

Ambient temperature ZrO₂-doped TiO₂ crystalline photocatalysts: Highly efficient powders and films for water depollution

Julien G. Mahy^{a, *}, Stéphanie D. Lambert^a, Rémi G. Tilkin^{a, b}, Cédric Wolfs^a, Dirk Poelman^c, François Devred^d, Eric M. Gaigneaux^d, Sigrid Douven^a

^a Department of Chemical Engineering – Nanomaterials, Catalysis & Electrochemistry, University of Liège, B6a, Quartier Agora, Allée du six Août 11, 4000 Liège, Belgium

^b Centre Interfacultaire des Biomatériaux (CEIB), University of Liège, Allée du Six Août 11, 4000 Liège, Belgium

^c LumiLab, Department of Solid State Sciences, Ghent University, Belgium

^d Institute of Condensed Matter and Nanosciences – Molecular Chemistry, Materials and Catalysis (IMCN/MOST), Université catholique de Louvain, Place Louis Pasteur 1, Box L4.01.09, 1348 Louvain-La-Neuve, Belgium

ARTICLE INFO

Article history:

Received 3 April 2019

Received in revised form

6 June 2019

Accepted 18 June 2019

Keywords:

Ambient crystallization

Photocatalysis

ZrO₂ doping

Titania

Sol-gel process

ABSTRACT

In this paper, several TiO₂ materials doped with zirconia precursor (0.7, 1.4, 1.6 and 2.0 mol%) were synthesized by an easy aqueous sol-gel synthesis at ambient temperature. This method consists in the peptization of the TiO₂ colloid in presence of HNO₃. The corresponding pure TiO₂ material was also synthesized for comparison. The performances and the physico-chemical properties of these materials were compared to the well-known Evonik P25 photocatalyst.

The physico-chemical characterizations showed that nano-crystalline anatase-brookite particles were produced with the sol-gel process, with higher specific surface area than P25 (~200 m² g⁻¹ vs. 47 m² g⁻¹). All samples presented a higher visible absorption than P25. The XPS spectra showed that all the samples were doped with nitrogen and that mixed TiO₂-ZrO₂ oxide materials were obtained when doping with zirconia precursor.

Photoactivity was evaluated through the degradation of *p*-nitrophenol in water. On the one hand, under UV/visible light, the ZrO₂ doping increased the degradation efficiency of the pure TiO₂ catalyst due to a better charge separation in the mixed TiO₂-ZrO₂ oxides. The activity of the sample with the highest dopant content was even higher than the one of P25. On the other hand, under visible light, all samples were much more efficient than P25. This activity shift towards visible range was due to the N-doping of the catalysts, with a slight improvement for the doped ones.

Finally, the feasibility of producing films starting from an aqueous suspension of the photocatalyst was assessed on P25, pure TiO₂ and the best doped material. The photoactivity of these films, evaluated on the degradation of methylene blue under UV-A light, showed that the sample with the highest dopant concentration had an efficiency 4 times higher than pure TiO₂ and 20 times higher than P25.

© 2019 Elsevier Ltd. All rights reserved.

1. Introduction

During the 20th century, industrialization intensified in a growing number of countries around the world, and in various industries, particularly the chemical, pharmaceutical, cosmetics and petroleum ones. This intense industrialization has resulted in

* Corresponding author. Department of Chemical Engineering – Nanomaterials, Catalysis & Electrochemistry, University of Liège, B6a, Quartier Agora, Allée du six Août 11, 4000 Liège, Belgium.

E-mail address: julien.mahy@uliege.be (J.G. Mahy).

the emergence of Refractory Organic Compounds (ROCs) such as dyes, aromatics, pesticides, solvents, EDCs (Endocrine Disrupting Chemicals) and PPCPs (Pharmaceuticals and Personal Care Products) causing disturbances of aquatic life and risks to human health [1]. These contaminants mostly escape conventional wastewater treatments. For example, the issue of endocrine disruptors in wastewater is today one of the priorities for most environmental agencies in industrialized countries (e.g. Canada, the US, and the EU) [2]. In order to limit the dispersion of these organic contaminants in the environment, waste water must be subjected to more

advanced (and yet to be developed at an industrial scale) pollution abatement treatments.

These past decades, Advanced Oxidation Processes (AOPs) have also attracted increasing attention for water treatment, as shown by the large number of fundamental and applied research works [3]. These processes consist in treatments performed at room temperature and normal pressure. They are based on the *in situ* generation of a powerful oxidizing agent, such as hydroxyl radicals ($\bullet\text{OH}$), at a sufficient concentration to efficiently decontaminate water [3]. Among AOPs, photocatalysis is well established for the effective and sustainable removal of a large range of organic pollutants [3]. This phenomenon consists of a set of oxidation-reduction (redox) reactions between organic compounds (*i.e.* pollutants) and active species formed from an illuminated photocatalyst. The most widely used photocatalyst is TiO_2 [4,5], which is a non-toxic and cheap semiconductor sensitive to UV radiation [5]. However, the use of TiO_2 as photocatalyst has two main limitations [6]: (i) the fast charge recombination and (ii) the high band gap value which needs UV light for activation. To prevent these limitations, several studies have been conducted [4,7] (i) to increase the recombination time and (ii) extend the activity towards the visible range. Most works consisted in modifying TiO_2 materials by doping with different elements or molecules such as Ag [8], P [9], N [6,10], Fe [11], and dye photosensitive molecules [12] as porphyrin [13,14]. Titania has also been combined with other semiconductor such as ZnO [15,16], SnO_2 [17], CeO_2 [18] or ZrO_2 [19] in order to increase the specific surface, the photocatalytic activity or decrease the formation of free radicals. Regarding the ZrO_2 – TiO_2 combination, it has been previously reported that zirconia doping increases the specific surface area [20,21], the surface acidity [22], the transition temperature between anatase and rutile [21–23], the adsorption and the hydrophilic properties [20,24]. However, in most studies [19,21–23], the doped materials require a calcination step to obtain crystalline materials.

