%) photocatalysts are shown in figure 55a - b, while the corresponding Kubelka-Munk functions for an effective presentation of the Au SPR are illustrated in figure 55c -d, respectively. Executed band gap estimations by absorption edge linearization reveal an increasing trend of the band gap energies with increasing  $Cs_{0.68}Ti_{1.83}O_4$ calcination temperature. A minor band gap increase after calcination, except for  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) on  $Cs_{0.68}Ti_{1.83}O_4$  (800 °C), can be observed. The actual band gaps show that all Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au (1 wt.-%) photocatalysts are exclusively active under UV light irradiation to an extended band gap of 3.62 eV, despite of the deep violet coloring of the photocatalyst powder. The powder coloring originates from the SPR of nanosized Au particles, which exhibit a distinct absorption in the visible light region at a wavelength of around 550 nm or rather at an energy of 2.25 eV, as shown in figure 55. Furthermore, dried Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au (1 wt.-%) photocatalysts on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcined at 700 and 800 °C show a distinct rutile absorption in the high energy region (> 3.0 eV). However, the rutile impurity is already known for higher calcined  $Cs_{0.68}Ti_{1.83}O_4$ , as described in chapter 5.1.1. After calcination, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au (1 wt.-%) on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> (700 °C) experiences a lower rutile



absorption as in the dried version. Nevertheless, the rutile impurity is still not observable in the diffraction patterns.

**Figure 55:** Tauc plots of a) dried and b) calcined  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) prepared on  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600, 700 and 800 °C with corresponding absorption edge linearization and band gap energies (Eg). Kubelka-Munk functions for the presentation of Au SPR signals of c) dried and d) calcined  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%). Graphic c) and d) exhibit an equivalent intensity scale.

Plotted Kubelka-Munk functions in figure 55c and d reveal a different quality of the Au SPR signal, depending on the used  $Cs_{0.68}Ti_{1.83}O_4$  support, as well as differences between the dried and calcined version of the  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) photocatalysts. The Au SPR signal of the dried as well as of the calcined material of  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) on the 600 °C support shows the highest intensity compared to the other recorded spectra. Interestingly,  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) on  $Cs_{0.68}Ti_{1.83}O_4$  (700 °C) after drying shows no Au SPR signal at all, while on  $Cs_{0.68}Ti_{1.83}O_4$  (800 °C) prepared  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) experiences a minor Au SPR signal. Nevertheless, after calcination on  $Cs_{0.68}Ti_{1.83}O_4$  (700 and 800 °C),  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) photocatalysts show a clear Au SPR signal but with a lowered intensity to Au nanoparticles on  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C). This confirms the necessity of the

calcination step for the complete formation of the  $Cs_{0.68}Ti_{1.83}O_4/Au$  photocatalyst or rather for fully reduced Au co-catalyst particles. Furthermore, the symmetric and narrow shape of the Au SPR signal induces the existence of spherical Au nanoparticles with a narrow particle size distribution.<sup>[184, 200]</sup> The intensity differences, especially after calcination, indicate also a difference in the actual deposited amount of the Au co-catalyst on the respective  $Cs_{0.68}Ti_{1.83}O_4$ surface. According to this assumption,  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600 °C offers more deposition sites for Au nanoparticles than at 700 and 800 °C calcined  $Cs_{0.68}Ti_{1.83}O_4$ , arising from a larger surface area of the lower annealed support material. The effective visible light absorption of deposited Au nanoparticles may induce the ability for an overall visible light activity of the  $Cs_{0.68}Ti_{1.83}O_4/Au$  photocatalyst by a direct activation of the Au SPR.

Photocatalytic  $H_2$  Production via Sacrificial Agent Reforming with  $Cs_{0.68}Ti_{1.83}O_4/Au$  on Stabilized  $Cs_{0.68}Ti_{1.83}O_4$ 

Photocatalytic H<sub>2</sub> production with  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) prepared by wet impregnation is performed in long term experiments in the photocatalytic reforming of methanol, ethanol and glycerol. Average H<sub>2</sub> production rate values with corresponding error indicators, calculated by the standard deviation of the included measuring points between 5 - 10 h, are illustrated in figure 56. Executed long term experiments for the calculated average H<sub>2</sub> production rate values can be found in the appendix.



**Figure 56:** Average H<sub>2</sub> evolution rates of  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) on  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600, 700 and 800 °C with measurement error indicators of long term experiments in the photocatalytic reforming of methanol, ethanol and glycerol.

Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au (1 wt.-%) on differently calcined Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> support shows a familiar trend in the photocatalytic sacrificial agent reforming efficiency, as already described in chapter 5.1.3 for photodeposited noble metal co-catalysts on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>. A constant reforming efficiency trend in the order methanol > glycerol > ethanol is still present with a decreasing photocatalytic activity with increasing  $Cs_{0.68}Ti_{1.83}O_4$  calcination temperature. An exception in the stated trend is on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> (800 °C) prepared Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au photocatalyst, which shows a higher activity in glycerol reforming than in the conversion of methanol. However, the minor discrepancy in the reforming trend cannot be classified as significant due to the narrow measuring range in the vicinity of the detection limit of the used thermal conductivity detection unit in the GC. Furthermore, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au prepared by wet impregnation experiences a decreased activity compared to the photodeposited analogue, being much less active than after impregnation with Cu, e.g. figure 43d. The discrepancy in the absolute value of the photocatalytic activity may arise from the circumstance that the photodeposited Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au photocatalyst is a recovered photocatalyst and re-used for the upcoming long term experiment, which exhibits naturally an increased activity compared to the as-synthesized material due to the increased surface area. However, the stated increased interaction between the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> support and Au particles does not lead to an increased photocatalytic activity, as previously estimated. Whether a connection between the Au<sub>0.919</sub>Ti<sub>0.081</sub> impurity and low photocatalytic performance is present could not be clarified, due to the unknown photocatalytic abilities of Au<sub>0.919</sub>Ti<sub>0.081</sub>. Furthermore, an immobilization of the Au co-catalyst in  $Au_{0.919}Ti_{0.081}$  and the resulting exclusion from the photocatalytic process may also be an explanation for the reduced reforming efficiency of the impregnated Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au (1 wt.-%) photocatalysts.

## In-situ SPR Measurements of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au (1 wt.-%) in Sacrificial Agent Reforming

For a better understanding of the reduced photocatalytic activity of Au modified  $Cs_{0.68}Ti_{1.83}O_4$ , impregnated  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) on  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C) is investigated in regard of the in-situ formation of the Au co-catalyst during the photocatalytic reforming of methanol, ethanol and glycerol.  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) on  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C) is chosen for the Au SPR tracking experiments, due to its improved activity compared to the photocatalysts prepared on 700 and 800 °C annealed  $Cs_{0.68}Ti_{1.83}O_4$ . Selected Au SPR spectra of the performed reforming reactions with  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) are presented in figure 57a - c.
In-situ measured Au SPR spectra reveal a similarity of the Au co-catalyst behavior during the examined sacrificial agent reforming reactions. In the initial blank spectrum (0 h), Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au show a defined Au SPR signal at approximately 540 nm in each used sacrificial agent solution. The actual Au SPR signal is in the typical wavelength range for spherical Au nanoparticles deposited on a TiO<sub>2</sub> surface, which is used as a reference for the actual Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> support.<sup>[201-202]</sup> Another consistence in the performed in-situ measurements is the immediate rise of the Au SPR signal with an increased intensity compared to the blank spectrum after 0.5 h of irradiation and the upcoming constant intensity drop during the entire measuring time. The increased Au SPR signal after 0.5 h of illumination indicates the reduction of an oxidized Au species. However, the actual content and structure of the oxidized Au precursor is unknown. It is possible that Au<sup>+</sup> cations are formed in the same manner as  $Cu^+$  and are located in the interlayer structure of  $Cs_{0.68}Ti_{1.83}O_4$ and further reduced during the irradiation process. The intensity decrease of the Au SPR signal is connected with an intensity drop of the signal basis, visible at wavelengths lower than 500 nm. The observed signal basis drop and the unchanged Au SPR signal shape indicates that the amount of the Au co-catalyst on the photocatalyst surface stays constant throughout the estimated measuring period. This intensity drop may arise from the known transformation of the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> support, caused by the exposition with the sacrificial agent solution during the photocatalytic process.

The stable signal shape of the Au SPR induces highly stable Au co-catalyst particles on the photocatalyst surface, which are not influenced by possible decomposition products, which are formed during the conversion of the respective sacrificial agent. The stability of the Au co-catalyst is also reflected in a stable H<sub>2</sub> evolution rate during the entire measuring time in each reforming reaction. Furthermore,  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) on  $Cs_{0.68}Ti_{1.83}O_4$  (600 - 800°C) do not experienced an elongated activation time as the Cu impregnated photocatalysts, as shown in figure 42. The final photocatalytic performance is established in the beginning of the irradiation process (0.5 h). This photocatalytic behavior can be observed in each performed reforming reaction with  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) on  $Cs_{0.68}Ti_{1.83}O_4$  (600 - 800°C). In conclusion, the deposited Au co-catalyst requires a minor initial reduction during the first 30 min of irradiation, which is probably referred to a reduction of interlayer Au<sup>+</sup> cations. Metallic Au nanoparticles are mainly formed after the calcination step, visible by the measurable Au SPR signals as presented in figure 55c - d or as already mentioned after 30 min of illumination. However, performance of Au modified  $Cs_{0.68}Ti_{1.83}O_4$ .



**Figure 57:** Selected in-situ SPR spectra recorded during a) methanol, b) ethanol and c) glycerol reforming with  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) prepared on  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 600 °C. Each spectra ensemble exhibits an equivalent intensity scale on the ordinate axis.

## Post Characterization of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au (1 wt.-%) on Stabilized Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>

Each  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) photocatalyst prepared on  $Cs_{0.68}Ti_{1.83}O_4$  (600 - 800 °C) is recovered after the performed photocatalytic process and characterized by XRD and diffuse reflectance spectroscopy. Diffraction patterns of recovered  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) photocatalysts can be found in the appendix. The tested Au modified photocatalysts prepared by wet impregnation show again a similar structural change after a performed reforming reaction as the Cu modified analogues. The formed cesium salt CsCl is not detected in the diffraction patterns of each  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) photocatalyst. Analogous to the  $Cs_2SO_4$  impurity in Cu impregnated  $Cs_{0.68}Ti_{1.83}O_4$  (600 - 800 °C), CsCl is also washed out of the photocatalyst bulk material during the photocatalytic reforming reaction, caused by the aqueous sacrificial agent solution. Contrary to the CsCl impurity, the formed gold titanium alloy  $Au_{0.919}Ti_{0.081}$  remains in each photocatalyst bulk material, analogous to TiO<sub>2</sub> (anatase) in  $Cs_{0.68}Ti_{1.83}O_4/Cu after sacrificial agent reforming. Due to the lack of information about the$  photocatalytic capabilities of  $Au_{0.919}Ti_{0.081}$ , a possible composite formation with the  $Cs_{0.68}Ti_{1.83}O_4$  support material can be neither be proved nor denied. Nevertheless, the  $Au_{0.919}Ti_{0.081}$  alloy does not have any positive effect on the photocatalytic activity of  $Cs_{0.68}Ti_{1.83}O_4/Au$  or provide a different trend in the photocatalytic reforming of methanol, ethanol and glycerol. Additionally,  $Cs_{0.68}Ti_{1.83}O_4/Au$  experiences the known structure transformation of the  $Cs_{0.68}Ti_{1.83}O_4$  support material towards its protonated  $H_{0.68}Ti_{1.83}O_4$  form, independent of the  $Cs_{0.68}Ti_{1.83}O_4$  calcination temperature.

Tauc plots of  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) on  $Cs_{0.68}Ti_{1.83}O_4$  (600 - 800 °C), presented in figure 58a, c and e, reveal an overall band gap increase after each performed reforming reaction. A band gap increase up to 3.66 eV is taking place. Furthermore, Au impregnated  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 800 °C still exhibits a distinct rutile absorption in the high energy range (> 3 eV) after methanol, ethanol and glycerol reforming. In accordance with the recorded in-situ Au SPR spectra of  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) on  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C) each photocatalyst material shows a defined Au SPR signal after each photocatalytic process, as shown in figure 58b, d and f.

The similarity of the Au SPR signals after methanol and ethanol reforming (Figure 58b and d) of all tested photocatalysts induces an equivalent constitution of the Au co-catalyst on the photocatalyst surface. Interestingly,  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) on  $Cs_{0.68}Ti_{1.83}O_4$  (700 °C) shows an increased Au SPR signal after glycerol reforming compared to the other tested Au impregnated photocatalysts, as shown in figure 58f. The difference in the Au SPR signal intensity cannot be fully explained. Minor discrepancies in the weighed Au precursor amount could be a possible explanation of the differences in the Au SPR intensity. Also a higher degree of the formed alloy  $Au_{0.919}Ti_{0.081}$ , which probably immobilizes Au particles, may have also an effect on the Au SPR signal. However, the overall symmetric and narrow signal shape of the Au SPR induces a stable constitution of the co-catalyst particle during each performed reforming reaction. Furthermore, the wet impregnation process enables a consisted reproduction of the same co-catalyst form, independent of the used  $Cs_{0.68}Ti_{1.83}O_4$  support. Contrary, an increased photocatalytic performance by an improved SMSI-effect could not be achieved through the utilization of the wet impregnation process.



**Figure 58:** Tauc plots of  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) prepared on  $Cs_{0.68}Ti_{1.83}O_4$  (600 - 800 °C) with corresponding absorption edge linearization and band gap energies (E<sub>g</sub>) after a) methanol, c) ethanol and e) glycerol reforming. Kubelka-Munk functions of Au SPR signals of  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) after b) methanol, d) ethanol and f) glycerol reforming. Graphic b), d) and f) exhibit an equivalent intensity scale.

#### 5.2.5 Summary

Wet impregnation enables a simple and direct loading of a photocatalyst with a desired cocatalyst material, overcoming a time consuming photodeposition procedure as in the case of the photodeposition of metallic Cu on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> surface. Impregnation of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> with solved  $CuSO_4 \cdot 5 H_2O$  results in a complex photocatalyst composition, containing three different components. Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu consists of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu, depending on the impregnated Cu amount, TiO<sub>2</sub> (anatase) and Cs<sub>2</sub>SO<sub>4</sub>. Cu impregnated Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> experiences an increasing photocatalytic activity in H<sub>2</sub> production with increasing Cu content. Additional sacrificial agent reforming experiments executed with the three most active Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (5 - 7 wt.-%) photocatalysts reveal a different trend in the reforming efficiency compared to the photodeposited Cu analogue in the order glycerol > methanol > ethanol. The new trend in sacrificial reforming indicates a change in the oxidative capabilities of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu, which provides new pathways in the conversion of the used sacrificial agents, especially for glycerol conversion. Post characterization of recovered photocatalysts reveals a significant change in the photocatalyst composition after a performed photocatalytic process. Cs<sub>2</sub>SO<sub>4</sub> is washed out of the bulk structure and therefore does not participate in the photocatalytic mechanism. Furthermore, an increasing TiO<sub>2</sub> (anatase) content with increasing Cu loading is observed and quantified by the formation of a TiO<sub>2</sub> I(011)/Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> I(130) ratio. The rising TiO<sub>2</sub> amount with Cu loading or rather with Cs<sub>2</sub>SO<sub>4</sub> leads to the conclusion, that the formation of both components is linked. The removal of  $Cs^+$  by  $SO_4^{2-}$  ions from the interlayers provokes a collapse of the sheet-like layered structure of  $Cs_{0.68}Ti_{1.83}O_4$ , which results in the generation of pure TiO<sub>2</sub>. Cu impregnation on higher annealed Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> (700 and 800 °C) support may embank the TiO<sub>2</sub> formation through the stabilization of Cs<sup>+</sup> in the interlayers but cannot prevent it completely. Basing on the recorded diffraction patterns of recovered Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu photocatalysts, the formation of a photocatalyst composite by the participating semiconductors Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> and TiO<sub>2</sub> is evident. A postulated charge carrier transport mechanism (Figure 53), basing on the actual band alignment of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> and TiO<sub>2</sub>, leads to the assumption that an effective charge carrier separation is present in the formed composite. Assuming two pathways for the trapping of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> CB electrons either on the Cu co-catalyst or on TiO<sub>2</sub> itself. However, an estimation which electron trapping pathway is occurring, cannot be made. Additionally, TiO<sub>2</sub> offers also new reaction sites for sacrificial agent oxidation, concluding that in-situ generated TiO<sub>2</sub> is mainly responsible for the observed reforming efficiency trend and increased photocatalytic activity of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu prepared by wet impregnation. Initially recorded low band gap energies,

which possibly arise from incorporated  $Cu^+$  cations into the lattice or rather in the interlayers of  $Cs_{0.68}Ti_{1.83}O_4$ , are lost after a performed photocatalytic reforming reaction. The overall band gap energy increase denies an application of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  for visible light driven heterogeneous photocatalysis. Furthermore, additional experiments towards overall water splitting without any sacrificial agents reveal that  $Cs_{0.68}Ti_{1.83}O_4/Cu$  photocatalysts prepared by wet impregnation are not capable to perform the overall water splitting reaction.

Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au prepared by photodeposition provides only a minor photocatalytic activity in the reforming of methanol, ethanol and glycerol which originates from the weak SMSI-effect between Au nanoparticles and Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>. Wet impregnation is utilized to improve the and semiconductor.  $Cs_{0.68}Ti_{1.83}O_4$ interaction between metal impregnation with HAuCl<sub>4</sub> · 3 H<sub>2</sub>O leads to the formation of three different components, which determine the photocatalyst composition. Beside the  $Cs_{0.68}Ti_{1.83}O_4$  support, also CsCl and the alloy Au<sub>0.919</sub>Ti<sub>0.081</sub> are identified in the diffraction patterns of the calcined Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au photocatalyst. The CsCl impurity is formed by the removal of Cs<sup>+</sup> from the interlayers by Cl<sup>-</sup> from the used Au precursor. It can be assumed that Cs<sup>+</sup> cations are replaced by Au<sup>+</sup> cations as in the corresponding Cu impregnated photocatalyst. Due to the low Au precursor content of only 1 wt.-%, the removal of  $Cs^+$  does not provoke a collapse of the layered  $Cs_{0.68}Ti_{1.83}O_4$ structure and therefore does not form TiO<sub>2</sub> either in anatase of rutile modification. Therefore, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> remains as the dominant component in the impregnated Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au photocatalyst. On the other hand, the calcination step forms a gold titanium alloy of the form  $Au_{0.919}Ti_{0.081}$ , which probably stabilizes the titanate sheets, resulting in a prevention of the structure collapse. Independent of the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcination temperature, both impurities are formed. Furthermore, the Au<sub>0.919</sub>Ti<sub>0.081</sub> alloy is a physical evidence for an improved SMSIeffect in Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au. However, despite of the improved interaction between metal component and semiconductor support, the observed sacrificial agent reforming efficiency shows a low photocatalytic performance of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au prepared by wet impregnation. Post characterization of recovered Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au photocatalysts shows a removal of CsCl and remaining Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> and Au<sub>0.919</sub>Ti<sub>0.081</sub>. If a composite formation between Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> and Au<sub>0.919</sub>Ti<sub>0.081</sub> is occurring<sub>081</sub> cannot be assumed yet, due to the lack of information about the electronic band structure of Au<sub>0.919</sub>Ti<sub>0</sub>. Additional experiments towards visible light activity by a direct excitation of the Au surface plasmons as well as towards overall water splitting were not successful.

In-situ tracking of Cu and Au SPR signals during a running photocatalytic reforming reactions enables a direct view on the Cu and Au co-catalyst formation. In case of Cu cocatalysts, a correlation between the co-catalyst formation and actual development of the H<sub>2</sub> evolution rate can be made. The long activation period of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu corresponds directly with the slow Cu co-catalyst formation, due to the slow reduction of the oxidic Cu precursor, especially in glycerol reforming. Contrary, Au co-catalyst particles are mainly formed after calcination and do not change significantly after 30 min of irradiation during the photocatalytic reforming reaction, independent of the used sacrificial agent. Both co-catalysts show a symmetric and narrow SPR signal in the visible light range. The SPR signal shape allows an estimation of the actual co-catalyst constitution. The presented SPR signals indicate the existence of spherical particles with uniform particle sizes. However, a clear visualization of deposited Au particles by electron microscopy was not successful for clarification of the stated assumption about the co-catalyst particle constitution. The required sample preparation for TEM measurements, which includes a treatment in ultrasonic bath for around 1 h may remove the deposited co-catalyst particles from the photocatalyst surface. Another sample pre-treatment in order to break the particle agglomerations but to remain the co-catalyst content constant for TEM measurements has to be established. However, chapter 5.3 presents successfully recorded TEM-images of impregnated Cu particles on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>.

### 5.3 Copper modification of Layered Cesium Titanate by Sol-Gel Process

Basing on chapter 5.2, the observed band gap decrease due to possibly incorporated Cu cations in the  $Cs_{0.68}Ti_{1.83}O_4$  host lattice, leads to the idea of a direct insertion of Cu cations into a sol-gel synthesis, forming a quaternary photocatalyst of the general chemical formula  $Cs_{0.68}Ti_{1.83-(x/2)}Cu_xO_4$ , by assuming an exclusive B-site occupation. The direct Cu insertion into the host matrix of  $Cs_{0.68}Ti_{1.83}O_4$  should stabilize the cationic doping effect to hold a small band gap energy for visible light driven heterogeneous photocatalysis for H<sub>2</sub> production. For comparison,  $Cs_{0.68}Ti_{1.83}O_4/Cu$  were prepared by wet impregnation and photodeposition with an equivalent Cu amount as the studied  $Cs_{0.68}Ti_{1.83-(x/2)}Cu_xO_4$  photocatalyst in regard of their photocatalytic activity in H<sub>2</sub> production and Cu SPR development.

### 5.3.1 Synthesis and Characterization

For the synthesis of the quaternary photocatalyst  $Cs_{0.68}Ti_{1.83-(x/2)}Cu_xO_4$ , the sol-gel approach described in chapter 4.1.1 has been applied. In first proximity, the maximum installable Cu amount has to be determined, in order to avoid the formation of any impurity components as different cesium titanate conformations or CuO cluster. For this reason, a synthesis series with five different Cu contents between a stoichiometric amount of x = 0.05 - 0.3 is applied for the optimum Cu content determination. Up to a stoichiometric Cu content of x = 0.1 the quaternary photocatalyst Cs<sub>0.68</sub>Ti<sub>1.83-(x/2)</sub>Cu<sub>x</sub>O<sub>4</sub> shows no impurity components, except of TiO<sub>2</sub> in anatase phase, in the respective diffraction patterns. Higher Cu contents, especially larger than x = 0.17, which resembles the stoichiometric of theoretical vacancies of the unmodified  $Cs_{0.68}Ti_{1.83}O_4$ , an increased formation of the cesium titanate conformation  $Cs_2Ti_4O_9$  is observed. Corresponding diffraction patterns of  $Cs_{0.68}Ti_{1.83-(x/2)}Cu_xO_4$  with x = 0.17 - 0.3 can be found in the appendix. For further studies with  $Cs_{0.68}Ti_{1.83-(x/2)}Cu_xO_4$ , Cu contents of x = 0.05 and 0.1 have been chosen. The addition of further cations into the host lattice of  $Cs_{0.68}Ti_{1.83}O_4$  leads to a charge discrepancy in the bulk material. For the compensation of Cu substitutions, a decrease in the titanium and cesium content or an increase in the vacancy amount may occur. For clarification of the accurate stoichiometry of Cs<sub>0.68</sub>Ti<sub>1.83-(x/2)</sub>Cu<sub>x</sub>O<sub>4</sub> with x = 0.05 and 0.1, X-ray fluorescence analysis (XFA) has been utilized for the determination of the respective element composition. Basing on the XFA measurements, the calculated chemical formulas of the cesium copper titanates are Cs<sub>0.63</sub>Ti<sub>1.82</sub>Cu<sub>0.05</sub>O<sub>4</sub> and Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub>. According to the lowered stoichiometric amount of titanium and cesium relative to the unmodified  $Cs_{0.68}Ti_{1.83}O_4$ , the chemical formulas indicate that Cu cations occupy unspecific either cesium or titanium positions. In conclusion, Cu cations cannot be

exclusively incorporated into the titanate sheets or rather on the B-site as assumed previously. However, an increased Cu content leads to a more favorite incorporation into the titanate sheets. Nevertheless, a clear trend in the mentioned behavior cannot be pointed out due to the missing of further XFA data. Recorded diffraction patterns of  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ , plotted with the corresponding unmodified  $Cs_{0.68}Ti_{1.83}O_4$  and presented in figure 59a, show a defined lepidocrocite  $\gamma$ -FeOOH type structure with minor TiO<sub>2</sub> (anatase) impurities. The low applied calcination temperature of 600 °C leads to a reflex broadening comparable to that of the unmodified  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C) in the respective diffraction patterns (Figure 27c). However, the random occupation of Cu cations on different crystallographic positions prevents the formation of any Cu oxide species in  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ .



