

Photocatalytic degradation of selected organic pollutants in water on zirconium modified TiO₂ photocatalyst

A dissertation accepted for the degree of Doctor of Science

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2018

This doctoral thesis was carried out between October 2015 and September 2018 at the Institute für Chemie, Facult V, Carl Von Ossietzky Universität Oldenburg, Germany under the supervision of Prof. Dr. Michael Wark.

First referee:	Prof. Dr. Michael Wark, University of Oldenburg
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Defense date:	12/18/2018

Acknowledgment

I wish to express my sincere gratitude to my supervisor, Prof. Dr. Michael Wark for his fruitful discussion, guidance and continuous support throughout my PhD research. I would like to extend my appreciation to Prof. Dr. Gunther Wittstock through whom I got a chance to do my research at Oldenburg University.

I would like to thank Dr. Dereje Taffa for introducing me to various instrumental techniques and also for his useful advice and suggestions during my research.

I am also grateful to Mrs. Nicole Lenkering and Heike Hilmer for their help in administrative and personal issues; Mr. Rainer Bolts for his technical assistance in the lab and all other group member for their support and making my stay in the working group more enjoyable.

Thanks to German Academic Exchange Service (DAAD) for their financial support during the first two years of my research.

My special thanks to my husband and son for the great sacrifices they made to see to it that my PhD study was a success. Special thanks to my late DAD who first introduced me to the Chemical Periodic Table and instilled in me the curiosity behind analysis at a very young age during our work in the farm. Thanks to my sweet mum, who always gave me a shoulder to cry on and encouraged me every day. Thanks to my brothers, sisters, my in-laws and friends for their unconditional support and encouragement.

All glory to God almighty through Him all things are possible.

Dedication

This thesis is dedicated to my parents; the late Johnson Mbiri and Lucy Mbiri

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Abstract

Though applications of TiO_2 photo-catalyst in environmental pollution remediation are promising, up to date, photocatalytic efficiency is still a challenge due to relatively low quantum efficiency of pure TiO_2 . The high recombination rate of photo-induced electron-hole pairs at or near its surface on TiO_2 reduces its photodegradation efficiency. Stability of the photocatalyst is also a key important factor for practical application of the semiconductor in the environment. Herein, we report enhanced photocatalytic activity of mesoporous TiO₂ powder and thin films towards degradation of organic pollutants in water due to their modification with zirconium. Powder catalysts were prepared by sol-gel and evaporation induced self-assembly (EISA) methods while highly stable, uniform transparent thin films were prepared using EISA via dipcoating. Characterization of the catalysts was carried out using different techniques; XRD, XPS, BET, HRTEM, SEM, RAMAN, UV-Vis DRS, electrochemical, photoluminescence and fluorescence. The effects of Zr addition on the morphology, structure, crystallinity and photoactivity of the catalyst were investigated. Incorporation of Zr to Ti positions in the TiO₂ crystal lattice enhanced the charge separation, improved surface area, increased stability of anatase phase as well as controlled the crystal growth as confirmed from photoluminescence, N_2 adsorption and X-ray diffraction analysis. Zirconium modified TiO₂ catalysts showed higher photocatalytic activity compared to pure TiO₂ catalyst. High calcination temperatures and high amount of Zr led to formation of composite whose activity was lower than doped TiO₂. The optimum loading of Zr was dependent on method of synthesis and type of catalyst ranging from 0.05 to 0.14 mol ratio. Photocatalytic degradation performance of powder was far much better than that of films. The results in this study show that modification of TiO_2 is a promising method in improving photocatalytic activity of TiO₂ towards degradation of organic pollutants in water.

1 Introduction

The world demand for clean and safe drinkable water is ever growing due to the increasingly stress on water resources by ground water over-abstraction, climate change and pollution. It has been estimated that 80 percent of world used water is released into the environment untreated leading to environmental pollution. Most of the pollution comes from industrial, agricultural house hold waste. It includes dyes, pesticides, detergents, pharmaceuticals, oils, pathogens, inorganic waste like lead, mercury, noxious gases among others. Both the organic and inorganic pollutants can cause adverse effect on both human health and the ecosystems [1-3].

One promising sustainable water management to meet up with the high water demand is by reuse of treated agricultural and industrial wastewater [4, 5]. The current water treatment technologies like biotechnology, physical, chemical integrated practices suffer from various disadvantages e.g. incomplete removal of the pollutants, high demand of chemical reagent, time consuming, high treatment cost, and generation of toxic secondary pollutant [6-8]. They mostly involve removal of coliforms, suspended solids and organic pollutants. Unfortunately for persistent organic pollutants (POPs) (pesticides, phenolic waste, surfactants, pharmaceuticals, coloring matter and endocrine disruptive chemicals), the methods are both tedious and expensive due to their stability of the pollutants. Presence of POPs and their intermediates has been reported in studies carried out on treated wastewater from sewage, surface and groundwater [6, 9, 10]. This suggests a possible bioaccumulation of these pollutants in food chains which can lead to a negative effect on both human and animals. Thus the need of advanced treatment technologies of POPs in water is essential.

In the past decades, advanced oxidation processes (AOP) has attracted increasing attention due to their promising, efficient and eco-friendly methods of removing POPs from water [4, 6, 9-11]. AOPs involve *in situ* formation of reactive free radicals through chemical, photochemical, sonochemical or electrochemical reactions, with the most important radical being the hydroxyl radical (OH[•]) [12, 13]. These radicals can degrade organic molecules into CO₂, H₂O or mineral acids. The processes can be broadly categorized as heterogeneous and homogenous processes. Heterogeneous processes have attracted more attention compared to homogenous ones due to the ease in catalyst separation and recovery thus the catalyst can be recycled after the reaction [14] . Additionally, heterogeneous catalysts are both thermally and chemically more stable and hence can withstand more harsh environments. Successful application of heterogeneous photocatalytic degradation of organic molecules such as alcohols, pesticides, amines, carboxylic acids, dyes, and aldehydes on semiconductors is well documented [12, 15]. Apart from water purification, the process is also used in purification of air and self-cleansing surfaces [15].

Among the semiconductors used as catalyst in heterogeneous processes TiO_2 is the most common one. Electron-hole recombination is detrimental to the photocatalytic efficiency of most TiO_2 nanomaterials as it depends on the ratio of the rate of surface charge carrier transfer to the rate of electron-hole generation. This can be overcome by preparation of materials with high crystallinity (less defects and grain boundaries) and high surface area (in order to capture charge carriers in the vicinity of their generation). Unfortunately, the amorphous to crystalline transition in TiO_2 requires relatively high calcination temperatures; which possibly leads to a collapse of the mesostructure and increased crystal growth. Choice of the method of synthesis is of great importance as it determines the crystallinity and mesostructure of the final catalyst. Low temperature synthesis method like evaporation induced self-assembly (EISA) route allows to achieve both, high surface area and high wall crystallinity [16-19].

Doping and surface modification of TiO_2 films with metals, non-metals or dyes are further strategies used for improving their photocatalytic efficiency in the UV, but especially in the visible light region [4]. For example, Choi and coworkers reported that surface chelation, surface derivatization and platinization and selective metal ion doping can be used in modification of TiO_2 with a goal to enhance interfacial charge-transfer reactions [20]. According to their study the presence of a controlled amount of selected metal ion impurities in the TiO_2 matrix acts as electron or hole traps which in turn decrease the rate of electron-hole recombination. On the other hand, too high levels of dopants can either act as recombination centers being detrimental for the photocatalytic activity or can lead to phase separation resulting in the formation of nanocomposites. Thus care must be taken on the type of the doping element and the amount introduced. Doping is also applied to enhance thermal stability, increase specific surface area and create more hydroxyl groups on TiO₂ which in return leads to better activity [4, 21-23].

For reduced aggregation and ease catalyst recovery, TiO_2 can be loaded on support material such as glass, steel or quartz. The activity of supported catalyst is generally lower than that of suspended or slurry systems as the immobilization can reduce the active sites and also decrease the mass-transfer rate. For this reason, a photocatalyst which can offer high activity and easy recovery is still a priority. TiO_2 thin films has been used widely for the preparation of different nanomaterial photocatalysts such as nanopowder, nanotubes, nanorods and more importantly thin films [4, 11, 19, 24]. Mesoporous crystalline TiO_2 thin films have potential applications in solar cells, self-cleaning coatings, gas sensors, photocatalytic water splitting and degradation of pollutants [25-30]. High chemical stability, optical transparency, fast photoinduced electron transfer and high accessibility of pores are important factors; the latter is especially achieved by high surface areas established in films with ordered mesoporosity [19, 31, 32]. As a result of high surface area and large pore volume, mesoporous films have more actives sites which create more interaction between the catalyst and the pollutant.

1.1 Aim of the study

This thesis reports the investigation into the synthesis of Zr modified mesoporous TiO_2 nanopowder and films that contribute to enhanced photocatalytic activity in environmental photocatalysis. The photocatalytic activity tests focused on aqueous degradation of selected organic pollutants under UV light.

As it has been proposed that zirconium enhances the photocatalytic activity of TiO_2 , this study gives more understanding of the effect of zirconium on both the characteristics and the photocatalytic activity of Zr modified TiO_2 using chloridazon as the main test molecule. This was achieved by:

- Synthesis of Zr modified TiO₂ nanopowder using different synthesis methods (sol-gel and EISA)
- Synthesis of Zr modified TiO₂ thin films by EISA method via dip-coating.
- Determination of the effect of different parameters such as; amount of zirconium, type precursor, solvent, aging conditions, and calcination temperature, on the structure and activity of the catalyst.
- Characterization of catalyst through; SEM, TEM, XPS, UV-DRS, N₂ physisorption analysis, RAMAN, among others.
- Photocatalytic degradation test of chloridazon, phenol and 4-chlorophenol on the prepared catalysts.

2 Literature review

2.1 Titanium dioxide

In photocatalysis, titanium dioxide (TiO₂) is the extensively studied metal oxide due to its versatility, high efficiency, widespread, availability, and low cost, physical and chemical stability. It is practically applied in; catalysis as photocatalyst, paints and cosmetics as white pigment, Li-based batteries, solar cells for production of hydrogen and electric energy, as an optical coating, in ceramics and sensors among others [4, 25, 26, 28, 30]. TiO₂ exists in three major different structures rutile (tetragonal), anatase (tetragonal) and brookite (rhombohedral). Among the existing structures, only rutile and anatase plays any role in the applications of TiO₂ [33, 34]. Fig. 1 shows the crystal structures of anatase and rutile, the basic building block consists of titanium atom surrounded by six oxygen atoms in a nearly distorted octahedral configuration while oxygen-titanium bond is slightly longer. Anatase draws more attention in photocatalysis as it is more photoactive as a result of its higher adsorption affinity for organic molecules and low recombination rate [35-37].

 TiO_2 is an n-type semiconductor with a band gap of 3.2 eV for anatase and 3.0 eV for rutile. Therefore, as a photocatalyst it can only be activated with irradiation in the UV region < 387 nm. Studies have shown that modifying TiO_2 using transition metals, noble metals, non-metals or dyes as sensitizers can improve its activity under visible light [4].

Common synthesis methods for preparation of nanocrystalline TiO_2 include sol-gel, hydrothermal, solvothermal, chemical vapor deposition, direct oxidation and template method. Sol-gel method is the most preferred method because of the homogeneity and purity of the products and ease in introduction of dopants. Sol-gel method combined with evaporation induced self-assembly (EISA) of triblock polymers with complexation of molecular inorganic species has enabled the preparation of mesoporous TiO₂ catalysts (powder and films) with high surface area [39]



Fig. 1 Crystal structure of anatase, rutile and brookite [34, 38].

2.2 Photocatalysis

This is an important chemical process behind the development of the key renewable energy and environmental technologies such as cheaper solar-cells with high-efficiency, hydrogen from water splitting and photocatalytic water/air purification [26, 30, 40]. The process involves three major steps: photoexcitation, bulk diffusion and surface transfer of charge carriers. Exposing a semiconductor photocatalyst to UV/visible light energy greater than its band gap, the energy excites electrons from the valence band (VB) to the conduction band (CB), generating electron/hole pair on the semiconductor surface. The holes in the valence band are very strong oxidants (redox potentials of +1.0 to +3.5 V versus normal hydrogen electrode (NHE), while the electrons in the conduction band act as good reductants (redox potentials of -1.5 V to +0.5 V vs NHE) [23]. Most organic photodegradation reactions utilize the oxidizing power of the holes either directly or indirectly. The primary requirement of a good semiconductor photocatalyst for

degradation of organic molecules is that the redox potential (E° ($H_2O/OH^2 = -0.28$ V vs. NHE) lies within the band gap domain of the material and the catalyst is stable for longer period. WO₃ ($E_g = 2.8$ eV), TiO₂ ($E_g = 3.2$ eV), SrTiO₃ ($E_g = 3.2$ eV), ZnO ($E_g = 3.2$ eV) and ZnS ($E_g = 3.6$ eV) are among the semiconductors whose band gap energies are sufficient for chemical reactions [41]. TiO₂ is more studied for its high photocatalytic activity and stability in aqueous media.

2.3 Principle of TiO₂ photocatalysis

Since the discovery of photocatalytic water splitting on TiO₂ under UV light by Fujishima and Honda in 1972, a lot of studies have been carried out to understand the photocatalytic mechanism of TiO₂ and at the end many promising applications have been found [42]. Heterogeneous photocatalytic reactions on TiO₂ involve reduction or oxidation of reactants e.g. organic pollutants on its surface. Upon irradiation of TiO₂ with light energy equal or greater than its band gap energy, electron is excited from the valence band to conduction band resulting in formation of conduction band electron (e^-_{CB}) and valence band hole ($/h^+_{VB}$) pairs fig. 2, eqn 1.

$$TiO_2 + h\upsilon \rightarrow h_{vb}^+ + e_{cb}^- \qquad (1)$$



Fig. 2 Principle of photocatalytic degradation of water pollutant (R) on TiO₂.

The pair generated has very short life span and can undergo; recombination (eqn 2), become trapped in metastable state or interfacial charge transfer to the surface of TiO_2 particle.

$$h_{vb}^+ + e_{cb}^- \rightarrow TiO_2 + heat$$
 (2)

Surface trapped electrons and holes have longer life span compared to those in the bulk [43-45]. In presence of water and air, generated electron-hole pair at the surface reacts with surface hydroxyl, adsorbed water molecules, dissolved oxygen, to form highly reactive species like hydroxyl radicals and superoxide anions (O_2^-) and peroxides (O_2^{2-}) (eqn 3-10).

 $\begin{aligned} H_{2}O + h_{vb}^{+} &\to OH^{\bullet} + H^{+} \quad (3) \\ O_{2} + e_{cb}^{-} &\to O_{2}^{\bullet-} & (4) \\ O_{2}^{\bullet-} + H^{+} &\to HO_{2}^{\bullet} & (5) \\ HO_{2}^{\bullet} + HO_{2}^{\bullet} &\to H_{2}O_{2} + O_{2} & (6) \\ O_{2}^{\bullet-} + HO_{2}^{\bullet} &\to O_{2} + HO_{2}^{-} & (7) \\ HO_{2}^{-} + H^{+} &\to H_{2}O_{2} & (8) \\ H_{2}O_{2} + e_{cb}^{-} &\to OH^{\bullet} + OH^{-} (9) \\ \end{aligned}$

In absence of air or water, charge recombination can also occur at the surface of TiO_2 with formation of heat (eqn 2). Depending on the experimental conditions, the photogenerated holes (h_{vb}^+), hydroxyl radical(OH[•]), hydroperoxide(HO₂[•]), oxygen radical ($O_2^{\bullet-}$) can take part in TiO₂ photocatalytic reactions (eqn 11).