A TiO_2 commercial product has been developed by the Degussa Company (currently called Evonik), the Evonik P25. This material has been used as a titania standard photocatalyst. Indeed, Evonik P25 remains the most used and efficient photocatalyst under UV light on a large range of molecules [25–28]. This material is prepared by an aerosol process which involves high temperature treatments (1000–1300 °C) [26]. This material is a powder composed of anatase and rutile phase in 80/20 proportion [29,30]. In numerous researches [31], Evonik P25 is used alone or with dopant to increase the photo efficiency of different systems [32,33].

The aim of this paper is the development of a TiO_2 -based photocatalyst with enhanced characteristics compared to Evonik P25: a better photoactivity under both UV and visible light, a more environmentally-friendly synthesis, and a more versatile use such as, for example, coatings on various substrates. To reach these goals, the TiO_2 -based materials were synthesized from titanium and zirconium alcoxides in water at ambient temperature, allowing to produce crystalline TiO_2 without any calcination step. The dried materials were characterized by XRD, nitrogen adsorption-desorption measurements, DR-UV-Vis, and XPS. The obtained physicochemical properties were compared to the Evonik P25 ones. The photoactivity of all materials were assessed, based on the degradation of *p*-nitrophenol under both UV and visible light. The feasibility of preparing stable aqueous suspensions from powders of both Evonik P25 and the TiO_2 -based samples was explored, with the aim of producing photoactive films. Photoactivity of the films prepared by bar coating was assessed on the methylene blue (MB) degradation under UV-A lamp.

2. Materials and methods

2.1. Pure TiO_2 synthesis

Titanium (IV) tetraisopropoxide (TTIP, > 97%, Sigma-Aldrich), nitric acid (HNO_3 , 65%, Merck), 2-Methoxyethanol (MEtOH, 99.8%, Sigma-Aldrich), and distilled water are used as starting materials.

Firstly, 250 mL of distilled water is acidified with HNO_3 to reach a pH of 1. In a second vessel, 35 mL of TTIP is mixed with 15 mL of MEtOH for 15 min. Then, the TTIP-MEtOH mixture is added to the water under stirring at ambient temperature. After 24 h, a light blue sol is obtained. Half of the volume is dried under ambient air to obtain a white powder. The pure sample is denoted pure TiO_2 .

Evonik P25 TiO_2 material is used as reference material and is denoted P25.

2.2. Zr-doped TiO_2 synthesis

Zr-doped samples are synthesized using Zirconium (IV) tert-butoxide (98%, Sigma Aldrich) as zirconium precursor. The synthesis steps are identical to pure TiO_2 synthesis ones, where the precursor is added to the TTIP-MEtOH mixture. After reaction at ambient temperature for 24 h, similar light blue sols are obtained. Again, half of the volume is dried under ambient air to obtain a powder.

Four Zr-doping ratios are studied: 0.7, 1.4, 1.6 and 2.0 mol%. Samples are denoted as TiO_2/ZrX where X corresponds to the dopant amount.

2.3. Material characterizations

The hydrodynamic aggregate sizes (D_{DLS}) of the colloids are measured by dynamic light scattering (DLS) with a device Zetasizer from Malvern Panalytical. The experimental procedure is as follows: for each sample, 50 consecutive measurements are made and a mean D_{DLS} is calculated; this procedure is repeated 3 times. Therefore the D_{DLS} is calculated on 150 experiments over 25 min of measurement time. Moreover, the stability has been assessed by measuring D_{DLS} after three months of storage with the same procedure as above and compared to the initial value.

The actual amount of zirconium in the Zr-doped TiO_2 sample is determined by inductively coupled plasma–atomic emission spectroscopy (ICP–AES), equipped with an ICAP 6500 THERMO Scientific device. Solutions for analysis are prepared as follows [34]: (i) 2 g of Na_2O_2 , 1 g of NaOH and 0.1 g of sample are mixed in a vitreous carbon crucible; (ii) the mixture is heated beyond the melting point (up to 950 °C); (iii) after cooling and solidification, the mixture is digested in 30 mL of HNO_3 (65%); (iv) the solution is then transferred into a 500 mL calibrated flask that is finally filled with deionized water [34]. The solution is then analyzed using an ICP-AES device.

The crystallographic properties are observed through the X-ray diffraction (XRD) patterns recorded with a Bruker D8 Twin-Twin powder diffractometer using Cu-K_α radiation. The Scherrer formula (Eq. (1)) is used to determine the size of the TiO_2 crystallites, d_{XRD} [35]:

$$d_{\text{XRD}} = 0.9 \frac{\lambda}{B \cos(\theta)} \quad (1)$$

where d_{XRD} is the crystallite size (nm), B the peak full-width at half maximum after correction of the instrumental broadening (rad), λ the wavelength (nm), and θ the Bragg angle (rad).

The repartition of the crystallographic phases is estimated with the Rietveld method using “Profex” software [36]. The proportion of

amorphous-crystalline phase is estimated with CaF₂ (calcium fluoride, Sigma-Aldrich, anhydrous powder, 99.99% trace metal basis) internal standard methods and then processing the data with “Profex” software [37].