**Figure 59:** a) XRD patterns and b) Tauc plots with corresponding absorption edge linearization and band gap energy ( $E_g$ ) of  $Cs_{0.68}Ti_{1.83}O_4$ ,  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ .

Furthermore, the insertion of Cu into the titanate sheets as well as into the interlayers leads to a minor shift of the diffraction patterns to higher  $2\theta$  values, visible on the most intensive (130) reflex shifting from 27.9° 2 $\theta$  for unmodified Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> to 28.1° 2 $\theta$  for Cs<sub>0.63</sub>Ti<sub>1.82</sub>Cu<sub>0.05</sub>O<sub>4</sub> as well as for Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub>. This indicates a smaller distance between the crystallographic lattice planes. Calculated sheet to sheet distance of 1.61 nm for Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> compared to a sheet distance of 1.64 nm for unmodified Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> confirms the stated shrinking of lattice distance. However, sheet distance calculation in the examined scale is error-prone and therefore not significant enough for a conformation. Titanate sheet distance determinations by HR-TEM images are further discussed in the post characterization section of this chapter. Beside of the structural effects, Cu incorporation into the layered cesium titanate lattice results in a significant shift of the band gap energy from initially 3.4 eV into the visible light region to 3.0 and 2.9 eV for  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  respectively. The band gap reduction arises from the  $\Delta_{oct}$ -splitting of formed CuO<sub>6</sub>-octahedrons inside the titanate sheets. The lower band gap of  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  relative to  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  originates therefore from a higher incorporated amount of Cu in the titanate sheets, visible by the reduced stoichiometric titanium amount and increased cesium amount compared to  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$ . Nevertheless the extrapolation of the absorption edges of the copper modified cesium titanates is not straightforward, due to the absorption shoulder beginning at around 3.2 eV followed by a rise in the low energy region (< 2 eV). The absorption shoulder can be mainly referred to the broad interband transitions, which occur in Cu oxide species. However, the band gap shift into the visible light region through the insertion of Cu ions into the common sol-gel approach enables a simple and direct synthesis of visible light absorbing photocatalysts.

Inserted stoichiometric Cu amounts of x = 0.05 and 0.1 corresponds to loadings of metallic Cu of 1.285 and 2.57 wt.-%, respectively, and are utilized for the preparation of wet impregnated analogous of the sol-gel based photocatalysts. Diffraction patterns of CTO-Cu<sub>0.05</sub>-WI (Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (1.285 wt.-%)) and CTO-Cu<sub>0.1</sub>-WI (Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (2.53 wt.-%)) reveal the prior described structural transformation of the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> support material to TiO<sub>2</sub> in anatase modification as well as the formation of the Cs<sub>2</sub>SO<sub>4</sub> impurity with an increasing transformation degree with increasing Cu amount. Constructed Tauc plots from recorded diffuse reflectance spectra provide band gap energies of 3.31 and 3.15 eV for CTO-Cu<sub>0.05</sub>-WI and CTO-Cu<sub>0.1</sub>-WI, respectively. The wet impregnation process does not have an equivalent band gap decreasing effect as the utilized sol-gel approach. Nevertheless, the partly amorphous structure of the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> support material still enables an incorporation of impregnated Cu cations either into the vacancies of the host material crystal lattice or into the interlayer structure, which results in a minor band gap reduction. Corresponding diffraction patterns and Tauc plots with absorption edge linearization and band gap energies are listed in the appendix.

#### 5.3.2 Photocatalytic H<sub>2</sub> Production and In-Situ SPR Tracking

Representatively, only the results of  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ , CTO-Cu<sub>0.1</sub>-WI and CTO-Cu<sub>0.1</sub>-PD ( $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2.53 wt.-%)) prepared by photodeposition) in photocatalytic H<sub>2</sub> production and in-situ SPR tracking are presented in this section, due to the similarity of the recorded Cu SPR signals for the respective photocatalyst material. Obtained H<sub>2</sub> evolution rates of the corresponding Cu<sub>0.05</sub>-photocatalysts are present in table 5.1, while the actual H<sub>2</sub> production and SPR measurements with to Cs<sub>0.63</sub>Ti<sub>1.82</sub>Cu<sub>0.05</sub>O<sub>4</sub>, CTO-Cu<sub>0.05</sub>-WI and CTO-Cu<sub>0.05</sub>-PD (Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu (1.285 wt.-%)) can be found in the appendix.

Photocatalytic H<sub>2</sub> production tests in methanolic solution with  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  and  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  are initially performed under irradiation of a Xe-arc lamp. Unfortunately,  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  shows only a minor photocatalytic activity in methanol reforming, manifested in a H<sub>2</sub> evolution rate of approximately 5 µmol/h after totally 30 h of irradiation (Appendix), while  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  does not show any photocatalytic activity at all. In order to receive more insights about the photocatalytic properties of  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ , further photocatalytic performance tests are executed under irradiation of a Hg-midpressure immersion lamp in photocatalysis setup 1. For comparison wet impregnated and photodeposited photocatalyst are also tested in photocatalysis setup 1 under Hg-lamp irradiation. H<sub>2</sub> evolution experiment in methanolic solution with  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  and corresponding in-situ SPR spectra are presented in figure 60.



**Figure 60:** a) Photocatalytic H<sub>2</sub> production by methanol reforming performed in photocatalysis setup 1 and b) Selected in-situ recorded Cu SPR of  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ .

 $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  shows an unconventional behavior under the illumination of the utilized Hg-lamp. During 7 h of irradiation a constantly increasing H<sub>2</sub> rate could be observed.

Afterwards, an exponential increase in H<sub>2</sub> evolution is recorded with a maximum rate of 5.1 mmol/h after 8.5 h followed by a constant activity drop. Repetition experiments confirm the observed photocatalytic behavior of  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ . Simultaneously recorded SPR spectra, as shown in figure 60b, reveal a slow but constant reduction of an oxidic Cu precursor species during the entire measuring period. The assumption of oxidized Cu species in Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> can be confirmed, by considering the recorded SPR blank measurement (0 h), which shows no SPR signal of metallic Cu particles at all. During the first hour of irradiation, Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> provides a small H<sub>2</sub> production rate comparable to the photocatalytic activity of unmodified Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> (Figure 32a). The corresponding SPR spectrum shows no formation of an active Cu co-catalyst. However, after 2 h of constant irradiation the Cu SPR transition signal is simultaneously increasing with the H<sub>2</sub> evolution rate. A significant increase of Cu SPR signal intensity after 8 h corresponds to the observed exponential increase in the H<sub>2</sub> production rate, marking a strong activity due to the formation of a critical amount of metallic Cu, which acts as a H<sub>2</sub> evolution co-catalyst. Contrary, the observed Cu SPR signals are broad and asymmetric, indicating a broad particle size and shape distribution of Cu particles. Nevertheless, the long activation period can be explained by a slow diffusion of reduced Cu ions from the interlayers as well as from the titanate sheets to the photocatalyst surface. Hence, the photocatalytic H<sub>2</sub> production and the Cu precursor reduction are parallel reactions, which are occurring at the same time. Equivalent experiments under Xe-lamp irradiation for 24 h with Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> show no photocatalytic activity at all, indicating that a high energy input is required for the reduction of a bulk Cu precursor species. Nevertheless, the Hg-lamp irradiation leads to a color change of the photocatalyst suspension from faint yellow to black during the photocatalytic process. This color change indicates a high dispersion of metallic Cu co-catalyst particles on the photocatalyst surface. After an exposure to air, the photocatalyst suspension decolorizes to pale green, indicating an oxidation of exposed Cu nanoparticles. A photometric analysis of the reaction solution confirmed that Cu particles are still bound on the photocatalyst surface and not washed out during the photocatalytic process.

To confirm the stated assumption that Cu ions are removed from the bulk structure and rearranged on the photocatalyst surface, acting as  $H_2$  evolution co-catalyst, recovered  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  is re-used in an additional  $H_2$  production test with a coupled Cu SPR tracking experiment (Figure 61). Oxidized Cu co-catalyst particles, proven by the initial blank SPR spectrum (0 h), are immediately reduced in the beginning of the irradiation period, rebuilding the Cu co-catalyst. Contrary, the recovered  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  photocatalyst suffers

from a deterioration of activity which is reflected in a lowered initial H<sub>2</sub> production rate of 3.8 mmol/h. Furthermore, a slow but constant decrease in the photocatalytic activity is observed during the estimated measuring time. Until now, the origin of the decreasing photocatalytic performance cannot be fully clarified, due to the lack of information about deactivation effects concerning semiconductive photocatalysts. A stabilization of the incorporated Cu ions in the crystal structure of  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  can be simply achieved by an additional heat treatment at 800 °C for 10 h. However, the stabilizing effect of the performed calcination step leads to a decreased photocatalytic activity and a corresponding H<sub>2</sub> production rate of only 0.4 mmol/h even under Hg-lamp irradiation (Appendix). A constantly increasing H<sub>2</sub> rate, which indicates the formation of metallic Cu co-catalyst, could not be observed with  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  (800 °C) during the estimated measuring time.



**Figure 61:** a) Photocatalytic H<sub>2</sub> production by methanol reforming performed in photocatalysis setup 1 and b) Selected in-situ recorded Cu SPR of re-used  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ .

The impregnated photocatalyst CTO-Cu<sub>0.1</sub>-WI shows a similar photocatalytic behavior under Hg-lamp irradiation as  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ . After a certain activation period, an exponential increase followed by a slow deactivation can be observed, as presented in figure 62a. But, CTO-Cu<sub>0.1</sub>-WI experiences a higher initial H<sub>2</sub> production rate of around 1.4 mmol/h as well as a shorter activation period of only 2 h with a corresponding maximum H<sub>2</sub> rate of 3.6 mmol/h. The observed photocatalytic behavior indicates a structural similarity of CTO-Cu<sub>0.1</sub>-WI to the sol-gel based Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> photocatalyst. The found activation period of CTO-Cu<sub>0.1</sub>-WI can be referred to the reduction and the followed removal of Cu ions, which are partly incorporated in the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> lattice, from the bulk to the photocatalyst surface.

Corresponding in-situ Cu SPR spectra of CTO-Cu<sub>0.1</sub>-WI during methanol reforming are shown in figure 62b. Interestingly, CTO-Cu<sub>0.1</sub>-WI does not show any Cu SPR signal in the

first hour of irradiation. After 4 h a broad Cu SPR signal can be observed at a wavelength of around 590 nm. The appearance of the Cu SPR signal corresponds with the exponential increase in the H<sub>2</sub> evolution rate and marks the formation of the undefined critical Cu co-catalyst amount in order to reach the maximum photocatalytic activity. Despite of the decreasing H<sub>2</sub> production after reaching the maximum rate, recorded SPR spectra reveal a continuously rising Cu SPR signal. This leads to the assumption that the observed photocatalyst deactivation is not in relation with the Cu co-catalyst formation. Cu SPR from CTO-Cu<sub>0.1</sub>-WI show a narrower and more symmetric signal compared to Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub>, indicating spherical Cu co-catalyst particles with a narrower particle size distribution, as described in chapter 5.2.2.



**Figure 62:** a) Photocatalytic  $H_2$  production by methanol reforming performed in photocatalysis setup 1 and b) Selected in-situ recorded Cu SPR of CTO-Cu<sub>0.1</sub>-WI.

Photodeposition of Cu on  $Cs_{0.68}Ti_{1.83}O_4$  under Hg-lamp irradiation leads to the shortest activation period of approximately 1 h. The maximum H<sub>2</sub> evolution rate of 4.7 mmol/h is reached after 2 h of constant irradiation. On the other hand, CTO-Cu<sub>0.1</sub>-PD experiences a fast deactivation after the achievement of the maximum H<sub>2</sub> rate compared to the wet impregnated and sol-gel based materials. Nevertheless, in-situ recorded Cu SPR spectra coincide to the observed photocatalytic behavior of CTO-Cu<sub>0.1</sub>-PD. After an activation period of 1 h, a distinct SPR signal of metallic Cu at a wavelength of 600 nm appears, followed by the most intensive Cu SPR signal after 2 h, which marks the highest H<sub>2</sub> evolution rate in methanol reforming. Afterwards, a decreasing signal intensity of the Cu SPR can be observed, which nearly corresponds with the decreasing photocatalytic performance of CTO-Cu<sub>0.1</sub>-PD. The similarity of the CTO-Cu<sub>0.1</sub>-PD Cu SPR signal shape to the wet impregnated photocatalyst induces a complementary Cu particle size and shape distribution. Therefore, the photodeposition technique produces spherical Cu particles with a narrow particle size distribution equivalent to the wet impregnation process. Contrary, CTO-Cu<sub>0.1</sub>-PD is subjected to a faster deactivation compared to CTO-Cu<sub>0.1</sub>-WI and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ .



**Figure 63:** a) Photocatalytic  $H_2$  production by methanol reforming performed in photocatalysis setup 1 and b) Selected in-situ recorded Cu SPR of CTO-Cu<sub>0.1</sub>-PD.

 $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  shows a similar photocatalytic behavior as well as similar in-situ Cu SPR signals as  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ . But generally,  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  suffers from longer activation times and a lowered photocatalytic activity in methanol reforming for H<sub>2</sub> production. The extended activation time can be explained by a reduced probability of Cu ion reduction due to the low Cu content and the simultaneously operating photocatalytic process for H<sub>2</sub> production. The decreased H<sub>2</sub> evolution rate can also be referred to the lowered amount of active Cu co-catalyst. The corresponding wet impregnated and photodeposited Cu photocatalysts with a Cu loading of 1.285 wt.-% experience also longer activation times and a reduced activity in the formation of H<sub>2</sub>. Recorded maximum H<sub>2</sub> evolution rates and corresponding activation times of Cu<sub>0.05</sub> and Cu<sub>0.1</sub> photocatalysts are summarized in table 5.1.

**Table 5.1**: Activation times and corresponding maximum  $H_2$  evolution rates of  $Cu_{0.05}$  (1.285 wt.-%) and  $Cu_{0.1}$  (2.57 wt.-%) prepared by sol-gel process, wet impregnation and photodeposition.

Synthesis method	Activation Time   max. H <sub>2</sub> Evolution Rate			
	Cu <sub>0.05</sub> (1.285 wt%)	Cu <sub>0.1</sub> (2.57 wt%)		
Sol-Gel Process	8 h   3.9 mmol/h	7 h   5.1 mmol/h		
Wet Impregnation	4 h   3.2 mmol/h	2 h   3.6 mmol/h		
Photodeposition	3 h   3.0 mmol/h	1 h   4.7 mmol/h		

The recorded Cu SPR spectra of  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  during photocatalytic methanol reforming reveal that differently sized Cu co-catalyst particles are formed by the sol-gel process or rather during the Hg-lamp irradiation, resulting in broad Cu SPR signals. The formed Cu particles act as a suitable co-catalyst species on appropriate reaction sites. In contrast, the photodeposition technique leads to the formation of Cu co-catalyst particles, which suffer from a fast deactivation. CTO-Cu<sub>0.1</sub>-WI represents an intermediate between the sol-gel based and photodeposited Cu photocatalyst in regard of activation time and deactivation but suffers from lower photocatalytic activity.

# 5.3.3 Post Characterization

The color change of the photocatalyst powder after photocatalytic  $H_2$  production as well as the observed deactivation indicate changes in the crystal structure and optical properties of all studied Cu modified photocatalysts. Recorded diffraction patterns and constructed Tauc plots of recovered photocatalysts confirm this assumption. Figure 64 presents the diffraction patterns and Tauc plots of  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ , as-synthesized and recovered after  $H_2$ production.



**Figure 64:** a) Diffraction patterns with reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$ ,  $TiO_2$  (anatase) and  $H_2Ti_2O_5 \cdot H_2O$  and b) Tauc plots of as-synthesized  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  and recovered from photocatalytic methanol reforming for  $H_2$  production with absorption edge linearization and respective band gap (E<sub>g</sub>).

 $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  experiences the already discussed structural transformation towards the Cs<sup>+</sup> exchanged H<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub>. The structural transformation is characterized by the disappearance of the reflexes at 21.4° and 30.8° 2θ and the increased reflex intensity of the (020) reflex at 10.4° 2θ. Furthermore,  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  exhibits a minor TiO<sub>2</sub> (anatase) impurity, visible by the most intensive (011) reflex at 25.3° 2θ. An equivalent crystal structure transformation is also observed for the Cu photodeposited photocatalysts or rather for the

utilized Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> support. Also CTO-Cu<sub>0.1</sub>-WI experiences an equivalent structure transformation typical for Cu impregnated  $Cs_{0.68}Ti_{1.83}O_4$ . The  $Cs_2SO_4$  impurity is washed out of the bulk structure; while an increased TiO<sub>2</sub> (anatase) content is observed. However, CTO-Cu<sub>0.1</sub>-WI is also subjected to the structural transformation towards H<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> as the sol-gel based and photodeposited photocatalysts. The lost doping effect of incorporated Cu cations, due to their removal from the bulk of  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  is directly reflected in an increased band gap energy after the photocatalytic process, as seen in figure 64b. However, CTO-Cu<sub>0.1</sub>-WI shows also an increased band gap energy of 3.17 eV from initially 2.97 eV after photocatalytic methanol reforming. CTO-Cu<sub>0.1</sub>-PD provides also an increased band gap of 3.60 eV after the photocatalytic process. This fact reveals that in case of the sol-gel based material Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> nearly the entire content of incorporated Cu cations are reduced, removed from the bulk and attached on the photocatalyst surface. Whether the in-situ formation of H<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> additionally promotes the Cu leaching effect cannot be clarified yet. In order to confirm the stated assumption concerning the Cu cation removal from the photocatalyst bulk structure, dispersive X-ray spectroscopy (EDX) analysis of the assynthesized and recovered Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> material as well as from the corresponding wet impregnated and photodeposited photocatalysts is performed. Table 5.2 summarizes the calculated Cs/Ti and Cu/Ti ratios of the three respective Cu modified photocatalysts before and after the performed H<sub>2</sub> production experiment.

Table 5.2: Element ratios of Cs, Cu and Ti basing on EDX-analysis of as-synthesized	and after H <sub>2</sub>	production
recovered Cs <sub>0.64</sub> Ti <sub>1.79</sub> Cu <sub>0.1</sub> O <sub>4</sub> , CTO-Cu <sub>0.1</sub> -WI and CTO-Cu <sub>0.1</sub> -PD.		

Synthesis method	as-synthesized		after H <sub>2</sub> production	
	Cs/Ti	Cu/Ti	Cs/Ti	Cu/Ti
Sol-Gel Process	0.40	0.16	0.12	0.22
Wet Impregnation	0.34	0.10	0.11	0.20
Photodeposition	0.31	-	0.06	0.26

The reduced Cs/Ti ratio, observable in each photocatalyst material, confirms the stated structural transformation towards their respective proton exchanged analogues. Furthermore, the increased Cu/Ti ratio after photocatalytic methanol reforming indicates also a change of the Cu or rather Cu<sub>x</sub>O particle distribution on the surface of  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  and CTO-Cu<sub>0.1</sub>-WI. It can be assumed that reduced Cu particles are sintering together during the photocatalytic process, which leads to a punctual higher Cu concentration in the EDX measurement for recovered  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  and CTO-Cu<sub>0.1</sub>-WI.

For a detailed analysis of the as-synthesized materials of  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ , CTO-Cu<sub>0.1</sub>-WI and CTO-Cu<sub>0.1</sub>-PD as well as of the recovered photocatalysts, TEM and HR-TEM images are recorded especially for the clarification of the Cu co-catalyst particles status in order to confirm the stated assumptions concerning in-situ recorded Cu SPR spectra. Generally, all TEM images of the differently prepared cesium copper titanates show the same irregular and flake-like shape of the photocatalyst particles. As already mentioned, the photocatalyst particle shape arises from the gel-combustion step of the used sol-gel process for the synthesis of  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  and  $Cs_{0.68}Ti_{1.83}O_4$ , which is used as a support for CTO-Cu<sub>0.1</sub>-WI and CTO-Cu<sub>0.1</sub>-PD. Figure 65 presents TEM and HR-TEM images of as-synthesized and recovered  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ .



**Figure 65:** a) TEM and b) HR-TEM image with marked sheet distance of as-synthesized Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub>. c) TEM and d) HR-TEM image with marked sheet distance of recovered Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub>.

The photocatalyst particles tend to agglomerate to larger aggregates, which results in an inhomogeneity of the aggregate packing degree, manifesting in darker zones in the TEM image, as illustrated in figure 65a. Furthermore, the particle agglomeration does not follow a

defined order, resulting in a variety of differently formed photocatalyst particle aggregates. Coupled EDX element analysis of the as-synthesized Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> particles show punctual higher Cu contents compared to other particles and indicates an inhomogeneous distribution of Cu cations throughout the photocatalyst material. However, a clear visualization of Cu particles in the as-synthesized material could not be achieved neither in TEM nor HR-TEM magnification. Consequently, Cu cations are incorporated in the photocatalyst bulk and not deposited on the outer surface. Furthermore, HR-TEM analysis shows again the macroscopic layered structure formed by alternating cesium and titanate sheets. In as-synthesized Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub>, a layer-to-layer distance of 1.61 nm is present (Figure 65b), which is slightly decreased to the unmodified  $Cs_{0.68}Ti_{1.83}O_4$  material. Recovered  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  after photocatalytic methanol reforming experiences a partial break down of the particle agglomeration, forming smaller particle aggregates compared to the assynthesized material, as seen in figure 65c. The irregular packing degree of the photocatalyst primary particles remains after the photocatalytic process. Furthermore, HR-TEM images of the recovered Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> material (Figure 65d) reveal an increased layer-to-layer distance of 1.72 nm. According to the confirmed transformation towards the Cs<sup>+</sup> to proton exchanged H<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub>, a decreased layer-to-layer distance is expected, due to small ionic diameter of inserted H<sup>+</sup>. However, the chemical formula of  $H_2Ti_2O_5 \cdot H_2O$ , which is used for the identification of the proton exchanged material, implies the incorporation of a single H<sub>2</sub>O molecule into the crystal lattice. Inserted H<sub>2</sub>O molecules in the interlayer structure may be the reason for the increased layer-to-layer distance. But with a molecular diameter of 0.275 nm for a single H<sub>2</sub>O molecule, an appropriate increase in the layer distance should occur. Therefore, an ordered incorporation of H<sub>2</sub>O into the crystal lattice should be unlikely but a partial incorporation cannot be denied. Further EDX analyses of the recovered  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  show that irregularly shaped Cu particles are formed during photocatalytic methanol reforming (Appendix). Predominantly, metallic Cu particle agglomerations instead of defined Cu oxide particles are detected. Contradictory, no Cu SPR signal of metallic Cu particles could be detected in the initial time of a second run of a recovered Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> photocatalyst. Thus, it is quite likely that metallic Cu particles are formed under the influence of the electron beam during the imaging process. An estimation of an average particle size of the Cu co-catalyst particles by TEM is not possible, due to the strong agglomeration tendency. However, in-situ recorded Cu SPR spectra indicate a variety of different particle sizes and shapes, which manifest in a broad Cu SPR signal (Figure 60b).

Contrary to the sol-gel based material, the as-synthesized CTO-Cu<sub>0.1</sub>-WI shows spherical Cu particles on the photocatalyst surface as well as not-attached free Cu particle. Cu particles are framed in figure 66a. The loss of attachment can be explained by the TEM sample preparation, which includes 1 h of ultrasonic treatment in order to fragment the photocatalyst particle aggregates. Basing on the recorded image in figure 66a, Cu particle sizes between 92 - 150 nm are estimated. However, the shown image is not representative for the entity of the CTO-Cu<sub>0.1</sub>-WI composition and can be seen as an artifact. Nevertheless, additional EDX measurements of recovered CTO-Cu<sub>0.1</sub>-WI, which can be found in the appendix, prove the existence of oxidic Cu species throughout the photocatalyst material. Furthermore, the spherical shape of Cu particles is already indicated by recorded in-situ SPR spectra as shown in figures 44 and 62 and confirmed by TEM imaging.



**Figure 66:** a) TEM image of as-synthesized CTO- $Cu_{0.1}$ -WI with framed Cu particles and b) HR-TEM image with marked sheet distance of recovered CTO- $Cu_{0.1}$ -WI.

The complex composition of CTO-Cu<sub>0.1</sub>-WI prevents the estimation of the layer-to-layer distance, therefore no results concerning the sheet distance in the as-synthesized material of CTO-Cu<sub>0.1</sub>-WI are available. On the other hand, recovered CTO-Cu<sub>0.1</sub>-WI enables a calculation of the layer-to-layer distance with a value of 1.64 nm, which lies in the range of unmodified  $Cs_{0.68}Ti_{1.83}O_4$ . The sheet distance does not experience a significant increase for recovered CTO-Cu<sub>0.1</sub>-WI. It has to be considered that CTO-Cu<sub>0.1</sub>-WI forms a  $Cs_{0.68}Ti_{1.83}O_4/TiO_2$  composite and therefore does not exhibit an equivalent structure transformation as  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ . The composite formation may prevent excessive proton incorporation in the  $Cs_{0.68}Ti_{1.83}O_4$  interlayers.