 $h_{vb}^+/OH^{\bullet} + R \rightarrow CO_2 + H_2O + intermediates + mineral acids$ (11)

The type of superoxide involved in the reaction differs from one compound to the other based on the nature of the compound. It has been reported that superoxide and mostly hydroxyl radical are the active species in photocatalytic degradation of organic compounds [46].

2.4 Modification of TiO₂ with zirconium

Despite the positive attributes of TiO_2 , its practical application still suffers a major drawback related to the high rate of charge carrier recombination during their migration to the surface where adsorption and oxidation of molecules takes place. This results in low quantum efficiencies in photocatalytic reactions. Other factors that can limit the efficiency of TiO_2 include surface area, crystal structure, size distribution, porosity, surface hydroxyl group density and band gap.

Various strategies have been utilized to modify TiO_2 in the aim of overcoming these limitations. Incorporating low amount of transition metals (Fe, V, Cu, Zr, Mo) [5, 45, 47-49] noble metals (Pt, Pd, Ag, Au) [39, 50, 51] or non-metals (N, C, S) [4] or forming composites like C_3N_4 -TiO₂, SnO₂-TiO₂ and WO₃-TiO₂ [52, 53] has led to development of high efficient photocatalyst. Modification of TiO₂ can impressively enhance light absorption, organic molecules adsorption, interfacial charge transfer kinetics, leading to improved photocatalytic activity.

The metals ions (M^{n+}) become shallow trapping sites for charge carriers hence suppressing electron-hole recombination by increasing the life-time of the photo-generated charge carriers [20, 44]. For an enhanced photoactivity, the energy level of M has to lie slightly below the conduction band edge or above the valence band. This allows easy detrapping and migration of the charge carriers to the surface to avoid further trapped charge carriers recombination (eqn 12).

$$M^{n+} + e_{CB}^- / h_{VB}^+ \to M^{(n-1)+} / M^{(n+1)+}$$
 (12)

Zirconium has been reported to enhance the photocatalytic activity of TiO₂ towards degradation of dyes, phenolic compounds and water splitting [49, 54-57]. Different hypotheses are given on the enhanced activity of Zr modified TiO₂. Venkatachalam suggested in 2007 that substitution of Ti⁴⁺ with Zr⁴⁺ in TiO₂ lattice may enhance adsorption of molecules on TiO₂ as it creates charge compensating anion vacancy in the TiO₂ lattice points [58]. Also the enhanced activity may be due to created Lewis acid acids which act as adsorption as well as electron traps. Zirconium 4+ ions are known to stabilize the anatase phase by creating Ti³⁺ species which hinders atom transport in the anatase phase [49].

3 Experimental

This chapter presents the work on the synthesis of zirconium modified TiO₂ powders and thin films, their characterization and evaluation of their photocatalytic activity if irradiated with Xenon lamp light. Cut-off filters (320/340 nm) were used to vary the range of illumination whether UV or visible region. To compare effect of method of synthesis on the activity of the samples, TiO₂ and Zr modified TiO₂ samples were prepared through sol-gel method or evaporated-induced self- assembly method. In each method either/both amount of zirconium or calcination temperature was varied. Samples were labeled as eTiZrx-y, sTiZrx-y, or fTiZrx-y where e, s and f represents EISA, Sol-gel and films respectively while x and y represent the calcination temperature and the molar ratio of Zr/Ti.

3.1 Chemicals and Materials

Titanium (iv) n-butoxide (99%, Alfa-Aesar), titanium isopropoxide (99%, Aldrich), zirconium (IV) oxynitrate hydrate (99.99%, Aldrich), zirconium dichloride oxide hydrate (99.9%, Alfa-Aesar), [poly(ethylene glycol)-poly(propylene glycol)- poly(ethylene glycol)] (Pluronic P-123

Aldrich), [poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide)] (Pluronic F127, Aldrich), TiO₂ Evonik P25 (rutile/anatase mixture with about 20 % of rutile and about 20 nm crystal size), concentrated hydrochloric acid (37%, VWR-ProABO), absolute ethanol (Aldrich) chloridazon (99.7%, Fluka), phenol (99%, Aldrich), 4-chlorophenol (98%, Merck). All chemical were used as received.

3.2 Preparation of nanocomposites by evaporation-induced self-assembly (EISA)

Mesoporous TiO_2/ZrO_2 was prepared using a procedures based on those given by Fan et al. and Zhou et al. [59, 60]. 3.17 ml concentrated HCl was added into 3.5 ml titanium butoxide by vigorous stirring. After 20 min of stirring, a solution containing 1 g P123, 15.3 ml ethanol, and 0 - 0.2 mole ratio of zirconium oxychloride was added. The mixture was stirred for another 3 h then aged at 40 °C in an oven for 4 days to evaporate the solvent. The as obtained samples were then calcined in air at 350, 450, 500, 600, 700, and 750 °C at a heating rate of 1 °C/min for 4 h.

3.3 Preparation of nanocomposites by sol-gel method

In a separate route, mesoporous TiO_2/ZrO_2 composites were prepared by sol-gel method. 3.5 ml of titanium butoxide was dissolved in 10 ml absolute ethanol at room temperature under vigorous stirring. After 20 min, a solution of 1 g F127, 0 - 0.2 mole ratio zirconium (IV) oxynitrate in 10 ml deionized water was added dropwise. The pH value of the sol was adjusted to 3 using 0.5 M HCl after which the sol was continuously stirred for 3 h followed by aging for 24 h at room temperature. The resulting powder was centrifuged, washed with distilled water and ethanol to remove unreacted reagents. The samples were then dried overnight in an oven at 110 °C and subsequently calcined at 500, 600, 650, 700, or 750 °C for 4 h in air at a heating rate of 1 °C/ min.

3.4 Preparation of urea/thiourea doped nanocomposite via sol-gel method

The same procedure as 3.3 above was repeated but with addition of either urea (2, 5, 10 %) or thiourea (2, 5, 10, 15 %) in the zirconium precursor solution. After mixing the two precursor solution the mixture was aged for 24 hr at room temperature with constant stirring. The other part of the procedure was the same as 3.3 above.

3.5 Preparation of thin films via dip-coating

Sols for pure TiO₂ and Zr modified TiO₂ films were synthesized by the EISA route using Pluronic P123 as the structure directing agent [39]. With vigorous stirring concentrated HCl was added slowly into a beaker containing titanium butoxide. After 20 minutes of stirring, a solution containing P123, ethanol and zirconium dichloride oxide hydrate was added and the mixture was stirred for further 3 h. The typical mole ratios were: Ti/HCl/EtOH/P123/Zr = 0.01/0.1/0.26/0.00017/0-0.0025. The amount of ZrOCl₂ was varied to prepare films with different Zr content. The as-prepared sols were used for preparing films by dip-coating on microscope glass at a withdrawal rate of 1 mm per s. The films were then aged in a humidity chamber at 25 °C and 50 % RH for 24 h followed by calcination for 4 h in air at 350, 450, 500 and 550 °C, respectively, with a heating rate of 1 °C/min. Multi-layered films were prepared by repeating the dip-coating process with a 350 °C intermediate heat treatment for 1 h (heating rate: 3 °C/min) between each coating step.

3.6 Characterization

3.6.1 Scanning electron microscopy (SEM)

Scanning electron microscope uses a focused beam of high-energy electrons (primary electrons) to generate a variety of signals at the surface of solid specimen placed on carbon tape placed on a

metal stub. The interaction of the high energy electrons generate, secondary electrons, back scattered electrons, auger electrons, X-rays and photons of various energies as signals. Signals from secondary electrons (from the surface) and backscattered electrons (from the bulk) are commonly used for imaging samples [61]. Secondary electrons shows the morphology and topography while back scattered electrons illustrate contrasts in composition in multiphase samples. The X-rays can results in the compositional information about the sample incase the SEM instrument is equipped with energy dispersive X-ray spectrometer. Secondary electrons from the surface of the specimen are then attracted and collected by a positively biased grid or detector and translated into a signal. An SEM image is produced by sweeping the electron beam across the area being analyzed to produce many signals which are amplified, analyzed and translated into images of the topography being inspected.

SEM images and film thickness were obtained using Helios NanoLab 600i (FEI, Eindhoven, The Netherlands) scanning electron microscope. Secondary electron detector was at an acceleration voltage of 15 kV. Powder samples were sprinkled lightly on a carbon tape fixed on an aluminum stub while films were fixed directly on the stub and conductive silver put between film and the stub. Finally all samples were sputtered with a thin layer of carbon to avoid charging effect during measurement.

3.6.2 Transmission and High transmission electron microscopy (TEM/HRTEM)

Transmission electron microscope is a powerful tool for structural analysis in material science. It resembles optical microscopy, except electromagnetic radiations are used to focus an electron beam on the sample instead of optical lenses [62]. TEM is a technique that uses the interaction of energetic electrons with the sample in vacuum and provides morphological, compositional and crystallographic information. The electron emitted from filament passes through the multiple

electromagnetic lenses and make contact with the screen where the electrons are converted into light and an image is obtained. The speed of electrons is directly related with the electron wavelength and determines the image resolution. A modern TEM is composed of an illumination system, condenser lens system, an objective lens system, magnification system, and the data recording system. A set of condenser lens that focus the beam on the sample and an objective lens collects all the electrons after interacting with the sample and form image of the sample, and determines the limit of image resolution. Finally, a set of intermediate lenses that magnify this image and projects them on a phosphorous screen or a charge coupled device (CCD). TEM can be used for imaging and diffraction mode.

The high-resolution transmission electron microscopy (HRTEM) uses both the transmitted and the scattered beams to create an interference image. It is a phase contrast image and can be as small as the unit cell of crystal. In this case, the outgoing modulated electron waves at very low angles interfere with itself during propagation through the objective lens. All electrons emerging from the specimen are combined at a point in the image plane. HRTEM has been extensively and successfully used for analyzing crystal structures and lattice imperfections in various kinds of advanced materials on an atomic resolution scale. It can be used for the characterization of point defects, stacking faults, dislocations, precipitates grain boundaries, and surface structures.

The morphology and structure of the composites were studied using a Joel 2100F-FS high resolution transmission electron microscope (HRTEM) and energy dispersive X-ray spectroscopy (EDX) operating at 200 kV. Powder samples and flakes peeled-off from film samples were sonically dispersed in absolute ethanol and the diluted powder suspension was deposited on carbon-coated grid before examination.

3.6.3 X-ray powder diffraction (XRD)

XRD is one of the most powerful analytical techniques used to determine phase purity, phase composition, crystallinity, crystal size, lattice parameters, and geometry of crystalline material [63, 64]. This technique is based on constructive interference of monochromatic X-rays with the sample. X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate and then directed toward the sample, shown on fig. 3.



Fig. 3 A schematic illustration of X-rays scattered on parallel lattice planes.

Upon interaction with the sample, the X-rays undergo diffraction, produced by the planes that form the atoms of the crystal. The path difference between two waves: 2 * wavelength (λ) = 2dsin θ . When there is constructive interference of the scattered X-rays a diffraction peak is observed. This occurs when conditions satisfy Bragg's law ($n\lambda = 2d \sin\theta$), where n = an integer known as the order of reflection, λ = wavelength of X-rays, d = distance between lattice planes and θ = angle of interference. The law relates the wavelength of electromagnetic radiation to diffraction angle and lattice spacing in the crystalline sample.

The diffracted X-rays are then detected, processed and counted. By scanning through a range of 20 angles a diffraction pattern is obtained. Conversion of the d-spacing allows identification of the element as each element has a set of unique d-spacing. From the diffraction patterns, the phase purity, degree of crystallinity and unit cell parameters of the material can be determined.

The crystal sizes can be calculated using the Scherrer equation ($\tau = \frac{K\lambda}{\beta \cos\theta}$), where τ is the mean size of the crystalline domains, K is the dimensionless shape factor (= 0.8 - 1.0), λ is the X-ray wavelength and β is the full width half maximum (FWHM) of the intense peak at θ value. Both powder and films X-ray diffraction patterns were obtained on a PANalytical Empyrean X-ray diffractometer using CuK α = 1.54 Å. X-ray diffractograms were recorded over a range of 2 θ of 15 - 80 at 45 kV and 40 mA and crystal size were calculated using Scherrer equation and lanthanum hexaboride as the reference material.

3.6.4 X-ray Photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy is one of the surface analysis technique applied on broad range materials to provide quantitative and chemical state information [65]. XPS is typically accomplished by exciting a samples surface with mono-energetic X-rays causing photoelectrons to be emitted from the sample surface (fig. 4). An electron energy analyzer is used to measure the energy of the emitted photoelectrons. From the binding energy (BE) and intensity of a photoelectron peak, the elemental identity, chemical state, and quantity of a detected element can be determined. The BE is related to the measured photoelectron KE by the equation; BE = hv - KE, where h is the photon (x-ray) energy:



Fig. 4 Principle of X-ray photoelectron spectroscopy.

X-ray photoelectron spectroscopy measurements were carried out using a Thermo Fischer ESCALAB 250Xi equipped with monochromatic Al-K α X-ray source 1486.6 eV. Powder sample was pressed to form a thin wafer while the film was fixed on the sample holder using a tape. The binding energies (BE) were referenced to the surface adventitious carbon contamination C1s peak (284.8 eV). XP spectra were recorded with 10 eV pass energy and 0.02 eV step size.

3.6.5 Raman spectroscopy

Raman spectroscopy is a tool used to study vibrational, rotational and other lower frequency modes in physics and chemistry. It also provides information about the crystallinity and phase purity of materials. A sample is illuminated with a monochromatic laser beam which interacts with the electron cloud of the bonds of the sample molecules. The incident photon excites the molecule into a virtual state and shortly later falls back lower rotational and/or vibrational state releasing a scattered radiation whose frequencies are detected. The scattered radiations have different frequencies. The scattered radiation having a frequency different from that of incident light (inelastic scattering) is used to construct a Raman spectrum. Much of this scattered radiation has a frequency which is equal to frequency of incident radiation and constitutes Rayleigh scattering. When the frequency of incident radiation is higher than frequency of scattered radiation, Stokes lines appear in Raman spectrum. But when the frequency of incident radiation is lower than frequency of scattered radiation, anti-Stokes lines appear in Raman spectrum. Signal from Rayleigh scattering is filtered and only the signal from inelastic scattering is detected. Raman spectra arise due to inelastic collision between incident monochromatic radiation and molecules of sample.

Raman spectra in the range of 200 - 2000 cm⁻¹ were recorded with a Bruker Senterra Raman spectrometer using a 633 nm laser with 2 mW laser power.

3.6.6 Nitrogen physisorption analysis

The specific surface area and the pore size distribution are fundamental parameters for the characterization of solids. Surface area measurements are commonly carried out by gas physisorption method. The commonly used gas is nitrogen as it is less expensive, easily available, inert and able to penetrate even finest pores. Measurements are carried out at liquid nitrogen temperature (77 K).

Different adsorption isotherms have been Freundlich, Langmuir and Brunauer, Emmett and Teller (BET) theory. The most applied theory is the BET as it can be used to measure the surface area accurately both at low and high pressures. The mathematical model derived from BET theory has been adopted as standard method for determination of surface area. This physical adsorption of a gas over the entire exposed surface of a material and the filling of pores is called physisorption and is used to measure total surface area and pore size analysis of nanopores, micropores and mesopores. The specific surface area of a powder is estimated from the amount of nitrogen adsorbed in relationship with its pressure, at the boiling temperature of liquid nitrogen under normal atmospheric pressure. The measurement process of physisorption involves chilling the surface of the measured powder, using nitrogen to adhere to the surface -adsorption, then taking the chilling away – leading to desorption.