The nanoparticle sizes are measured with transmission electron microscopy (Phillips CM 100 device at an accelerating voltage of 200 kV). About one hundred particles are measured and an average value is estimated.

The sample textural properties are characterized by nitrogen adsorption-desorption isotherms in an ASAP 2420 multi-sampler adsorption-desorption volumetric device from Micromeritics. From these isotherms, the microporous volume is calculated using the Dubinin-Radushkevich theory (V_{DR}). The surface area is evaluated using the Brunauer, Emmett, and Teller theory (S_{BET}) [38]. An average particle size, d_{BET} , can be calculated from S_{BET} values by assuming spherical and non-porous TiO₂ anatase nanoparticles using the following formula [26]:

$$\frac{d_{BET}}{6} = \frac{1}{S_{BET} \rho_{anatase}} \quad (2)$$

where $\rho_{anatase}$ is the apparent density of TiO₂ anatase estimated to be equal to $3.89 \times 10^3 \text{ kg m}^{-3}$ [3,8].

Optical properties of TiO₂-based materials in the range of 300–800 nm region are obtained with diffuse reflectance measurements on a Varian Cary 500 UV–Vis–NIR spectrophotometer equipped with an integrating sphere (Varian External DRA-2500), and using BaSO₄ as reference. The absorbance spectra are transformed using the Kubelka–Munk function [26,40,41] to produce a signal, normalized for comparison between samples, and so to calculate the band gaps ($E_{g,direct}$ and $E_{g,indirect}$). The details of this treatment method are widely described elsewhere [4,10,42].

X-ray photoelectron spectra are obtained with a SSI-X-probe (SSX-100/206) spectrometer equipped with a monochromatized microfocused Al X-ray source (1486.6 eV), operating at 10 kV and 20 mA. Samples are placed in the analysis chamber where the residual pressure was about 10^{-6} Pa. The charging effect is adjusted using flood gun energy at 8 eV and a fine-meshed nickel grid placed 3 mm above the sample surface [43]. The pass energy is 150 eV and the spot size is 1.4 mm². The angle between the normal to the sample surface and the direction of electron collection is 55°. Under these conditions, the mid-height width (FWHM) of the Au 4f_{7/2} peak photo-peak measured on a standard sample of cleaned gold is about 1.6 eV. The following sequence of spectra is recorded: survey spectrum, C 1s, O 1s, N 1s, Zr 3d and Ti 2p and again C 1s to check the stability of charge compensation with time and absence of degradation of the samples.

The C- (C, H) component of the carbon C 1s peak is fixed at 284.8 eV to calibrate the scale in binding energy. Three other components of the carbon peak (C- (O, N), C = O or O–C–O and O–C=O) have been resolved, notably to determine the amount of oxygen involved in the carbon contamination. Data processing is carried out with the CasaXPS program (Casa Software Ltd, UK). Some spectra are decomposed using the Gaussian and Lorentzian function product model (least squares fitting) after subtraction of a nonlinear Shirley baseline [44]. The molar fractions are calculated using the normalized peak areas based on acquisition parameters and sensitivity factors supplied by the manufacturer.

2.4. Photocatalytic experiments

The photocatalytic properties of the materials are estimated through the degradation of a model pollutant, *p*-nitrophenol (PNP).

For each test, the degradation percentage of PNP, D_{PNPi} , is calculated by Eq. (3) [34]:

$$D_{PNPi}(\%) = \left(1 - \frac{[PNP]_i}{[PNP]_0}\right) * 100 \quad (3)$$

where $[PNP]_i$ represents the residual concentration of PNP at time $t = i$ h and $[PNP]_0$ represents the initial concentration of PNP at time $t = 0$ h.

The experimental set-up is described in a previous study [26,45]. The D_{PNP} is evaluated after 8 h under UV/visible light, thanks to a halogen lamp with a continuous spectrum from 300 to 800 nm (300 W, 220 V) measured with a Mini-Spectrometer TM-UV/vis C10082MD from Hamamatsu. The PNP degradation under visible light is evaluated after 24 h with the same halogen lamp covered by an UV filter that removes wavelengths shorter than 390 nm. The residual concentration of PNP is measured by UV/Vis spectroscopy (GENESYS 10S UV–Vis from Thermo Scientific) at 318 nm. For each tested catalyst, three flasks containing the catalytic powder are exposed to light to calculate the PNP degradation, and one is kept in the dark to evaluate PNP adsorption on the sample. One additional flask is exposed to light without catalyst to evaluate PNP natural decomposition under UV/visible or visible light only. In each flask, the initial concentrations of catalyst (if present) and PNP are equal to 1 g/L and 10^{-4} M respectively. The volume of each flask is 10 mL, and the flasks are agitated by a magnetic stirrer. Experiments are conducted in test tubes closed with a sealing cap. These tubes are placed in a cylindrical glass reactor with the halogen lamp in the center. The reactor is maintained at constant temperature (20 °C) by a cooling system with recirculating water. The lamp is also cooled by a similar system. Aluminum foil covers the outer wall of the reactor to prevent any interaction with the room lighting [4]. Each catalyst is tested under UV/visible light and under visible light.

2.5. Thin film deposition, characterization and photoactivity

Films are produced on pre-painted steel substrate (Solano®, ArcelorMittal, 7.5 cm × 5 cm × 0.2 cm) by bar-coating with an Elcometer 4340 Automatic Film Applicator with a bar-speed of 1 cm/s. Films are dried at 100 °C for 30 s, washed with distilled water, dried with compressed air, and finally dried again at 100 °C for 30 s to get a perfectly clean surface and to remove non-adherent TiO₂ material.