The photodeposition technique is commonly used in the deposition of co-catalyst materials on the photocatalyst surface and enables the formation of nanosized particles on photoactive reaction sites. Figure 67a presents a photocatalyst particle of recovered CTO-Cu<sub>0.1</sub>-PD. The illustrated particle shows the typical fragmentation of the particle agglomerations, visible by the less dense packed areas in the upper section of the aggregate. TEM and even HR-TEM imaging could not visualizes any Cu co-catalyst particles on the photocatalyst surface. While performed EDX analysis of different CTO-Cu<sub>0.1</sub>-PD particles reveal a homogeneously distributed Cu co-catalyst throughout the entire photocatalyst material. Nevertheless, HR-TEM imaging reveals an intact layered structure of the recovered photodeposited photocatalyst. Layer-to-layer distance analysis reveals a sheet spacing of 1.68 nm for recovered CTO-Cu<sub>0.1</sub>-PD. The sheet distance of CTO-Cu<sub>0.1</sub>-PD is slightly increased compared to the unmodified Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>, which is again mainly related to the incorporation of H<sub>2</sub>O molecules into the interlayer structure.



Figure 67: a) TEM and b) HR-TEM image with marked sheet distance of recovered CTO-Cu<sub>0.1</sub>-PD.

TEM and HR-TEM measurements partially confirm the stated assumptions concerning the Cu co-catalyst constitution in regard of the particle shape and size distribution and induce that insitu SPR measurements provide reliable information for an estimation of the Cu co-catalyst status during the running photocatalytic process. However, photodeposited Cu co-catalyst particles could not be visualized either at TEM or HR-TEM magnification. Nevertheless, CTO-Cu<sub>0.1</sub>-WI shows spherical Cu particles and equivalent Cu SPR signals as the photodeposited analog. Conversely, the photodeposition technique also generates spherical Cu particles on the photocatalyst surface, basing on the recorded in-situ Cu SPR signals. Furthermore, all examined Cu modified photocatalysts are subjected to a structural change, even the sol-gel based  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ . However, higher annealing temperatures may improve the structural stability but at the expense of activity. X-ray photoelectron spectroscopic (XPS) analysis are performed on the as-synthesized and recovered Cu modified photocatalysts in order to receive more insights about the photocatalyst status or rather the chemical evolution of photocatalyst surfaces before and after a photocatalytic process. Prior it should be highlighted that XPS analysis is used as an ex-situ characterization method for the determination of the Cu oxidation state and does not describe the actual operating co-catalyst during a photocatalytic reforming process for H<sub>2</sub> production. Pristine  $Cs_{0.68}Ti_{1.83}O_4$  is again utilized as a reference material.

**Table 5.3:** Binding energy values of O 1s, Ti 2p, Cs  $3d_{5/2}$  and Cu  $2p_{3/2}$  signals as well as kinetic energy values of the Cu<sub>LMM</sub> Auger parameter of as-synthesized and recovered Cu modified photocatalysts synthesized by photodeposition, sol-gel process and wet impregnation and pristine Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>.

as-synthesized	O 1s	Ti 2p	Cs 3d <sub>5/2</sub>	Cu 2p <sub>3/2</sub>	Cu <sub>LMM</sub>
$Cs_{0.68}Ti_{1.83}O_4$	529.6 eV	458.0 eV	724.0 eV	-	-
$Cs_{0.64}Ti_{1.79}Cu_{0.1}O_{4}\\$	529.8 eV	458.2 eV	724.0 eV	932.2 eV	1849.0 eV
CTO-Cu <sub>0.1</sub> -WI	529.9 eV	458.2 eV	723.0 eV	932.4 eV	1849.3 eV
recovered	O 1s	Ti 2p	Cs 3d <sub>5/2</sub>	Cu 2p <sub>3/2</sub>	Cu <sub>LMM</sub>
CTO-Cu <sub>0.1</sub> -PD	530.1 eV	458.4 eV	723.9 eV	932.3 eV	1848.1 eV
$Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$	530.4 eV	458.9 eV	724.3 eV	932.8 eV	1848.1 eV
CTO-Cu <sub>0.1</sub> -WI	529.9 eV	458.4 eV	723.7 eV	932.2 eV	1847.9 eV

The position of the Ti 2p and Cs  $3d_{5/2}$  signals of the as-synthesized and recovered photocatalysts display, after correction for charging effects based upon the position of the C 1s signal relative to adventitious carbon at 284.6 eV, the typical binding energies of Ti(IV) and Cs(I) in oxidic form, as listed in table 5.3. Corresponding XPS spectra of O 1s, Ti 2p and Cs  $3d_{5/2}$  of as-synthesized and recovered photocatalysts can be found in the appendix. By considering the Cu  $2p_{3/2}$  signal of the as-synthesized and recovered photocatalysts (Table 5.3 and Figure 68) after correction for charging effects, the presence of a Cu(I) (931.9 – 932.9 eV) species is evident, while Cu(II) is expected at larger binding energy (> 933.4 eV).<sup>[191, 203]</sup> The binding energy value of the Cu  $2p_{3/2}$  signal differs slightly after photocatalytic methanol reforming, in case of Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> and CTO-Cu<sub>0.1</sub>-WI. Interestingly, CTO-Cu<sub>0.1</sub>-PD shows also an oxidation of the formed metallic Cu co-catalyst during the photocatalytic process to a Cu(I) species after atmospheric exposition, according to its Cu  $2p_{3/2}$  signal.

To more accurately determine the Cu oxidation state, the kinetic energy of the Cu<sub>LMM</sub> Auger transition is used to calculate the respective Auger parameter, since the binding energy value of the Cu  $2p_{3/2}$  signal does not allow an unambiguous determination of the Cu oxidation state. In case of the sol-gel based Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> and impregnated CTO-Cu<sub>0.1</sub>-WI photocatalysts, the Cu Auger parameter shows different values for the as-synthesized and recovered materials as well as differ from the expected value of metallic Cu (1851.0 -1851.3 eV) reported in literature.<sup>[191, 203]</sup> Instead, these values seem to hint again at the presence of Cu(I) (1848.6 - 1849.6 eV), since Cu(II) is characterized by a higher Auger parameter (~ 1851.0 eV).<sup>[191, 203]</sup> XPS measurements show that Cu<sub>2</sub>O is the actual Cu species in the as-synthesized and recovered Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub>. Such formation of Cu(I) species from a Cu(II) precursor might be questionable since Cu<sub>2</sub>O can be formed by the thermal reduction of CuO only at temperatures above 800 °C. However, certain organic ligands as citric acid are capable to reduce Cu(II) to Cu(I).<sup>[204]</sup> The formation of Cu(I) species in the as-synthesized CTO-Cu<sub>0.1</sub>-WI from a Cu(II) precursor under the given synthesis conditions is quite unusual. It can be assumed that in terms of the maintenance of charge neutrality induced by the replacement of interlayer Cs<sup>+</sup> by Cu<sup>+</sup> cations, the Cu(II) precursor is reduced to a Cu(I) species. However, the reducing agent in CTO-Cu<sub>0.1</sub>-WI is still unknown.



**Figure 68:** XPS spectra of Cu  $2p_{1/2}$  and Cu  $2p_{3/2}$  signals corrected for charging effects of a) as-synthesized CTO-Cu<sub>0.1</sub>-WI and Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> as well as b) recovered CTO-Cu<sub>0.1</sub>-PD, CTO-Cu<sub>0.1</sub>-WI and Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub>.

Furthermore, XPS analyses reveal a decrease of the Cs  $3d_{3/2}$  and Cs  $3d_{5/2}$  signals of recovered photocatalysts from 4.6 at.-% to 1.0 at.-%, calculated by quantitative analysis of Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> (Appendix). This change in Cs content explains also the change in crystal structure after a photocatalytic process by the exchange of interlayer Cs<sup>+</sup> cations by protons. In conjunction with recorded diffraction patterns (Figure 64a), the formation of the proton exchanged form during a photocatalytic process in aqueous media can be verified.

Nevertheless,  $Cs^+$  cations are still present in recovered photocatalysts, leading to the assumption that both photocatalysts  $Cs_{0.64-x}Ti_{1.79}Cu_{0.1}O_4$  and  $H_xTi_{1.79}Cu_{0.1}O_4$  are coexisting in the bulk material and contribute to the overall photocatalytic performance.

# 5.3.4 Summary

The utilized sol-gel approach enables the synthesis of quaternary layered cesium copper titanates. Cu contents larger than the stoichiometric amount of x = 0.1 lead to the formation of undesired Cs<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub> conformation as well as to an increase TiO<sub>2</sub> (anatase) generation. Nevertheless, the chemical formulas, based on XFA measurements, of the formed titanates Cs<sub>0.63</sub>Ti<sub>1.82</sub>Cu<sub>0.05</sub>O<sub>4</sub> and Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> reveal that Cu cannot be selectively incorporated into the titanate sheets or rather on the B-site. Cu<sup>+</sup>, basing on XPS results, occupies partially Cs<sup>+</sup> positions in the interlayers, which is evident in the decreased Cs content compared to the unmodified  $C_{s_{0.68}}Ti_{1.83}O_4$ . Nevertheless, the incorporation of  $Cu^+$  into  $C_{s_{0.68}}Ti_{1.83}O_4$  leads to a significant shift of the band gap energy from 3.4 eV to 3.0 and 2.9 eV for Cs<sub>0.63</sub>Ti<sub>1.82</sub>Cu<sub>0.05</sub>O<sub>4</sub> and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  respectively. Unfortunately, the cationic doping effect of incorporated Cu<sup>+</sup> ions lead to an increased formation of crystal defects, which act as trap states for photoinduced electron/hole pairs and lead consequently to an increased recombination rate. The increased charge carrier recombination is directly reflected in the decreased activity of  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$ , while higher Cu amounts as in  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  lead to full deactivation of the photocatalyst under Xe-arc lamp irradiation. Nevertheless, under irradiation of a Hgmidpressure immersion lamp, Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> shows an interesting photocatalytic behavior manifested in a constantly increasing H<sub>2</sub> rate followed by an exponential rise. The observed progress in H<sub>2</sub> evolution can be referred to the reduction of the Cu dopant and the formation of a critical co-catalyst amount, causing the exponential increase in H<sub>2</sub> production. The Cu dopant reduction is tracked by in-situ SPR measurements during the running photocatalytic process. The broad Cu SPR of Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> can be referred to irregular shaped and differently sized Cu particles, which is confirmed by coupled TEM and EDX analysis. However, an equivalent reaction of either Cs<sub>0.63</sub>Ti<sub>1.82</sub>Cu<sub>0.05</sub>O<sub>4</sub> or Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> under Xearc lamp irradiation even at 24 h of constant illumination could not be achieved.

Post characterization of recovered  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  reveal an equivalent structural transformation to unmodified  $Cs_{0.68}Ti_{1.83}O_4$  as well as a band gap energy shift to 3.31 eV into the UV-range from initially 2.9 eV. The observed band gap increase arises from the lost doping effect of incorporated Cu<sup>+</sup> cations, which are removed from the interlayer structure as well as from the titanate sheets during the photocatalytic process. However, a similar structure

transformation but with a minor extend in band gap increase (3.2 eV) could be observed after an exposition of  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  in methanolic solution but without irradiation. The performed dark experiment shows that interlayer Cu<sup>+</sup> cations can be easily removed and replaced by protons as Cs<sup>+</sup>. On the other hand, the slightly increased band gap energy of  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  from the dark experiment provides the assumption that Cu<sup>+</sup> cations, which are incorporated in the titanate sheets, are not affected and still have a minor band gap reducing doping effect (Appendix). An additional heat treatment of the sol-gel based photocatalyst, e.g. at 800 °C for 10 h, has a stabilizing effect on the interlayer cations but also results in a reduced photocatalytic performance and without a reduction of incorporated Cu cations.

Corresponding wet impregnated and photodeposited photocatalysts CTO-Cu<sub>0.1</sub>-WI and CTO- $Cu_{0,1}$ -PD show a similar photocatalytic behavior to  $Cs_{0,64}Ti_{1,79}Cu_{0,1}O_4$  but a difference in regard of their in-situ Cu SPR signals. CTO-Cu<sub>0.1</sub>-WI and CTO-Cu<sub>0.1</sub>-PD experience also significantly shorter activation periods than  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  but on the other hand also a reduced photocatalytic activity. Furthermore, in-situ Cu SPR spectra of CTO-Cu<sub>0.1</sub>-WI and CTO-Cu<sub>0.1</sub>-PD show a narrow and defined signal of metallic Cu at a wavelength of around 590 nm, inducing spherical Cu co-catalyst particles with a narrow particle sizes distribution. The spherical character of Cu co-catalyst particles could be proven by TEM measurements in case of as-synthesized CTO-Cu<sub>0.1</sub>-WI, as shown figure 66a. Contrary, in case of CTO-Cu<sub>0.1</sub>-PD no Cu co-catalyst particles could be visualized either at TEM or HR-TEM magnification, despite of the fact that EDX analyses confirm a homogeneous Cu distribution throughout the photocatalyst material. The nanosized Cu co-catalyst particles are probably imbedded on densely packed sections of the particle aggregates, which prevent a clear imaging. However, a clear explanation for the non-visualizable Cu particles in CTO-Cu<sub>0.1</sub>-PD cannot be given. But in-situ recorded Cu SPR spectra of CTO-Cu<sub>0.1</sub>-PD indicate the existence of spherical Cu particle generated by photodeposition. Furthermore, the stated results concerning the Cu cocatalyst status in CTO-Cu<sub>0.1</sub>-WI and CTO-Cu<sub>0.1</sub>-PD is also transferable on the prior investigated Cu photodeposited photocatalyst in chapter 5.1.4 as well as on the examined wet impregnated photocatalysts in chapter 5.2.2, due to their equivalence in their respective Cu SPR signal.

XPS analysis reveals stable oxidation states of Ti(IV) and Cs(I) in all as-synthesized and recovered photocatalysts (Appendix). Interestingly, calculated binding energies of the Cu  $2p_{3/2}$  signal of as-synthesized as well as recovered Cu modified photocatalysts prepared by

sol-gel process and wet impregnation show a clear evidence of a Cu(I) species. A reduction of the used Cu(II) precursor by inserted complexing agents EDTA and citric acid, in case of the sol-gel process, can be assumed, while a concrete explanation of the Cu(I) presence in CTO- $Cu_{0,1}$ -WI cannot be given. A Cu(I) formation in order to keep charge neutrality induced by the intercalation of Cu<sup>+</sup> cations into the crystal interlayers, which are occupied by Cs<sup>+</sup>, can be used as an explanation while the reducing agent is still not indentified. The present Cu(I) species in sol-gel based Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> material lead to a new consideration of the chemical formula, providing a charge imbalance due to the missing positive charge of the prior assumed Cu(II) species. The actual charge discrepancy can be compensated by the formation of additional oxygen defects, leading to a chemical formula of  $Cs_{0.64}Ti_{1.79}Cu_{0.1}\square_{0.05}O_{3.95}$ . Nevertheless, oxygen vacancies cannot be considered in the model for the calculation of the chemical formula, basing on X-ray fluorescence data. Additional crystal structure investigations as Rietveld refinement in order to calculate the amount of oxygen vacancies have to be executed to determine the correct chemical formula of the solgel based Cu modified photocatalysts. Furthermore, the overall decrease of the Cs  $3d_{3/2}$  and Cs 3d<sub>5/2</sub> signals, recorded for recovered photocatalysts, matches with reduced Cs/Ti ratios calculated from EDX analysis (Table 5.2) and confirms the significant loss of Cs<sup>+</sup> from the interlayer structure.

In case of the sol-gel based material  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ , the presented results lead to a controversy that an inhomogenously distributed co-catalyst implies higher photocatalytic activity in the face of a well-dispersed co-catalyst. In spite of the inhomogeneity in dispersion, the inserted Cu precursor in  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  seems to occupy appropriate reaction sites for an effective reduction by the host photocatalyst, which leads to a high photocatalytic performance in H<sub>2</sub> production.

# 5.4 Chromium, Iron and Manganese Doped Layered Cesium Titanate

The lost doping effect of incorporated Cu ions in case of the quaternary photocatalysts  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ , due to the occurring reduction during the photocatalytic methanol reforming process, demands alternative doping agents for an effective and stable band gap reduction of  $Cs_{0.68}Ti_{1.83}O_4$ . Three transition metal cations  $Cr^{3+}$ ,  $Fe^{3+}$  and  $Mn^{3+}$  are chosen as dopants for  $Cs_{0.68}Ti_{1.83}O_4$ , due to their comparable ionic diameter to Ti<sup>4+</sup> (60.5 pm) of 61.5, 64.5 and 64.5 pm respectively.<sup>[134-135]</sup> A specific incorporation of the mentioned doping ions into the titanate sheets of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> will cause the formation of  $MO_6$  (M = Cr, Mn, Fe) octahedrons within the TiO<sub>6</sub>-network. Consequently, the formed  $MO_6$ octahedrons generate additional energy states in the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> band structure. Basing on the crystal field theory, sixfold coordinated transition metals experience an energetic splitting of the five energetic equivalent or rather deteriorated d-orbitals. The  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals are energetically increased and thereupon named as eg orbitals, while the orbitals dxy, dyz and dxz are lower in energy relatively to their deteriorated ground state in a spherically symmetric ligand field and named as t<sub>2g</sub> orbitals. Depending on the nature of the coordinating ligands, the d-electrons of the metal center are in the low or high spin configuration. Weak ligands as H<sub>2</sub>O causes high spin while strong ligands as halide anions induce low spin d-electron configuration at the coordinated metal center. However, in the formed MO<sub>6</sub>-coordination for  $M = Mn^{3+}$  and  $Fe^{3+}$ , a high spin configuration of the four and five d-electrons for  $Mn^{3+}$  and  $Fe^{3+}$  is expected.  $Cr^{3+}$  in MO<sub>6</sub> exhibits only three d-electrons, which are equally distributed in the three t<sub>2g</sub> orbitals according to the Pauli Exclusion Principle. The individual octahedral splitting  $\Delta_{oct.}$  of the utilized transition metal dopants in the titanate sheets is unknown. Therefore, four different energy state alignments of the split d-orbitals in an octahedral coordination field are possible: 1) eg and t<sub>2g</sub> orbitals are entirely imbedded either inside the VB or CB, having no band gap decreasing effect, 2) t<sub>2g</sub> orbitals are located in the semiconductor VB, while the empty or partially occupied eg orbitals are located in the forbidden zone, 3) eg orbitals are placed in the semiconductor CB, while the partially occupied  $t_{2g}$  orbitals are placed in the forbidden zone and 4)  $t_{2g}$  and  $e_g$  orbitals are located in the forbidden zone. In the second and third scenario, empty and partially occupied  $e_g$  and  $t_{2g}$ orbitals act as acceptor states for excited VB electrons, which can be further excited into the CB. The fourth case implies an additional electron excitation between the  $t_{2g}$  and  $e_g$  orbitals. Nevertheless, energy state alignment 2), 3) and 4) have a band gap decreasing effect caused by the reduced energy for electron transition to the dopant energy states. But, inserted dopant energy states act also as acceptor levels for VB holes and consequently as recombination

center, too. Therefore, the adjustment of the optimum doping concentration has to be established in order to receive a visible light active photocatalyst with an appropriate photocatalytic performance.

Basing on the results in chapter 5.3, an exclusive incorporation of the chosen doping metal ions  $Cr^{3+}$ ,  $Fe^{3+}$  and  $Mn^{3+}$  into the titanate sheets or rather into the crystallographic B-site cannot be guaranteed. Despite of the similarity in their ionic diameter, a possible incorporation into the interlayer of  $Cs_{0.68}Ti_{1.83}O_4$  or rather a substitution of the crystallographic A-site still persists. A-site occupation would inevitably result in a removal of the doping agent during the photocatalytic process and consequently to an increased band gap energy. Subsequent characterization of the recovered Cr, Fe and Mn doped photocatalysts will clarify the stated assumption.

### 5.4.1 Synthesis and Characterization

Basing on Merka et. al.,<sup>[134]</sup> three doping concentration of 0.1, 0.25 and 0.5 mol.-% referred to the actual titanium concentration are applied for each doping element. The utilized doping concentrations can be roughly approximate to a M/Ti (M = Cr, Fe, Mn) ratio of 1000, 400 and 200 for 0.1, 0.25 and 0.5 mol.-% respectively. Metal cation doped  $Cs_{0.68}Ti_{1.83}O_4$  is synthesized by the sol-gel approach, described in chapter 4.1.1, to ensure an effective distribution of the doping agent throughout the photocatalyst bulk material. Concentrations of citric acid and EDTA which are utilized as complexing agent are adjusted on the additional metal ion amount. According to the performed calcination studies on  $Cs_{0.68}Ti_{1.83}O_4$  and the resulting photocatalytic activities, the solid carbon contaminated precursors are calcined at 600 °C for 10 h in order to form the  $Cs_{0.68}Ti_{1.83}O_4$ :M (M = Cr, Fe, Mn) photocatalysts. Diffraction patterns of  $Cs_{0.68}Ti_{1.83}O_4$ :M (M = Cr, Fe, Mn) synthesized with 0.1, 0.25 and 0.5 mol.-% of the respective doping element are illustrated in figure 69.

According to the recorded diffraction patterns of  $Cs_{0.68}Ti_{1.83}O_4$ :M (M = Cr, Fe, Mn), an increased formation of the cesium titanate conformation  $Cs_2Ti_4O_9$  with increasing doping agent amount is observed. In order to prevent the formation of the undesired  $Cs_2Ti_4O_9$  component, the titanium amount is further increased up to 5% over the stoichiometric amount of the unmodified  $Cs_{0.68}Ti_{1.83}O_4$  to lower the Cs/Ti ratio towards the ratio of 0.37 for  $Cs_{0.68}Ti_{1.83}O_4$ . Nevertheless, increased titanium content leads to an increased formation of TiO<sub>2</sub> in anatase modification, while the formation of  $Cs_2Ti_4O_9$  is not prevented. The formation of  $Cs_2Ti_4O_9$  can be tracked by the (601) and (311) reflexes at 26.5° and 27.2° 20,

respectively, which are greenly marked in the diffraction patterns (Figure 69). Interestingly, larger ionic diameter of Fe<sup>3+</sup> and Mn<sup>3+</sup> compared to Cr<sup>3+</sup> provoke a Cs<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub> formation even at the lowest doping concentration of 0.1 mol.-%. Furthermore, each doped Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> photocatalyst exhibits a TiO<sub>2</sub> (anatase) impurity, visible by the most intensive (011) reflex at 25.3° 20.



Figure 69: Diffraction patterns of sol-gel based  $Cs_{0.68}Ti_{1.83}O_4$  doped with a) Cr, b) Fe and c) Mn cations in different concentrations of 0.1, 0.25 and 0.5 mol.-%.

Diffraction patterns of Fe and Mn doped  $C_{s_{0.68}}Ti_{1.83}O_4$  are slightly shifted of around  $0.3^{\circ}$  to higher 2 $\theta$  values, which indicates a shrinking of the lattice plane distances. In summary, each doped  $C_{s_{0.68}}Ti_{1.83}O_4$  material consists of  $C_{s_{0.68}}Ti_{1.83}O_4$ :M (M = Cr, Fe or Mn),  $C_{s_2}Ti_4O_9$  and TiO<sub>2</sub> (anatase), while  $C_{s_{0.68}}Ti_{1.83}O_4$ :M is the dominating component. The formation of  $C_{s_2}Ti_4O_9$  indicates a replacement of cesium and titanium by the respective doping element on the crystallographic A- and B-site of  $C_{s_{0.68}}Ti_{1.83}O_4$  in order to keep charge neutrality. The removal of titanium from the B-site is directly connected to the formation of crystal defects or rather vacancy sites, which act as recombination centers for generated electron/hole pairs.



**Figure 70:** Tauc plots of sol-gel based  $Cs_{0.68}Ti_{1.83}O_4$  doped with a, b) Cr, c, d) Fe and c, f) Mn catios in different concentrations of 0.1, 0.25 and 0.5 mol.-% with absorption edge linearization and band gap energies ( $E_g$ ).

Diffuse reflectance spectra of the doped  $Cs_{0.68}Ti_{1.83}O_4$  photocatalysts are recorded for the characterization of their respective optical properties as well as for the determination of band gap energies. Tauc plots of  $Cs_{0.68}Ti_{1.83}O_4$ :M (M = Cr, Fe, Mn) are presented in figure 70.Each doping element induces a small decrease of the band gap energy of  $Cs_{0.68}Ti_{1.83}O_4$ . The band gap decreasing effect correlates with the inserted amount of the respective doping agent. Due

to the small inserted amounts of the respective doping element, a meaningful quantification of the doping concentration is not possible, even with XPS.