The BET equation can be represented as

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{(c - 1)p}{c v_m p_0}$$

Where C is a constant at a given temperature and is related to the heat of adsorption, v is the volume of gas adsorbed at equilibrium pressure p, v_m is the volume of adsorbate needed to form a monolayer on the surface and p_0 is the saturation vapor pressure of the adsorbate. According to this BET equation, the specific area S.A (BET) can be calculated by knowing v_m .

A value of v_m is measured at each of not less than 3 values of p/p_0 . Then the BET value:

$$\frac{1}{v(\frac{p_0}{p}-1)}$$

is plotted against p/p_0 . From the resulting linear plot, the slope (c-1)/v_mc and the intercept (1/v_mc, v_m can be determined. From the so determined value of v_m, the specific surface area is calculated by equation:

$$S.A_{(BET)} = v_m A_m N_A / v_{mol}$$

Nitrogen adsorption-desorption isotherms were collected either on a Micrometrics TriStar II 3020 or Micrometrics ASAP 2020 apparatus and the Brunauer-Emmett-Teller (BET) equation was used to calculate the specific surface area.

3.6.7 UV-Vis diffuse reflectance spectroscopy

UV-Vis spectroscopy is a technique applied preferably in liquid state for solids and insoluble samples UV-Vis reflectance or diffuse reflectance is more applicable. UV-Vis diffuse reflectance is a good method for powdered samples and rough solids.

When a beam of light is directed to an opaque (solid) sample, the light is reflected on the surface of the sample. Part of the light is reflected symmetrically with respect to the normal line (Specula reflection), while the other part is scattered in different directions (diffuse reflection). Using an integrating sphere, it is easy to avoid specular reflection by directing the light to the sample at an angle 0 °, specular reflected light exits the integrating sphere and only the diffuse reflection is concentrated on the detector. The inside of the sphere is coated with diffusive material like barium-sulfate. The obtained values are relative reflectance with respect to the reflectance of a reference white standard which is taken to be 100%.

The most commonly used model to describe diffuse reflection is the Kubelka-Munk function; it displays a linear relationship between absorption and scattering.

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

 R_{∞} is the reflectivity; K is the absorption coefficient while α is the scattering coefficient. From the above equation, E_{gap} is directly related to absorption coefficient can be determined using the Tauc-plot:

$$(h\upsilon\alpha)^{1/n} \propto A. (h\upsilon - E_{gap})$$

where h is the Plank-constant, v is the frequency and A is the proportionality constant. Absorption coefficient is directly proportional to the Kubelka-munk function, thus,

$$(F(R_{\infty})h\upsilon)^{1/n} \propto A. (h\upsilon - E_{gap})$$

The reciprocal exponential $n = \frac{1}{2}$ or 2, it represent the nature of electronic excitation in the material. Where $n = \frac{1}{2}$ is for direct band gap transition and n = 2 is for indirect band gap transition. E_{gap} can be obtained by plotting $(F(R_{\infty})hv)^{1/n}$ versus hv, extrapolating the linear part and determining the intercept.

UV-vis diffuse reflectance spectra (DRS) were measured on a VARIAN Carry 4000 spectrophotometer connected with an integrating sphere. The spectra were scanned in the range

of 200-800 nm and magnesium oxide used as the white standard. The indirect band-gap (E_{gap}) was determined from the intercept of the Tauc's plot of $(F(R\infty) * h\nu)^{\frac{1}{2}}$ vs hv.

3.6.8 Photoluminescence spectroscopy

The photoluminescence (PL) is as highly sensitivity and non-destructive technique which is widely used to investigate the structure and properties of the active sites on the surface of metal oxides and zeolites. Also, the PL technique is applied in the field of photocatalysis to understand the surface processes of semiconductors. PL spectrum is an effective way to study the electronic structure, optical and photochemical properties of semiconductor materials, by which information such as surface oxygen vacancies and defects, as well as the efficiency of charge carrier trapping, immigration and transfer can be obtained. PL signals of semiconductor materials result from the recombination of photo-induced charge carriers. In general, the lower the PL intensity, the lower the recombination rate of photo-induced electron–hole pairs, and the higher the photocatalytic activity of semiconductor photocatalysts. However, the photocatalytic activity of semiconductor photocatalysts can also increase as the PL intensity becomes stronger.

The electronic structure of a semiconductor consists of a valence band (VB), conduction band sometimes sub-bands in the band gap which is related to the surface defects and surface states Fig. 5. The band gap energy (E_g) is the energy difference between the CB bottom and VB top. When the semiconductor is excited with light energy equal or higher than its E_g , electrons in the VB are promoted to CB with different energies to become different excited states with generation of holes on the VB (process 1). However, the excited electrons are unstable and easily recombine with holes at VB releasing energy in form of heat or light (process 2, 3, 4).



Fig. 5 Main photophysical processes of a semiconductor excited by light with equal to or higher than band gap energy.

The light energy can be dissipated as radiation, which results in a luminescence emission of semiconductor material, called the PL phenomenon of the semiconductor. Electron transition can take place from of the lowest energy state of the CB to the top energy state of the VB (process 2) or electrons from bottom CB first undergoes relaxation (non-radiative) different sub-bands below the CB before moving to the top VB state with emission of radiation (process 3). In addition, the excited electrons at the CB bottom can come back to the VB directly or indirectly by nonradiative transitions, which is the process 4. The first phenomenon results into a band-band PL while the latter results into excitonic PL which mainly results from surface oxygen vacancies and defects of semiconductors. Mid-gap energy states (MG) caused by impurities acts as deep traps of charge carries and can results in indirect recombination of excited electrons in the CB with holes in the VB. These transitions are non-radiative (fig. 6a). On the other hand, donor or acceptor dopant can create donor/acceptor energy levels near the band edges which also results in indirect recombination centers (fig. 6b). Donor and acceptor energy levels acts as shallow traps for electrons. The electronic transitions involved in this case are radiative but are very rare at room temperatures.



Fig 6. Diagram illustration of the two different indirect recombination processes.

The photoluminescence spectra were measured at room temperature with a VARIAN Cary Eclipse fluorescence spectrophotometer using the 325 nm line of a Xe lamp as excitation source.

3.6.9 Mott-Schottky analysis

The semiconducting properties of a material can be estimated from Mott-Schottky plots. When a semiconductor is brought in contact with an electrolyte solution, a potential difference is established [66]. If the Fermi level (E_f) of the semiconductor lies above the potential of the solution, as in the case of n-type semiconductors, electrons will transfer from the semiconductor to the solution. The Fermi levels become equal. The semiconductor becomes positively charged (depleted) while the solution carries a negative charge. An upward band bending is observed (fig. 7a). A change in voltage of the semiconductor can result into separation of both Fermi levels and thus band bending varies depending on the applied voltage. Applying a voltage/potential greater than the electrostatic potential shifts the Fermi level upwards causing the bands to bend downward since the band edge positions at the interface remain fixed (fig. 7b). The semiconductor acquires excess charge carriers. The potential where no charge depletion and therefore no band bending appear, the semiconductor is said to be at its flat-band potential (E_{fb}) (fig. 7c).



Fig. 7 A schematic illustration of semiconductor/electrolyte interface under applied potential, in case of n-type semiconductor, a) $E > E_{fb}$, b) $E = E_{fb}$, and c) $E < E_{fb}$.

Using the Mott-Schottky relationship the E_{fb} can be estimated by measuring the capacitance as a function of the applied voltage under depletion conditions.

$$\frac{1}{C_{SC}^2} = \frac{2}{e\varepsilon\varepsilon_o N} * (E - E_{fb} - \frac{\kappa T}{e})$$

Where C_{sc} is the capacitance of the space charge region, ε is the dielectric constant of semiconductor, ε_{o} is the permittivity of free space, N is the electron donor density in case of n-type semiconductor, E is the applied potential, E_{fb} is the flat-band potential, K is the Boltzmann constant, T is the absolute temperature and e is the electron charge. Flat-band potential (E_{fb}) can be estimated as the intercept from the linear region from the plot of $1/C^2$ versus the applied voltage E while donor density is the slope of the curve.

Electrochemical measurements were carried out in a conventional three-electrode cell. A saturated Ag/AgCl (3 M NaCl) was used as the reference electrode (+0.209 V vs NHE at pH =0), 0.1 M Na₂SO₄ (pH = 5.6) was used as an electrolyte, a Pt-wire as counter electrode and the film coated on the glass substrate fixed with copper adhesive tape as working electrode. The measurements were performed on a ZAHNER Zennium potentiostat and evaluated with Thales 4.12 software. The space charge capacitance of the films were measured in the dark at various

frequencies 1, 10 and 100 kHz in the potential range of -0.7 - 0.5 V at a step size range of 30 - 50mV. Flat-band potentials were estimated from Mott-Schottky plots.

3.7 Photocatalytic activity studies

3.7.1 Photocatalytic degradation test on powder

Photocatalytic degradation reaction on powder samples were carried out in a 100 ml slurry double wall glass photo-reactor with a water cooling system (figure 8a). A specific amount (0 - 3 mg/L) of the powder was dispersed into 50 ml of aqueous solution. Each pollutant was illuminated with light from a 150 Xenon lamp light source with a 320 nm cutoff filter for UV region and 340 nm for visible region. The light source was placed approximately 5 cm above of the reactor as shown on. Prior to irradiation, the sample was stirred in the dark for 30 min to reach adsorption equilibrium. Adequate amount of aliquots of the sample were withdrawn after illumination periodic interval of irradiation filtered with Sartorius Minisart syringe filters before analysis.

3.7.2 Photocatalytic degradation test on films

The photocatalytic activities were tested for the degradation of three compounds, the herbicide chloridazon, phenol and 4-chlorophenol, under UV region irradiation. Chemical structures of the pollutants are shown on fig. A1. The reaction was carried out in a cylindrical quartz photoreactor placed 6 cm in front of a 300 W Xenon lamp fitted with a 320 nm cut-off filter (fig. 8 b). Each film was pretreated under UV irradiation for 6 h using a 365 nm UV lamp to clean the surface. For each experiment 50 ml aqueous chloridazon (0.005 mM, pH 5), phenol (0.001 mM, pH 5.45) or 4-chlorophenol (0.001 mM, pH 5.53), respectively, were put into the photoreactor and the clean film was placed inside in a way that around 7.5 cm² of the film (about 5 mg catalyst) could
be illuminated. Experiments were carried out at room temperature and without changing the respective pH value. Prior to irradiation, the films immersed into the solution and magnetically stirred for 30 min in the dark to reach adsorption/desorption equilibrium. After this the films were irradiated for 4 h.



Fig. 8 A photo of the photo-reactors used in photocatalytic tests (**a**) Glass reactor for powder samples (**b**) Quartz reactor for film samples.

The extent of pollutants degradation was monitored using UV-vis spectrophotometer (VARIAN Carry 4000) by following the decrease in absorption maxima at 283 nm, 270 nm and 280 nm for chloridazon, phenol and 4-chlorophenol respectively (figs. A4, A6, A7). Phenol and 4-chlorophenol aliquots obtained from powder samples were further analyzed with LC-20AT Shimadzu high performance liquid chromatograph equipped with UV-vis detector. The column was a PRP C-18 5 μ m (2.1 μ m x 250 mm) and acetonitrile: water (40:60) as the mobile phase. To get the quantitative information, calibration curves made from standard solutions were used. Since optimization of reaction variables will maximize the degradation efficiency, reaction parameters like catalyst loading and initial pollutant concentration were optimized.

3.7.3 Photocatalytic mechanism test

Using terephthalic acid as a probe molecule, OH• radicals were detected by fluorescence technique. Terephthalic acid reacts with hydroxyl radicals to produce 2-hydroxyterephthalic acid whose fluorescence intensity is proportional to the amount of OH• produced in water [67]. 50 mg of the catalyst was suspended in 50 ml of alkaline 3 mM terephthalic acid and irradiated with light from a 150 W Xenon lamp fitted with a 320 nm cutoff filter. A sample was taken every 1 h and its fluorescence spectrum at 320 nm was measured. In order to identify the primary reactive oxygen species responsible for chloridazon photodegradation, scavenger tests were performed using 10 mM potassium iodide (KI), 10 mM isopropanol (IPA), and 10 mM benzoquinone (BQ) as scavengers for holes (h⁺), hydroxyl radical (OH•), and oxygen radical (O₂•), respectively [68, 69]. Each scavenger was introduced into the chloridazon solution and the experiment carried out in a manner similar to photodegradation experiment above.

4 Results and discussion

4.1 Photocatalytic degradation of the herbicide chloridazon on mesoporous titania/zirconia nanopowders

4.1.1 TEM and HRTEM measurements

The morphology of the synthesized samples was studied with TEM imaging and the results are presented in Fig. 9a,b for the most active EISA and sol-gel samples. For the EISA samples, rectangular nanoparticles of 20–30 nm length and 10–15 nm width with rounded edges were obtained, while for the sol-gel samples, most of the particles exhibit spherical shape with diameter of ca. 40 nm.

As shown in Fig. A2 (a,b), the pure $eTiO_2$ and $sTiO_2$ samples exhibit similar morphological features indicating that the shapes of the particles are not affected with the addition of Zr. HRTEM images of the TiZr samples are also presented in Fig. 9c,d to assess their crystallinity of the samples. Both samples are highly crystalline and the measured lattice spacing for the (011) anatase plane are 0.3560 and 0.3562 nm for eTiZr-0.14-450 and sTiZr0.05- 700 samples, respectively. These values are slightly higher than values reported in the reference database for pure TiO₂ (d = 0.3537 nm, ICSD 98-000-9855) and can be attributed to the incorporation of some Zr^{4+} ions, which possess larger ionic radii (72 pm) than the Ti⁴⁺ ions (61 pm) [70]. In order to check the Zr distribution in the TiO₂ matrix, we performed EDX mapping on the most active samples prepared by both routes as shown in (Fig. 10). The Zr is uniformly distributed on

analysis and found to be 0.11 and 0.051 for EISA and sol-gel sample, respectively. These ratios are very close to the mixing ratio of the two metals used during the synthesis.

both the EISA and sol-gel prepared samples. The ratio of Zr/Ti was estimated from the EDX



Fig. 9 TEM micrographs of nanopowders (a) eTiZr0.14-450 (d) sTiZr0.05-700; HRTEM micrographs of (c) eTiZr0.14-450, (d) sTiZr0.05-700 showing the lattice spacing of the anatase (011).



Fig. 10 EDX mapping on samples eTiZr0.14-450 (a) and sTiZr0.05-700 (b), proofing uniform distribution of Zr.

4.1.2 XRD results

Fig. 11a presents selected X-ray diffraction patterns of the most active EISA and sol-gel samples showing the influence of both the calcination temperatures and the Zr/Ti molar ratio. All composites prepared by the EISA method and treated at temperatures lower than 600 °C did not show any zirconium oxide diffraction reflexes up to loadings of 0.2 mol% Zr (Fig. 11a and 11). However, as the temperature increases beyond 600 °C, the reflexes belonging to monoclinic ZrO_2 (2 theta = 31.4° and 45.3°) start to develop simultaneously to peak broadening of the anatase diffraction on samples with (Fig. 11b, Table 1). This indicates phase separation and/or the formation of new ZrO₂ phase combined with a decreased crystal coarsening of TiO₂. It might also be deduced that the formed new phases act as capping layer which hinders the crystal growth of TiO₂. Additionally, according to Fu et al., such peak broadening can be related to low crystallinity of the samples as zirconia inhibits densification and crystallite growth by providing dissimilar boundaries [54]. Interestingly, similar peak broadening was also observed for sol-gel samples containing Zr loadings higher than 0.05 mol% being annealed at 700 °C (Fig. 11c and Table 1). Fig. A3 shows of EISA samples with 0.05 mol% Zr above 600 °C. There was no observable Zr reflexes an indication of a substitution process at low Zr loading. All the ESIA samples show no rutile (ISCD 98-000-9161) modification even at higher calcination temperature (750 °C) (Fig. 11b). The thermodynamic transformation of anatase to rutile phase begins at around 500 °C [35]. However, doping TiO₂ with cations of valence +4 and higher including Zr^{4+} is known to stabilize the anatase phase by creating Ti³⁺ species which hinders atom transport in the anatase structure [49, 71] (Table 1). For the sol-gel samples calcined at 700 °C (Fig. 11c), diffraction reflexes of the rutile phase appeared at Zr loadings up to 0.05 mol%, but higher amounts of Zr led to the formation of TiO_2/ZrO_2 oxide nanocomposites.