Three suspensions are used for film application: pure TiO₂, TiO₂/Zr2.0 and P25 suspension.

The P25 suspension is made by dispersing 3 g of Evonik P25 powder in 100 mL of acidic water (pH of 1 with HNO₃) in order to reach the same concentration as sol-gel colloids. The mixture is placed in ultrasonic bath for 1 h.

For pure TiO₂ and TiO₂/Zr2.0 materials, initial colloids are used as well as a dispersion of its corresponding powder in acidic water (3 g in 100 mL of acidic water). The powders are completely redispersed in water giving similar colloids [46] as initial ones.

The film crystallinity is characterized by grazing incidence X-Ray diffraction (GIXRD) in a Bruker D8 diffractometer using Cu radiation and operating at 40 kV and 40 mA. The incidence beam angle is 0.25°. The bare substrate is first measured to highlight the presence of TiO₂ in the white painting.

The photocatalytic activity of TiO₂ films is evaluated by monitoring the degradation of methylene blue (MB) under ultraviolet light (Osram Sylvania, Blacklight-Bleu Lamp, F 18W/BLB-T8) over 17 h. Indeed, PNP is not used in this case because the photocatalytic installation is equipped with an ultraviolet light source which degrades PNP. The spectra of the lamps are measured with a Mini-

Spectrometer TM-UV/vis C10082MD from Hamamatsu. UV-A light can be considered as monochromatic with a wavelength $\lambda = 365$ nm. Each film is placed in a Petri dish with 25 mL of 2×10^{-5} M of MB solution. The degradation of MB is evaluated from absorbance measurements with a Genesys 10S UV–Vis spectrophotometer (Thermo Scientific) at $\lambda = 665$ nm. Adsorption tests are performed in the dark (dark tests) to show whether MB is adsorbed on the surface. A blank test, consisting in irradiating the pollutant solution for 17 h in a Petri dish without any catalyst or support, shows that MB concentration under UV-A illumination remains constant. The Petri dishes with catalysts and pollutant are stirred on orbital shakers and illuminated for 17 h. Aliquots of MB are sampled at the beginning of the test and after 17 h. The photocatalytic degradation is equal to the total degradation of MB taking the catalyst adsorption (dark test) into account. Each photocatalytic measurement is triplicated to assess reproducibility of the data.

3. Results and discussion

3.1. Macroscopic observation

The pure and doped TiO_2 sols have similar aspects: translucent white bluish liquid. The pure TiO_2 is cloudier than the doped ones. This observation is in agreement with the aggregate size measured with DLS, D_{DLS} (Table 1). Indeed, the aggregate size is lower for doped samples (i.e. around 30 nm) than for the pure TiO_2 (i.e. around 60 nm). This difference in size can result from a different surface charge of the particles, leading to a better stability for the doped samples [46]. All samples are stable over a three-month period since the D_{DLS} remains constant and no precipitate is observed.

Sol-gel powders, obtained after drying of the sols, have a similar white-yellow color for all samples (pure and doped). The P25 powder is white.

When the Evonik P25 sample is mixed with acidic water, it results in a milky unstable sol with a lot of precipitates. It is consistent with the high aggregate size measured by DLS, D_{DLS} (Table 1), around 750 nm.

When the pure and doped TiO_2 powders are mixed with acidic water, suspensions have a similar aspect to initial colloids with stability over time.

3.2. Sample crystallinity

The XRD patterns of all samples are represented in Fig. 1.

A similar pattern is obtained for each sample. The samples are mainly composed of anatase with a small amount of brookite (peak

at 30.8°). The crystallite sizes, d_{XRD} , are calculated using the Scherrer formula (Eq. (1)) and are displayed in Table 1. The crystallite size increases slightly from 4 to 6 nm when the Zr content increases from 0 to 2.0 mol%. This trend is related to the width of the XRD peaks. In fact, the peaks become narrower when the Zr content increases. This size of crystallite is typical of aqueous TiO_2 material synthesized by precipitation-peptization method which leads to the formation of small TiO_2 particles well dispersed in water [47–49]. No peak associated to ZrO_2 species is observed.

For the Evonik P25, the XRD pattern is depicted in Fig. 2, anatase and rutile phases are present as widely reported [30]. The crystallite size is around 18 nm for the anatase phase and 8 nm for the rutile phase.

The phase distributions are reported in Table 1. The amorphous fraction is higher in the pure TiO_2 than in the doped samples, around 50% for the former compared to 20–30% for the latter. The anatase represents around 50% for the pure TiO_2 while it reaches 65–70% for the doped ones. The remaining phase is brookite, which lies between 5 and 8%. The doping seems to promote the crystallization, since the doped samples have a quite high crystallinity (i.e. around 75%) without any calcination step.

Evonik P25 is composed of 86% of anatase and 14% of rutile, a ratio widely reported in the literature [30].

3.3. TEM micrographs

TEM micrographs for pure TiO_2 , $\text{TiO}_2/\text{Zr}1.4$ and $\text{TiO}_2/\text{Zr}2.0$ samples are presented in Fig. 3. For all samples, TiO_2 aggregates are observed. These aggregates are composed of TiO_2 nanoparticles with spherical shapes [10]. The particles are not perfectly separated from each other because the material was first dried and then deposited on the TEM grid for measurement [10]. Additionally, the TiO_2 nanoparticles are not very clearly observable by TEM because of their relatively low contrast in bright-field TEM conditions [10]. TiO_2 nanoparticles have a size of about 7 nm (Table 1). As no different morphology is observed between the pure and Zr-doped samples, a hybrid TiO_2 – ZrO_2 structure can be assumed for the doped samples.