Cr doped  $Cs_{0.68}Ti_{1.83}O_4$  shows two distinct absorption edges in the respective Tauc plots. The main absorption edge in the high energy range between 3.5 - 4.0 eV can be referred to  $Cs_{0.68}Ti_{1.83}O_4$ , while the absorption shoulder in the lower energy range between 3.0 - 3.5 eV arises from  $Cs_{0.68}Ti_{1.83}O_4$ :Cr. A linearization of the absorption shoulders reveals band gap energies of 2.86, 2.85 and 2.78 eV for 0.1, 0.25 and 0.5 mol.-% of Cr respectively. Therefore, the yellow coloring of the  $Cs_{0.68}Ti_{1.83}O_4$ :Cr photocatalyst powders can be directly referred to the absorption shoulders in the visible light range. A similar light absorption behavior is observed from Li et. al.<sup>[44]</sup> for Cr doped SrTiO<sub>3</sub> as well as from Merka et. al.<sup>[134]</sup> for Cr doped non-stoichiometric  $Y_2Ti_2O_7$ . In both cases, Cr doping generates a defined absorption shoulder in the visible light region instead of a complete absorption edge shift, even at higher Cr contents as in SrTiO<sub>3</sub>. Probably a stoichiometric Ti-substitution by Cr is required for a homogeneous absorption edge shift. An incorporation of Cr<sup>3+</sup> ions into the interlayers of  $Cs_{0.68}Ti_{1.83}O_4$ , forming Cr<sub>2</sub>O<sub>3</sub> should also be taken into account.

Fe doping applied on  $Cs_{0.68}Ti_{1.83}O_4$  leads also to a stepwise reduction of the band gap energy of around 0.1 eV per increased Fe doping content, as illustrated in figure 70c. But with a decreased band gap of 3.23 eV for a Fe content of 0.5 mol.-%, the Fe doped Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> is still not capable for visible light absorption. Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>:Fe shows also characteristic absorption bands of Fe<sub>2</sub>O<sub>3</sub> (hematite) below 3.0 eV, as presented in figure 70d.<sup>[150]</sup> However, the observed Fe<sub>2</sub>O<sub>3</sub> absorption is shifted to higher energies compared to bulk Fe<sub>2</sub>O<sub>3</sub>. Bulk Fe<sub>2</sub>O<sub>3</sub> normally shows electron transitions at around 1.5 eV (d-d-transition) and 2.0 eV, as shown in the appendix. The shift to larger energies, as seen in figure 70d, can be referred to the quantum confinement effect, assuming nanosized Fe<sub>2</sub>O<sub>3</sub> particles.<sup>[205]</sup> Nevertheless, Fe<sub>2</sub>O<sub>3</sub> absorption is less defined and much lower in intensity as the absorption shoulder of  $Cs_{0.68}Ti_{1.83}O_4$ :Cr, which manifests in a non-coloring of the  $Cs_{0.68}Ti_{1.83}O_4$ :Fe photocatalyst powder. This leads to the assumption that Fe<sup>3+</sup> is not successfully incorporated into the titanate sheets, probably forming  $Fe_2O_3$  in the interlayer structure, which does not interact with the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> host. The interlayer incorporation of Fe<sub>2</sub>O<sub>3</sub> may provoke the formation of the mentioned nanosized  $Fe_2O_3$  particle, induced by the narrow interlayer spacing between 1.59 - 1.64 nm (Figure 29c and d). Therefore, a real Fe doping of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> is not accomplished. Furthermore, it can be assumed that Fe<sup>3+</sup>cations may form FeO<sup>+</sup>-species<sup>[206]</sup> in order to keep the overall charge neutrality, while replacing  $Cs^+$  in the interlayers. The formation of FeO<sup>+</sup>-species is known for Fe<sup>3+</sup> cation exchanged zeolites.<sup>[206-207]</sup> But the existence as well as the optical properties of the mentioned FeO<sup>+</sup>-species in  $Cs_{0.68}Ti_{1.83}O_4$ :Fe are not experimentally clarified yet and require further investigations.

Mn doping of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> has an insignificant effect on the band gap energy in the concentrations of 0.1 and 0.25 mol.-% with energies of 3.36 and 3.34 eV, respectively. On the other hand, a Mn content of 0.5 mol.-% provokes a band gap reduction down to 3.21eV, as illustrated in figure 70e. In the overall  $C_{s_{0.68}}T_{i_{1.83}}O_4$  doping study in chapter 5.4, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>:Mn (0.5 mol.-%) experiences the greatest band gap decrease of the main absorption edge. However, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>:Mn shows also a defined absorption shoulder of probably an oxidic Mn species in the visible light region below 2.5 eV, as presented in figure 70f.<sup>[208]</sup> This absorption shoulder indicates as well as in case of Fe doping that Mn cations are not successfully incorporated in the titanate sheets rather than in the interlayers replacing Cs<sup>+</sup>. Due to the easily oxidizable Mn<sup>2+</sup> cation, which is used as a precursor in form of Mn(NO<sub>3</sub>)<sub>2</sub> · 4 H<sub>2</sub>O, into Mn<sup>3+</sup> or Mn<sup>4+</sup>, a specific Mn oxide in Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>:Mn cannot be specified.<sup>[209]</sup> The low Mn content prevents a detailed element analysis and oxidation state determination by XPS. The Mn doping causes also a broad absorption between 3.5 - 2.5 eV, which hinders the absorption edge linearization for a clear band gap determination. Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>:Mn powders turn from white to gray with increasing Mn amount, inducing a broad light absorption, which arises particular from three light absorption edges.

In summary, each doped  $Cs_{0.68}Ti_{1.83}O_4$ :M (M = Cr, Fe, Mn) photocatalyst exhibits a TiO<sub>2</sub> (anatase) and  $Cs_2Ti_4O_9$  impurity, according to the diffraction patterns, which interestingly do not influence the optical properties of the photocatalyst material. Contrary, each dopant could not be entirely incorporated on the crystallographic B-site, which may lead to the formation of the respective oxidic form of the doping element in the interlayers. On the other hand, the respective doping element may also form a MO<sup>+</sup>-species (M = Cr, Fe and Mn) in the interlayers, replacing Cs<sup>+</sup> on the A-site. It has to be considered that a MO<sup>+</sup>-species with Cr and Mn were not observed up until now. Therefore, the stated assumption cannot be verified. The status of the doping element is further discussed in chapter 5.4.3. While Cr and Mn doped  $Cs_{0.68}Ti_{1.83}O_4$  exhibit visible light absorbing capabilities, evidentially by the colored powder material, Fe doped  $Cs_{0.68}Ti_{1.83}O_4$  does not show any visible light absorption ability.

## 5.4.2 Photocatalytic H<sub>2</sub> Production with Cr, Fe and Mn Doped Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>

 $Cs_{0.68}Ti_{1.83}O_4:M$  (M = Cr, Fe, Mn) photocatalysts are tested in the photocatalytic methanol reforming for H<sub>2</sub> production, executed in the stepwise photodeposition of 0.0125 wt.-% of Rh. Recorded H<sub>2</sub> evolution rates of Cr, Fe and Mn doped  $Cs_{0.68}Ti_{1.83}O_4$  with doping concentrations of 0.1, 0.25 and 0.5 mol.-% are illustrated in figure 71. Photocatalytic performance tests with  $Cs_{0.68}Ti_{1.83}O_4:M$  (M = Cr, Fe, Mn) are executed in photocatalysis setup 2 under the irradiation of a Xe-arc lamp.



**Figure 71:** Sequential photodeposition of 0.0125 wt.-% Rh on a) Cr, b) Fe and c) Mn doped  $Cs_{0.68}Ti_{1.83}O_4$  for photocatalytic H<sub>2</sub> production in methanolic solution, with unmodified  $Cs_{0.68}Ti_{1.83}O_4$  as reference.

Basing on the presented results in H<sub>2</sub> production, a general trend in regard of the inserted doping concentration can be extracted. A constant activity drop with increasing doping content is observed for each doping element. Furthermore, all tested doped photocatalysts experience a lower photocatalytic activity than the unmodified  $Cs_{0.68}Ti_{1.83}O_4$ , except of  $Cs_{0.68}Ti_{1.83}O_4$ :Mn (0.1 mol.-%) which shows a 25% increased activity to  $Cs_{0.68}Ti_{1.83}O_4$  in the same Rh loading range. Nevertheless, the decreasing photocatalytic activity is referred to an increased formation of crystal defects or rather trap states, which increase the recombination

probability of photogenerated electron/hole pairs. Also an activity trend in regard of the doping element can be extracted, excluding the exception of  $Cs_{0.68}Ti_{1.83}O_4$ :Mn (0.1 mol.-%). A trend in the order Cr > Mn > Fe can be formed, which conforms to the results of Merka et. al.<sup>[134]</sup> for Cr, Fe and Mn doped non-stoichiometric Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>.

According to Merka. et. al.<sup>[134]</sup>, the observed activity trend correlates with the visible light absorbing ability of the respective doped photocatalyst, while the exception  $Cs_{0.68}Ti_{1.83}O_4$ :Mn (0.1 mol.-%) does not conform with the stated assumption. The stated assumption implies that a higher light fraction of the visible light region is additionally absorbed, causing a larger number of photoinduced electron/hole pairs for the photocatalytic process. Contrary, the increased number of the charge carriers is directly consumed by the coherently increased number of trap states resulting in a decreased activity compared to Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>. The significant activity drop of Fe doped Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> even at low Fe contents as well as the nonexisting band gap reduction effect lead to the conclusion that Fe is an inappropriate doping element for Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>. However, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>:Mn (0.1 mol.-%) provides a sufficient photocatalytic activity even higher than  $C_{s_0 68}Ti_{1 83}O_4$ , which implies a balanced material in regard of inserted foreign elements and coherently produced crystal defects, while higher Mn concentrations (> 0.1 mol.-%) have an adverse effect on the activity. The insertion of a Mn amount lower than 0.1 mol.-%, e.g. 0.05 mol.-% does not have any further positive effect on the photocatalytic activity of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>:Mn. Sequential photodeposition of 0.0125 wt.-% of Rh on  $Cs_{0.68}Ti_{1.83}O_4$ : Mn (0.05 mol.-%) can be found in the appendix.

Additional photocatalytic performance tests under visible light irradiation with each Cr, Fe and Mn doped  $Cs_{0.68}Ti_{1.83}O_4$  photocatalysts do not lead to any photocatalytic response. The inability of visible light absorption of  $Cs_{0.68}Ti_{1.83}O_4$ :M (M = Cr, Fe, Mn) leads to the assumption that the utilized doping elements are not strongly incorporated on the crystallographic B-site and rather loosely bond on the A-site interlayer. Nevertheless, an influence of the identified TiO<sub>2</sub> (anatase) and Cs<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub> impurities on the photocatalytic performance cannot be confirmed. For the clarification of a present TiO<sub>2</sub> (anatase) and Cs<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub> effect on the activity, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>:M (M = Cr, Fe, Mn) are recovered after the photocatalytic process and again characterized by XRD and diffuse reflectance spectroscopy.
#### 5.4.3 Post Characterization

Each doped photocatalyst  $Cs_{0.68}Ti_{1.83}O_4$ :M (M = Cr, Fe, Mn) is recovered and further characterized. Diffraction patterns as well as constructed Tauc plots from the respective diffuse reflectance spectra of  $Cs_{0.68}Ti_{1.83}O_4$ :M (M = Cr, Fe, Mn) are shown in figure 72.



**Figure 72:** Diffraction patterns of recovered a) Cr, c) Fe and e) Mn doped  $Cs_{0.68}Ti_{1.83}O_4$  with reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$ ,  $H_2Ti_2O_5 \cdot H_2O$  and greenly mark (011) reflex of TiO<sub>2</sub> (anatase). Tauc plots of recovered b) Cr, d) Fe and f) Mn doped  $Cs_{0.68}Ti_{1.83}O_4$  with absorption edge linearization and band gap energy ( $E_g$ ).

Recovered  $Cs_{0.68}Ti_{1.83}O_4:M$  (M = Cr, Fe, Mn) photocatalysts show an equivalent crystal structure transformation towards their respective proton exchanged version, as described in chapter 5.1.2. Interestingly, the previously recorded  $Cs_2Ti_4O_9$  impurity is no longer detected in each diffraction pattern of the recovered doped  $Cs_{0.68}Ti_{1.83}O_4$  materials. This indicates that  $Cs_2Ti_4O_9$  is washed out of the photocatalyst bulk material and therefore does not influence the photocatalytic performance at all. On the other hand, TiO<sub>2</sub> (anatase) remains in the bulk structure, while in case of  $Cs_{0.68}Ti_{1.83}O_4:Fe$  which holds only a minor anatase impurity, TiO<sub>2</sub> (anatase) is no longer available in the photocatalyst bulk. Despite of the remaining TiO<sub>2</sub> (anatase) impurity, the diffraction patterns of each  $Cs_{0.68}Ti_{1.83}O_4:M$  (M = Cr, Fe, Mn) photocatalyst show an equivalent material in regard of their crystal structure.

Furthermore, the removable  $Cs_2Ti_4O_9$  impurity provides also new insights about the  $Cs_{0.68}Ti_{1.83}O_4$  preparation approach. If a minor  $Cs_2Ti_4O_9$  impurity is present in the assynthesized material, the purity of  $Cs_{0.68}Ti_{1.83}O_4$  will not be affected, because  $Cs_2Ti_4O_9$  will be removed from the bulk material during the photocatalytic process due to the exposition in the aqueous reaction solution. On the other hand, TiO<sub>2</sub> (anatase) persists in the  $Cs_{0.68}Ti_{1.83}O_4$  material even after a photocatalytic process, concluding that the TiO<sub>2</sub> (anatase) formation should be prevented instead of  $Cs_2Ti_4O_9$ . However, TiO<sub>2</sub> (anatase) has no positive or negative on the photocatalytic performance of  $Cs_{0.68}Ti_{1.83}O_4$ :M (M = Cr, Fe, Mn). Beside structural changes,  $Cs_{0.68}Ti_{1.83}O_4$ :M (M = Cr, Fe, Mn) experiences also changes in their light absorption capabilities.

Tauc plots of recovered  $Cs_{0.68}Ti_{1.83}O_4:M$  (M = Cr, Fe, Mn) photocatalysts are shown in figure 72b, d and f. In first proximity, an overall band gap energy increase is observed in a range between 3.48 - 3.59 eV, which lies in the typical range for recovered unmodified  $Cs_{0.68}Ti_{1.83}O_4$  (chapter 5.1.2). The increased band gap energy can be mainly referred to the structural transformation induced by the exposition in the aqueous sacrificial agent solution. Furthermore, each Tauc plot of  $Cs_{0.68}Ti_{1.83}O_4:M$  (M = Cr, Fe, Mn) confirms the disappearance of the absorption shoulders in the visible light region, which could be prior observed in the Tauc plots of as-synthesized materials (Figure 70). The disappearance of the additional absorption shoulders manifests in a discoloration of the  $Cs_{0.68}Ti_{1.83}O_4:M$  (M = Cr, Mn) powder materials. Basing on the Tauc plots, the inserted doping elements Cr, Fe and Mn are also removed from the photocatalyst bulk structure during the photocatalytic process in the same manner as  $Cs^+$  from the interlayers. This leads to the assumption that  $Cr^{3+}$ ,  $Fe^{3+}$  and  $Mn^{3+}$  are exclusively inserted on the crystallographic A-site instead of the desired B-site,

forming probably their respective oxidic forms or  $MO^+$ -species (M = Cr, Fe, Mn) in the interlayers. Occupation of the crystallographic A-site by pure  $M^{3+}$  cations (M = Cr, Fe, Mn) would lead to a charge discrepancy, which causes the removal of three cesium cations in the interlayers in order to restore charge neutrality. Additionally, the smaller ionic radii of  $Cr^{3+}$ (61.5 pm),  $\text{Fe}^{3+}$  (64.5 pm) and  $\text{Mn}^{3+}$  (64.5 pm) compared to  $\text{Cs}^+$  (260 pm)<sup>[115]</sup> may provoke the formation of their respective oxidic form, due to the large distance between the  $M^{3+}$  cation and the negatively charged titanate sheets. To avoid a charge discrepancy, the  $M^{3+}$  cations may also form  $MO^+$ -species (M = Cr, Fe, Mn) instead of its oxide, which is not proven yet. The preferential A-site occupation by the utilized doping cations induces an avoidance of a Bsite occupation in order to prevent any crystal disorders or rather defect formations in the titanate sheets caused by trivalent Cr<sup>3+</sup>, Fe<sup>3+</sup> and Mn<sup>3+</sup> cations. But a cationic A-site occupation is evidently adverse for the establishment of visible light absorption. In order to provoke an effective B-site occupation in case of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>, a stoichiometric Tisubstitution like for the quaternary  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  photocatalyst has to be executed. Nevertheless, an increased doping amount will definitely cause a lowered band gap energy but in cost of an appropriate photocatalytic performance either under visible or UV light irradiation.

According to the post characterization studies on recovered  $Cs_{0.68}Ti_{1.83}O_4$ :M (M = Cr, Fe, Mn) photocatalysts, the cation doping method for band gap energy reduction cannot be seen as an appropriate tool for the production of visible light active layered cesium titanate of the form  $Cs_{0.68}Ti_{1.83}O_4$ :M (M = transition metal cation). The preferential A-site occupation by cationic doping agents and the subsequent removal from the interlayers during a photocatalytic process in an aqueous reaction medium hinders the application of cation modified  $Cs_{0.68}Ti_{1.83}O_4$  in visible light driven photocatalytic H<sub>2</sub> production.

### 5.4.4 Summary

The utilized sol-gel based synthesis approach for transition metal cation doped  $Cs_{0.68}Ti_{1.83}O_4$ does not enable the preparation of pristine  $Cs_{0.68}Ti_{1.83}O_4$ :M (M = Cr, Fe, Mn). Synthesized Cr, Fe and Mn doped  $Cs_{0.68}Ti_{1.83}O_4$  exhibits either a TiO<sub>2</sub> (anatase) and  $Cs_2Ti_4O_9$  impurity, which are confirmed by XRD analysis of the photocatalyst powders. Further attempts with an alternating titanium content in order to decrease the actual Cs/Ti ratio towards  $Cs_{0.68}Ti_{1.83}O_4$  is also not successful. Despite of the low doping concentrations of 0.1, 0.25 and 0.5 mol.-% referred to the titanium content of the unmodified  $Cs_{0.68}Ti_{1.83}O_4$  and the used sol-gel process for preparation, the inserted doping elements could not be homogeneously incorporated on the crystallographic B-site or rather into the titanate sheets, visible by defined absorption shoulders in the constructed Tauc plots (Figure 70b, d and f). Inserted doping elements have only a minor effect on the main absorption edge, resulting in a lowered band gap energy of a factor between 0.1 -0.2 eV relative to unmodified  $Cs_{0.68}Ti_{1.83}O_4$  with a band gap of 3.4 eV.

Photocatalytic H<sub>2</sub> production tests in methanolic solution (10 vol.-%) with  $C_{s_0 68}Ti_{1.83}O_4$ :M (M = Cr, Fe, Mn) reveal an overall reduced photocatalytic activity in methanol reforming compared to pristine Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>, except Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>:Mn (0.1 mol.-%) which shows an increased photocatalytic performance. Nevertheless, the decreased activity of doped Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> can be directly referred to an increased formation of energetic trap states, which act as recombination centers for photogenerated electron/hole pairs. Therefore, a correlation between inserted dopant amount and observed activity drop is evident. Excluding  $Cs_{0.68}Ti_{1.83}O_4$ :Mn (0.1 mol.-%), also a trend in the used doping elements in the order Cr > Mn > Fe can be extracted from the present H<sub>2</sub> evolution rates. According to Merka et. al.<sup>[134]</sup> the observed trend arises from the respective capability for visible light absorption. But in case of  $Cs_{0.68}Ti_{1.83}O_4:M$  (M = Cr, Fe, Mn) photocatalysts, which exhibit no visible light absorption abilities after the photocatalytic process, due to the removal of inserted doping cations from the bulk, the stated explanation by Merka et. al.<sup>[134]</sup> is not valid for doped  $Cs_{0.68}Ti_{1.83}O_4$ , due the lost doping effect after the photocatalytic process. Nevertheless, the actual activity differences indicate a partial B-site occupation of the doping element, while a preferential Asite occupation is evident. The low doping concentrations prevent a qualitative as well as a quantitative element analysis of  $C_{s_{0.68}}T_{i_{1.83}}O_4$ :M (M = Cr, Fe, Mn) photocatalysts.

XRD analysis of recovered  $Cs_{0.68}Ti_{1.83}O_4$ :M (M = Cr, Fe, Mn) photocatalysts reveal an equivalent structural transformation independent of the inserted doping element. Furthermore,

the  $Cs_2Ti_4O_9$  impurity is removed from the bulk structure during the photocatalytic process and therefore does not affect the photocatalytic performance of doped  $Cs_{0.68}Ti_{1.83}O_4$ .

The low extent in band gap energy lowering and the decreased photocatalytic activity caused by cation doping lead to the conclusion that either an A-site or B-site occupation by transition metal cations have no positive effect on the light absorption ability as well as on the activity of  $Cs_{0.68}Ti_{1.83}O_4$ . Anionic doping with ammonia to form  $Cs_{0.68}Ti_{1.83}O_{4-x}N_x$  has an equivalent adverse effect on the photocatalytic performance of  $Cs_{0.68}Ti_{1.83}O_4$  as cationic doping in photocatalytic H<sub>2</sub> production.<sup>[42]</sup> Therefore an alternative method for the production of visible light active  $Cs_{0.68}Ti_{1.83}O_4$  has to be established. In order to maintain the photocatalytic performance of pristine  $Cs_{0.68}Ti_{1.83}O_4$ , a combination with a stable visible light absorbing semiconductor like graphitic carbon nitride of the form g-C<sub>3</sub>N<sub>4</sub> in order to form a type II photocatalyst composite system has to be considered for future work.<sup>[107, 210]</sup>

Quaternary layered cesium copper titanates of the form Cs<sub>0.63</sub>Ti<sub>1.82</sub>Cu<sub>0.05</sub>O<sub>4</sub> and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  show a sufficient visible light absorption, according to the homogeneous absorption edge shift in the respective Tauc plots, but a poor photocatalytic performance in  $H_2$ production under Xe-arc lamp irradiation. In order to utilize the visible light harvesting ability of layered cesium copper titanates, Cs<sub>0.63</sub>Ti<sub>1.82</sub>Cu<sub>0.05</sub>O<sub>4</sub> and Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> are chosen as raw materials for the preparation of visible light active photoelectrodes. A connection to an external bias should improve the separation of photoinduced electron/hole pairs by the dissipation of electrons to the Pt counter electrode of the 3-electrode system, while VB holes are transferred to photoelectrode surface towards the semiconductor electrolyte interface, oxidizing the electrolyte itself. Unmodified  $Cs_{0.68}Ti_{1.83}O_4$  is used as a reference material in order to investigate the extended of band structure changes induces by the incorporated Cu cations. Capacitance measurements are executed for the construction of Mott-Schottky plots in order to determine the CB edge of the examined photocatalyst. Additional chopped light voltammetry (CLV) experiments are performed for the quantification of the induced photocurrent by a UV-lamp with a defined wavelength of 375 nm and a full spectra white light source for the simulation of realistic irradiation conditions.

#### **5.5.1 Photoelectrode Preparation**

The doctor blading technique is utilized for the deposition of the powdered photocatalysts on the surface of a conductive glass substrate. Glass plates with a thin fluorine doped tin oxide (FTO) layer are used as electric conductive substrates for the immobilization of photocatalyst powders to form photoelectrodes. Initially, photocatalyst powders calcined at 600 °C are utilized for photoelectrode preparation, in order to enable a direct comparison with previously performed H<sub>2</sub> production tests. After powder deposition on the FTO-glass substrate, the photoelectrodes are dried for 1 h at 80 °C for solvent evaporation and afterwards calcined at 600 °C for 3 h to improve the semiconductor-substrate contact. Unfortunately, immobilized photocatalyst powders calcined at 600 °C are not stable on the FTO-glass substrate when exposed to the aqueous electrolyte. Further attempts with lower powder amounts as well as longer calcination times do not provoke a stabilization of the photocatalyst on the FTO-glass substrates. The irregular shape of the photocatalyst primary particles as well as the loosely bound particle aggregates and the low crystallinity may weaken the semiconductor-substrate contact. Therefore, the powder material of  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  is additionally calcined at 700 and 800 °C for 10 h to increase the average particle size and to stabilize the particle agglomerations. Diffraction patterns of  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  calcined at 600, 700 and 800 °C are presented in figure 73a and b respectively.



**Figure 73:** Diffraction patterns of a)  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and b)  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  calcined at 600, 700 and 800 °C for 10 h with reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$ , TiO<sub>2</sub> in anatase and rutile modification.