Fig. 11 XRD patterns of EISA and sol-gel samples showing the influence of the Zr content at fixed calcination temperatures of 450 and 700 $^{\circ}$ C (a, c), the effect of different calcination temperatures at Zr contents of 0.14 and 0.05 mol%, respectively (b,d).

EISA samples	FWHM	XRD crystal	Sol-gel samples	FWHM	XRD crystal
	(degrees)	size (nm)		(degrees)	size (nm)
eTiO ₂ -450	0.6998	12.7	sTiO ₂ -700	0.2832	37
eTiZr0.14-450	0.643	13.7	sTiZr0.05-500	1.1342	7.6
eTiZr0.14-500	0.283	35.7	sTiZr0.05-600	0.5339	17
eTiZr0.14-600	0.274	37.5	sTiZr0.05-650	0.5083	19
eTiZr0.14-700	0.592	15.2	sTiZr0.05-700	0.3038	33
eTiZr0.14-750	0.511	17.9	sTiZr0.05-750	0.2485	42
eTiZr0.1-450	0.6091	14.7	sTiZr0.01-700	0.2353	44.9
eTiZr0.05-450	0.6165	14.5	sTiZr0.1-700	0.3737	25.6
eTiZr0.2-450	0.5826	15.4	sTiZr0.2-700	0.6706	13.2

Table 1 FWHM in PXRDs and crystallite sizes obtained by use of the Scherrer equation

Note that for the sol-gel samples, the rutile phase also appeared at temperatures of 700 °C and above (Fig. 11d). This reveals the anatase to rutile phase transformation is still inhibited in the s-TiZr samples compared to the thermodynamic transition temperature. The similar phenomenon was also reported by Neppolian et al. [72]. The measured full width at half maximum (FWHM) for the most intense anatase reflex at 2 theta = 25.1° and the calculated crystal sizes with the Scherrer equation is shown in Table 1. At the optimum Zr loading, the calculated crystal sizes show a coarsening of the nanoparticles for EISA up to 600 °C but lower crystal sizes are observed at T \geq 700 °C. On the other hand, for the sol-gel prepared samples, the crystal size increases continuously with the calcination temperature. The variation of the Zr/Ti ratio at constant calcination temperature has no significant influence for the EISA samples, but for the sol-gel samples, smaller crystallites were obtained as the Zr/Ti ratio increases. This is probably due to the phase separation and ZrO₂ may act as capping layer to inhibit further growth of the TiO₂. For the most active samples, eTiZr0.14–450 and sTiZr0.05–700 crystallite sizes of 13.7 and 33 nm are obtained, respectively, which agrees very well with the TEM measurements.

4.1.3 XPS results

Fig. 12a and b shows XP spectra of the Ti 2p and Zr 3d peaks of sample eTiZr0.14-450. There was no peak shift due to the presence of Zr; the binding energy of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ was found to be 459.0 and 464.79 eV on both pure TiO₂ and the TiZr sample.

From the observed binding energies and the spin-orbit splitting ($\Delta = 5.58 \text{ eV}$), it is evident that also in the TiZr sample the oxidation state of Ti is +4 [73]. The binding energies of the Zr 3d_{5/2} and Zr 3d_{3/2} peaks were found to be 182.43 and 184.57 eV, respectively. These results are in agreement to literature, where binding energies of Ti 3p_{3/2} and Zr 3d_{5/2} were reported to be 459.0 and 182.0 eV, respectively [21]. The Zr/Ti ratio was calculated to 0.10 from the integrated areas under the Ti 2p and Zr 3d peaks, which is close to the mole ratios used in the synthesis and found by EDX as presented above. The O 1s peak consists of two peaks centered at 530.0 eV (lattice oxygen, M-O) and 531.5 eV (oxygenated carbon, C-O), the latter originating from the thermal decomposition of the templates.



Fig. 12 Core level XP spectra of (a) Ti 2p and (b) Zr 3d and (c) O 1s of sample eTiZr0.14 annealed at 450 °C.

4.1.4 UV-Vis diffuse reflectance spectroscopy results

To investigate the effect of Zr on the band structure of TiO_2 photocatalyst, diffuse reflectance UV-Vis absorption analysis was carried out. The spectra or the different samples are shown in fig. 13 (a,b). All samples were found to absorb at UV region, absorption ascribed to the band-band transition. The band gaps were for EISA samples were estimated to range between 3.05 - 3.2 eV (fig. 13a) while those for sol-gel ranged between 3.0 - 3.05 eV (fig. 13b). Zirconium is a wide band gap semiconductor (5.0 eV) compared to TiO₂ which has (3.2 or 3.0 eV) depending on the phase [41]. Addition of up to 0.14 mol% led to a slight blue-shift in the band gap and above this resulted to a red-shift in the band gap in EISA method. Interestingly, the decrease in the band gap occurred at lower Zr concentration in sol-gel method 0.01 mol%. Method of synthesis, type of precursors and calcination temperature has an effect on the band gap of the

catalysts. A blue-shift shows the effect of incorporation of Zr in the TiO_2 lattice but a red-shift could be as a result of formation of composite $ZrTiO_4$ [55].

Addition of urea and thiourea into sol-gel sample sTiZr0.05-700 changed the colour of the powder from white to bright yellow. The band gap of the composite shifted from 3.04 eV to 2.99 eV for thiourea, and to 2.94 eV for urea added samples. This confirms that nitrogen or nitrogen/sulphur was been doped into TiO₂ lattice. Replacement of oxygen on the TiO₂ lattice with N or S resulted into decrease the band gap. The results in this study are comparable to those reported by Cha et al, using hexadecyltremethylammonium as the nitrogen source they synthesized TiO₂-N/ZrO₂ composite with a band gap of 2.81 eV [74]. Similar red shifts were on nitrogen doped TiO₂/ZrO₂ observed by Yu et al and Wang et al [75, 76].



Fig. 13 Tauc plots transformed reflectance spectra (a) EISA (b) Sol-gel samples (c) urea/thiourea doped sol-gel samples.

4.1.5 Photoluminescence results

Photoluminescence (PL) emission spectra of samples $eTiO_2-450$, eTiZr0.14-450, $sTiO_2$, and sTiZr0.05-700 excited at 340 nm were recorded to study the recombination of photogenerated electron-hole pairs (Fig. 14a,b). It can be seen that a broad emission band from 475 to 575 nm was formed in all samples indicating the presence of defect states which serve as recombination

centers. Semiconductors exhibit complicated photoluminescence spectra due to different fluorescence signals caused by surface states and bulk defects among other factors. The PL emission intensities of both TiZr samples were lower than those of the pure TiO_2 counterparts. This suggests that introduction of Zr enhances the separation of the photogenerated charge carriers and, hence, contributes to the observed increase in the photoactivity. Previous reports on sol gel synthesized Zr-doped TiO_2 also showed similar PL trends [77].



Fig. 14 Photoluminescence tests on eTiZr0.14-450 (a) and sTiZr-0.05-700 (b), each incomparison to pure anatase TiO_2 .

4.1.6 Raman results

Raman spectroscopy was carried out for both EISA and sol-gel samples to supplement the XRD data and get more insight on the influence of Zr on the TiO₂ structure. From Fig. 15, the Raman bands observed at 143 cm⁻¹(E_g), 198 cm⁻¹(E_g), 396 cm⁻¹($B1_g$), 517 cm⁻¹ (A_{1g}), and 638 cm⁻¹ (E_g) correspond to the vibrational modes of the anatase phase [78]. Avery weak band of rutile at 322 cm⁻¹ [79] was observed for the sTiZr-x-700 samples. However, this vibrational band can also be assigned to the ZrO₂ according to Hirata et al. [80]. The other ZrO₂ vibrational bands only appear at higher Zr content since the Raman cross section of ZrO₂ lower than TiO₂ [78]. In

our study, Raman bands related to ZrO_2 only appear at higher Zr content; the identification becomes ambiguous at lower Zr amount as the Raman cross section of ZrO_2 is much lower than TiO₂ and due to overlap of rutile peaks [72, 81]. Furthermore, the eTiZr-x-450 samples only display Raman bands related to anatase suggesting the successful integration of the Zr atoms into the TiO₂ structure. These observations on the Raman spectra are consistent with the XRD data.



Fig. 15 Raman bands of EISA (a) and sol-gel (b) synthesized TiZr samples showing main bands assigned to anatase.

4.1.7 N₂ adsorption results

Fig. 16 represents nitrogen adsorption-desorption isotherms for the different samples. All samples show type IV isotherms which are related to the presence of mesopores formed between interconnected particles according to the IUPAC classifications [60, 82]. For EISA samples (Fig. 16a), there was a gradual increase in surface area with increasing Zr amount up to 0.05 mol% which was followed by decrease in surface area above this value. It has been suggested that, presence of Zr^{4+} which has larger ionic radius than Ti⁴⁺ inhibits densification which leads to less crystal growth by providing dissimilar boundaries [54].



Fig. 16 Nitrogen adsorption desorption isotherms for composites prepared by EISA (a,b) and sol gel method (c,d): influence of Zr /Ti ratio at fixed calcination temperature (a,c), effect of calcinations temperatures (b,d).

Note that the type of hysteresis changes from type IV to II isotherm at higher Zr content indicating the formation of larger pores (macropores) which supports that higher amounts of Zr inhibit densification leading to wider interparticle voids. However, for the sol-gel samples, the BET area increases with Zr content indicating the formation of ZrO_2 is accompanied by additional adsorption sites or favorable interaction with the adsorbate (Fig. 16c).

In general, as the calcination temperature increases, the pore sizes also increase as result of progressed removal of the templating polymer or a merging of smaller pores. This suggests that the interparticle mesopores partly survive the calcination process (Table 2). On the other hand, there was no observable trend in the pore size with variation of the amount of Zr. In general,

high-temperature treatment in sol-gel synthesis resulted in samples with lower surface area than those prepared by EISA method (due to larger crystallite sizes).

EISA	BET-specific	Pore size	Sol-gel	BET-specific	Pore size
	surface area	(nm)		surface area	(nm)
	$(\mathbf{m}^2/\mathbf{g})$			$(\mathbf{m}^2/\mathbf{g})$	
eTiO ₂ -450	85	15.9	sTiO ₂ -700	23	15.4
eTiZr0.14-450	90	12.8	sTiZr0.05-500	97	6.5
eTiZr0.14-500	86.6	6.72	sTiZr0.05-600	75	8.5
eTiZr0.14-600	46.3	11.1	sTiZr0.05-650	58	13.7
eTiZr0.14-700	49.6	16.6	sTiZr0.05-700	33	18.3
eTiZr0.14-750	42.7	16.8	sTiZr0.05-750	27	18.9
eTiZr0.1-450	101	14.0	sTiZr0.01-700	23	13.0
eTiZr0.05-450	90	12.8	sTiZr0.1-700	43	16.2
eTiZr0.2-450	87	12.1	sTiZr0.2-700	53	12

Table 2 BET surface area and average pore size from N₂ gas adsorption experiments

4.1.8 Photocatalytic activity tests under UV and Visible light

To determine; the best method of synthesis, optimum calcination temperature and amount of Zr, chloridazon was used as the model pollutant. After getting the optimum parameters, the pure and modified TiO_2 samples with the highest activity for degradation of chloridazon were used in degradation of phenol and 4-chlorophenol. The tests were carried out either under UV or visible light illumination using cut-filters.

4.1.8.1 Photocatalytic degradation of Chloridazon

Photodegradation activity of the composites towards degradation of aqueous solutions of the herbicide chloridazon under Xenon lamp illumination was determined from the absorbance peak

at 283 nm on a UV-vis spectrophotometer (Fig. A4). Both chloridazon and its metabolites absorb in the UV region with overlapping absorption maxima (around 280 and 230 nm (Fig. A5). Thus, it was difficult to differentiate them in the aqueous solution using UV spectroscopy.

4.1.8.1.1 Degradation of chloridazon under UV light

4.1.8.1.1.2 Effect of catalyst loading

Photocatalytic degradation of chloridazon against amount of catalyst is shown on fig. 17. From the results it is clear that the photocatalytic activity increased with increase in the amount of catalyst loading and reaches an optimum value above which the activity began to decrease. The initial increase in photocatalytic activity is a result of the increase in the number of illuminated particles, hence higher production of reactive electron-hole pairs. Nevertheless, there is a limit of the catalyst loading corresponding to the total absorption of the photons coming from the light source. For this case, the optimum value was 3 g/L. At high catalyst loading turbidity of the mixture prevents further penetration of light in the reactor lowering the performance of the catalyst.



Fig. 17 Influence of catalyst loading on the degradation of chloridazon.

4.1.8.1.1.3 Effect of amount of zirconium and calcination temperature

Fig. 18a–d shows representative data for changes in concentration of chloridazon with respect to the initial concentration (C/C_0). As expected, the control experiment containing only chloridazon and no photocatalyst showed only negligible degradation after 6 h of irradiation suggesting no photolysis (self-degradation).



Fig. 18 Plots of degradation of chloridazon on EISA (a,b) and sol-gel samples (c,d). The Zr content (a,c) and the calcination temperatures (b,d) were varied.

Photocatalytic activity of the samples increased with increasing calcination temperature up to the optimum temperatures was 450 °C for the EISA samples and 700 °C for the sol-gel route, and then decreased with further increase in temperature. The high-temperature decrease can be interpreted as a result of crystal growth, and hence, a decrease in BET specific surface area (Table 2). As stated by Shao et al., [82], photocatalytic activity does not depend on specific

surface area alone but also on crystallinity and morphology of the catalyst. This is evident from samples eTiZr0.14-350 and sTiZr0.05-500 which display the highest surface areas of 175 and 97 m²/g but had the lowest activities due to poor crystallinity resulting from low calcination temperature. EISA-prepared nanopowders showed higher activity than eTiO₂ and commercial Evonik P25. This could be attributed to the higher surface area and reduced electron-hole recombination compared to that of TiO₂ and P25 caused by the presence of Zr. From powder XRD measurements, the EISA samples consist exclusively of the anatase phase which is photocatalytically more active than the rutile phase. The optimum activity was obtained with the sample containing 0.14 mol% Zr calcined at 450 °C. A further increase in Zr content resulted in decrease in activity which was a result of poor anatase crystallinity and decrease in surface area. Samples synthesized by sol-gel exhibited lower activities than the EISA samples and commercial P25, with the highest activity recorded for sample sTiZr0.05-700. There are various reasons contributed for the low activity (i) large crystal size leading to lower BET surface area (Table 2), (ii) different crystal phases (anatase vs. rutile) and phase separation leading to the formation of ZrO_2 as demonstrated by the XRD results (Table 1). ZrO_2 is a wide-band semiconductor (ca. 5.2) eV) being only activated in the deep UV. Thus, it will not participate in the light absorption process. The presence of different phases may facilitate charge carrier recombination at grain boundaries. However, the low activity of P25 and sample sTiZr0.01-700 which had both anatase (major) and rutile phase compared to eTiZr0.05-450 with pure anatase phase supports the suggestion by Ohtani et al. that there is no synergetic effect between anatase and rutile on the photoactivity P25 [84]. Additionally, the different molecular weight of the polymers and type of zirconium precursor used in the synthesis could also have contributed to the differences in the photoactivity [59].