3.4. Surface properties

The nitrogen adsorption-desorption isotherms are depicted in Fig. 4 for pure TiO_2 and $\text{TiO}_2/\text{Zr}2.0$ samples. All other isotherms present a similar shape. In both cases, a sharp increase at low pressure is followed by a plateau which corresponds to a microporous solid from the BDDT classification (type I isotherm) [38]. The corresponding specific surface area, S_{BET} , and micropore volume,

Table 1
Textural and optical properties of TiO_2 -based photocatalysts.

Samples	Theoretical dopant content (mol/mol %)	Actual dopant content (mol/mol %)	Phase distribution (%) ± 5	S_{BET} (m^2g^{-1}) ± 5	V_{DR} (cm^3g^{-1}) ± 0.01	d_{BET} (nm) ± 1	d_{XRD} (nm) ± 1	d_{TEM} (nm) ± 1	D_{DLS} (nm) ± 10	$E_{\text{g,direct}}$ (eV) ± 0.01	$E_{\text{g,indirect}}$ (eV) ± 0.01
P25	—	—	A[86%] + R[14%]	50	0.03	31	18^{a} – 8^{b}	—	750	3.51	3.12
Pure TiO_2	—	—	Am[47%] + A[48%] + B[5%]	225	0.12	7	4	5	60	3.35	2.97
$\text{TiO}_2/\text{Zr}0.7$	0.7	0.7	Am[25%] + A[71%] + B[4%]	215	0.12	7	4	5	33	3.39	2.98
$\text{TiO}_2/\text{Zr}1.4$	1.4	1.4	Am[23%] + A[73%] + B[4%]	210	0.11	7	5	5	30	3.37	3.00
$\text{TiO}_2/\text{Zr}1.6$	1.7	1.6	Am[20%] + A[72%] + B[8%]	210	0.11	7	6	6	32	3.36	2.98
$\text{TiO}_2/\text{Zr}2.0$	2.0	2.0	Am[29%] + A[64%] + B[7%]	230	0.13	7	6	7	35	3.37	2.99

Am: amorphous TiO_2 phase; A: Anatase TiO_2 phase; B: Brookite TiO_2 phase; R: Rutile TiO_2 phase; S_{BET} : specific surface area determined by the BET method; V_{DR} : specific micropore volume determined by Dubinin–Raduskevitch theory; d_{BET} : mean diameter of TiO_2 nanoparticles calculated from S_{BET} values; d_{XRD} : mean diameter of TiO_2 crystallites measured by the Scherrer method; d_{TEM} : mean diameter of TiO_2 nanoparticles measured by TEM; D_{DLS} : hydrodynamic diameter of TiO_2 particles aggregates measured by DLS; $E_{\text{g,direct}}$: direct optical band-gap values calculated using the transformed Kubelka–Munk function; $E_{\text{g,indirect}}$: indirect optical band-gap values calculated using the transformed Kubelka–Munk function; ^a: measured for anatase peak; ^b: measured for rutile peak.

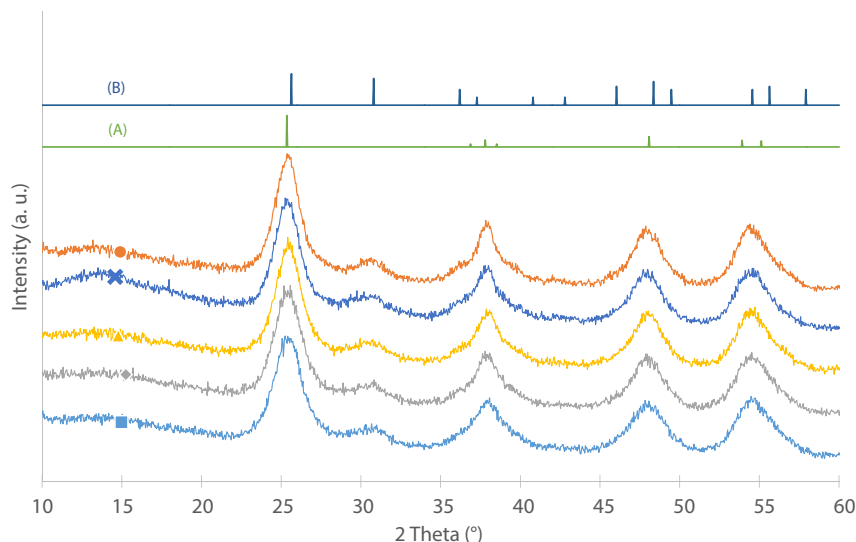


Fig. 1. X-ray diffraction (XRD) patterns of samples: (■) pure TiO_2 , (◆) $\text{TiO}_2/\text{Zr}0.7$, (▲) $\text{TiO}_2/\text{Zr}1.4$, (×) $\text{TiO}_2/\text{Zr}1.6$ and (●) $\text{TiO}_2/\text{Zr}2.0$. (A) reference pattern of anatase and (B) reference pattern of brookite.

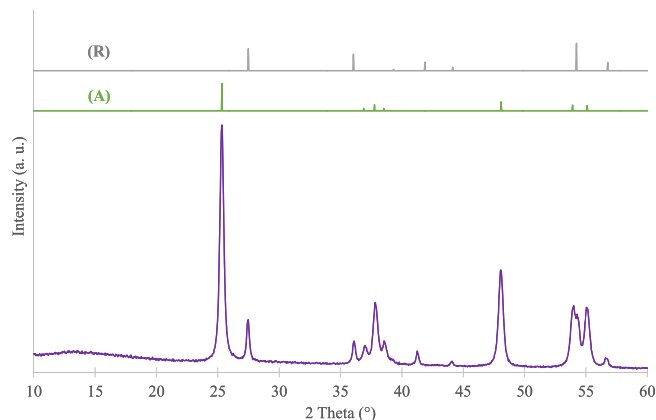


Fig. 2. X-ray diffraction (XRD) pattern of Evonik P25 sample. (A) reference pattern of anatase and (R) reference pattern of rutile.