Diffraction patterns of 600 °C calcined  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  are characterized by a distinct reflex broadening and a minor TiO<sub>2</sub> (anatase) impurity. An additional calcination step at 700 °C, leads to the formation of a more crystalline photocatalyst material, which is confirmed by the observed reflex narrowing visible in the respective diffraction patterns. Furthermore, calcination temperatures higher than 600 °C lead to a transformation of the TiO<sub>2</sub> anatase phase to the more thermodynamic stable rutile modification, which can be observed by the appearance of the most intensive (110) reflex of rutile at 27.7° 20. Interestingly, a higher rutile content in  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  compared to  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  is present, basing on the rutile (110) reflex intensity. A correlation between inserted Cu content and the formed amount of TiO<sub>2</sub> (anatase and rutile) cannot be confirmed. Nevertheless, an additional annealing step at 800 °C for 10 h produces a highly crystalline  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  material, visible by the sharp and narrow reflexes of the respective diffraction patterns. An increased formation of  $TiO_2$  in rutile modification cannot be observed, assuming a constant amount of the TiO<sub>2</sub> impurity in the bulk material. Despite of the 700 °C materials of  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ , which exhibit high rutile contents relative to the formed amount of crystalline layered cesium copper titanate, the lepidocrocite crystal structure of the layered cesium titanate is the dominating component in the 600 and 800 °C materials. Unmodified Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcined at 700 and 800 °C is used as a reference material for equally calcined layered cesium copper titanates. Diffraction patterns and Tauc plots of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> (700 and 800 °C) are illustrated in figure 27c and d respectively. Contrary to  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ , unmodified Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> does not exhibit any TiO<sub>2</sub> impurities in the corresponding diffraction patterns, while constructed Tauc plots show a defined absorption shoulder of a rutile impurity, which indicates a rutile amount below the detection limit of XRD analysis. In order to investigate the annealing temperature effect on the optical properties of  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ , diffuse reflectance spectra are recorded for the construction of Tauc plots for band gap energy determination. Tauc plots of  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  annealed between 600 - 800 °C are shown in figure 74.



**Figure 74:** Tauc plots of a)  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and b)  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  calcined at 600, 700 and 800 °C for 10 h with corresponding absorption edge linearization and band gap energies ( $E_{e}$ ).

Additional calcinations of the 600 °C material of  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  at 700 and 800 °C lead to a significant band gap energy decrease down to 2.62 ( $Cu_{0.05}$ ) and 2.49 eV ( $Cu_{0.1}$ ) at 700 °C and to 2.86 ( $Cu_{0.05}$ ) and 2.53 eV ( $Cu_{0.1}$ ) at 800 °C calcined photocatalysts. The decreased band gap energy can be referred to an improved incorporation of Cu cations into the overall crystal structure of the quaternary photocatalyst system. Nevertheless, a discrepancy in the band gap energy trend between the 700 and 800 °C

material within Cs<sub>0.63</sub>Ti<sub>1.82</sub>Cu<sub>0.05</sub>O<sub>4</sub> and Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> is evident. Interestingly, Cs<sub>0.63</sub>Ti<sub>1.82</sub>Cu<sub>0.05</sub>O<sub>4</sub> and Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> calcined at 700 °C exhibit smaller band gap energies as the corresponding 800 °C material. The differences in band gap energy can be referred to the different rutile contents in the 700 and 800 °C material of Cs<sub>0.63</sub>Ti<sub>1.82</sub>Cu<sub>0.05</sub>O<sub>4</sub> and Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub>. An increased TiO<sub>2</sub> rutile content relative to the actual amount of crystalline layered cesium copper titanate provokes a lowered band gap energy compared to the 600 and 800 °C material. This can be referred to the formation of nanocomposites consisting of Cs<sub>0.63</sub>Ti<sub>1.82</sub>Cu<sub>0.05</sub>O<sub>4</sub> or Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> and rutile. The increased rutile content manifests also in a defined absorption shoulder between 2.75 - 3.25 eV in the Tauc plots, shown in figure 74. The rutile absorption shoulder is slightly shifted to lower energies, which induces a partial Cu doping of the rutile impurity and hinders a clear approximation of the band gap energies of the layered cesium copper titanates. The increased band gap energy of the 800 °C materials compared to the 700 °C photocatalysts can be explained by the formation of a larger amount of crystalline Cs<sub>0.63</sub>Ti<sub>1.82</sub>Cu<sub>0.05</sub>O<sub>4</sub> and Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub>, which causes an additional band gap shift towards higher energies. Nevertheless, this effect is less pronounced in  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  than in  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$ . However, higher calcination temperatures produce a photocatalyst material with appropriate visible light absorbing abilities.

Due to the larger photocatalyst particles as well as to the increased stability of the particle aggregates, the photocatalyst paste preparation required 1 h of ultrasonic treatment in order to receive a fine colloidal suspension for the upcoming doctor blading process. The deposited photocatalyst films on FTO-glass were afterwards dried and again calcined for 3 h at 600 °C. Received photoelectrodes with 700 and 800 °C materials of the respective photocatalyst are stable under electrolyte exposition and can be used for further (photo)-electrochemical investigations.

#### **5.5.2 Capacitance Measurements**

Determination of CB edges of  $Cs_{0.68}Ti_{1.83}O_4$ ,  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  calcined at 700 and 800 °C is executed by capacitance measurements at three different constant frequencies of 100 Hz, 1 kHz and 10 kHz, for the construction of a Mott-Schottky plot according to equation 4.8. The execution of the capacitance measurement at three different frequencies is necessary to determine a frequency plateau where the CB edge potential remains constant. According to equation 4.8, the CB edge potential is accessible by the extrapolation of the linear part of the Mott-Schottky plot towards the abscissa. The

intercept of the linear extrapolation with the abscissa determines the CB edge potential. All capacitance measurements are executed in  $0.1 \text{ M Na}_2\text{SO}_4$  solution.

Figure 75 shows representatively the frequency dependant capacitance measurements of  $Cs_{0.68}Ti_{1.83}O_4$  and  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  calcined at 700 °C, performed at frequencies of 100 Hz, 1 kHz and 10 kHz. All utilized Mott-Schottky plots for CB edge potential determination and for the construction of respective photocatalyst band structure are summarized in the appendix.



**Figure 75:** Mott-Schottky plots measured at frequencies of 100 Hz, 1 kHz and 10 kHz of a)  $Cs_{0.68}Ti_{1.83}O_4$  and b)  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  calcined at 700 °C.

According to the capacitance measurement of unmodified  $Cs_{0.68}Ti_{1.83}O_4$ , the frequency plateau is achieved at a frequency of 1 kHz, while a plateau for  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  is already achieved at a low frequency of 100 Hz, visible by the consistent CB edge potential. The quaternary photocatalyst  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  experiences a significant CB edge drop towards a more positive potential, indicating additional energy states induced by inserted Cu cations below the former CB edge. Furthermore, all performed capacitance measurements show a baseline increase after the linear capacitance drop. The baseline increase becomes more distinct with increasing frequency value. Actually, the Mott-Schottky plot is strictly valid for an ideal compact semiconductor film without surface state formation. In first proximity, the tested photoelectrodes do not form a closed compact film on the FTO-glass substrate due to the utilized doctor blading technique, which is subjected by the manual handling of the operator. The manual handling produces an inhomogeneous film in regard of the film thickness throughout the coated area. But the formation of charged surface states is more convenient for the explanation of the observed baseline increase, due to the observed frequency dependency of the baseline shift. Surface states influence the space charge layer, inducing additional charges, which are not considered in the Mott-Schottky theory. Nevertheless, the observed baseline upwards shift does not affect the CB edge determination significantly. The determined CB edge of  $Cs_{0.68}Ti_{1.83}O_4$  at - 0.67 V vs NHE is in good accordance with the proclaimed CB edge potential of unmodified  $Cs_{0.68}Ti_{1.83}O_4$ , prepared by solid state reaction, by Liu et. al.<sup>[37]</sup> at - 0.75 V vs NHE. Nevertheless, the shapes of the recorded Mott-Schottky plots reveal that all examined photocatalyst can be categorized as n-type semiconductors. P-type semiconductors would generate a mirrored Mott-Schottky plot to a n-type semiconductor. The VB edge is directly accessible by the subtraction of the band gap energy, extracted from the respective Tauc plot, from the CB edge position, as described in electronic properties of solids in chapter 3.1.1. Figure 76 illustrates the determined band structure of  $Cs_{0.68}Ti_{1.83}O_4$ ,  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  calcined at 700 °C, constructed from respective Mott-Schottky and Tauc plots.



**Figure 76:** Electronic potential diagram of  $Cs_{0.68}Ti_{1.83}O_4$ ,  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  calcined at 700 °C plotted against the normal hydrogen electrode (NHE) and redox potentials of H<sup>+</sup>/H<sub>2</sub> and H<sub>2</sub>O/O<sub>2</sub>.

The constructed potential diagrams of the 700 °C material of  $Cs_{0.68}Ti_{1.83}O_4$ ,  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  reveal that each synthesized photocatalyst is theoretically capable to perform the overall water splitting reaction but only from the thermodynamic point of view. Incorporation of Cu into the host lattice of  $Cs_{0.68}Ti_{1.83}O_4$  leads to a shrinking of the electronic band structure, while the CB potential edge is shifted downwards to a more positive potential and the VB potential edge is shifted upwards to a more negative potential. This leads to the assumption that inserted Cu cations form additional energy states in the vicinity of the CB and VB edge potential, induced by the octahedral splitting of deteriorated d-orbitals into  $t_{2g}$  and  $e_g$  orbitals in the octahedral coordination of B-

site occupying Cu cations. An additional calcination at 800 °C for 10 h has only minor effect on the electronic band structure of  $Cs_{0.68}Ti_{1.83}O_4$ ,  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ , as shown in figure 77.

The increased band gap energy of  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  does not affect the CB edge potential position, while the VB edge position is shifted downwards towards a more positive potential.



**Figure 77:** Electronic potential diagram of  $Cs_{0.68}Ti_{1.83}O_4$ ,  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  calcined at 800 °C plotted against the normal hydrogen electrode (NHE) and redox potentials of H<sup>+</sup>/H<sub>2</sub> and H<sub>2</sub>O/O<sub>2</sub>.

By a simple consideration of the electronic band structures,  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  provide ideal conditions for visible light active photocatalysts, which are capable to perform the overall water splitting reaction. But in the real application of overall water splitting, both Cu modified photocatalysts failed in the actual performance. Even with the assistance of a sacrificial agent as methanol.  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  show only a minor or no activity under irradiation of a Xe-arc lamp, due to the increased number of crystal defects, induced by Cu cations, which act recombination centers for electron/hole pairs.

Concluding, the performed capacitance measurements for the construction of Mott-Schottky plots to determine the CB edge, enables the construction of the electronic band structure, when combined with constructed Tauc plots for band gap energy estimation. The received complete picture of the electronic band structure enables the selection of qualified photocatalysts for water splitting. But, the actual performance test is still unavoidable to clarify the real photocatalytic activity or photocurrent.

#### **5.5.3 Photocurrent Measurements**

Photocurrent measurements are performed as chopped light voltammograms (CLV) in order to quantify the potential of  $Cs_{0.68}Ti_{1.83}O_4$  as well as of the Cu modified layered cesium titanates  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  as photoelectrochemical cells. CLVs are executed in two different electrolytes, in 0.1 M Na<sub>2</sub>SO<sub>4</sub> and in a mixture of 0.1 M Na<sub>2</sub>SO<sub>4</sub> and 0.1 M KI. KI is acting as a hole scavenger to reduce the electron/hole pair recombination and thereby to increase the number of electrons which are transferred to the external circuit. To confirm the n-type semiconductive character of the tested photocatalysts, which is previously described by the constructed Mott-Schottky plots, a front and back side illumination experiment is performed with  $Cs_{0.68}Ti_{1.83}O_4$  (800 °C), as shown in figure 78.



**Figure 78:** Photovoltammograms of front and back side illuminated  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 800 °C for 10 h, performed under irradiation of an UV light emitting diode ( $\lambda = 375 \pm 4 \text{ nm}$ ; 60 W/m<sup>2</sup>) in 0.1 M Na<sub>2</sub>SO<sub>4</sub>.

Back side illumination executed on a  $Cs_{0.68}Ti_{1.83}O_4$  (800 °C) photoelectrode provides an increased current density compared to a front side illuminated photoelectrode and confirms the n-type semiconductivity of unmodified and transition metal modified layered cesium titanates. N-type semiconductor photoelectrodes experience a higher photocurrent under back side illumination because electrons, which are the majority charge carrier in an n-type semiconductor, are directly transferred to the external circuit while holes are transferred towards the semiconductor/electrolyte interface, oxidizing the electrolyte itself. On the other hand, front side illuminated n-type semiconductor photoelectrodes, because electrons are produced on the semiconductor/electrolyte interface and move through the photocatalyst bulk towards the

semiconductor/substrate interface. The electron transfer process increases the probability to be trapped on defect sites and to recombine with holes. Front side illumination is generally used on p-type semiconductor photoelectrodes. Therefore, all photocurrent measurements are executed under back side illumination. Furthermore, the performed front-back side illumination experiment enables also an estimation of an recombination degree of produced electron/hole pairs. Front side illumination causes a current density reduction of approximately 71% from 56  $\mu$ A/cm<sup>2</sup> down to 16  $\mu$ A/cm<sup>2</sup>, extracted from recorded current densities at a potential of 0.6 V vs. (Ag/AgCl). This careful estimation does not represents the actually occurring recombination of electron/hole pairs, due to the exclusion of the incident photon energy by the used light source which provide the effective number of theoretically produced electron/hole pairs. In order to receive the real photo efficiency) measurements have to be performed in the future.

Figure 79 presents the performed CLVs with  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 700 and 800 °C in 0.1 M Na<sub>2</sub>SO<sub>4</sub> (a) and in 0.1 M Na<sub>2</sub>SO<sub>4</sub>/0.1 M KI (b).



**Figure 79:** Photovoltammograms of  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 700 and 800 °C for 10 h, performed under back side irradiation of an UV light emitting diode ( $\lambda = 375 \pm 4$  nm; 60 W/m<sup>2</sup>) in a) 0.1 M Na<sub>2</sub>SO<sub>4</sub> and in b) 0.1 M Na<sub>2</sub>SO<sub>4</sub>/0.1 M KI.

According to the recorded current densities of  $Cs_{0.68}Ti_{1.83}O_4$  (700 and 800 °C) either in 0.1 M Na<sub>2</sub>SO<sub>4</sub> or 0.1 M Na<sub>2</sub>SO<sub>4</sub>/0.1 M KI, the presented results are contradictory to the performed H<sub>2</sub> evolution tests with the same photocatalyst materials (Figure 30c).  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 800 °C provides in both utilized electrolytes an increased current density than the corresponding 700 °C material. On the other,  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 700 °C experiences an increased photocatalytic activity in the reforming of methanol for H<sub>2</sub> production. The main

discrepancy between the 700 and 800 °C material of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> is the average particle size as described in chapter 3.1.1 and can be used as an explanation for the observed activity difference in both evaluation tests. While the increased average particle size of  $Cs_{0.68}Ti_{1.83}O_4$ (800 °C) causes a decreased photocatalytic activity in methanol reforming due to the increased recombination probability of electron/hole pairs, the same photocatalyst material enables the coating of a denser packed photocatalyst film on the FTO-glass substrate. The denser packed film and the coherently improved photocatalyst/substrate contact lead to a more efficient dissipation of photoinduced electrons to the external circuit than for  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 700 °C. On the other hand,  $Cs_{0.68}Ti_{1.83}O_4$  (700 °C) shows an improved photocatalytic activity compared to the 800 °C material of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> due to the reduced average particle size which lowers the recombination probability of electron/hole pairs but weakens the photocatalyst/substrate contact. The poor photocatalyst/substrate contact caused by low calcined Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> material is evident, especially for the 600 °C material, which prevents the preparation of a stable film on the FTO-glass substrate. An equivalent trend can be observed in the mixed Na<sub>2</sub>SO<sub>4</sub>/KI electrolyte, as shown in figure 79b. Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcined at 800 °C shows a higher current density than the corresponding 700 °C material. Interestingly, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> experiences a lowered current density of 40 µA/cm<sup>2</sup> at 0.3 V vs. (Ag/AgCl), in the mixed electrolyte than in pure 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution, visible in the magnified section imbedded in figure 79b. During the photoelectrochemical process, iodide anions are oxidized by photoinduced holes on the semiconductor/electrolyte interface to elemental iodine (2I/I<sub>2</sub> +0.54 V vs NHE)<sup>[115]</sup>, visible through the brown coloring of the electrolyte solution. Furthermore, the increasing baseline shift at larger potentials can be referred to the photoelectrochemical decomposition of the KI electrolyte component, which is crosschecked by a CLV experiment in 0.1 M KI solution (Appendix). The steep increase of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> (800 °C) above 0.4 V vs. (Ag/AgCl) can be referred to the higher photoresponse compared to the 700 °C material. The additional KI decomposition effectively reduces the electrolyte concentration and thereby affects the charge carrier transport.

Cu modified layered cesium titanates of the form  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ show only a minor photocurrent density under back side illumination of an UV light emitting diode. Figure 80 shows the CLV experiments with highest achieved current density with  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  calcined at 700 °C for 10 h.  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  calcined at 800 °C shows only a minor current density of 0.5  $\mu$ A/cm<sup>2</sup>, while  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  calcined at 700 and 800 °C shows no photocurrent at all even under UV light irradiation. However, also the observable current density of  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  (700 °C) is probably referred to the present rutile impurity as from the Cu photocatalyst itself. The non-existing photocurrent response of  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  correlate with their inactivity in the photocatalytic methanol reforming reaction under Xe-arc lamp irradiation, which is referred to the high number of trap states and the coherently high recombination probability.



**Figure 80:** Photovoltammograms of  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  calcined at 700 °C for 10 h, performed under back side irradiation of an UV light emitting diode ( $\lambda = 375 \pm 4$  nm; 60 W/m<sup>2</sup>) in a) 0.1 M Na<sub>2</sub>SO<sub>4</sub> and b) 0.1 M Na<sub>2</sub>SO<sub>4</sub>/ 0.1 M KI.

Additional photocurrent experiments with  $Cs_{0.68}Ti_{1.83}O_4$ ,  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  calcined at 700 and 800 °C under the irradiation of a white light source do not result in any photocurrent response and therefore denies their application as visible light active photocatalysts and photoelectrodes.

### 5.5.4 Summary

The instable coated photocatalyst film, consisting of a 600 °C material of the respective layered cesium titanate on a FTO-glass substrate prevents a comparison of the performed photocatalytic investigations concerning sacrificial agent reforming for  $H_2$  production with CLV experiments. The weak photocatalyst/substrate contact can be referred to the loosely agglomerated primary particles of the 600 °C material as well as to the irregular shape of the photocatalyst particles, which hinder an effective adhesion on the utilized substrate. Additional calcination steps at 700 and 800 °C for 10 h generate photocatalyst materials with an increased average particle size and enable the coating of a more dense packed film on the FTO-glass substrate, which experiences an improved substrate adhesion after calcination. Beside of the increase in the average particle size, calcination at 700 and 800 °C has also an effect on the photocatalyst bulk composition as well as on the optical properties of the tested

photocatalysts. Unmodified Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> shows a distinct rutile absorption in the Tauc plot of the corresponding 700 and 800 °C material, while this rutile impurity is not detected in the diffraction patterns, indicating only a minor rutile amount in the bulk. Cs<sub>0.63</sub>Ti<sub>1.82</sub>Cu<sub>0.05</sub>O<sub>4</sub> and Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> calcined at 700 and 800 °C show a significant rutile impurity in the corresponding diffraction patterns and an additional absorption edge shift towards the visible light region. The observed band gap shift indicates an improved incorporation of Cu cations in the host lattice but can also be related to a partial Cu doping of the rutile impurity. Therefore, the source of the band gap reduction cannot be fully clarified. Performed capacitance measurements for the construction of Mott-Schottky plots enable the determination of the CB edge potential position and with the knowledge of the corresponding band gap energy also the construction of the electronic potential diagram. Figures 76 and 77 show the constructed potential diagrams of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>, Cs<sub>0.63</sub>Ti<sub>1.82</sub>Cu<sub>0.05</sub>O<sub>4</sub> and Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> calcined at 700 and 800 °C. According to the constructed potential diagrams, each tested photocatalyst is capable to perform the overall water splitting reaction, form the thermodynamic point of view. Especially,  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  shows an ideal electronic band structure as well as a sufficient band gap energy for visible light absorption but fails in the actual reaction performance even with the assistance of a sacrificial agent for hole scavenging. The inactivity of Cu modified layered cesium titanates can be referred to a high number of additional trap states induced by incorporated Cu cations. The photocatalytic inactivity of Cs<sub>0.63</sub>Ti<sub>1.82</sub>Cu<sub>0.05</sub>O<sub>4</sub> and Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> under Xe-arc lamp irradiation is also reflected in their application as photoelectrode materials. Minor recorded photocurrents of Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> calcined at 700 °C, arises probably from the rutile impurity, which is detected by XRD analysis. Unmodified Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> provides an appropriate photocurrent under the irradiation of an UV light emitting light source, as shown in figure 79. Unfortunately, Cs<sub>0.63</sub>Ti<sub>1.82</sub>Cu<sub>0.05</sub>O<sub>4</sub> and Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> calcined at 700 and 800 °C show also no detectable photocurrent under irradiation of a full spectra white light source.

Molecular scale as well as stoichiometric doping of  $Cs_{0.68}Ti_{1.83}O_4$  leads equally to a significant deactivation of the photocatalyst material. An externally applied bias, in order to improve the dissipation of photoinduced electrons has no effect at all if the effective number of generated electron/hole pairs cannot be increased. Concluding, Cu modified layered cesium titanates of the form  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  are not sufficient photocatalysts in the applications of water splitting or rather H<sub>2</sub> production under visible light irradiation as well as not suitable in the application as photoelectrode materials.

# **6** Conclusion

183

The presented thesis is aligned with the catalyst development scheme presented in figure 1, starting with the preparation of pristine Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> by a Pechini method based sol-gel approach followed by a detailed characterization of the crystal structure, optical properties and particle morphology and finishing with an activity evaluation, as carried out in chapter 5.1. The utilized sol-gel process enables the synthesis of  $Cs_{0.68}Ti_{1.83}O_4$  at lower calcination temperatures and shorter calcination times compared to the conventional solid state reaction, resulting in a more photocatalytically active material. Low calcination temperatures enable the formation of photocatalyst particles with smaller average particle sizes, which are confirmed by XRD analysis, than calcination temperatures greater or equal to 800 °C. Lower calcined photocatalysts, e.g. at 600 °C, experience an increased photocatalytic performance than higher calcined photocatalysts. Smaller particles shorten the diffusion length for photoinduced electron/hole pairs from the bulk to the photocatalyst surface and hence reduce the probability to be trapped by crystal defects and to recombine. Particle morphology analysis by SEM and HR-TEM reveal an irregular shaped powder material of  $Cs_{0.68}Ti_{1.83}O_4$ . Flake-like shaped photocatalyst particles tend to agglomerate to larger aggregates, which results in a low surface area despite of the low average particle size of  $Cs_{0.68}Ti_{1.83}O_4$  particles produced at 600 °C. Activity evaluation is executed primary in the photocatalytic H<sub>2</sub> production via sacrificial agent reforming.

The activity evaluation test is also used in the stepwise photodeposition of different cocatalyst materials in order to determine the optimum loading of the respective co-catalyst. Prior,  $Cs_{0.68}Ti_{1.83}O_4$  calcined between 500 · 800 °C is tested in the stepwise Rh photodeposition to investigate the calcination temperature effect on the photocatalytic performance. Essentially for a systematic catalyst development is a post characterization of the recovered photocatalysts after a performed photocatalytic process in order study possible changes in crystal structure, optical properties and particle morphology and to investigate their effect on the photocatalytic performance. XRD analysis of  $Cs_{0.68}Ti_{1.83}O_4$ /Rh (500 -800 °C) reveals a crystal structure change towards a  $Cs^+$  to proton exchanged material of the form  $H_{0.68}Ti_{1.83}O_4$ , which is identified by the  $H_2Ti_2O_5 \cdot H_2O$  phase.  $H_2Ti_2O_5 \cdot H_2O$  exhibits an equivalent crystal structure to  $H_{0.68}Ti_{1.83}O_4$ . Higher calcined  $Cs_{0.68}Ti_{1.83}O_4$  materials are less affected by the  $Cs^+$  to proton exchange but suffer from lower photocatalytic activities. Characterization of the particle morphology of recovered  $Cs_{0.68}Ti_{1.83}O_4$ /Rh shows a segregation of the particle aggregates which can be referred to the mechanical stress induced by the turbulent stirring of the photocatalyst suspension in the reactor system. The particle segregation manifests in an increased surface area and also in an increased activity. The photocatalyst post characterization provokes a preselection of the prior synthesized  $Cs_{0.68}Ti_{1.83}O_4$  materials. Selection criteria must be established in order to choose between photocatalytic activity or structural stability.