Further increase in calcination temperature to 750 °C led to better crystallinity but low photoactivity due to more pronounced decrease in surface area and more anatase-to-rutile phase transformation.

4.1.8.1.1 Degradation chloridazon under visible light

Sol-gel sample sTiZr0.05-700 doped with nitrogen or nitrogen and sulphur was tested for degradation of aqueous chloridazon under visible light. The results are as shown on fig. 19 a,b. Degradation of chloridazon under visible light in absence of photocatalyst was negligible. As expected, the undoped sTiZr0.05-700 recorded the lowest activity incomparison with the doped samples. The low activity is as a result of the wide band gap (3.04 eV) as depicted on the UV-DRS results. The absorption band of the undoped sample is more into UV region compared to that of doped samples. An increase in the amount of thiourea from 2 to 10 % showed a gradual increase in activity but 15 % thiourea resulted in decrease in activity. For urea 5% showed better activity compared to 2 % and 10 %. Excess dopant ions can act as recombination centers hence decreasing the activity of the catalyst. Although there was a small shift of the band gap towards the visible region, the photocatalytic activity under visible light was very low compared to the activity under UV light. Could be presence of nitrogen or sulphur ions in the TiO₂ lattice caused structural defects which act as recombination centers of charge carriers or the shift was not large enough to activate the catalyst under visible illumination. Also, the composite formed after doping could be unstable hence poor activity. Mrowetz et al argued that the narrowing of the band gap due to nitrogen doping is largely due to creation of occupied stated above the valence band of TiO₂ and the oxidizing species generated at the interface after promotion of such states by means of visible irradiation are thermodynamically or kinetically unable to oxidize some organic pollutants [85].



Fig. 19 Plots of degradation of chloridazon on NS (a) and (b) N doped sTiZr0.05-700.

4.1.8.2 Photocatalytic degradation of phenol and 4-chlorophenol

The widespread occurrence of phenols in wastewater and associated environmental hazards has heightened concern over public health. Phenols and their derivatives are well known for their biorecalcitrant (resistance to biodegradation) and acute toxicity. Fig. 20 (a,b) shows photocatalytic degradation results for phenol and 4-chlorophenol on sample $eTiO_2$ -450 and eTiZr0.14-450 after 4 h illumination with a Xenon lamp source. In the absence of photocatalyst, the photodegradation was negligible. Zirconium modified powder exhibited better degradation performance than both pure TiO₂ and commercial Evonik P25. The enhanced activity is attributed by the increase in surface area and decrease in charge recombination due to presence of Zr in TiO₂ lattice. These results are consistent with those observed for degradation of chloridazon. Venkatachalam et al., [58] suggested higher photocatalytic degradation of 4chlorophenol on Zr doped TiO₂ is a result of enhanced adsorption of the molecule on the catalyst site due to creation of more Lewis acidic sites and also the high surface area . Same results were observed by Macmanamon et al., [86] on degradation of phenol.



Fig. 20 Plots of degradation of phenol (a) and 4-chlorophenol (b) on EISA samples under Xenon lamp illumination.

HPLC analysis results for degradation of phenol and 4-chlorophenol on nanopowder catalysts are shown on fig. 21 (a,d). To confirm the degradation of phenol, 4-chlorophenol and their intermediates, we tried to identify some of the common intermediates; benzoquinone (BQ), hydroquinone (HQ), and catechol (C) [87, 88]. Using acetonitrile: water (40:60) solvent system, phenol peak eluted at 3.6 min while 4-chlorophenol appeared at 7.5 min. The phenol (fig. 21a) and 4-chlorophenol (fig. 21b) peak decreases with increase in irradiation time, a similar trend observed from the UV analysis results. An expansion of the chromatogram shows formation of some intermediates during the degradation of both phenol (fig. 21c) and 4-chlorophenol (fig. 21d). But it was not easy to identify all the intermediates from the chromatograph and their degradation trend was not consistent. This could be as a result of our solvent system or the column (PRP C-18.5 μ m) used in this study. It has also been reported that HPLC alone as a detection method for the intermediates is not enough due to the need of calibration standards yet many intermediates are unknown and the fact that some intermediates have the same retention time [88]



Fig. 21 HPLC chromatogram of (a), (c) Phenol (b), (d) 4-chlorophenol on eTiZr0.14-450.

4.1.8.3 Results for photocatalytic mechanism test

In order to elucidate the mechanism of the degradation and the reactive species involved in the process, hydroxylation of terephthalic acid and scavenger tests were performed (Fig.22a– d). The enhanced activity of the composites was determined by the amount of hydroxyl radicals produced, which is one of the active species in photocatalytic degradation reactions. For both syntheses, the intensity of the OH• radical peak increased with increasing amount of Zr up to the optimum value and then decreases with further addition of Zr. Sample eTiZr0.14-450 produced more OH• than EISA samples with different Zr loading or TiO₂ and P25 (Fig. 22a). Among the sol gel samples, sTiZr0.05-700 has the highest fluorescence intensity (Fig. 22b), but slightly lower than that of eTiZr0.14-450. Thus, the photocatalytic most active samples show the highest

OH• radical formation, confirming that OH• radicals are involved in the photocatalytic degradation of chloridazon.



Fig. 22 Hydroxylation test of terephthalic acid: EISA samples with different amount of Zr calcined at 450 $^{\circ}$ C (a) and sol-gel samples with varying Zr content calcined at 700 $^{\circ}$ C (b). Scavenger tests with eTiZr0.14-450 (c) and sTiZr-0.05-700 (d).

In the presence of the OH• scavenger (IPA), little or no degradation of chloridazon was observed (Fig. 22c,d). On the other hand, addition of h⁺ scavenger (KI) resulted in only 3% degradation after 6 h of UV irradiation. This implies the primary oxidizing agent in the photodegradation of chloridazon is mainly OH• radical and the role of photo-induced holes is not significant. However, tests for superoxide radicals using BQ or ascorbic acid were not successful, as result of chemical reactions between the scavenger and chloridazon dark yellow solutions were formed.

4.1.9 Conclusion

The degradation of chloridazon on the surface of UV- irradiated Zr-loaded TiO₂ was investigated. Nanopowders prepared by the EISA route were found to be more active than TiO₂ and Evonik P25. The anatase modification is the sole composition of the EISA samples without any other impurities for calcination temperatures up to 750 °C. The optimum value of zirconium was found to be 0.14 mol% and the highest photodegradation activity towards chloridazon was observed after calcination at 450 °C. However, for nanopowders prepared by the sol-gel route, the formation of composites of anatase and rutile phase TiO₂ and ZrO₂ is found. The highest activity was observed with the Zr/Ti composition of 0.05 mol% at 700 °C; the samples show lower activity than the EISA-prepared ones due to the recombination at grain boundaries of the different polymorphs and lower surface area. For both preparation methods, the calcination temperature significantly affects the photoactivity. Higher temperatures (T \geq 700 °C) lead to phase separation forming ZrO₂ which are photocatalytically less active.

Modification of TiO_2 catalyst with zirconium shows enhanced photocatalytic degradation activity on other organic compounds rather than chloridazon. This is clear from the high photocatalytic activity of sample eTiZr0.14-450 towards degradation of phenol and 4chlorophenol as compared to pure eTiO₂-450 sample.

4.2 Zirconium doped mesoporous TiO₂ multilayer thin films: Influence of the zirconium content on the photodegradation of organic pollutants

4.2.1 SEM and HRTEM results

Mesostructural changes due to addition of Zr, calcination temperatures, and number of deposited layers are illustrated by the SEM micrographs presented in Fig 23a-e. The obtained thin films were mesoporous, optically transparent and with majority of the particles are spherical in shape. The mesoporosity was less ordered especially for films calcined at high temperatures. For films calcined at 500 °C addition of some Zr (Zr/Ti = 0.05) in Fig. 23b resulted in comparison to the pure TiO₂ film (Fig. 23a) to a decrease in the particle size, but also to a more pronounced distortion of the mesostructure.

The thickness of films depends on many factors; method of synthesis, type of substrate, ratio of the reagents, dip-coating withdrawal rate, number of coatings, aging parameters and calcination temperature. A withdrawal rate of 1 mm/s applied in this study has been reported to produce films with uniform thickness. As determined from the cross-sectional SEM image the thickness of three layer pure TiO₂ film was 645 nm in good agreement to earlier reports [12] while that of a three layer Zr modified mesoporous TiZr0.05-500 film was about 417 nm showing a decrease of 35%. A single layer of TiZr0.05-500 film had a thickness of 340 nm (Fig. 23e and Table 1), thus the increase goes not linear with the number of coatings in contrast to earlier studies on pure TiO₂ [32]. Studies on Zr doped TiO₂ single layer films carried out by Juma et al. and Oluwabi et al. reported film thickness of 200-330 nm [21, 22].

The thickness of the films not only depended on the number of coating cycles, but also on the calcination temperature and the amount of Zr added during the synthesis. An increase in calcination temperature resulted in decrease in the film thickness. As the temperature increases

the mesoporosity is lost hence leading to a film contraction. On the other hand, the increase in Zr content led to a decrease in film thickness due to the formation of a more viscous sol which results more compact films (Table 2).



Fig. 23 SEM images of pristine (A) TiO_2 film and the film fTiZr0.05-500 both calcined at 500 °C. Further SEM images show the films fTiZr0.05-450 (C) and fTiZr0.05-550 (D). The cross-sectional image of a three layer fTiZr0.05-500 film is shown in (E) and (F) shows a HRTEM image of flakes peeled-off from fTiZr0.05-500.

The morphology and structure of the composites were studied using HRTEM. HRTEM images (Fig. 23f) from film scratches mounted on Cu grids exhibit average TiO₂ crystallite sizes of 13

nm for the sample film fTiZr0.05-500. In agreement with our earlier work on powdered samples [21] flakes taken from the film fTiZr0.05-500 exhibit average particle sizes of 13 nm in HRTEM images (Fig. 23f); moreover the particles are highly crystalline. From site specific EDX analysis the Zr: Ti atomic ratios vary between 0.06 and 0.09 which is slightly higher than in the mixed precursor sol (0.05).

4.2.2 X-Ray diffraction and N₂ adsorption results

X-ray diffractograms of TiO₂ and Zr modified TiO₂ thin films calcined at 350 - 550 °C are shown in Fig. 24 a-d. The diffraction reflexes become sharper with increasing in calcination temperature (Fig. 24b), an indication of enhanced crystallinity. On the other hand, an increase in concentration of Zr led to a slight decrease in crystallinity (Fig. 24a). Anatase phase dominated in all samples (Reference ICDD: 98.015.4602). The absence of the rutile phase even at 550 °C indicates the stabilization of anatase phase by Zr [21, 49, 89, 90]. There is no additional impurity phase below Zr/Ti rations of 0.10 suggesting the lattice substitution of Ti⁴⁺ ions by Zr⁴⁺ ions in these samples. Thus, the Zr^{4+} ions act as dopant. However, if the Zr/Ti ratio was raised up to 0.18 a very weak diffraction reflex at $2\theta = 31.4^{\circ}$ and 45.5° were observed, which can be related to monoclinic zirconium oxide (ZrO₂, ICSD 98-008-0043) [90, 91]. Interestingly, the formation ZrO_2 depends not only on the Zr/Ti ratio, but also on the number of layers (Fig. 24c). As the number of layers increases (> 3 layers) the formation of ZrO₂ is more pronounced due to the repeated steps of intermediate thermal treatment. However, it seems that independent on classical sol-gel route or EISA route and independent on the mesoporosity of the samples the anatase TiO₂ crystal lattice can tolerate only a maximum of about 10 % of the slightly larger Zr^{4+} ions. Excess Zr^{4+} ions form with the amorphous TiO₂ phase, which is present up to 400 °C, in the oxygen-rich atmosphere the mixed metal oxide ZrTiO₄ [56, 90] or, as in our case, a TiO₂/ZrO₂ [89, 92] composite in the oxygen-rich atmosphere. Study carried out by Wang et al reported that $ZrTiO_4$ is formed depending on the concentration of the Zr^{4+} and the calcination temperature [90]. They observed a weak reflex of $ZrTiO_4$ at 2 theta = 30.3 ° for TiO₂ doped with 20 molar percentage of Zr calcined at 800 °C while for 40 molar percentage $ZrTiO_4$ was formed at 500 °C. Unlike in our results where a reflex at 31.4 ° and 45.5 ° were observed, the XRD patterns in this study do not contain a reflex at 45.5 ° which according to reference ICSD 98-008-0043 belongs to ZrO_2 , thus confirming the presence of $ZrTiO_4$ (fig. 25a,b). Gnatyuk et al reported formation of a titanate solid together with anatase which caused the anatase reflex (101) to shift to lower 2theta angles due to the ionic radius difference in Zr^{4+} and Ti⁴⁺ [56].

The inset in Fig 24a shows a shift of the anatase (101) diffraction line at around $2\theta = 25^{\circ}$ to lower 2 θ angles with addition of Zr. If the Zr⁴⁺ ions (ionic radius: 0.072 nm) substitute the somewhat smaller Ti⁴⁺ ions (ionic radius: 0.065 nm) in the anatase lattice, this can causes distortion of the crystal parameters, which becomes obvious by an increased d-spacing (Table 1). Due to the incorporation of the Zr⁴⁺ ions the distance between the crystal planes increases slightly [22, 57, 90, 93].

The effects of the amount of Zr incorporated on the crystallite sizes and surface area of the mesoporous films are demonstrated for films calcined at 500 °C (Table 3). The crystallite sizes were calculated from the widths of the XRD reflexes at $2\theta \approx 25^{\circ}$ and $2\theta \approx 48^{\circ}$ using the Scherrer equation [94]. In general the crystallite sizes range between 15 - 21 nm whereas they as expected increase with the calcination temperature. It is remarkable that the crystallite sizes of films calcined at 500 °C stay in the 15 nm range as long as the Zr/Ti ratio does not exceed 0.1; i.e. as long as lattice substitution takes place. For higher Zr/Ti ratios, i.e. when the nanocomposites with ZrO₂ crystallites grow, the crystallite sizes increase to about 20 nm.



Fig. 24 GI-XRD diffractograms of thin films showing effects of the Zr content (A), inset shows the shift of (101) peak, the calcination temperature (B), the number of layers for films with Zr/Ti = 0.05, intermediate heat treatment at 350°C and final calcination at 500 °C (C), and the temperature of the intermediate heat treatment in the preparation of 3-layer films with Zr/Ti = 0.05 (D).



Fig. 25 A series of XRD patterns of samples calcined at A) 500 °C and B) 1000 °C [90].

Table 3. Lattice parameters, crystal sizes obtained from analyzing XRD peak widths with the Scherrer equation, and BET surface areas from nitrogen physisorption results for differently prepared 3-layer films. For the crystallite sizes error ranges of about ± 2 nm and for the BET surface areas error ranges of about $\pm 5 \text{ m}^2/\text{m}^2$ must be considered.