V_{DR} , are reported in Table 1. These two values are similar for all samples, between 210 and 230 $\text{m}^2 \text{g}^{-1}$ for S_{BET} and between 0.11 and 0.13 $\text{cm}^3 \text{g}^{-1}$ for V_{DR} . These surface area properties are usually found in samples prepared with the peptization-precipitation method [26,39]. A model has been previously developed considering that these materials are made of spherical shape nanoparticles with small voids (*i.e.* < 2 nm, micropores) between the particles [26,42]. Therefore, a particle size, d_{BET} , can be estimated with the S_{BET} and Equation (2) assuming spherical shape for the particles. The values are reported in Table 1. For all samples, the d_{BET} is around 7 nm. This value can be compared with the particle sizes

measured (i) by XRD, d_{XRD} (Section 3.2.), and (ii) by TEM, d_{TEM} (Section 3.3.). The three values are in the same order of magnitude, *i.e.* between 4 and 7 nm. It can be assumed that the material is composed of spherical shape nanoparticles, each one corresponding to one crystallite.

Evonik P25 sample has a different isotherm (Fig. 4), characteristic of macroporous solid. At high pressure, the adsorbed volume increases asymptotically like in type II isotherm (macroporous solid) [38]. The S_{BET} and V_{DR} values are lower than pure and doped TiO_2 samples' ones with values of 50 $\text{m}^2 \text{g}^{-1}$ and 0.03 $\text{cm}^3 \text{g}^{-1}$ respectively.

3.5. Optical properties

The normalized Kubelka–Munk function is represented in Fig. 5 for pure TiO_2 , $\text{TiO}_2/\text{Zr}2.0$, and Evonik P25 samples. There is a clear shift towards longer wavelengths for the samples of this study, compared to Evonik P25. In fact, in Fig. 5, the absorption begins around 350 nm for Evonik P25 while it begins around 360–365 nm for other samples. The difference can be due to nitrogen insertion, inherent to this type of aqueous synthesis. Indeed, it has been previously shown that N doping happens when using nitric acid as peptizing agent, even for pure TiO_2 synthesis [10]. The N-doping is confirmed by the XPS measurements (see Section 3.7, Fig. 6c).

The band gap values are calculated and reported in Table 1. The doped samples present slightly higher values of the band gap than the pure TiO_2 . This shift can be due to the use of ZrO_2 [21,22], a semiconductor with a higher band gap than TiO_2 (5.2 vs. 3.2 eV) [19].

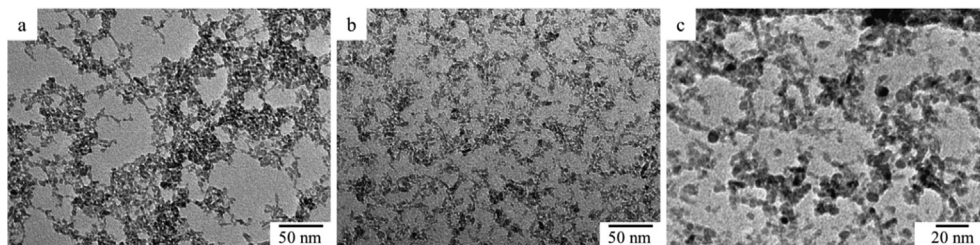


Fig. 3. TEM micrographs of samples: (a) pure TiO_2 , (b) $\text{TiO}_2/\text{Zr}1.4$ and (c) $\text{TiO}_2/\text{Zr}2.0$.

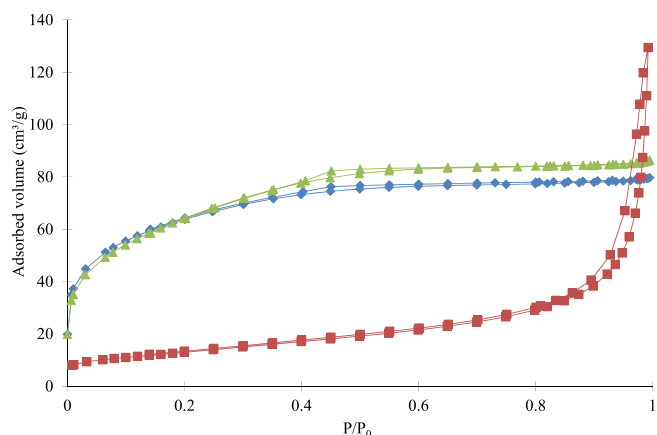


Fig. 4. Nitrogen adsorption-desorption isotherms of samples: (◆) pure TiO₂, (▲) TiO₂/Zr_{2.0} and (■) Evonik P25.