Due to its superior activity, Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> calcined at 600 °C is selected as the standard photocatalyst for co-catalyst studies in sacrificial agent reforming, despite of the occurring structure change. The effect of noble metal as well as earth abundant co-catalysts on the sacrificial agent reforming capabilities of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> is investigated to receive a benchmark for the photocatalytic activity for later bulk structure modified Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>. Rh, Au and Pt are utilized as noble metal co-catalysts for the photocatalytic reforming of methanol, ethanol and glycerol, while Cu is selected as an alternative earth abundant co-catalyst. After the stepwise photodeposition of the optimum co-catalyst amount, recovered Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/M (M = Rh, Au, Pt, Cu) are re-used in long term experiments for the investigation of the respective photocatalyst stability in each tested reforming reaction. Basing on the activity evaluation results, two activity trends can be extracted: 1) Co-catalyst trend in the order Pt > Rh > Cu > Au, basing on methanol reforming activities and 2) sacrificial agent efficiency trend in the order methanol > glycerol > ethanol. It has to be remarked that only a minor activity difference is present between Rh and Cu in methanol reforming, while Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu shows a higher ethanol and glycerol reforming efficiency than Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Rh. The sufficient photocatalytic activity of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu confirms that even earth abundant co-catalysts provide a performance in the range of noble metal cocatalysts. But a long preparation time of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  by photodeposition is a significant drawback of the Cu co-catalyst. Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Au shows only minor activity in sacrificial agent reforming, which is referred to a weak SMSI-effect between Au particles and  $Cs_{0.68}Ti_{1.83}O_4$  support.

In order to overcome the major drawbacks of  $Cs_{0.68}Ti_{1.83}O_4/M$  (M = Cu, Au), both photocatalyst systems are prepared by the wet impregnation technique, seen in chapter 5.2. This preparation technique enables an easy and fast deposition of the desired co-catalyst amount on the photocatalyst surface and shortens the preparation time of  $Cs_{0.68}Ti_{1.83}O_4/Cu$ significantly. But as a consequence of the  $Cs_{0.68}Ti_{1.83}O_4$  impregnation with the CuSO<sub>4</sub> precursor, a type I photocatalyst composite of the form  $Cs_{0.68}Ti_{1.83}O_4/TiO_2$  (anatase) is produced. The TiO<sub>2</sub> formation is caused by the removal of interlayer Cs<sup>+</sup> by the sulfate anion of the impregnated Cu precursor, forming Cs<sub>2</sub>SO<sub>4</sub> as a product. The Cs<sup>+</sup> removal causes a collapse of the layered sheet structure, which results in the formation of  $TiO_2$  in the anatase phase. The formed composite Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/TiO<sub>2</sub> provides new pathways for the sacrificial agent reforming, which manifests in a new trend in the sacrificial reforming efficiency in the order glycerol > methanol > ethanol. The observed trend in reforming efficiency is induces by the oxidative capability of the in-situ formed TiO<sub>2</sub> (anatase) component, because a deposited  $H_2$  formation co-catalyst does not change the oxidative abilities of  $Cs_{0.68}Ti_{1.83}O_4$ . Nevertheless, the highly active  $Cs_{0.68}Ti_{1.83}O_4/TiO_2$  composite with Cu as co-catalyst in the reforming of glycerol resembles the desire photocatalyst for the photocatalytic conversion of a cheap and abundant feedstock as glycerol to solar H<sub>2</sub>. The in-situ formation of TiO<sub>2</sub> in the process of wet impregnation cannot be entirely prevented even by use of a stabilized  $C_{s_0 68}T_{i_{1,83}}O_4$  support. Also the utilization of other Cu precursors as nitrate or chloride Cu salts cannot hinder the removal of Cs<sup>+</sup> from the interlayers and the corresponding structure collapse, which results in the formation of TiO<sub>2</sub>. The challenging problem is the cesium salt production initiated by the Cu precursor anion. Interlayer Cs<sup>+</sup> form preferentially a strong ionic bond with the induced precursor anion than to be weakly coordinated by titanate sheets. Therefore, another alternative preparation route has to be chosen in order to produce a pure Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu photocatalyst with the optimum Cu co-catalyst amount. The impregnation of Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> with HAuCl<sub>4</sub>, in order to strengthen the interaction between Au particles and Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> support, does not result in an improved photocatalytic activity.

 $Cs_{0.68}Ti_{1.83}O_4/Cu$  prepared by wet impregnation experiences a band gap decrease with increasing Cu content. In order to utilize the band gap decreasing effect of Cu cations, Cu is directly inserted in the sol-gel process for a selective incorporation of Cu into the crystal structure of the layered cesium titanate, seen in chapter 5.3. Two quaternary photocatalysts of the form  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  are prepared with a minor TiO<sub>2</sub> (anatase) impurity and with band gaps of 3.0 and 2.9 eV respectively. The chemical formulas of layered cesium copper titanates reveal that Cu is either occupying the crystallographic A- and B-site, concluding that a selective B-site occupation in a simple one step synthesis is not successful. Furthermore, both photocatalysts are not active under the irradiation of a Xe-arc lamp or show only a minor performance. Under Hg-midpressure immersion lamp irradiation,  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  show an interesting photocatalytic behavior, manifested in a constantly increasing H<sub>2</sub> evolution rate followed by an exponential increase until their respective maximum activity. This photocatalytic behavior is directly referred to a constant reduction of incorporated Cu cations until the formation of a critical Cu co-catalyst amount, which causes the observed exponential activity increase. The formation of active metallic Cu co-catalyst is tracked by in-situ SPR analysis of the photocatalyst suspension under operating conditions. Adverse effect, Cu cations are removed from the crystal lattice, resulting in an increased band gap energy after the photocatalytic process. Higher calcination temperatures may stabilize the Cu cations inside the lattice but also result in a decreased photocatalytic activity. Analogous photocatalysts with a equivalent Cu loading prepared by photodeposition and wet impregnation show a similar photocatalytic behavior as the sol-gel based  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  but differ in terms of a shorter activation time and a lowered activity.

In-situ SPR analysis of the photocatalyst suspension at operating conditions enables a direct view on the Cu co-catalyst formation and basing on the SPR signal shape and position, an estimation of the Cu co-catalyst constitution can be made. Sol-gel based Cu-containing photocatalysts generate a slowly developing and broad Cu SPR signal, indicating an irregular Cu particle shape as well as an inhomogeneous particle size distribution. Wet impregnated Cu-containing photocatalysts experience also a slow Cu co-catalyst formation but not in the same extend as their sol-gel analogous and show also a more defined Cu SPR signal. This extreme difference in the Cu SPR signal shape indicates a contrary Cu co-catalyst particle constitution compared to the sol-gel based Cu photocatalysts. The observed narrow Cu SPR signal at around 590 nm indicates spherically shaped Cu particle and a homogeneous particle size distribution. Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/Cu prepared by photodeposition shows equivalent Cu SPR signals to the wet impregnated photocatalyst, which implies a similar Cu co-catalyst constitution. The indicated Cu particle shapes by recorded Cu SPR spectra are confirmed by TEM measurement instead for the photodeposited photocatalyst. The harsh pretreatment conditions for TEM samples cause a removal of Cu particle from the Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> surface in case of the photodeposited Cu co-catalyst. Nevertheless, in-situ SPR measurements provide a reliable tool for the investigation of SPR active co-catalysts and enable to connect the actual photocatalytic performance with the co-catalyst formation.

The stoichiometric Cu incorporation leads to a tremendous deactivation of the photocatalyst material under Xe-arc lamp irradiation. In order to minimize the degree of deactivation as well as to prevent a possible reduction of the foreign incorporated cations, three transition metal cations in the order  $Cr^{3+}$ ,  $Fe^{3+}$  and  $Mn^{3+}$ , which exhibit a similar ionic radii as  $Ti^{4+}$  are chosen as doping element for band gap reduction. Chapter 5.4 deals with the influence of  $Cr^{3+}$ ,  $Fe^{3+}$  and  $Mn^{3+}$  on  $Cs_{0.68}Ti_{1.83}O_4$ . Each transition metal cation is inserted with a

concentration of 0.1, 0.25 and 0.5 mol.-% into the host matrix of  $Cs_{0.68}Ti_{1.83}O_4$ . The metal cation incorporation has only a minor decreasing effect on the band gap energy, evident by small decreased main absorption edges in the Tauc plots. Each doped  $Cs_{0.68}Ti_{1.83}O_4$ :M (M = Cr, Fe, Mn) photocatalyst exhibits a distinct absorption shoulder in the visible light region, induced by the added metal cations. As expected, transition metal doped  $Cs_{0.68}Ti_{1.83}O_4$  experiences a reduced photocatalytic activity in methanol reforming for H<sub>2</sub> production relatively to pristine  $Cs_{0.68}Ti_{1.83}O_4$  with increasing doping element content. However,  $Cs_{0.68}Ti_{1.83}O_4$ :Mn (0.1 mol.-%) shows an increased reforming efficiency compared to unmodified  $Cs_{0.68}Ti_{1.83}O_4$  and therefore resembles a promising photocatalyst for further photocatalytic studies. Unfortunately, none of the chosen metal cations could be selectively incorporated in the crystallographic B-site, visible by the lost visible light absorption in the Tauc plots of recovered doped photocatalysts. Therefore  $Cs_{0.68}Ti_{1.83}O_4$ :M (M = Cr, Fe, Mn) are not suitable photocatalysts for visible light driven heterogeneous photocatalysis.

To utilize the visible light absorption ability of the sol-gel based  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ , both photocatalysts are used as raw materials for the preparation of visible light active photoelectrodes, as described in chapter 5.5. Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub> is used as a reference material. Photocatalysts calcined at 700 and 800 °C provide suitable particle constitutions for a stable film on the FTO-glass substrate. Capacitance measurements at three different frequencies for the construction of a Mott-Schottky plot enable the determination of the individual CB edge position. In combination with estimated band gaps, extracted from the respective Tauc plot, the individual electronic band diagram is constructed. According to the electronic band diagrams each synthesized photocatalyst is capable to perform the overall water splitting reaction from the thermodynamic point of view. Especially  $C_{s_0}_{63}Ti_{1}_{82}Cu_{0.05}O_4$ and  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  exhibit an ideal band alignment as well as a sufficient band gap energy for visible light driven overall water splitting but fail in the actual application. Also photoelectrochemical photocurrent experiments confirm their inactivity even under UV light irradiation. Basing on the results of cation doped Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>, the doping technique enables a simple synthesis of visible light absorbing semiconductors as well as a coherent tunable electronic band alignment but leads constantly to a significant deactivation, caused by induced crystallographic defects. Therefore, an alternative technique instead of cation doping has to be utilized to achieve visible light activity.

In summary,  $Cs_{0.68}Ti_{1.83}O_4$  can be exclusively applied in the photocatalytic reforming of a hole scavenging sacrificial agent for H<sub>2</sub> production. While noble metal co-catalysts still provide an effective electron trapping ability, which results in an increased H<sub>2</sub> evolution rate, Cu as an earth abundant co-catalyst resembles an alternative co-catalyst material with a comparable photocatalytic activity to noble metals. The Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/TiO<sub>2</sub> composite with Cu co-catalyst, show an increased efficiency in glycerol reforming compared to the reforming of methanol and ethanol. Glycerol as a byproduct of bio fuel production resembles an abundant feedstock for photocatalytic H<sub>2</sub> production and in combination with Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/TiO<sub>2</sub> also a cheap alternative to methanol reforming with Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>/M (M = Rh, Au and Pt).

# 7 Outlook

Cationic doping of semiconductors resembles a simple and controllable method for band gap energy reduction. But in case of the layered cesium titanate  $Cs_{0.68}Ti_{1.83}O_4$ , inserted foreign cations occupy either the crystallographic A- and B-site, while a exclusive B-site occupation is desired. To ensure an entire B-site occupation an alternative synthesis route has to be considered, e.g. the sol-gel assisted solid state reaction (SASSR) developed by the workgroup of Poul Norby.<sup>[43]</sup> The formation of B-site doped  $Cs_{0.68}Ti_{1.83}O_4$  is divided into two parts: 1) Sol-gel synthesis of a cationic doped TiO<sub>2</sub> material and 2) Solid state reaction of the sol-gel based doped TiO<sub>2</sub> material with  $Cs_2CO_3$  to generate the final doped layered cesium titanate. Due to the doped TiO<sub>2</sub>, received from the first synthesis step, incorporated cations are already placed in the desired B-site for the final layered cesium titanate. Contrary of the SASSR synthesis approach is the utilization of high calcination temperatures ( $\geq 800$  °C) and long reaction periods of totally 48 h, which are required for the second synthesis step. Basing on the executed calcination series, presented in figure 27c, high calcination temperatures may form a highly crystalline material but on the cost of the photocatalytic performance as shown in figure 30c. Nevertheless, an attempt towards visible light activity has to be performed.

Cu as an earth abundant co-catalyst resembles a promising alternative to noble metal cocatalyst but suffers in case of  $Cs_{0.68}Ti_{1.83}O_4$  from a long preparation time, due to the slow photodeposition kinetic. Also the alternative wet impregnation process leads to an undesired TiO<sub>2</sub> (anatase) formation, despite of the resulting highly active  $Cs_{0.68}Ti_{1.83}O_4/TiO_2$  composite. Therefore, an alternative and fast deposition of high Cu contents on the surface of  $Cs_{0.68}Ti_{1.83}O_4$  without the formation of any byproducts is still required. The chemical vapor deposition (CVD) represents an alternative deposition process of high Cu amounts on  $Cs_{0.68}Ti_{1.83}O_4$  without the formation of  $TiO_2$ .<sup>[211]</sup> The CVD technique prevents the usage of an aqueous phase as well as a contact of the  $Cs_{0.68}Ti_{1.83}O_4$  support with the used Cu precursor, which provokes a removal of Cs<sup>+</sup> from the interlayers by a cesium salt formation. However, a suitable Cu precursor with a low vapor pressure has to be found for a Cu-CVD process on  $Cs_{0.68}Ti_{1.83}O_4$ .

Even the sufficient photocatalytic activity of the  $Cs_{0.68}Ti_{1.83}O_4/TiO_2$  composite with Cu as cocatalyst is impractical due to the required UV light irradiation for activation. Therefore the production of a visible light active photocatalyst system, in order to utilize the incident sun light is unavoidable. The executed attempts with cation doped  $Cs_{0.68}Ti_{1.83}O_4$  is not satisfactory for visible light driven photocatalysis. In order to keep the photocatalytic performance of a photocatalyst system, e.g.  $Cs_{0.68}Ti_{1.83}O_4/TiO_2$ , the chosen photocatalyst can be applied in a visible absorbing composite photocatalyst system. A coupled photocatalyst system ideally a type II composite (Figure 14), consisting of the highly UV light active photocatalyst and a visible light absorbing photocatalyst with a higher CB edge than the UV light active component is required. This coupled photocatalyst system utilizes the active reaction sites of the UV light active photocatalyst, which are activated by visible light induced electrons from the visible light absorbing photocatalyst. The UV light active photocatalyst acts as an electron acceptor for visible light induced electrons of the visible light absorbing component, in the described system can be graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), which provides a sufficient visible light absorbing ability.<sup>[210, 212-213]</sup> On the basis of coupled photocatalysts, the formation of a so called Z-scheme can be applied on Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>, in order to overcome the inability to perform the overall water splitting reaction. A Z-scheme is characterized by the coupling of a H<sub>2</sub> evolution photocatalyst with an O<sub>2</sub> evolution photocatalyst, assisted by a redox-mediator, which acts as a dual sacrificial agent for hole and electron scavenging.<sup>[32]</sup>

Beside the great potential in photocatalysis,  $Cs_{0.68}Ti_{1.83}O_4$  holds also great potentials in the application as a photoelectrode material, especially B-site doped  $Cs_{0.68}Ti_{1.83}O_4$ , but in the form of exfoliated nanosheets. Pure B-site doped  $Cs_{0.68}Ti_{1.83}O_4$  received for example from a SASSR, resembles a suitable starting material for nanosheet synthesis. It has to be considered that visible light absorbing doped  $Cs_{0.68}Ti_{1.83}O_4$  will experience a band gap energy increase due to the occurring quantum confinement effect after a complete exfoliation of the material. Nevertheless, differently doped exfoliated titanate nanosheets enable the preparation of designed photoelectrodes. Exfoliated nanosheets can be deposited on an electric conductive substrate by the electrostatic sequential deposition technique. This method enables the architecture of doped titanate nanosheet photoelectrodes.

# **8** References

- [1] S. Ahmad, G. Baiocchi, F. Creutzig, *Environ. Sci. Technol.* **2015**, *49*, 11312-11320.
- [2] G. Akhmat, K. Zaman, T. Shukui, D. Irfan, M. M. Khan, *Environ. Sci. Pollut. Res. Int.* **2014**, *21*, 5940-5951.
- [3] in *Energiestatistiken Internationaler Energiemarkt* (Ed.: B. f. W. u. Energie), **2015**, pp. 1-10.
- [4] B. Petroleum, in *BPstats*, Vol. 64, **2015**, pp. 1-48.
- [5] S. Farhani, J. Rejeb, Int. J. Energy Econom. Pol. 2012, 2, 71-81.
- [6] J. Yuan, Y. Xu, Z. Hu, C. Zhao, M. Xiong, J. Guo, *Energy Policy* **2014**, *68*, 508-523.
- [7] D. A. Castelo Branco, M. C. P. Moura, A. Szklo, R. Schaeffer, *Energy Policy* 2013, 61, 1221-1235.
- [8] L. C. de Freitas, S. Kaneko, *Energy Policy* **2011**, *39*, 1495-1504.
- [9] G. De Martino Jannuzzi, *Aspen Forum* **2005**, 1-41.
- [10] H. Statista GmbH, in *statista*, **2016**, pp. 1-8.
- [11] B. Petroleum, in *BPstats, Vol. 63*, **2014**, pp. 1-48.
- [12] Y.-P. Yuan, L.-W. Ruan, J. Barber, S. C. Joachim Loo, C. Xue, *Energy Environ. Sci.* **2014**, *7*, 3934-3951.
- [13] B. Viswanathan, V. Subramanian, J. S. Lee, *Materials and Processes for Solar Fuel Production*, Springer, **2014**.
- [14] N. S. Lewis, D. G. Nocera, Proc. Natl. Acad. Sci. USA 2006, 103, 15729-15735.
- [15] H.-S. Kim, S. H. Im, N.-G. Park, J. Phys. Chem. C. 2014, 118, 5615-5625.
- [16] B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737-740.
- [17] S. Chandra, Proc. Natl. Acad. Sci. Sect. A Phys. Sci. 2012, 82, 5-19.
- [18] R. M. Navarro Yerga, M. C. Alvarez Galvan, F. del Valle, J. A. Villoria de la Mano, J. L. Fierro, *ChemSusChem* 2009, 2, 471-485.
- [19] X. Chen, S. Shen, L. Guo, S. S. Mao, *Chem. Rev.* **2010**, *110*, 6503-6570.
- [20] K. Shimura, H. Yoshida, *Energy Environ. Sci.* **2011**, *4*, 2467-2481.
- [21] W. Wei, W. Du, J. Xu, X. Bao, Int. J. Chem. React. Eng. 2011, 9, 1-21.
- [22] Y. Qian, Q. Yang, J. Zhang, H. Zhou, S. Yang, Ind. Eng. Chem. Res. 2014, 53, 19970-19978.

- [23] R. M. Navarro, M. C. Alvarez-Galván, J. A. Villoria de la Mano, S. M. Al-Zahrani, J. L. G. Fierro, *Energy Environ. Sci.* 2010, *3*, 1865.
- [24] L. Chen, X. Dong, F. Wang, Y. Wang, Y. Xia, Chem. Commun. 2016.
- [25] S. M. M. Ehteshami, S. H. Chan, *Energy Policy* **2014**, *73*, 103-109.
- [26] A. Kudo, Y. Miseki, Chem. Soc. Rev. 2009, 38, 253-278.
- [27] R. Ramachandran, R. K. Menon, Int. J. Hydrogen Energy 1998, 23, 593-598.
- [28] P. J. Boddy, J. Electrochem. Soc. 1968, 115, 199-203.
- [29] K. Honda, A. Fujishima, *Nature* **1972**, *238*, 37-38.
- [30] F. E. Osterloh, *Chem. Mater.* **2008**, *20*, 35-54.
- [31] A. Y. Ahmed, T. A. Kandiel, T. Oekermann, D. Bahnemann, J. Phys. Chem. Lett. 2011, 2, 2461-2465.
- [32] S. S. K. Ma, T. Hisatomi, K. Domen, J. Jpn. Petrol. Ins. 2013, 56, 280-287.
- [33] J. W. Phair, S. P. S. Badwal, Sci. Technol. Adv. Mater. 2006, 7, 792-805.
- [34] M. R. Allen, A. Thibert, E. M. Sabio, N. D. Browning, D. S. Larsen, F. E. Osterloh, *Chem. Mater.* **2010**, *22*, 1220-1228.
- [35] Y. Hosogi, H. Kato, A. Kudo, J. Phys. Chem. C. 2008, 112, 17678-17682.
- [36] S. Ivanova, A. Penkova, M. d. C. Hidalgo, J. A. Navío, F. Romero-Sarria, M. Á. Centeno, J. A. Odriozola, *Appl. Catal.*, *B* **2015**, *163*, 23-29.
- [37] G. Liu, L. Wang, C. Sun, X. Yan, X. Wang, Z. Chen, S. C. Smith, H.-M. Cheng, G. Q. Lu, *Chem. Mater.* 2009, 21, 1266-1274.
- [38] T. Gao, P. Norby, H. Okamoto, H. Fjellvag, *Inorg. Chem.* 2009, 48, 9409-9418.
- [39] H. Hattori, Y. Ide, S. Ogo, K. Inumaru, M. Sadakane, T. Sano, *ACS Catal.* **2012**, *2*, 1910-1915.
- [40] H. Song, A. O. Sjåstad, H. Fjellvåg, H. Okamoto, Ø. B. Vistad, B. Arstad, P. Norby, J. Solid State Chem. 2011, 184, 3135-3143.
- [41] T. Sumida, Y. Takahara, R. Abe, M. Hara, J. N. Kondo, K. Domen, M. Kakihana, M. Yoshimura, *Phys. Chemi. Chem. Phys.* **2001**, *3*, 640-644.
- [42] G. Liu, P. Niu, L. Wang, G. Q. Lu, H.-M. Cheng, *Catal. Sci. & Tech.* 2011, 1, 222.
- [43] H. Song, A. O. Sjastad, O. B. Vistad, T. Gao, P. Norby, *Inorg. Chem.* 2009, 48, 6952-6959.
- [44] H. Li, S. Yin, Y. Wang, T. Sekino, S. W. Lee, T. Sato, J. Catal. 2013, 297, 65-69.

- [45] G. Liu, C. Sun, L. Wang, S. C. Smith, G. Q. Lu, H.-M. Cheng, J. Mater. Chem. 2011, 21, 14672.
- [46] S. Y. Chae, M. K. Park, S. K. Lee, T. Y. Kim, S. K. Kim, W. I. Lee, *Chem. Mater.* 2003, 15, 3326-3331.
- [47] J. Z. Bloh, R. Dillert, D. W. Bahnemann, J. Phys. Chem. C. 2012, 116, 25558-25562.
- [48] X. Zhang, J. Qin, Y. Xue, P. Yu, B. Zhang, L. Wang, R. Liu, Sci. Rep. 2014, 4, 4596.
- [49] X. Zong, Z. Xing, H. Yu, Z. Chen, F. Tang, J. Zou, G. Q. Lu, L. Wang, Chem. Commun. 2011, 47, 11742-11744.
- [50] M. A. Fox, M. T. Dulay, *Chem. Rev.* **1993**, *93*, 341-357.
- [51] T. Nakayama, N. Ichikuni, S. Sato, F. Nozaki, Appl. Catal., A 1997, 158, 185-199.
- [52] O. Merka, O. Raisch, F. Steinbach, D. W. Bahnemann, M. Wark, J. Nino, J. Am. Ceram. Soc. 2012, 634-642.
- [53] L. Schwertmann, M. Wark, R. Marschall, *RSC Adv.* **2013**, *3*, 18908.
- [54] T. Gao, H. Fjellvåg, P. Norby, J. Mater. Chem. 2009, 19, 787-794.
- [55] M. Ohashi, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A 2000, 341, 265-270.
- [56] J. Yang, D. Wang, H. Han, C. Li, Acc. Chem. Res. 2012, 46, 1900-1909.
- [57] G. R. Bamwenda, S. Tsubota, T. Nakamura, M. Haruta, J. Photochem. Photobiol., A 1995, 89, 177-189.
- [58] K. J. McDonald, K.-S. Choi, *Chem. Mater.* **2011**, *23*, 1686-1693.
- [59] J. Ohyama, A. Yamamoto, K. Teramura, T. Shishido, T. Tanaka, *ACS Catal.* **2011**, *1*, 187-192.
- [60] M. Hmadeh, V. Hoepfner, E. Larios, K. Liao, J. Jia, M. Jose-Yacaman, G. A. Ozin, *ChemSusChem* **2014**, *7*, 2104-2109.
- [61] F. Gartner, S. Losse, A. Boddien, M. M. Pohl, S. Denurra, H. Junge, M. Beller, *ChemSusChem* 2012, 5, 530-533.
- [62] T. Nogawa, T. Isobe, S. Matsushita, A. Nakajima, *Mater. Lett.* **2012**, *82*, 174-177.
- [63] M. Yoshida, K. Maeda, D. Lu, J. Kubota, K. Domen, J. Phys. Chem. C. 2013, 117, 14000-14006.
- [64] K. Maeda, N. Sakamoto, T. Ikeda, H. Ohtsuka, A. Xiong, D. Lu, M. Kanehara, T. Teranishi, K. Domen, *Chem. Eur. J.* **2010**, *16*, 7750-7759.
- [65] W. J. Foo, C. Zhang, G. W. Ho, *Nanoscale* **2013**, *5*, 759-764.
- [66] M. Hara, T. Kondo, M. Komoda, S. Ikeda, K. Shinohara, A. Tanaka, J. N. Kondo, K. Domen, *Chem. Commun.* **1998**, 357-358.