Sample	(101) 20	d-spacing	Crystallite	S _{BET}	Thickness
(3 layers)	(°)	(Å)	size (nm)	(m^2/m^2)	(nm)
TiO ₂ -500	25.25	3.525	14.80	48	645
TiZr0.01-500	25.20	3.531	15.01	50	-
TiZr0.05-500	25.19	3.532	14.57	72	417
TiZr0.10-500	25.17	3.535	14.15	102	420
TiZr0.14-500	25.16	3.537	20.91	113	-
TiZr0.18-500	25.15	3.538	19.89	134	-
TiZr0.05-350	25.23	3.527	14.77	169	-
TiZr0.05-400	25.21	3.528	14.91	142	587
TiZr0.05-450	25.20	3.532	16.24	89	-
TiZr0.05-550	25.19	3.531	31.27	37	272

The BET surface areas were in the range of $37 - 169 \text{ m}^2/\text{m}^2$ depending on the Zr/Ti ratio and the calcination temperature. Since the surface areas obtained from N₂ adsorption are related to the geometric area of the films, the high values indicate a high mesoporosity. However, no ordering of the mesopores is visible in the SEM images (Fig. 23) and also no XRD diffraction peaks at small angles (below $2\theta < 3^\circ$) could be detected. The surface areas decrease strongly with the calcination temperature due to the crystal growth and loss of mesoporosity as the film structure collapse [32, 39]. At constant calcination temperature (500 °C) the BET surface area increases with the Zr loading. As long as the Zr level is below 10%, substitution of Ti⁴⁺ by the Zr⁴⁺ at the lattice positions in the anatase probably leads to the formation of some lattice defects and the increase in BET area remains moderate. However, for the films TiZr0.14-500 and TiZr0.18-500, in which nanocomposites of Zr-doped anatase and ZrO₂ are present, the increase in surface area is quite significant. This might indicate that the newly formed ZrO₂ phase is porous as well, and the mesoporosity does not only result from interstitial voids between the crystallites. The film

TiZr0.10-500 shows intermediate behavior, with small crystallite size but already increased surface area. This is probably due to the start of some ZrO_2 formation which stays below the detection limit of the XRD.

4.2.3 XPS analysis results

By X-ray photoelectron spectroscopy a slight shift in the binding energy of Ti 2p electrons from 458.06 eV to 458.27eV for $2p_{3/2}$ and 463.78 eV to 464.01 eV for $2p_{1/2}$ was observed for sample fTiZr0.05-500 compared to pure TiO₂ (Fig. 26a). Studies carried out by Wang et al. [90] and Gnatyuk et al.[56] relate this phenomenon to the presence of the more electronegative Zr⁴⁺ ion in the TiO₂ lattice which reduces the electron density around the Ti⁴⁺ ions hence increasing the binding energy. Fig. 26b shows the XP spectra for Zr 3d, 181.37 eV and 183.74 eV represent the Zr 3d_{5/2} and Zr 3d_{3/2} peaks, respectively. These results are in good agreement with reported data for Zr⁴⁺ ion [21, 55, 89].



Fig. 26 XP spectra of Ti 2p (A) Zr 3d (B) of films f-TiO₂-500 and f-TiZr0.05-500;(C) C 1s of f-TiO₂-500 before and after UV illumination.

The effect of UV illumination on the films was done by analysis of the XP spectra of carbon before and after illumination. The results fig. 26c shows a significant decrease of the carbon peak after the irradiation. This explains the reason behind the poor photocatalytic performance of the films before the UV treatment due to the carbon contamination covering the active sites on the surface of the films.

4.3.4 UV-Vis diffuse reflectance and photoluminescence results

Fig. 27a shows the influence of Zr incorporation on the optical band gaps of the TiO₂ film. Notably, addition of up to Zr/Ti = 0.10 led to a slight continuous blue-shift in the indirect band gap absorption onset of TiO₂, resulting in a band gap widening from 3.29 eV to 3.35 eV as calculated from Tauc plots. In contrast, a further increase in the Zr/Ti resulted in a red-shift. This is probably due to the formation of the ZrTiO₄ at high levels of Zr doping. Gao et al., [55] reported a similar red-shift for TiO₂ powder by adding a much higher content of Zr (35%) but suggested this shift to the presence of ZrTiO₄. Maybe also in that case, additional ZrO₂ was formed, since the X-ray diffractograms shown in that work look closer to those in our study (Fig. 2) than in a recent paper by Polliotto et al. on ZrTiO₄ [95]. In that work, Polliotto et al. determined a band gap of 3.65 eV for ZrTiO₄, leading to an optical blue shift with respect to TiO₂.

Charge recombination is one of the limitations for practical application of TiO₂ catalyst. Several strategies have been applied to improve the charge transport properties of TiO₂ including introduction of both metal and non-metal ions into TiO₂ lattice [4]. Photoluminescence (PL) analysis was carried out to study the influence of Zr doping in the TiO₂ thin films on the recombination of photogenerated species electrons (fig 27b). Comparing pure TiO₂ films and films with a low Zr doping level (Zr/Ti = 0.05) the luminescence intensity drastically decreases due to presence of Zr. At such low doping levels, the more electronegative Zr^{4+} ions may act as electron traps during the band gap excitation of TiO₂. Thus, a better charge distribution and

stabilization seems to occur documenting the favoring doping. This suggestion is also supported by the observed slight binding energy shift of the Ti 2p electrons (Fig. 27a). Higher doping levels of $Zr/Ti \ge 0.10$, however, lead again to an increase of the photoluminescence intensity. These films contain ZrO_2 as impurity phase forming grain boundaries for recombination with the TiO₂ crystallites. Furthermore, structural defects might be introduced in the crystal lattice due to the progressive substitution of Ti⁴⁺ ions by Zr^{4+} ions. Such structural defects can act as mid-gap states and increase, thus, the electron-hole recombination [89, 93].



Fig. 27 Tauc plots (C) and photoluminescence (D) of films, which were calcined at 500 °C, with varied amount of Zr.

4.3.5 Mott-Schottky measurements

Mott-Schottky analysis of EIS spectra for the most active film (fTiZr0.05-500) and pure TiO₂ film are shown on fig. 28 a,b. The positive slopes in the region where the $1/C^2$ vary linearly with the potential indicate that both samples exhibit n- type semiconductivity. The flat band potentials (E_{fb}) were estimated from the linear part of the curve. Using the Mott-Shottky equation the E_{fb} for fTiO₂-500 and fTiZr0.05-500 were found to be -0.02 V and -0.11 V versus NHE respectively. Addition of Zr 0.05 mole% led to a slight negative shift of TiO₂ E_{fb}. This behavior is related to

grain boundaries generated due to formation of TiO_2/ZrO_2 ; their interface produces defects in the TiO_2 lattice hence the shift of E_{fb} of TiO_2 to more negative values. The E_{fb} values in this study are comparable to those reported by Imahori et al -0.08 V for TiO_2 and -0.19 V for Ti-Zr versus NHE [96].



Fig. 28 Mott-Schottky plots of fTiZr0.05-500 and fTiO₂-500 at 100 Hz in 0.1 M Na₂SO₄ (pH = 5.6) versus NHE reference electrode.

4.3.6 Photocatalytic degradation test under UV light

Photocatalytic tests towards the degradation of organic pollutants were performed using chloridazon, phenol and 4-chlorophenol. For all the three molecules photolysis tests proved the stability of the molecules under Xenon lamp irradiation in absence of catalyst.

4.3.6.1 Photocatalytic degradation of chloridazon

The effect of Zr modification on the photocatalytic activity of TiO_2 thin films was investigated by using 0.005 mM chloridazon as the organic pollutant (Fig. 29a). The TiZr0.05-500 film degraded about 99 % of the pollutant while pure TiO_2 films only removed 69 % of the chloridazon in 4 h. This is related to a better charge separation, the increase in surface area as well as stabilization of anatase phase as illustrated on photoluminescence, BET and XRD results. Although still under debate some studies have suggested that the increase of the band gap may contribute to the improved activity of Zr doped TiO_2 , due to a shift of the conduction band to a slightly more negative potential [93]. This was concluded from a small negative shift of the flat band potentials for Zr doped TiO_2 as shown on the Mott-Schottky plots above and reported in other studies [96, 97].

While films with Zr/Ti ratios up to 0.05 showed an increase in activity, higher Zr amounts caused a decreasing activity. The increasing amounts of structural defects as well as grain boundaries with the ZrO₂, which starts to grow, act as recombination centers for the photogenerated charge carriers hence decreasing the activity. As ZrO₂ is a wide band gap oxide semiconductor (5.0 eV) it will only be excited in the deep UV region (\leq 250 nm) which is not accessible with the used light source. Additionally, the injection of photoexcited charge carriers from TiO₂ to ZrO₂ is not possible due to the mismatch of the band positions. Thus, ZrO₂ either blocks the active centers or creates grain boundaries for charge recombination, both effects being detrimental to the photoactivity.

The influence of the calcination temperature on the photocatalytic activity of the catalyst is evident on Fig. 29b. The rate of degradation improved gradually with increase in calcination temperature from 350 °C to 500 °C. This trend is related to the transformation of amorphous to crystalline TiO₂ anatase phase (Fig. 24b). However, a further increase in temperature (> 500 °C) led to an increase in crystal size and a complete collapse of the mesostructure (as shown on SEM images), which may reduce the accessibility of the active sites and the interactions between the catalyst and chloridazon molecules. Temperatures beyond 550 °C could not be tested due to the instability of the microscopic glass supports. However, previous studies showed that higher temperatures resulted in the diffusion of sodium ions into the films, decreasing their

photoactivity even further [98, 99]. Interestingly, the films fTiZr0.05-400 and fTiZr0.05-450 showed some ordered mesoporosity, but their activity was poor compared to fTiZr0.05-500 and fTiZr0.05-550 which possess only disordered mesoporosity. The results suggest that mesoporosity and crystallinity are more key factors for the photocatalytic performance than the order of the mesopores [100].



Fig. 29 Photocatalytic activity of fTiZr0.05-500 films in dependence on the Zr content (A), the calcination temperature (B).

4.3.6.1.1 Effect of number of layers on degradation

The correlation between the number of layers and the photocatalytic activity is shown in Fig. 30. The optimum number of coatings in this study was found to be 3, addition of more layers led to a slight decrease in activity. As the number of coatings increases, the amount of the catalyst material deposited on the substrate increases, leading to the generation of more holes which are responsible for the oxidation of the pollutants. As the thickness of the film increases, the penetration of light and pollutant molecules to the bulk of the film decreases. Therefore, the degradation can only occur on the outer/exposed surface of the film. This could be the reason for the slight decrease in degradation on films with four and five layers. Moreover, for multilayer films the formation of ZrO_2 is pronounced as shown in the XRD patterns (Fig. 24c).

Furthermore, the intermediate (consolidation) heat treatment at 25, 100 or 350 °C between the coating steps of the multi-layer films showed in general no significant effect on the photocatalytic activity, the repeated tempering of the four and five layer films might cause the formation of too much grain boundaries acting as recombination centers. Photogenerated holes produced in the bulk can easily recombine with electrons due to the longer diffusion length required to reach the surface of the film to interact with the pollutant.



Fig. 30 Effect of the number of layers on degradation of chloridazon.

4.3.6.2 Degradation of phenol and 4-chlorophenol

We have extended the photocatalytic activity tests towards the degradation of phenol (Fig 31a) and 4-chlorophenol (Fig. 31b) for the pure TiO₂ film (fTiO₂-500) and the most active Zr doped film fTiZr0.05-500. The decreases in absorbance of the three pollutants with time are depicted on Fig. A4, Fig. A6 and Fig. A7. The Zr doped film showed in all cases the superior photocatalytic activity. For phenol the rate of degradation was lowest, indicating the high stability of the aromatic ring. Prior to illumination adsorption-desorption tests on the fTiZr0.05-500 film were performed in the dark for 30 minutes. During this time the absorbance (at the absorption maxima) of the solutions of the different pollutants decreased in the order: phenol (16%) < 4-chlorophenol (30%) < chloridazon (34%). This decrease is due to the adsorption of the pollutants

on the film surface. The different degrees of adsorption, which might also be a reason for the varying rates of degradation under illumination, are closely related to the pH of the solution, the isoelectric point (surface charge) of the oxide and the relative valence and conduction band positions following Nernst's law [101]. Fu et al. reported the isoelectric point of Zr modified TiO_2 catalyst to be 6.4 [54]. Thus, at pH values below 6.4 the films will be positively charged while at pH values above 6.4 they will be negatively charged. For phenol (pK_a 9.99) and 4-chlorophenol (pK_a 9.41) [102] at solution pH values 5.5 and 5.6, respectively, the film surface as well as the pollutant surface will be positively charged which might hinder the adsorption of the two molecules due to electrostatic repulsion. On the other hand, the adsorption chloridazon (pK_a 3.38) [103] at pH 5 is favorable at the positively charged surface since chloridazon possesses net negative charge, resulting in better photocatalytic degradation.



Fig. 31 Plots of degradation of phenol (a) and 4-chlorophenol (b) on $eTiO_2$ -500 and fTiZr0.05-500 under Xenon lamp illumination.

4.3.6.3 Photocatalytic mechanism results

The amount of hydroxyl radicals formed was determined qualitatively by fluorescence spectroscopy using 50 ml of alkaline 0.3 mM terephthalic acid. The fluorescence intensity at ca. 430 nm (Fig. 32a) resulted from the formation of 2-hydroxy terephthalic acid, which is related to
the amount of hydroxyl radicals formed on the illuminated films. The intensity, i.e. •OH radical formation, is highest for fTiZr0.05-500 and correlates well with the photocatalytic degradation results in Fig. 29a.

In order to identify the main reactive oxygen species responsible for the degradation, we conducted different scavenger tests using 50 ml of 0.001 mM phenol solution and 10 mM of either potassium iodide (KI), isopropanol (IPA) or benzoquinone (BQ). Addition of IPA (•OH scavenger) and KI (h^+ scavenger) resulted in little or no degradation of phenol (Fig. 32b). However, in presence of BQ, a scavenger for superoxide radicals $\bullet O_2^-$, degradation of phenol occurred at lower but significant rate. The results suggest that direct hole oxidation or hydroxide radical (•OH) mediated oxidation are the main reaction pathways in the degradation of the pollutants on fTiZr0.05-500 film. The •OH radicals seem to be mainly formed by the reaction of holes with OH⁻ ions from the aqueous solution. But also the superoxide radicals might be involved; they are formed via the reaction of oxygen molecules with irradiated electrons. With water they form •OH radicals in a subsequent step. A similar mechanism was observed for degradation of chloridazon over zirconia/titania powder in our former studies [89].



Fig. 32 Terephthalic acid hydroxylation test (a) and scavenger tests (b).

4.3.7 Conclusion

Zr-doped mesoporous TiO₂ thin films with enhanced photocatalytic activity towards degradation of organic pollutants (chloridazon, phenol and 4-chlorophenol) under Xe lamp irradiation were successfully prepared. At low Zr/Ti ratios up to about 0.08 - 0.1 the Zr⁴⁺ ions are substituting Ti⁴⁺ ions in the anatase TiO₂ lattice. This lowers the charge carrier recombination as evidenced from photoluminescence measurements and consequently increases the photocatalytic activity. With progressing Zr introduction the formation of structural defects increases and above Zr/Ti ratios of 0.1 the formation of ZrO₂ as a second phase occurs. The formed nanocomposites of Zr-doped anatase and ZrO₂ show an increased crystallite size, but surprisingly also an increased surface area indicating the formed nanocomposite is also porous. The photocatalytic activity of films with high Zr content decreases, since nanocomposite formation leads to more grain boundaries acting as recombination centers and also blocks active centers. Optimization of parameters such as Zr loading, calcination temperature and number of layers is crucial in determining the best overall photocatalytic performance of the films.