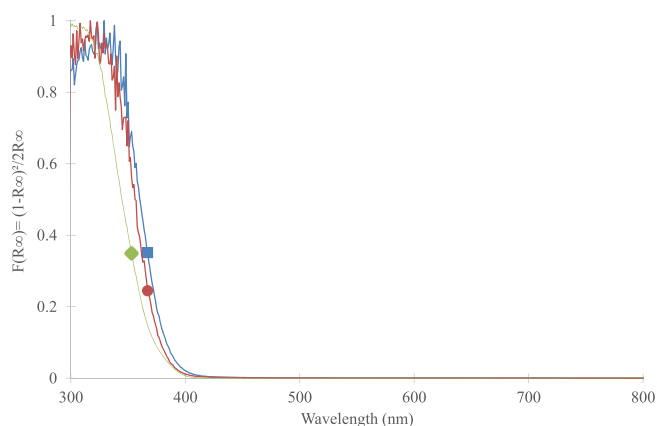


Fig. 5. Normalized Kubelka–Munk function $F(R_{\infty})$ calculated from DR-UV-Vis spectra for samples: (■) pure TiO₂, (●) TiO₂/Zr_{2.0} and (◆) Evonik P25.

The shift of the absorption towards the visible region enhances the photocatalytic activity under visible light for the pure and doped TiO₂, in comparison with Evonik P25. This is confirmed by the photocatalytic experiments of Section 3.7.

3.6. XPS analysis

Ti 2p, O 1s, N 1s, and Zr 3d spectra are presented in Fig. 6 for pure TiO₂ and TiO₂/Zr_{2.0}. For all doped samples, similar spectra are obtained. On the Ti 2p spectrum (Fig. 6a), for both samples the Ti 2p_{1/2} and Ti 2p_{3/2} are observed at 464 and 459 eV respectively. They are attributed to Ti⁴⁺ species [10,20,24] and thus TiO₂. No differences between samples can be noticed in the Ti 2p area. For the O 1s spectrum, both samples present a peak at 530 eV corresponding to Ti–O in TiO₂ [50]. The tail at higher binding energy in the O1s peak is hardly exploitable because of the presence of a non-negligible amount of oxygen involved in the carbonaceous contamination. For the N 1s spectrum (Fig. 6c), two peaks are observed for TiO₂/Zr_{2.0}, i.e. one centered on 400 eV, as for pure TiO₂, and a small one around 407 eV. In the literature, a N 1s peak around 400 eV may correspond to interstitial Ti–O–N [51,52] leading to visible absorption. It is in accordance with the diffuse reflectance measurements (Fig. 5). Indeed, the N-doping allows a higher visible absorption than Evonik P25. The second peak at 407 eV is attributed to residual nitrate due to the residual nitric acid from the synthesis as shown in Ref. [10]. This contribution is not taken into account in

the latter quantification. For the Zr 3d spectrum (Fig. 6d), for Zr-doped samples only, two peaks are observed at 182.4 eV and 185.0 eV and correspond to Zr 3d_{3/2} and Zr 3d_{5/2} electronic states [24,53,54]. These peaks correspond to ZrO₂ material and could be indicative of the production of hybrid TiO₂–ZrO₂ nanoparticles as reported in Refs. [24,50,55]. Indeed, TEM micrographs do not show a difference of morphology between pure and Zr-doped TiO₂ samples, indicating that a TiO₂–ZrO₂ mixed structure is very likely. The atomic ratios N/Ti and Zr/Ti estimated with XPS measurements are presented in Table 2. The N/Ti ratio is quite similar for each sample, meaning that the nitrogen doping is identical. It is in agreement with the absorption spectrum of the samples (Table 1 and Fig. 5), which is quite similar. Concerning the Zr/Ti ratio, it increases logically with the dopant content. The ratio Zr/Ti is calculated also from the ICP-AES measurements (Table 2), the values are a bit lower than the ratios measured by XPS but stay in the same range. So, the ZrO₂ seems to be localized rather at the surface of the samples.

3.7. Photocatalytic activity

3.7.1. Experiments under UV–Visible light

The photocatalytic degradation of PNP after 8 h under UV–visible light is presented in Fig. 7. Without photocatalyst, no degradation is observed, meaning there is no spontaneous decomposition of PNP under illumination. For the samples of this study, the degradation increases with the dopant content, starting from 20% for the pure TiO₂ to 96% for the highest doping (TiO₂/Zr_{2.0}). In comparison, the commercial Evonik P25 sample degrades 84% of PNP.

The increase of activity under UV–visible light with ZrO₂ doping can be explained by: i) an increase of the crystallinity between the pure and Zr-doped samples; ii) the decrease in aggregate size in suspension and iii) the formation of mixed TiO₂–ZrO₂ oxides. First, regarding the crystallinity (Table 1), the phase distribution estimated with *Profex* software shows that the amorphous fraction is higher for the pure TiO₂ sample. An increase in the amount of crystalline material induces a better photoactivity. Furthermore, when TiO₂ is doped with zirconia, the increased phase fraction is anatase. It is well-known that anatase is the most photoactive phase of TiO₂ materials [26].

Concerning the decrease in aggregate size, it is observed in Table 1 that D_{DLS} decreases when the materials are doped with ZrO₂. This size decrease in suspension can lead to less light scattering and to the illumination of more catalyst particles. Indeed, the particles are very small compared to the wavelength of light (max 60 nm vs. min 390 nm). Then the scattering can be described as Rayleigh scattering, which scales as R^4 , with R the radius of the particles. If the concentration of particles remains constant, then the number of particles per volume scales with R^{-3} , i.e. the smaller the particles, the more particles per volume. Therefore, the scattering power per volume scales with R : so the smaller the particles, the less light scattering.