- [67] K. Maeda, T. Ohno, K. Domen, Chemi. Sci. 2011, 2, 1362.
- [68] Q. Guo, C. Xu, Z. Ren, W. Yang, Z. Ma, D. Dai, H. Fan, T. K. Minton, X. Yang, J. *Am. Chem. Soc.* **2012**, *134*, 13366-13373.
- [69] M. Shen, M. A. Henderson, J. Phys. Chem. Lett. 2011, 2, 2707-2710.
- [70] S. Chen, S. V. Jenkins, J. Tao, Y. Zhu, J. Chen, J. Phys. Chem. C. 2013, 117, 8924-8932.
- [71] T. Ghodselahi, H. Zahrabi, M. H. Saani, M. A. Vesaghi, J. Phys. Chem. C. 2011, 115, 22126-22130.
- [72] X. Zhou, G. Liu, J. Yu, W. Fan, J. Mater. Chem. 2012, 22, 21337.
- [73] S. Linic, P. Christopher, D. B. Ingram, *Nature materials* **2011**, *10*, 911-921.
- [74] A. Kubacka, G. Colón, M. Fernández-García, Catal. Today 2009, 143, 286-292.
- [75] J. Zhang, J. Xi, Z. Ji, J. Mater. Chem. 2012, 22, 17700.
- [76] J. Bandara, C. P. Udawatta, C. S. Rajapakse, *Photochem. Photobiol. Sci.* 2005, 4, 857-861.
- [77] H. W. P. Carvalho, M. V. J. Rocha, P. Hammer, T. C. Ramalho, J. Mater. Sci. 2013, 48, 3904-3912.
- [78] Y. Yalçın, M. Kılıç, Z. Çınar, Appl. Catal., B 2010, 99, 469-477.
- [79] K. Z. Zhang, B. Z. Lin, Y. L. Chen, B. H. Xu, X. T. Pian, J. D. Kuang, B. Li, J. Colloid. Interface Sci. 2011, 358, 360-368.
- [80] B. Tian, C. Li, J. Zhang, *Chem. Eng. J.* **2012**, *191*, 402-409.
- [81] P. L. Richardson, M. L. N. Perdigoto, W. Wang, R. J. G. Lopes, *Appl. Catal., B* **2012**, *126*, 200-207.
- [82] S. Paul, P. Chetri, A. Choudhury, J. Alloys Compd. 2014, 583, 578-586.
- [83] T. Gao, H. Fjellvåg, P. Norby, *Chem. Mater.* **2009**, *21*, 3503-3513.
- [84] M. Ohashi, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A 1998, 311, 51-56.
- [85] P. R. Ghediya, T. K. Chaudhuri, J. Mater. Sci.: Mater. Electron. 2014, 26, 1908-1912.
- [86] K. Xiong, L. Hou, M. Wu, Y. Huo, W. Mo, Y. Yuan, S. Sun, W. Xu, E. Wang, Sol. Energy Mater. Sol. Cells 2015, 132, 252-259.
- [87] P. W. Atkins, J. de Paula, *Physical Chemistry*, 8 ed., Oxford University Press, 2006.
- [88] B. T. Mei, Ruhr-Universität Bochum (Bochum), 2013.
- [89] R. E. Hummel, *Electronic Properties of Materials*, 4 ed., Springer 2011.

- [90] L. Schwertmann, Ruhr-Universität Bochum (Bochum), 2014.
- [91] R. G. Mortimer, *Physical Chemistry*, 2 ed., Academic Press, 2000.
- [92] R. P. Huebener, Conductors, Semiconductors, Superconductors An Introduction to Solid State Physics, Springer, 2015.
- [93] B. D. Fahlmann, *Materials Chemistry* 2ed., Springer 2011.
- [94] A. W. Bott, Curr. Sep. 1998, 17, 87-91.
- [95] A. J. Cowan, J. R. Durrant, *Chem. Soc. Rev.* **2013**, *42*, 2281-2293.
- [96] A. Hernandez-Ramirez, I. Meduna-Ramirez, *Photocatalytic Semiconductors*, Springer, **2015**.
- [97] A. Kubacka, M. Fernandez-Garcia, G. Colon, Chem. Rev. 2012, 112, 1555-1614.
- [98] R. Marschall, Adv. Funct. Mater. 2014, 24, 2421-2440.
- [99] R. Beranek, Adv. Phys. Chem. 2011, 2011, 1-20.
- [100] A. L. Linsebigler, G. Lu, J. T. Yates, Chem. Rev. 1995, 95, 735-758.
- [101] R. van de Krol, M. Grätzel, *Photoelectrochemical Hydrogen Production*, Springer, **2012**.
- [102] R. Beranek, in *Material Properties: Lecture Skript*, Ruhr-Universität Bochum, **2013**, pp. 1-46.
- [103] M. D. McNaught, A. Wilkinson, in *IUPAC Gold Book* (Ed.: 2), Blackwell Scientific Publications, Oxford, **1997**.
- [104] M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, *Chem. Rev.* 1995, 95, 69-96.
- [105] H. Park, Y. Park, W. Kim, W. Choi, J. Photochem. Photobiol. C. 2013, 15, 1-20.
- [106] T. Hisatomi, K. Takanabe, K. Domen, Catal. Lett. 2014, 145, 95-108.
- [107] T. Hisatomi, J. Kubota, K. Domen, Chem. Soc. Rev. 2014, 43, 7520-7535.
- [108] A. Kudo, *Catal. Surv. Asia* **2003**, *7*, 31-38.
- [109] J. Schneider, D. W. Bahnemann, J. Phys. Chem. Lett. 2013, 4, 3479-3483.
- [110] J. Ran, J. Zhang, J. Yu, M. Jaroniec, S. Z. Qiao, Chem. Soc. Rev. 2014, 43, 7787-7812.
- [111] U. o. Cambridge, Creative Commons Attribution-NonCommercial-ShareAlike 2.0: England & Wales License, **2004-2015**.
- [112] F. Yan, Y. Wang, J. Zhang, Z. Lin, J. Zheng, F. Huang, ChemSusChem 2014, 7, 101-104.

- [113] Q. Fu, T. Wagner, Surf. Sci. Rep. 2007, 62, 431-498.
- [114] M. Wark, in *Material Properties: Lecture Skript*, Ruhr-Universität Bochum, pp. 1-45.
- [115] D. R. Linde, *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Ranton FL, 2005.
- [116] K. Maeda, D. Lu, K. Domen, Chem. Eur. J. 2013, 19, 4986-4991.
- [117] K. Domen, S. Naito, M. Soma, T. Onishi, K. Tamaru, J. Chem. Soc., Chem. Commun. 1980, 543.
- [118] M. Bledowski, L. Wang, A. Ramakrishnan, A. Betard, O. V. Khavryuchenko, R. Beranek, *Chem. Phys. Chem.* **2012**, *13*, 3018-3024.
- [119] D. Ravelli, D. Dondi, M. Fagnoni, A. Albini, *Chem. Soc. Rev.* **2009**, *38*, 1999-2011.
- [120] T. Kawai, T. Sakata, J.C.S. Chem. Comm. 1980, 384, 694-695.
- [121] C. Wang, H. Groenzin, M. J. Shultz, J. Am. Chem. Soc. 2004, 126, 8094-8095.
- [122] L. M. Peter, *Chem. Rev.* **1990**, *90*, 753-769.
- [123] S. Hoang, S. P. Berglund, N. T. Hahn, A. J. Bard, C. B. Mullins, J. Am. Chem. Soc. 2012, 134, 3659-3662.
- [124] S. Saadi, A. Bouguelia, A. Derbal, M. Trari, J. Photochem. Photobiol. A. 2007, 187, 97-104.
- [125] H. Suzuki, O. Tomita, M. Higashi, R. Abe, Catal. Sci. Technol. 2015, 5, 2640-2648.
- [126] R. Marschall, L. Wang, *Catal. Today* **2014**, 225, 111-135.
- [127] H. Tong, S. Ouyang, Y. Bi, N. Umezawa, M. Oshikiri, J. Ye, Adv. Mater. 2012, 24, 229-251.
- [128] W. Hou, S. B. Cronin, Adv. Funct. Mater. 2013, 23, 1612-1619.
- [129] M. Ni, M. K. H. Leung, D. Y. C. Leung, K. Sumathy, *Renew. Sust. Energ. Rev.* 2007, *11*, 401-425.
- [130] T. Takata, K. Domen, J. Phys. Chem. C. 2009, 113, 19386-19388.
- [131] Z. Zheng, J. Zhao, Y. Yuan, H. Liu, D. Yang, S. Sarina, H. Zhang, E. R. Waclawika, H. Zhu, *Chem. Eur. J.* 2013, 19, 5731-5741.
- [132] G. Liu, L. Wang, C. Sun, Z. Chen, X. Yan, L. Cheng, H. M. Cheng, G. Q. Lu, Chem. Commun. 2009, 1383-1385.
- [133] G. Liu, L. Wang, H. G. Yang, H.-M. Cheng, G. Q. Lu, J. Mater. Chem. 2010, 20, 831-843.
- [134] O. Merka, Leibniz Universität Hannover (Hannover), **2012**.

- [135] R. D. Shannon, Acta Cryst. 1976, 32, 751-767.
- [136] X. Dong, M. Osada, H. Ueda, Y. Ebina, Y. Kotani, K. Ono, S. Ueda, K. Kobayashi, K. Takada, T. Sasaki, *Chem. Mater.* 2009, 21, 4366-4373.
- [137] I. Ganesh, P. P. Kumar, A. K. Gupta, P. S. C. Sekhar, K. Radha, G. Padmanabham, G. Sundararajan, *Process. Appl. Ceram.* **2012**, *6*, 21-36.
- [138] R. Chen, H. Liu, J. Chin. Chem. Soc. 2011, 58, 947-954.
- [139] I. Ganesh, A. K. Gupta, P. P. Kumar, P. S. Chandra Sekhar, K. Radha, G. Padmanabham, G. Sundararajan, *Mater. Chem. Phys.* **2012**, *135*, 220-234.
- [140] B. Mei, M. D. Sánchez, T. Reinecke, S. Kaluza, W. Xia, M. Muhler, J. Mater. Chem. 2011, 21, 11781.
- [141] A. Heciak, A. W. Morawski, B. Grzmil, S. Mozia, *Appl. Catal.*, B 2013, 140-141, 108-114.
- [142] T. Umebayashi, T. Yamaki, H. Itoh, K. Asai, J. Phys. Chem. Solids 2002, 63, 1909-1920.
- [143] S. G. Kumar, L. G. Devi, J. Phys. Chem. A. 2011, 115, 13211-13241.
- [144] J. Rabani, J. Phys. Chem. 1989, 93, 7707-7713.
- [145] X. Wang, Q. Xu, M. Li, S. Shen, X. Wang, Y. Wang, Z. Feng, J. Shi, H. Han, C. Li, Angew. Chem. Int. Ed. Engl. 2012, 51, 13089-13092.
- [146] B. Ohtani, O. O. Prieto-Mahaney, D. Li, R. Abe, J. Photochem. Photobiol., A 2010, 216, 179-182.
- [147] A. Y. Ahmed, T. A. Kandiel, I. Ivanova, D. Bahnemann, *Appl. Surf. Sci.* **2014**, *319*, 44-49.
- [148] A. C. Cakir, P. Guloglu, M. Bilgin, S. Erten-Ela, J. Optoelectron. Adv. M. 2012, 14, 230-237.
- [149] Q. Mi, Y. Ping, Y. Li, B. Cao, B. S. Brunschwig, P. G. Khalifah, G. A. Galli, H. B. Gray, N. S. Lewis, J. Am. Chem. Soc. 2012, 134, 18318-18324.
- [150] M. Barroso, A. J. Cowan, S. R. Pendlebury, M. Gratzel, D. R. Klug, J. R. Durrant, J. *Am. Chem. Soc.* **2011**, *133*, 14868-14871.
- [151] H. N. Kim, T. W. Kim, I. Y. Kim, S.-J. Hwang, Adv. Funct. Mater. 2011, 21, 3111-3118.
- [152] Q. Xiang, J. Yu, M. Jaroniec, J. Am. Chem. Soc. 2012, 134, 6575-6578.
- [153] Y. Miseki, H. Kato, A. Kudo, Energy & Environ. Sci. 2009, 2, 306.
- [154] K. Iwashina, A. Kudo, J. Am. Chem. Soc. 2011, 133, 13272-13275.
- [155] R. Ma, T. Sasaki, Adv. Mater. 2010, 22, 5082-5104.

- [156] L. Wang, T. Sasaki, Chem. Rev. 2014, 114, 9455-9486.
- [157] I. E. Grey, C. Li, I. C. Madsen, J. A. Watts, J. Solid State Chem. 1987, 66, 7-19.
- [158] K. Nakagawa, K. Yamaguchi, K. Yamada, K.-I. Sotowa, S. Sugiyama, M. Adachi, *Eur. J. Inorg. Chem.* **2012**, 2012, 2741-2748.
- [159] J. A. Ayllon, A. Figueras, S. Garelik, L. Spirkova, J. Durand, L. Cot, J. Mater. Sci. Lett. 1999, 18, 1319-1321.
- [160] Q. Zeng, J. Bai, J. Li, L. Xia, K. Huang, X. Li, B. Zhou, J. Mater. Chem. A 2015, 3, 4345-4353.
- [161] J. Wang, P. Zhang, X. Li, J. Zhu, H. Li, Appl. Catal., B 2013, 134-135, 198-204.
- [162] A. Mukherji, R. Marschall, A. Tanksale, C. Sun, S. C. Smith, G. Q. Lu, L. Wang, *Adv. Funct. Mater.* **2011**, *21*, 126-132.
- [163] N. Masaki, S. Uchida, T. Sato, J. Mater. Chem. 2002, 12, 305-308.
- [164] J. Guo, S. Zhu, Z. Chen, Y. Li, Z. Yu, Q. Liu, J. Li, C. Feng, D. Zhang, Ultrason. Sonochem. 2011, 18, 1082-1090.
- [165] T. Alammar, I. Hamm, M. Wark, A.-V. Mudring, Appl. Catal., B. 2015, 178, 20-28.
- [166] L. Pan, X. Liu, Z. Sun, C. Q. Sun, J. Mater. Chem. A 2013, 1, 8299.
- [167] G. Hyett, J. A. Darr, A. Mills, I. P. Parkin, Chem. Vap. Deposition 2010, 16, 301-304.
- [168] D. H. Taffa, I. Hamm, C. Dunkel, I. Sinev, D. Bahnemann, M. Wark, *RSC Adv.* 2015, 5, 103512-103522.
- [169] A. J. Nozik, Ann. Rev. Phys. Chem. 1978, 29, 189-222.
- [170] W. H. Brattain, C. G. B. Garrett, Bell. Syst. Tech. J. 1955, 34, 129-176.
- [171] A. J. Bard, *Science* **1980**, *207*, 139-144.
- [172] M. Alcala, C. Real, Solid State Ionics 2006, 177, 955-960.
- [173] U. Heiz, U. Landman, *Nanocatalysis*, Springer, 2008.
- [174] S. Jung, C. Lu, H. He, K. Ahn, R. J. Gorte, J. M. Vohs, *J. Power Sources* **2006**, *154*, 42-50.
- [175] J. W. Niemantsverdriet, Spectroscopy in Catalysis 3rd, 3 ed., Wiley-VCH, 2007.
- [176] J. H. Nobbs, Rev. Prog. Coloration 1985, 15, 66-75.
- [177] Y. Aoyagi, K. Kajikawa, Optical Propertie of Advanced Materials, Vol. 168, Springer, 2013.
- [178] V. Štengl, T. M. Grygar, Int. J. Photoener. 2011, 2011, 1-13.

- [179] J. Tauc, R. Grigorovici, A. Vancu, Phys. Stat. Sol. 1966, 15, 627-637.
- [180] H. Amekura, B. Johannessen, D. J. Sprouster, M. C. Ridgway, *Appl. Phys. Lett.* **2011**, *99*, 043102.
- [181] L. B. Sagle, L. K. Ruvuna, J. A. Ruemmele, R. P. Van Duyne, *Nanomedicine* **2011**, *6*, 1447-1462.
- [182] L. J. Sherry, S. Chang, G. C. Schatz, R. P. Van Duyne, Nano Lett. 2005, 5.
- [183] G. Jia, J. Wang, L. Zhang, H. Liu, R. Xu, C. Liu, Europhys. Lett. 2013, 101, 57005.
- [184] J. Chen, J. C. S. Wu, P. C. Wu, D. P. Tsai, J. Phys. Chem. C. 2011, 115, 210-216.
- [185] H. K. Cammenga, M. Epple, Angew. Chem. 1995, 107, 1284-1301.
- [186] C. B. Murphy, Anal. Chem. 1974, 46, 451-459.
- [187] C. de Mello Donega, *Nanoparticles*, Springer, 2014.
- [188] S. J. Pennycook, P. D. Nellist, *Scanning Transmisson Electron Microscopy, Vol. 11*, Springer, **2011**.
- [189] B. Fultz, J. Howe, *Transmission Electron Microscopy and Diffractometry of Materials, Vol. 3*, Springer, **2008**.
- [190] C. C. Chusuei, D. W. Goodman, in *Encyclopedia of Physical Science and Technology*, *Vol. 17*, 3 ed., **2002**.
- [191] A. V. Naumkin, A. Kraut-Vass, S. W. Gaarenstroom, C. J. Powell, NIST X-ray Photoelectron Spectroscopy Database 20, Version 4.1, National Institute of Standards and Technology and Material Measurement Laboratory, 2000.
- [192] B. Mei, H. Byford, M. Bledowski, L. Wang, J. Strunk, M. Muhler, R. Beranek, Sol. Energy Mater. Sol. Cells 2013, 117, 48-53.
- [193] K. Shimura, H. Yoshida, in *Biomass for Sustainable Applications: Pollution Remediation and Energy*, RSC Publishing **2013**, pp. 335-365.
- [194] G. Halasi, I. Ugrai, F. Solymosi, J. Catal. 2011, 281, 309-317.
- [195] R. Chong, J. Li, X. Zhou, Y. Ma, J. Yang, L. Huang, H. Han, F. Zhang, C. Li, *Chem. Commun.* 2014, 50, 165-167.
- [196] F. Mafuné, T. Kondow, Chem. Phys. Lett. 2003, 372, 199-204.
- [197] P. Panagiotopoulou, E. E. Karamerou, D. I. Kondarides, *Catal. Today* 2013, 209, 91-98.
- [198] T. Yamaguchi, E. Kazuma, N. Sakai, T. Tatsuma, Chem. Lett. 2012, 41, 1340-1342.
- [199] Y. S. Park, H. K. Chae, *Chem. Mater.* **2010**, *22*, 6280-6290.
- [200] L. Liu, S. Ouyang, J. Ye, Angew. Chem. 2013, 52, 6689-6693.

- [201] G. Wang, X. Wang, J. Liu, X. Sun, Chemistry 2012, 18, 5361-5366.
- [202] L. Du, A. Furube, K. Yamamoto, K. Hara, R. Katoh, M. Tachiya, *J. Phys. Chem. C.* **2009**, *113*, 64546462.
- [203] J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy*, Eden Prairie, MN: Perkin Elmer Corporation, **1992**.
- [204] F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry* 4ed., John Wiley & Sons 1982.
- [205] L. Zhang, G. C. Papaefthymiou, J. Y. Ying, J. Appl. Phys. 1997, 81, 6892-6900.
- [206] M. S. Batista, M. Wallau, E. A. Urquieta-Gonzalez, *Stud. Surf. Sci. Catal.* **2004**, *154*, 2493-2500.
- [207] H. G. Karge, H. K. Beyer, Stud. Surf. Sci. Catal. 1991, 69, 43-64.
- [208] Y. Chen, X. J. Ma, Adv. Mater. Res. 2014, 989-994, 531-535.
- [209] A. Pérez-Larios, A. Hernández-Gordillo, G. Morales-Mendoza, L. Lartundo-Rojas, A. Mantilla, R. Gómez, *Catal. Today* 2016, 266, 9-16.
- [210] Y. Wang, X. Wang, M. Antonietti, Angew. Chem. 2012, 51, 68-89.
- [211] X. Xu, G. Huang, Ind. Eng. Chem. Res. 2016, 55, 1380-1386.
- [212] F. Dong, Y. Sun, L. Wu, M. Fu, Z. Wu, Catal. Sci. Technol. 2012, 2, 1332.
- [213] S. Ye, L.-G. Qiu, Y.-P. Yuan, Y.-J. Zhu, J. Xia, J.-F. Zhu, J. Mater. Chem. A 2013, 1, 3008.
# 9 Appendix

### 9.1 Additional Information to Chapter 4.1

	molar mass /	mass /	density /	volume /	molar amount /
	(g/mol)	g	(g/cm <sup>3</sup> )	mL	mmol
CsNO <sub>3</sub>	194.91	1.36	3.7	-	7
Ti(O-nBu) <sub>4</sub>	340.32	6.47	0.99	6.53	19
$Cu(NO_3)_2\cdot 3H_2O$	241.6	0.12	2.05	-	0.5
EDTA	292.25	8.13	0.86	-	27.8
$C_6H_8O_7\ H_2O$	210.14	8.35	1.67	-	39.9
$Cs_{0.7}Ti_{1.95}Cu_{0.05}O_4$	253.55	2.46	-	-	9.7

Table A1: Synthesis of  $Cs_{0.7}Ti_{1.95}Cu_{0.05}O_4$  by sol-gel process.

Table A2: Synthesis of  $Cs_{0.7}Ti_{1.9}Cu_{0.1}O_4$  by sol-gel process.

	molar mass /	mass /	density /	volume /	molar amount /
	(g/mol)	g	(g/cm <sup>3</sup> )	mL	mmol
CsNO <sub>3</sub>	194.91	1.36	3.7	-	7
$Ti(O-nBu)_4$	340.32	6.47	0.99	6.53	19
$Cu(NO_3)_2 \cdot 3H_2O$	241.6	0.24	2.05	-	1
EDTA	292.25	8.29	0.86	-	28.4
$C_6H_8O_7\ H_2O$	210.14	8.51	1.67	-	40.5
Cs <sub>0.7</sub> Ti <sub>1.9</sub> Cu <sub>0.1</sub> O <sub>4</sub>	254.34	2.47	-	-	9.7

	molar mass /	mass /	density /	volume /	molar amount /
	(g/mol)	g	(g/cm <sup>3</sup> )	mL	mmol
CsNO <sub>3</sub>	194.91	1.36	3.7	-	7
Ti(O-nBu) <sub>4</sub>	340.32	6.47	0.99	6.53	19
$Cr(NO_3)_3 \cdot 9H_2O$	400.21	0.007	1.85	-	0.019
EDTA	292.25	7.98	0.86	-	27.3
$C_6H_8O_7\ H_2O$	210.14	8.2	1.67	-	39
Cs <sub>0.68</sub> Ti <sub>1.83</sub> O <sub>4</sub> :Cr	242	2.35	-	-	9.7

Table A3: Synthesis of  $Cs_{0.68}Ti_{1.83}O_4$ :Cr 0.1 mol.-% by sol-gel process.