In dependence of the acidity of the pollutant, which shall be degraded; the pKa values of the pollutant, the pH value changes and with that the surface charge of the Zr doped TiO_2 films and the adsorption rate of the pollutant. Hydroxyl radicals are the dominant active species in the degradation reactions.

5 General conclusion

In this research two types of Zr modified TiO₂ catalyst (powder and films) were successfully prepared and their photocatalytic activity towards degradation of three organic pollutants was investigated. Considering the method of preparation, EISA method was found to be more preferable method compared to sol-gel method as it resulted to samples with high surface area and also higher photocatalytic activity Presence of Zr in the modified samples were confirmed from the HRTEM-EDX, XRD and XPS results. Addition of Zr⁴⁺ ions into TiO₂ resulted in either substitution of Ti⁴⁺ with Zr⁴⁺ (low Zr content) or formation of TiO₂/ZrO₂ composite (high Zr content). Although other studies have reported formation of mixture of anatase and ZrTiO₄, our samples showed presence of either pure anatase or anatase with ZrO₂. In general, presence of Zr increased the band gap of the samples except in at very high amount of Zr a decrease in band gap was observed. This was as result of formation of composite. Mott-Schottky analysis showed that Zr can results in decrease in the flat-band potential of TiO₂ which is related to change in conduction band.

This study reports an improved photocatalytic performance of TiO_2 towards degradation of selected organic pollutants due to modification with Zr^{4+} ions compared to pure TiO_2 catalyst. Also, for powder samples the Zr modified sample showed better activity compared to the commercial Evonik P25 especially for samples prepared through EISA method. Increase in surface area, better charge separation, small crystal size and better adsorption of organic molecules on surface catalyst were among the major reasons for the increase in photocatalytic activity. The optimum Zr concentration and calcination temperature varied depending on the type of catalyst and the method of synthesis. Sol-gel prepared powder samples and EISA films showed highest activity at lower Zr content 0.05 mol% while EISA prepared samples required

higher Zr concentration (0.14 mol%). Above Zr 0.05 mol%, sol-gel powder and EISA film formed TiO_2/ZrO_2 composites while EISA powder samples formed only anatase phase. Anatase phase is known to be the most photocatalytic active phase of TiO_2 . In case of a mixture of anatase and ZrO_2 phase, ZrO_2 which has a wide band-gap does not participate much in light absorption during the degradation. Between films and powder type of catalyst, powder samples recorded superior photocatalytic activity which is expected due to the large mass of particles as compared to the small amount of particles on the film. Although the photocatalytic activity of films a lower films are better in terms of ease in catalyst recovery.

6 Outlook

Although the improvement of photocatalytic activity of TiO_2 by modification of with Zr shows positive results, the increase is still low for its practical application. More work is still needed to optimize the performance of the catalyst. Especially the films as they can ease the tedious work of water treatment. Further investigation of the effect of Zr on the electronic structure of TiO_2 could help in better understanding of its contribution towards the increase in activity and hence optimization of the same. Electrochemical methods like cyclic voltammetry and transient photocurrent could help in understanding of the changes in the conduction bands and efficiency of the charge carrier separation due to Zr.

In this study only three organic pollutants were tested where else there are many other known and also emerging pollutants which need to be investigated. Could be the modified catalyst has even higher activity towards other pollutants. In addition, due to limited time and facility few degradation products were determined. In future, it would be important to analyze the degradation products to avoid formation of new persistent molecules which could be more toxic than the original pollutant.

Finally, the world is searching for cheaper, safer and easily available sources of energy and one of them is by use of the visible energy from the sun. Zr modified TiO_2 are only active under UV light which is a limitation as only 5% of the sunlight is within UV region. In this work, known methods of decreasing the band gap of TiO_2 using elements like nitrogen and sulphur from urea and thiourea were applied but little or no activity was observed under visible region. Further modifications are possible to make this catalyst visible light active as it is known that doping/modification of TiO_2 with Zr results into a very stable catalyst. Recent advances has shown that formation C_3N_4 can be coupled with the semiconductors to make them visible active.

5 References

D. Bahnemann, Photocatalytic water treatment: solar energy applications, Solar Energy, 77
 (2004) 445-459.

[2] A. Di Paola, E. Garcia-Lopez, G. Marci, L. Palmisano, A survey of photocatalytic materials for environmental remediation, J Hazard Mater, 211 (2012) 3-29.

[3] A. Vidal, Developments in solar photocatalysis for water purification, Chemosphere, 36 (1998) 2593-2606.

[4] H. Dong, G. Zeng, L. Tang, C. Fan, C. Zhang, X. He, Y. He, An overview on limitations of TiO2-based particles for photocatalytic degradation of organic pollutants and the corresponding countermeasures, Water Res, 79 (2015) 128-146.

[5] P.A. Xu, G.M. Zeng, D.L. Huang, C.L. Feng, S. Hu, M.H. Zhao, C. Lai, Z. Wei, C. Huang, G.X. Xie, Z.F. Liu, Use of iron oxide nanomaterials in wastewater treatment: A review, Sci Total Environ, 424 (2012) 1-10.

[6] N. Miranda-García, S. Suárez, B. Sánchez, J.M. Coronado, S. Malato, M.I. Maldonado, Photocatalytic degradation of emerging contaminants in municipal wastewater treatment plant effluents using immobilized TiO_2 in a solar pilot plant, Applied Catalysis B: Environmental, 103 (2011) 294-301.

[7] G.M. Zeng, M. Chen, Z.T. Zeng, Risks of Neonicotinoid Pesticides, Science, 340 (2013) 1403-1403.

[8] Y. Zhou, L. Tang, G. Zeng, J. Chen, Y. Cai, Y. Zhang, G. Yang, Y. Liu, C. Zhang, W. Tang, Mesoporous carbon nitride based biosensor for highly sensitive and selective analysis of phenol and catechol in compost bioremediation, Biosens Bioelectron, 61 (2014) 519-525. [9] G. Buttiglieri, M. Peschka, T. Fromel, J. Muller, F. Malpei, P. Seel, T.P. Knepper, Environmental occurrence and degradation of the herbicide n-chloridazon, Water Res, 43 (2009) 2865-2873.

[10] P.V.A. Padmanabhan, K.P. Sreekumar, T.K. Thiyagarajan, R.U. Satpute, K. Bhanumurthy,P. Sengupta, G.K. Dey, K.G.K. Warrier, Nano-crystalline titanium dioxide formed by reactive plasma synthesis, Vacuum, 80 (2006) 1252-1255.

[11] K. Nakata, A. Fujishima, TiO₂ photocatalysis: Design and applications, J Photoch Photobio C, 13 (2012) 169-189.

[12] M.N. Chong, B. Jin, C.W. Chow, C. Saint, Recent developments in photocatalytic water treatment technology: a review, Water Res, 44 (2010) 2997-3027.

[13] M. Pera-Titus, V. García-Molina, M.A. Baños, J. Giménez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, Applied Catalysis B: Environmental, 47 (2004) 219-256.

[14] D. Astruc, F. Lu, J.R. Aranzaes, Nanoparticles as recyclable catalysts: the frontier between homogeneous and heterogeneous catalysis, Angew Chem Int Ed Engl, 44 (2005) 7852-7872.

[15] J.M. Herrmann, Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants, Catal Today, 53 (1999) 115-129.

[16] E.L. Crepaldi, G.J.D.A. Soler-Illia, D. Grosso, F. Cagnol, F. Ribot, C. Sanchez, Controlled formation of highly organized mesoporous titania thin films: From mesostructured hybrids to mesoporous nanoanatase TiO₂, J Am Chem Soc, 125 (2003) 9770-9786.

[17] L. Mahoney, R.T. Koodali, Versatility of Evaporation-Induced Self-Assembly (EISA) Method for Preparation of Mesoporous TiO₂ for Energy and Environmental Applications, Materials (Basel), 7 (2014) 2697-2746. [18] C. Sanchez, C. Boissiere, D. Grosso, C. Laberty, L. Nicole, Design, synthesis, and properties of inorganic and hybrid thin films having periodically organized nanoporosity, Chem Mater, 20 (2008) 682-737.

[19] I.L. Violi, M.D. Perez, M.C. Fuertes, G.J. Soler-Illia, Highly ordered, accessible and nanocrystalline mesoporous TiO_2 thin films on transparent conductive substrates, ACS Appl Mater Interfaces, 4 (2012) 4320-4330.

[20] W.Y. Choi, A. Termin, M.R. Hoffmann, The Role of Metal-Ion Dopants in Quantum-Sized TiO₂ - Correlation between Photoreactivity and Charge-Carrier Recombination Dynamics, J Phys Chem-Us, 98 (1994) 13669-13679.

[21] A. Juma, I. Oja Acik, A.T. Oluwabi, A. Mere, V. Mikli, M. Danilson, M. Krunks, Zirconium doped TiO_2 thin films deposited by chemical spray pyrolysis, Applied Surface Science, 387 (2016) 539-545.

[22] A.T. Oluwabi, A.O. Juma, I.O. Acik, A. Mere, M. Krunks, Effect of Zr doping on the structural and electrical properties of spray deposited TiO₂ thin films, P Est Acad Sci, 67 (2018) 147-157.

[23] H. Wang, L. Zhang, Z. Chen, J. Hu, S. Li, Z. Wang, J. Liu, X. Wang, Semiconductor heterojunction photocatalysts: design, construction, and photocatalytic performances, Chem Soc Rev, 43 (2014) 5234-5244.

[24] A.H. Mamaghani, F. Haghighat, C.-S. Lee, Photocatalytic oxidation technology for indoor environment air purification: The state-of-the-art, Applied Catalysis B: Environmental, 203 (2017) 247-269.

[25] J. Bai, B. Zhou, Titanium dioxide nanomaterials for sensor applications, Chem Rev, 114(2014) 10131-10176.

[26] M.A. Henderson, A surface science perspective on TiO_2 photocatalysis, Surface Science Reports, 66 (2011) 185-297.

[27] M.D. Hernández-Alonso, I. Tejedor-Tejedor, J.M. Coronado, M.A. Anderson, Operando FTIR study of the photocatalytic oxidation of methylcyclohexane and toluene in air over TiO_2 -ZrO₂ thin films: Influence of the aromaticity of the target molecule on deactivation, Applied Catalysis B: Environmental, 101 (2011) 283-293.

[28] A. Nakajima, K. Hashimoto, T. Watanabe, K. Takai, G. Yamauchi, A. Fujishima, Transparent superhydrophobic thin films with self-cleaning properties, Langmuir, 16 (2000) 7044-7047.

[29] D.F. Ollis, Photocatalytic purification and remediation of contaminated air and water, Cr Acad Sci Ii C, 3 (2000) 405-411.

[30] B. Oregan, M. Gratzel, A Low-Cost, High-Efficiency Solar-Cell Based on Dye-Sensitized
 Colloidal TiO₂ Films, Nature, 353 (1991) 737-740.

[31] P. Hartmann, D.K. Lee, B.M. Smarsly, J. Janek, Mesoporous TiO₂: Comparison of Classical Sol-Gel and Nanoparticle Based Photoelectrodes for the Water Splitting Reaction, Acs Nano, 4 (2010) 3147-3154.

[32] A.A. Ismail, D.W. Bahnemann, J. Rathousky, V. Yarovyi, M. Wark, Multilayered ordered mesoporous platinum/titania composite films: does the photocatalytic activity benefit from the film thickness?, Journal of Materials Chemistry, 21 (2011) 7802.

[33] U. Diebold, The surface science of titanium dioxide, Surface Science Reports, 48 (2003) 53-229.

[34] L. Koči, D.Y. Kim, J.S. de Almeida, M. Mattesini, E. Isaev, R. Ahuja, Mechanical stability of TiO₂ polymorphs under pressure:ab initiocalculations, Journal of Physics: Condensed Matter, 20 (2008).

[35] D.A.H. Hanaor, C.C. Sorrell, Review of the anatase to rutile phase transformation, Journal of Materials Science, 46 (2010) 855-874.

[36] T. Luttrell, S. Halpegamage, J. Tao, A. Kramer, E. Sutter, M. Batzill, Why is anatase a better photocatalyst than rutile?--Model studies on epitaxial TiO₂ films, Sci Rep, 4 (2014) 4043.

[37] L. Ma, S.X. Tu, Removal of arsenic from aqueous solution by two types of nano TiO_2 crystals, Environ Chem Lett, 9 (2011) 465-472.

[38] V. Etacheri, C. Di Valentin, J. Schneider, D. Bahnemann, S.C. Pillai, Visible-light activation of TiO₂ photocatalysts: Advances in theory and experiments, Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 25 (2015) 1-29.

[39] I. Bannat, K. Wessels, T. Oekermann, J. Rathousky, D. Bahnemann, M. Wark, Improving the Photocatalytic Performance of Mesoporous Titania Films by Modification with Gold Nanostructures, Chem Mater, 21 (2009) 1645-1653.

[40] X.B. Chen, C. Li, M. Gratzel, R. Kostecki, S.S. Mao, Nanomaterials for renewable energy production and storage, Chemical Society Reviews, 41 (2012) 7909-7937.

[41] M. Gratzel, Photoelectrochemical cells, Nature, 414 (2001) 338-344.

[42] A. Fujishima, X. Zhang, D. Tryk, TiO₂ photocatalysis and related surface phenomena, Surface Science Reports, 63 (2008) 515-582.

[43] A. Furube, T. Asahi, H. Masuhara, H. Yamashita, M. Anpo, Direct observation of a picosecond charge separation process in photoexcited platinum-loaded TiO_2 particles by femtosecond diffuse reflectance spectroscopy, Chem Phys Lett, 336 (2001) 424-430.

71

[44] M.R. Hoffmann, S.T. Martin, W.Y. Choi, D.W. Bahnemann, Environmental Applications of Semiconductor Photocatalysis, Chemical Reviews, 95 (1995) 69-96.

[45] J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, D.W.
Bahnemann, Understanding TiO₂ photocatalysis: mechanisms and materials, Chem Rev, 114
(2014) 9919-9986.

[46] S. Ahmed, M.G. Rasul, R. Brown, M.A. Hashib, Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: a short review, J Environ Manage, 92 (2011) 311-330.

[47] B. Liu, H.M. Chen, C. Liu, S.C. Andrews, C. Hahn, P.D. Yang, Large-Scale Synthesis of Transition-Metal-Doped TiO₂ Nanowires with Controllable Overpotential, J Am Chem Soc, 135 (2013) 9995-9998.

[48] W.-H. Lu, C.-S. Chou, C.-Y. Chen, P. Wu, Preparation of Zr-doped mesoporous TiO₂ particles and their applications in the novel working electrode of a dye-sensitized solar cell, Advanced Powder Technology, 28 (2017) 2186-2197.

[49] J. Lukáč, M. Klementová, P. Bezdička, S. Bakardjieva, J. Šubrt, L. Szatmáry, Z. Bastl, J. Jirkovský, Influence of Zr as TiO₂ doping ion on photocatalytic degradation of 4-chlorophenol, Applied Catalysis B: Environmental, 74 (2007) 83-91.

[50] A. Yamakata, T. Ishibashi, H. Onishi, Electron- and HoleCapture Reactions on PtTiO₂ Photocatalyst Exposed to Methanol Vapor Studied with Time-Resolved Infrared Absorption Spectroscopy, J. Phys. Chem, 106 (2002) 9122-9125.

[51] W.L. S. I. Shah, C.-P. Huang, O. Jung, C. Ni, Study of Nd3, Pd2, Pt4, and Fe3 dopant effect on photoreactivity of TiO_2 nanoparticles, Proceedings of the National Academy of Sciences of the United States of America, 99 (2002).

[52] R. Fagan, D.E. McCormack, S.J. Hinder, S.C. Pillai, Photocatalytic Properties of g-C(3)N(4)-TiO(2) Heterojunctions under UV and Visible Light Conditions, Materials (Basel), 9 (2016).

[53] C.H. Wang, C.L. Shao, X.T. Zhang, Y.C. Liu, SnO₂ Nanostructures-TiO₂ Nanofibers Heterostructures: Controlled Fabrication and High Photocatalytic Properties, Inorg Chem, 48 (2009) 7261-7268.

[54] X.Z. Fu, L.A. Clark, Q. Yang, M.A. Anderson, Enhanced photocatalytic performance of titania-based binary metal oxides: TiO₂/SiO₂ and TiO₂/ZrO₂, Environ Sci Technol, 30 (1996) 647-653.

[55] B. Gao, T.M. Lim, D.P. Subagio, T.-T. Lim, Zr-doped TiO₂ for enhanced photocatalytic degradation of bisphenol A, Applied Catalysis A: General, 375 (2010) 107-115.

[56] Y. Gnatyuk, N. Smirnova, O. Korduban, A. Eremenko, Effect of zirconium incorporation on the stabilization of TiO_2 mesoporous structure, Surface and Interface Analysis, 42 (2010) 1276-1280.

[57] J. Song, X. Wang, J. Yan, J. Yu, G. Sun, B. Ding, Soft Zr-doped TiO₂ Nanofibrous Membranes with Enhanced Photocatalytic Activity for Water Purification, Sci Rep, 7 (2017) 1636.

[58] N. Venkatachalam, M. Palanichamy, B. Arabindoo, V. Murugesan, Enhanced photocatalytic degradation of 4-chlorophenol by Zr^{4+} doped nano TiO₂, Journal of Molecular Catalysis A: Chemical, 266 (2007) 158-165.

[59] M.Q. Fan, S.X. Hu, B. Ren, J. Wang, X.Y. Jing, Synthesis of nanocomposite TiO₂/ZrO₂ prepared by different templates and photocatalytic properties for the photodegradation of Rhodamine B, Powder Technol, 235 (2013) 27-32.

73

[60] W. Zhou, K. Liu, H. Fu, K. Pan, L. Zhang, L. Wang, C.C. Sun, Multi-modal mesoporous TiO(₂)-ZrO(₂) composites with high photocatalytic activity and hydrophilicity, Nanotechnology, 19 (2008) 035610.

[61] R. Gauvin, K. Robertson, P. Horny, A.M. Elwazri, S. Yue, Materials characterization using high-resolution scanning-electron microscopy and X-ray microanalysis, Jom-Us, 58 (2006) 20-26.

[62] R.b.P.D. Brown, Transmission Electron Microscopy, Microscopy and Microanalysis, 5 (2003) 452-453.

[63] R. Jenkins, Introduction to Xray, 1996 John Wiley & Sons, Inc.1996.

[64] Z.l. Wang, characterization of nanophase materials, Wiley-VCH, Germany, 2001.

[65] J.C. Vickerman, Surface analysis: The principal techniques, John Wiley & Sons2009.

[66] M.G. Kibria, S. Zhao, F.A. Chowdhury, Q. Wang, H.P.T. Nguyen, M.L. Trudeau, H. Guo,

Z. Mi, Tuning the surface Fermi level on p-type gallium nitride nanowires for efficient overall water splitting, Nat Commun, 5 (2014).

[67] A.F. Ken-ichi Ishibashi , Toshiya Watanabe , Kazuhito Hashimoto Detection of active oxidative species in TiO2 photocatalysis using the fluorescence technique, Electrochemistry Communications, 2 (2000) 207-210.

[68] H. Li, Y. Cui, W. Hong, S. Fan, L. Zhu, Photocatalytic performance of Pr/In/Nd composite oxides synthesized by solid state reaction, Ceramics International, 39 (2013) 6583-6589.

[69] M. Li, X.C. Li, G.L. Jiang, G.H. He, Hierarchically macro-mesoporous ZrO₂-TiO₂ composites with enhanced photocatalytic activity, Ceramics International, 41 (2015) 5749-5757.

[70] R.D. Shannon, Revised Effective Ionic-Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides, Acta Crystallogr A, 32 (1976) 751-767.

[71] K. Okada, N. Yamamoto, Y. Kameshima, A. Yasumori, K.J.D. MacKenzie, Effect of silica additive on the anatase-to-rutile phase transition, J Am Ceram Soc, 84 (2001) 1591-1596.

[72] B. Neppolian, Q. Wang, H. Yamashita, H. Choi, Synthesis and characterization of ZrO₂-TiO2 binary oxide semiconductor nanoparticles: Application and interparticle electron transfer process, Appl Catal a-Gen, 333 (2007) 264-271.

[73] K.V. Bineesh, D.K. Kim, D.W. Park, Synthesis and characterization of zirconium-doped mesoporous nano-crystalline TiO₂, Nanoscale, 2 (2010) 1222-1228.

[74] J.-A. Cha, S.-H. An, H.-D. Jang, C.-S. Kim, D.-K. Song, T.-O. Kim, Synthesis and photocatalytic activity of N-doped TiO₂/ZrO₂ visible-light photocatalysts, Advanced Powder Technology, 23 (2012) 717-723.

[75] Y. Yu, P. Zhang, Y. Kuang, Y. Ding, J. Yao, J. Xu, Y. Cao, Adjustment and Control of Energy Levels for TiO₂–N/ZrO₂–xNx with Enhanced Visible Light Photocatalytic Activity, The Journal of Physical Chemistry C, 118 (2014) 20982-20988.

[76] X. Wang, J.C. Yu, Y. chen, L. Wu, X. Fu, ZrO₂-Modified Mesoporous nanocrystalline TiO2-xNx as efficient visible light photocatalysts, Environ. Sci. Technol., 40 (2006) 2369-2374.

[77] C.X. Fu, Y.Y. Gong, Y.T. Wu, J.Q. Liu, Z. Zhang, C. Li, L.Y. Niu, Photocatalytic enhancement of TiO₂ by B and Zr co-doping and modulation of microstructure, Applied Surface Science, 379 (2016) 83-90.

[78] W.F. Zhang, Y.L. He, M.S. Zhang, Z. Yin, Q. Chen, Raman scattering study on anatase TiO2 nanocrystals, J Phys D Appl Phys, 33 (2000) 912-916.

[79] U. Balachandran, N.G. Eror, Raman-Spectra of Titanium-Dioxide, J Solid State Chem, 42 (1982) 276-282.

75

[80] T. Hirata, E. Asari, M. Kitajima, Infrared and Raman-Spectroscopic Studies of ZrO₂ Polymorphs Doped with Y₂O₃ or CeO₂, J Solid State Chem, 110 (1994) 201-207.

[81] A. Gajovic, I. Djerdj, K. Furic, R. Schlogl, D.S. Su, Preparation of nanostructured $ZrTiO_4$ by solid state reaction in equimolar mixture of TiO_2 and ZrO_2 , Cryst Res Technol, 41 (2006) 1076-1081.

[82] G.N. Shao, S.M. Imran, S.J. Jeon, M. Engole, N. Abbas, M.S. Haider, S.J. Kang, H.T. Kim, Sol-gel synthesis of photoactive zirconia-titania from metal salts and investigation of their photocatalytic properties in the photodegradation of methylene blue, Powder Technol, 258 (2014) 99-109.

[83] J.A. Navio, G. Colon, J.M. Herrmann, Photoconductive and photocatalytic properties of ZrTiO4. Comparison with the parent oxides TiO₂ and ZrO₂, J Photoch Photobio A, 108 (1997) 179-185.

[84] B. Ohtani, O.O. Prieto-Mahaney, D. Li, R. Abe, What is Degussa (Evonik) P25? Crystalline composition analysis, reconstruction from isolated pure particles and photocatalytic activity test, Journal of Photochemistry and Photobiology A: Chemistry, 216 (2010) 179-182.

[85] M. Mrowetz, W. Balcerski, A.J. Colussi, M.R. Hoffmann, Oxidative power of nitrogendoped TiO₂ photocatalysts under visible illumination, J Phys Chem B, 108 (2004) 17269-17273.

[86] C. McManamon, J.D. Holmes, M.A. Morris, Improved photocatalytic degradation rates of phenol achieved using novel porous ZrO₂-doped TiO₂ nanoparticulate powders, J Hazard Mater, 193 (2011) 120-127.

[87] S. Ahmed, M.G. Rasul, W.N. Martens, R. Brown, M.A. Hashib, Heterogeneous photocatalytic degradation of phenols in wastewater: A review on current status and developments, Desalination, 261 (2010) 3-18.

76

[88] Z. Guo, R. Ma, G. Li, Degradation of phenol by nanomaterial TiO₂ in wastewater, Chemical Engineering Journal, 119 (2006) 55-59.

[89] A. Mbiri, G. Wittstock, D.H. Taffa, E. Gatebe, J. Baya, M. Wark, Photocatalytic degradation of the herbicide chloridazon on mesoporous titania/zirconia nanopowders, Environ Sci Pollut Res Int, (2017).

[90] J. Wang, Y. Yu, S. Li, L. Guo, E. Wang, Y. Cao, Doping Behavior of Zr⁴⁺ Ions in Zr⁴⁺-Doped TiO₂ Nanoparticles, The Journal of Physical Chemistry C, 117 (2013) 27120-27126.

[91] D.G. Mieritz, A. Renaud, D.K. Seo, Unusual Changes in Electronic Band-Edge Energies of the Nanostructured Transparent n-Type Semiconductor Zr-Doped Anatase TiO_2 (Ti1-xZrxO₂; x < 0.3), Inorg Chem, 55 (2016) 6574-6585.

[92] D. Guerrero-Araque, D. Ramírez-Ortega, P. Acevedo-Peña, F. Tzompantzi, H.A. Calderón, R. Gómez, Interfacial charge-transfer process across ZrO₂ -TiO₂ heterojunction and its impact on photocatalytic activity, Journal of Photochemistry and Photobiology A: Chemistry, 335 (2017) 276-286.

[93] S. Huang, Y. Yu, Y. Yan, J. Yuan, S. Yin, Y. Cao, Enhanced photocatalytic activity of TiO₂ activated by doping Zr and modifying Pd, RSC Advances, 6 (2016) 29950-29957.

[94] A.L. Patterson, The Scherrer Formula for X-Ray Particle Size Determination, Physical Review, 56 (1939) 978-982.

[95] V. Polliotto, E. Albanese, S. Livraghi, P. Indyka, Z. Sojka, G. Pacchioni, E. Giamello, Fifty-Fifty Zr-Ti Solid Solution with a TiO₂-Type Structure: Electronic Structure and Photochemical Properties of Zirconium Titanate ZrTiO₄, J Phys Chem C, 121 (2017) 5487-5497.

[96] H. Imahori, S. Hayashi, T. Umeyama, S. Eu, A. Oguro, S. Kang, Y. Matano, T. Shishido, S. Ngamsinlapasathian, S. Yoshikawa, Comparison of electrode structures and photovoltaic

properties of porphyrin-sensitized solar cells with TiO(2) and Nb, Ge, Zr-added TiO(2) composite electrodes, Langmuir, 22 (2006) 11405-11411.

[97] N. Smirnova, Y. Gnatyuk, A. Eremenko, G. Kolbasov, V. Vorobetz, I. Kolbasova, O. Linyucheva, Photoelectrochemical characterization and photocatalytic properties of mesoporousTiO₂/ZrO₂ films, International Journal of Photoenergy, 2006 (2006) 1-6.

[98] H.K. Chen, W.F. Chen, P. Koshy, E. Adabifiroozjaei, R. Liu, L.R. Sheppard, C.C. Sorrell, Effect of tungsten-doping on the properties and photocatalytic performance of titania thin films on glass substrates, J Taiwan Inst Chem E, 67 (2016) 202-210.

[99] J.G. Yu, X.J. Zhao, Effect of substrates on the photocatalytic activity of nanometer TiO2 thin films, Mater Res Bull, 35 (2000) 1293-1301.

[100] B. Elgh, N. Yuan, H.S. Cho, D. Magerl, M. Philipp, S.V. Roth, K.B. Yoon, P. Muller-Buschbaum, O. Terasaki, A.E.C. Palmqvist, Controlling morphology, mesoporosity, crystallinity, and photocatalytic activity of ordered mesoporous TiO_2 films prepared at low temperature, Apl Mater, 2 (2014).

[101] J. Theurich, M. Lindner, D.W. Bahnemann, Photocatalytic degradation of 4-chlorophenol in aerated aqueous titanium dioxide suspensions: A kinetic and mechanistic study, Langmuir, 12 (1996) 6368-6376.

[102] E.M. Woolley, L.G. Hepler, Apparent Ionization-Constants of Water in Aqueous Organic Mixtures and Acid Dissociation-Constants of Protonated Co-Solvents in Aqueous-Solution, Anal Chem, 44 (1972) 1520-&.

[103] M. Zimpl, M. Kotoucek, K. Lemr, J. Vesela, J. Skopalova, Electrochemical reduction of chloridazon at mercury electrodes, and its analytical application, Fresen J Anal Chem, 371 (2001) 975-982.

6 Appendix



Fig. A1 Pollutant structure (a) Chloridazon (b) Phenol and (c) 4-chlorophenol



Fig. A2 TEM micrographs of pure TiO_2 samples prepared by the two methods (a) $eTiO_2$ -450 and (b) $sTiO_2$ -700



Fig. A3 XRD patterns of EISA samples showing the effect of different calcination temperatures at Zr content of 0.05 mol%.



Fig. A4. Absorbance change during the photodegradation of chloridazon on eTiZr0.14-500.



Fig. A5. Chemical structure of chloridazon and its metabolites.



Fig. A6. Absorbance change during the photodegradation of phenol on fTiZr0.05-500.



Fig. A7. Absorbance change during the photodegradation of 4-chlorophenol on fTiZr0.05-500.

7 Curriculum Vitae

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Publications

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Environmental Science and Pollution Research, 2017, https://doi.org/10.1007/s11356-017-1023-x

"Zirconium doped mesoporous TiO₂ multilayer thin films: Influence of the zirconium content on the photodegradation of organic pollutants"

Anne Mbiri, Dereje H. Taffa, Erastus Gatebe and Michael Wark

Submitted manuscript (10/11/2018) for Catalysis Today

Posters Contribution

"Photocatalytic degradation of chloridazon on mesoporous titania/zirconia nanocomposites" Anne Mbiri, Gunther Wittstock, Dereje H. Taffa, Erastus Gatebe, Joseph Baya and Michael Wark

Environmental Applications of Advanced Oxidation Processes, 2017, Prague, Czech Republic

"Evaporation-induced self-assembly synthesis of mesoporous TiO₂ /ZrO₂ and nanopowders for degradation of selected pesticides" Anne Mbiri, Michael Wark, Gunther Wittstock, Dereje H. Taffa, Erastus Gatebe and Joseph Baya Semiconductor Photochemistry, 2017, Oldenburg, Germany

"A comparative study of photocatalytic activity of Zr modified TiO2 thin films and nanopowder towards degradation of organic pollutants" Anne Mbiri, Michael Wark, Gunther Wittstock, Dereje H. Taffa and Joseph Baya

10th European Meeting on Solar Chemistry and photocatalysis: Environmental Applications, 2018, Almeria, Spain

8 Declaration

I hereby declare that this thesis is my summary of original PhD work and has not been presented or submitted to any other University. All the sources and materials used in this thesis are duly acknowledged and cited.

Oldenburg, December

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Anne Wanjira Mbiri