Table A4: Synthesis of  $Cs_{0.68}Ti_{1.83}O_4$ :Cr 0.25 mol.-% by sol-gel process.

	molar mass /	mass /	density /	volume /	molar amount /
	(g/mol)	g	(g/cm <sup>3</sup> )	mL	mmol
CsNO <sub>3</sub>	194.91	1.36	3.7	-	7
Ti(O-nBu) <sub>4</sub>	340.32	6.47	0.99	6.53	19
$Cr(NO_3)_3 \cdot 9H_2O$	400.21	0.019	1.85	-	0.047
EDTA	292.25	7.99	0.86	-	27.3
$C_6H_8O_7\ H_2O$	210.14	8.21	1.67	-	39
Cs <sub>0.68</sub> Ti <sub>1.83</sub> O <sub>4</sub> :Cr	242	2.35	-	-	9.7

Table A5: Synthesis of  $Cs_{0.68}Ti_{1.83}O_4$ :Cr 0.5 mol.-% by sol-gel process.

	molar mass /	mass /	density /	volume /	molar amount /
	(g/mol)	g	$(g/cm^3)$	mL	mmol
CsNO <sub>3</sub>	194.91	1.36	3.7	-	7
Ti(O-nBu) <sub>4</sub>	340.32	6.47	0.99	6.53	19
$Cr(NO_3)_3 \cdot 9H_2O$	400.21	0.038	1.85	-	0.094
EDTA	292.25	8.0	0.86	-	27.4
$C_6H_8O_7\ H_2O$	210.14	8.22	1.67	-	39.1
Cs <sub>0.68</sub> Ti <sub>1.83</sub> O <sub>4</sub> :Cr	242	2.35	-	-	9.7

	molar mass /	mass /	density /	volume /	molar amount /
	(g/mol)	g	(g/cm <sup>3</sup> )	mL	mmol
CsNO <sub>3</sub>	194.91	1.36	3.7	-	7
Ti(O-nBu) <sub>4</sub>	340.32	6.47	0.99	6.53	19
$Fe(NO_3)_3 \cdot 9H_2O$	403,86	0.0077	1.68	-	0.019
EDTA	292.25	7.98	0.86	-	27.3
$C_6H_8O_7\ H_2O$	210.14	8.2	1.67	-	39
Cs <sub>0.68</sub> Ti <sub>1.83</sub> O <sub>4</sub> :Fe	242	2.35			9.7

Table A6: Synthesis of  $Cs_{0.68}Ti_{1.83}O_4{:}Fe\ 0.1\ mol.-\%$  by sol-gel process.

Table A7: Synthesis of  $Cs_{0.68}Ti_{1.83}O_4{:}Fe\ 0.25\ mol.-\%$  by sol-gel process.

	molar mass /	mass /	density /	volume /	molar amount /
	(g/mol)	g	(g/cm <sup>3</sup> )	mL	mmol
CsNO <sub>3</sub>	194.91	1.36	3.7	-	7
Ti(O-nBu) <sub>4</sub>	340.32	6.47	0.99	6.53	19
$Fe(NO_3)_3 \cdot 9H_2O$	403,86	0.019	1.68	-	0.047
EDTA	292.25	7.99	0.86	-	27.3
$C_6H_8O_7\ H_2O$	210.14	8.21	1.67	-	39
Cs <sub>0.68</sub> Ti <sub>1.83</sub> O <sub>4</sub> :Fe	242	2.35			9.7

Table A8: Synthesis of  $Cs_{0.68} Ti_{1.83} O_4{:}Fe\ 0.5\ mol.-\%$  by sol-gel process.

	molar mass /	mass /	density /	volume /	molar amount /
	(g/mol)	g	$(g/cm^3)$	mL	mmol
CsNO <sub>3</sub>	194.91	1.36	3.7	-	7
Ti(O-nBu) <sub>4</sub>	340.32	6.47	0.99	6.53	19
$Fe(NO_3)_3 \cdot 9H_2O$	403,86	0.038	1.68	-	0.094
EDTA	292.25	8.0	0.86	-	27.3
$C_6H_8O_7\ H_2O$	210.14	8.22	1.67	-	39
Cs <sub>0.68</sub> Ti <sub>1.83</sub> O <sub>4</sub> :Fe	242	2.35	-	-	9.7

	molar mass /	mass /	density /	volume /	molar amount /
	(g/mol)	g	$(g/cm^3)$	mL	mmol
CsNO <sub>3</sub>	194.91	1.36	3.7	-	7
$Ti(O-nBu)_4$	340.32	6.47	0.99	6.53	19
$Mn(NO_3)_2 \cdot 4H_2O$	251,01	0.0048	2.13	-	0.019
EDTA	292.25	7.98	0.86	-	27.3
$C_6H_8O_7\ H_2O$	210.14	8.2	1.67	-	39
Cs <sub>0.68</sub> Ti <sub>1.83</sub> O <sub>4</sub> :Mn	242	2.35	-	-	9.7

Table A9: Synthesis of  $Cs_{0.68}Ti_{1.83}O_4{:}Mn\ 0.1\ mol.-\%$  by sol-gel process.

Table A10: Synthesis of  $Cs_{0.68}Ti_{1.83}O_4$ :Mn 0.25 mol.-% by sol-gel process.

	molar mass /	mass /	density /	volume /	molar amount /
	(g/mol)	g	$(g/cm^3)$	mL	mmol
CsNO <sub>3</sub>	194.91	1.36	3.7	-	7
$Ti(O-nBu)_4$	340.32	6.47	0.99	6.53	19
$Mn(NO_3)_2\cdot 4H_2O$	251,01	0.012	2.13		0.047
EDTA	292.25	7.99	0.86	-	27.3
$C_6H_8O_7$ $H_2O$	210.14	8.21	1.67	-	39
Cs <sub>0.68</sub> Ti <sub>1.83</sub> O <sub>4</sub> :Mn	242	2.35	-	-	9.7

Table A11: Synthesis of  $Cs_{0.68} Ti_{1.83} O_4{:}Mn \ 0.5 \ \text{mol.-\%}$  by sol-gel process.

	molar mass /	mass /	density /	volume /	molar amount /
	(g/mol)	g	$(g/cm^3)$	mL	mmol
CsNO <sub>3</sub>	194.91	1.36	3.7	-	7
$Ti(O-nBu)_4$	340.32	6.47	0.99	6.53	19
$Mn(NO_3)_2\cdot 4H_2O$	251,01	0.024	2.13	-	0.094
EDTA	292.25	8.0	0.86	-	27.3
$C_6H_8O_7\ H_2O$	210.14	8.22	1.67	-	39
Cs <sub>0.68</sub> Ti <sub>1.83</sub> O <sub>4</sub> :Mn	242	2.35	-	-	9.7

Cs <sub>0.68</sub> Ti <sub>1.83</sub> O <sub>4</sub> /	Cu /	$CuSO_4 \cdot 5H_2O$ /	Cu molar amount	Cu mass /
g	wt%	g	/ mmol	g
0.55	$(Cu_{0.05})$ 1.285	0.0278	0.11	0.0071
0.55	2	0.0432	0.17	0.0110
0.55	(Cu <sub>0.1</sub> ) 2.57	0.0555	0.22	0.0141
0.55	3	0.0648	0.26	0.0165
0.55	4	0.0864	0.35	0.0220
0.55	5	0.1080	0.43	0.0275
0.55	6	0.1297	0.52	0.0330
0.55	7	0.1513	0.61	0.0385

Table A12: Synthesis of wet impregnated  $Cs_{0.68}Ti_{1.83}O_4/Cu$ .

Table A13: Synthesis of wet impregnated  $Cs_{0.68}Ti_{1.83}O_4/Au.$ 

Cs <sub>0.68</sub> Ti <sub>1.83</sub> O <sub>4</sub> /	Au /	$HAuCl_4 \cdot 3H_2O$ /	Au molar amount	Au mass /
g	wt%	g	/ mmol	g
0.55	1	0.0110	0.027	0.0055



### 9.2 Additional Information to Chapter 4.4

**Figure A1:** GC calibration curves with linear fit as origin function constructed by integrated peak areas of TCD signals of the respective gas plotted against  $H_2/O_2$  concentration. a)  $H_2$  calibration curves plotted in a concentration range between 0.005 - 5 vol.-%. b)  $H_2$  calibration curves plotted in a concentration range between 0.005 - 0.2381 vol.-%. c)  $O_2$  calibration curves plotted in a concentration range between 0.005 - 5 vol.-%. d)  $O_2$  calibration curves plotted in a concentration range between 0.005 - 0.2381 vol.-%. c)  $O_2$  calibration curves plotted in a concentration range between 0.005 - 0.2381 vol.-%.

#### 9.3 Additional Information to Chapter 5.1



**Figure A2:** Diffraction patterns of  $Cs_{0.68}Ti_{1.83}O_4$  from sol-gel process calcined at 900 and 1000 °C with reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$ ,  $Cs_2Ti_4O_9$  and  $Cs_{1.1}Ti_8O_{16}$ .



Figure A3: Sequential photodeposition of a) Pt and b) Au in 0.0125 wt.-% up to a total loading of 0.0375 wt.-%.



**Figure A4:** Long term experiments with  $Cs_{0.68}Ti_{1.83}O_4/M$  a) M = Rh 0.0375 wt.-%, b) M = Au 1 wt.-% and c) M = Pt 1 wt.-% at optimum co-catalyst loading in the photocatalytic reforming of methanol, ethanol and glycerol for H<sub>2</sub> production.



**Figure A5:** Sequential photodeposition of Cu in 0.0125 wt.-% steps on  $Cs_{0.68}Ti_{1.83}O_4$ , divided into three subsequent deposition phases.



**Figure A6:** Long term experiments with  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (3 wt.-%) in the photocatalytic reforming of a) methanol, b) ethanol and c) glycerol, with respective sequential photodeposition of 2 and 3 wt.-% of Cu for H<sub>2</sub> production.



**Figure A7:** a) Diffraction patterns with reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$  and  $H_2Ti_2O_5 \cdot H_2O$  and b) Tauc plots with respective absorption edge linearization and band gap energy (Eg) of recovered  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (3 wt.-%) prepared by photodeposition after long term experiments in the photocatalytic reforming of methanol, ethanol and glycerol.



**Figure A8:** a) Diffraction patterns of as-synthesized  $H_xCs_yTi_{1.83}O_4$  with reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$ , TiO<sub>2</sub> (anatase) and  $H_2Ti_2O_5 \cdot H_2O$ , b) Tauc Plots with respective absorption edge linearization and band gap energy (E<sub>g</sub>) of as-synthesized and recovered  $H_xCs_yTi_{1.83}O_4$  and c) Photocatalytic  $H_2$  production with  $H_xCs_yTi_{1.83}O_4$  in the stepwise photodeposition of Rh in 0.0125 wt.-% in methanolic solution (10 vol.-%).



**Figure A9:** a) Sequential photodeposition of initially Rh followed by  $Cr_2O_3$  photodeposition in 0.0125 wt.-% steps with  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C) under Xe-arc lamp irradiation. b) Sequential photodeposition of initially Cu followed by  $Cr_2O_3$  photodeposition in 0.0125 wt.-% steps with  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C) under Xe-arc lamp irradiation. c) Sequential photodeposition of initially Rh followed by  $Cr_2O_3$  photodeposition in 0.0125 wt.-% steps with  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C) under Xe-arc lamp irradiation. c) Sequential photodeposition of initially Rh followed by  $Cr_2O_3$  photodeposition in 0.0125 wt.-% steps with  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C) under Hg-midpressure immersion lamp irradiation. d) Sequential photodeposition of initially Cu followed by  $Cr_2O_3$  photodeposition in 0.0125 wt.-% steps with  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C) under Hg-midpressure immersion lamp irradiation. d) Sequential photodeposition of initially Cu followed by  $Cr_2O_3$  photodeposition in 0.0125 wt.-% steps with  $Cs_{0.68}Ti_{1.83}O_4$  (600 °C) under Hg-midpressure immersion lamp irradiation.

# 9.4 Additional Information to Chapter 5.2



**Figure A10:** Long term experiments with  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) prepared by wet impregnation on a)  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 700 °C for 10 h and b)  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 800 °C in the photocatalytic reforming of methanol, ethanol and glycerol.



**Figure A11:** Diffraction patterns of dried, calcined, recovered after methanol, ethanol and glycerol reforming of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) prepared by wet impregnation on  $Cs_{0.68}Ti_{1.83}O_4$  calcined at a) 600 °C, c) 700 °C and e) 800 °C. Tauc plots with respective absorption edge linearization and band gap energy (Eg) of dried, calcined, recovered after methanol, ethanol and glycerol reforming of  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) prepared by wet impregnation on  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) prepared by wet impregnation on  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (5 wt.-%) prepared by wet impregnation on  $Cs_{0.68}Ti_{1.83}O_4$  calcined at b) 600 °C, d) 700 °C and f) 800 °C.



**Figure A12:** Diffraction patterns of dried, calcined, recovered after methanol, ethanol and glycerol reforming of  $C_{s_{0.68}}Ti_{1.83}O_4/Au$  (1 wt.-%) prepared by wet impregnation on  $C_{s_{0.68}}Ti_{1.83}O_4$  calcined at a) 600 °C, c) 700 °C and e) 800 °C with reference patterns of  $C_{s_{0.68}}Ti_{1.83}O_4$ , CsCl and  $Au_{0.919}Ti_{0.081}$ . Tauc plots with respective absorption edge linearization and band gap energy ( $E_g$ ) of dried, calcined, recovered after methanol, ethanol and glycerol reforming of  $C_{s_{0.68}}Ti_{1.83}O_4/Au$  (1 wt.-%) prepared by wet impregnation on  $C_{s_{0.68}}Ti_{1.83}O_4$  calcined at b) 600 °C, d) 700 °C and f) 800 °C.



**Figure A13:** Long term experiments with  $Cs_{0.68}Ti_{1.83}O_4/Au$  (1 wt.-%) prepared by wet impregnation on  $Cs_{0.68}Ti_{1.83}O_4$  calcined at a) 600 °C, b) 700 °C and c) 800 °C in the photocatalytic reforming of methanol, ethanol and glycerol for H<sub>2</sub> production.

### 9.5 Additional Information to Chapter 5.3



**Figure A14:** Diffraction patterns of sol-gel based  $Cs_{0.7}Ti_{1.83}Cu_{0.17}O_4$ ,  $Cs_{0.7}Ti_{1.8}Cu_{0.2}O_4$  and  $Cs_{0.7}Ti_{1.7}Cu_{0.3}O_4$  with reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$ ,  $TiO_2$  (anatase) and  $Cs_2Ti_4O_9$ .



**Figure A15:** Photocatalytic  $H_2$  production with  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  in methanolic solution under Xe-lamp irradiation and performed in photocatalysis setup 2.



**Figure A16:** a) Diffraction patterns of as-synthesized and recovered  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  synthesized by sol-gel process with reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$ , TiO<sub>2</sub> (anatase) and  $H_2Ti_2O_5 \cdot H_2O$ . b) Tauc plots with respective absorption edge linearization and band gap energy (Eg) of as-synthesized and recovered  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  synthesized by sol-gel process. c) Photocatalytic H<sub>2</sub> production performed with sol-gel based  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  in methanolic solution (10 vol.-%) under Hg-midpressure immersion lamp irradiation in photocatalysis setup 1; irradiation period is marked by Hg-lamp switching on and off. d) In-situ Cu SPR spectra of  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  recorded during photocatalytic H<sub>2</sub> production in methanolic solution (10 vol.-%) shown in figure A11c.



**Figure A17:** a) Diffraction patterns of as-synthesized and recovered  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (1.285 wt.-%) (CTO- $Cu_{0.05}$ -WI) synthesized by wet impregnation process with reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$ , TiO<sub>2</sub> (anatase) and  $Cs_2SO_4$ . b) Tauc plots with respective absorption edge linearization and band gap energy ( $E_g$ ) of as-synthesized and recovered  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (1.285 wt.-%) (CTO- $Cu_{0.05}$ -WI) synthesized by wet impregnation process. c) Photocatalytic H<sub>2</sub> production performed with CTO- $Cu_{0.05}$ -WI in methanolic solution (10 vol.-%) under Hg-midpressure immersion lamp irradiation in photocatalysis setup 1; irradiation period is marked by Hg-lamp switching on and off. d) In-situ Cu SPR spectra of CTO- $Cu_{0.05}$ -WI recorded during photocatalytic H<sub>2</sub> production in methanolic solution (10 vol.-%) shown in figure A12c.



**Figure A18:** a) Diffraction patterns of as-synthesized and recovered  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (1.285 wt.-%) (CTO- $Cu_{0.05}$ -PD) synthesized by photodeposition process with reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$ , TiO<sub>2</sub> (anatase) and  $H_2Ti_2O_5 \cdot H_2O$ . b) Tauc plots with respective absorption edge linearization and band gap energy ( $E_g$ ) of as-synthesized and recovered  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (1.285 wt.-%) (CTO- $Cu_{0.05}$ -PD) synthesized by photodeposition process. c) Photocatalytic  $H_2$  production performed with CTO- $Cu_{0.05}$ -PD in methanolic solution (10 vol.-%) under Hg-midpressure immersion lamp irradiation in photocatalysis setup 1; irradiation period is marked by Hg-lamp switching on and off. d) In-situ Cu SPR spectra of CTO- $Cu_{0.05}$ -PD recorded during photocatalytic  $H_2$  production (10 vol.-%) shown in figure A13c.



**Figure A19:** a) Diffraction patterns of as-synthesized and recovered  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2.57 wt.-%) (CTO- $Cu_{0.1}$ -WI) synthesized by wet impregnation process with reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$ , TiO<sub>2</sub> (anatase) and  $Cs_2SO_4$ . b) Tauc plots with respective absorption edge linearization and band gap energy (E<sub>g</sub>) of as-synthesized and recovered  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2.57 wt.-%) (CTO- $Cu_{0.1}$ -WI) synthesized by wet impregnation process.



**Figure A20:** a) Diffraction patterns of as-synthesized and recovered  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2.57 wt.-%) (CTO- $Cu_{0.1}$ -PD) synthesized by photodeposition process with reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$ , TiO<sub>2</sub> (anatase) and  $H_2Ti_2O_5 \cdot H_2O$ . b) Tauc plots with respective absorption edge linearization and band gap energy (E<sub>g</sub>) of as-synthesized and recovered  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2.57 wt.-%) (CTO- $Cu_{0.1}$ -PD) synthesized by photodeposition process.



**Figure A21:** a,b) STEM images of recovered  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  synthesized by sol-gel process with 1 µm scale bar. Selected particles of recovered  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  for EDX measurements.

Element	O / atom %	Ti / atom %	Cu / atom %	Cs / atom %	
spectra 1	0.00	0.00	100.00	0.00	
spectra 2	0.00	7.95	92.05	0.00	
spectra 3	0.00	0.00	100.00	0.00	

**Table A14:** Element composition of framed particle area in figure A21.



**Figure A22:** STEM image of recovered  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2.57 wt.-%) (CTO-Cu<sub>0.1</sub>-WI) synthesized by wet impregnation process with 1 µm scale bar. Selected particles for EDX measurements.

Element	O / atom %	Ti / atom %	Cu / atom %	Cs / atom %
spectra 1	48.41	0.00	35.74	15.84
spectra 2	0.00	0.00	100.00	0.00
spectra 3	n.a.	n.a.	n.a.	n.a.

**Table A15:** Element composition of framed particle area in figure A22.



Figure A23: STEM image of recovered  $Cs_{0.68}Ti_{1.83}O_4/Cu$  (2.57 wt.-%) (CTO-Cu<sub>0.1</sub>-PD) synthesized by photodeposition process with 100 nm scale bar. Selected particles for EDX measurements.

Element	O / atom %	Ti / atom %	Cu / atom %	Cs / atom %
spectra 1	79.21	17.33	1.88	1.58
spectra 2	79.26	17.32	1.94	1.48

**Table A16:** Element composition of framed particle area in figure A23.



**Figure A24:** Photocatalytic H<sub>2</sub> production with  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  calcined at 800 °C for 10 h in methanolic solution (10 vol.-%) and performed in photocatalysis setup 1.



**Figure A25:** Tauc plot with respective absorption edge linearization and band gap energy ( $E_g$ ) of as-synthesized and recovered  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  after 8 h of stirring in 10 vol.-% methanolic solution in the dark.



**Figure A26:** XPS spectra of a) Cs  $3d_{5/2}$  (as-synthesized), b) Cs  $3d_{5/2}$  (recovered), c) Ti  $2p_{1/2}$  and Ti  $2p_{3/2}$  (as-synthesized), d) Ti  $2p_{1/2}$  and Ti  $2p_{3/2}$  (recovered), e) O 1s (as-synthesized) and f) O 1s (recovered) from as-synthesized Cs<sub>0.68</sub>Ti<sub>1.83</sub>O<sub>4</sub>, Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> and CTO-Cu<sub>0.1</sub>-WI as well as from recovered CTO-Cu<sub>0.1</sub>-PD, Cs<sub>0.64</sub>Ti<sub>1.79</sub>Cu<sub>0.1</sub>O<sub>4</sub> and CTO-Cu<sub>0.1</sub>-WI.



#### 9.6 Additional Information to Chapter 5.4

**Figure A27:** a) Diffraction patterns of as-synthesized and recovered  $Cs_{0.68}Ti_{1.83}O_4$ :Mn (0.05 mol.-%) with reference patterns of  $Cs_{0.68}Ti_{1.83}O_4$  and  $H_2Ti_2O_5 \cdot H_2O$ , b) Tauc plots with respective absorption edge linearization and band gap energy (Eg) of as-synthesized and recovered  $Cs_{0.68}Ti_{1.83}O_4$ :Mn (0.05 mol.-%) and c) Sequential photodeposition of 0.0125 wt.-% of Rh on  $Cs_{0.68}Ti_{1.83}O_4$ :Mn (0.05 mol.-%) in methanolic solution.



Figure A28: Tauc plot with respective absorption edge linearization and band gap energy (Eg) of Fe<sub>2</sub>O<sub>3</sub>.

#### 9.7 Additional Information to Chapter 5.5



**Figure A29:** Mott-Schottky plots measured at frequencies of 100 Hz, 1 kHz and 10 kHz of a)  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 800 °C for 10 h, b)  $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$  calcined at 800 °C for 10 h, c)  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  calcined at 700 °C for 10 h and d)  $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$  calcined at 800 °C.



**Figure A30:** Photovoltammograms of  $Cs_{0.68}Ti_{1.83}O_4$  calcined at 700 and 800 °C for 10 h, performed under backside irradiation of an UV light emitting diode ( $\lambda = 375 \pm 4$  nm; 60 W/m<sup>2</sup>) in 0.1 M KI.

# **10 Curriculum Vitae**

# Martin Pilarski

## **Personal Data**

Born:	June 18 <sup>th</sup> , 1987 in Tarnowitz, Poland
Nationality:	German
Marital Status:	Single

# Academic Education

10/2015 - present	Ph.D. Student Chemistry, Carl von Ossietzky University Oldenburg		
10/2012 - 09/2015	Ph.D. Student Chemistry, Ruhr-University Bochum		
10/2010 - 09/2012	Master of Science in Chemistry, Ruhr-University Bochum		
10/2007 - 09/2010	Bachelor of Science in Chemistry, Ruhr-University Bochum		
08/2003 - 07/2006	Final Secondary-School Examinations (Abitur), Albert-Martmöller-		
	Gymnasium, Witten		

## **Additional Education**

10/2012 - 03/2013	Ruhr-Lehrverbund-Katalyse, organized by the Ruhr-University
	Bochum, der Technical University Dortmund and the Max Planck
	Institute for Coal Research in Mülheim an der Ruhr
10/2012 - 10/2013	Intellectual Property Rights, Ruhr-University Bochum
02/2013	Quantitative Phase Analysis: Introduction to the Rietveld method,
	Institute for Geology, Ruhr-University Bochum
10/2013	Workshop: Basic Scientific Presentation for Doctoral Fellows from the
	Life Sciences, Natural Sciences and Engineering, Ruhr-University
	Bochum
11/2013	Workshop: Optimizing Writing Strategies for Doctoral Researchers
	from the Life Sciences, Natural Sciences and Engineering, Ruhr-
	University Bochum

## **Research Interests**

- Photocatalysis and Photoelectrochemistry
- Solar fuels: Photocatalytic hydrogen production

- Preparation of mixed metal oxides and heterogeneous catalysis
- Semiconductor science
- Industrial Chemistry

## **Publications**

**M. Pilarski**, R. Marschall, S. Gross, M. Wark, *Copper modified layered cesium titanates for photocatalytic hydrogen production*, **in preparation**.

## **Conference Presentations**

M. Pilarski, R. Marshall, M. Wark

Poster: Layered cesium titanates for photocatalytic hydrogen production

46. Jahrestreffen Deutscher Katalytiker, 13 – 15.03.2013, Weimar, Germany

M. Pilarski, R. Marshall, M. Wark

Conference Talk: Copper modified layered cesium titanates for photocatalytic  $H_2$  production Photocatalytic Advanced Oxidation Technologies for Treatment of Water, Air, Soil and Surfaces, 09 – 12.09.2013, Danzig, Poland.

M. Pilarski, R. Marshall, M. Wark

Poster: Copper modified layered cesium titanates for photocatalytic H<sub>2</sub> production

IPS-20: 20<sup>th</sup> International Conference on Photochemical Conversion and Storage of Solar Energy, 27.07 - 01.08.2014, Berlin, Germany

### Erklärung

Hiermit versichere ich, dass ich diese Arbeit mit dem Titel "Heterogeneous Photocatalysis with Transition Metal Modified Layered Titanates for Solar Hydrogen Production" selbstständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe. Des Weiteren erkläre ich, dass die Dissertation weder in ihrer Gesamtheit noch in Teilen einer anderen wissenschaftlichen Hochschule zur Begutachtung in einem Promotionsverfahren vorliegt oder vorgelegen hat.

Martin Pilarski | Oldenburg, den