Regarding the mixed TiO₂–ZrO₂ oxide formation, the XPS spectrum (Fig. 6d) shows that ZrO₂ doping is well present in the samples with an increased content through the samples. The TEM micrographs (Fig. 3) shows no difference in the morphology of the samples, with the formation of spherical shape nanoparticles around 6–7 nm. Therefore, a mixed oxide between TiO₂ and ZrO₂ is formed. This mixed oxide can increase the photoactivity by increasing the recombination time between the charges (e^- and h^+). The mechanism is described in Fig. 8. Indeed, it is possible to calculate the conduction and valence band potentials [55–57] of TiO₂ and ZrO₂ with the estimated band gap (Table 1 and Fig. 5) for TiO₂ and the value of 5.2 eV for the ZrO₂ as reported in many studies

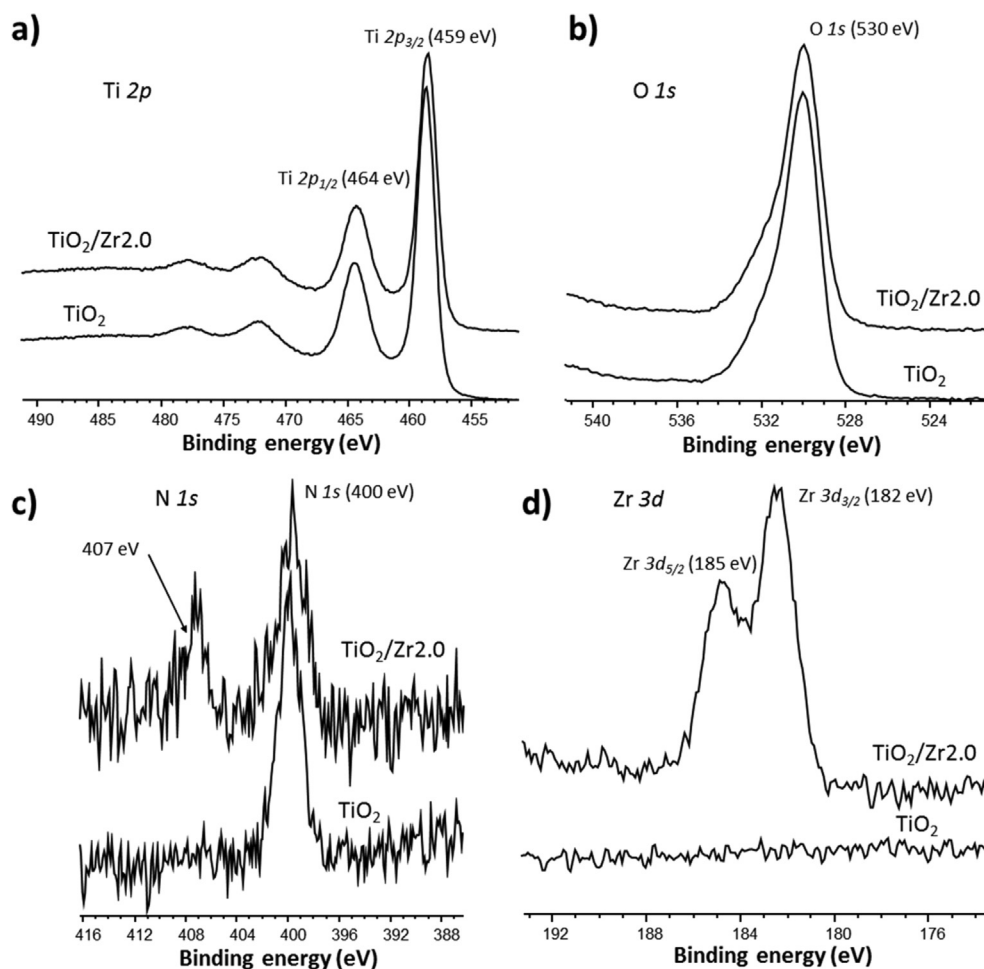


Fig. 6. XPS spectra of pure TiO_2 and $\text{TiO}_2/\text{Zr2.0}$: (a) Ti 2p region, (b) O 1s region, (c) N 1s region and (d) Zr 3d region.

Table 2

Molar ratios from XPS measurements and comparison with ICP-AES measurements.

Sample	N/Ti _{XPS}	Zr/Ti _{XPS}	Zr/Ti _{ICP}
Pure TiO_2	0.035	0.000	0.000
$\text{TiO}_2/\text{Zr0.7}$	0.029	0.011	0.007
$\text{TiO}_2/\text{Zr1.4}$	0.035	0.022	0.014
$\text{TiO}_2/\text{Zr1.6}$	0.033	0.023	0.016
$\text{TiO}_2/\text{Zr2.0}$	0.033	0.028	0.020

N/Ti_{XPS}: molar ratio of nitrogen to titanium from XPS measurements; Zr/Ti_{XPS}: molar ratio of zirconium to titanium from XPS measurements; Zr/Ti_{ICP}: molar ratio of zirconium to titanium from ICP-AES measurements.

[19,55,58]. The calculated energy levels for both oxides are represented in Fig. 8. The mechanism in the mixed oxide is interpreted as follows: when the samples are illuminated with UV–visible light, the TiO_2 materials are excited producing photogenerated electrons (e^-) and holes (h^+). Zirconia, with a larger band gap (5.2 eV), is poorly activated but electrons from its valence band can be transferred to the valence band of TiO_2 as the energy levels are close ($\Delta E \sim 1.1$ eV) [55]. A part of the photogenerated h^+ can be transferred to the valence band of zirconia. Therefore, the separation between the e^- and h^+ is larger, leading to a more efficient photoactivity than pure TiO_2 . In our samples (Fig. 7), when the doping content is low ($\text{TiO}_2/\text{Zr0.7}$), the efficiency of charge separation is quite low due to the low amount of zirconia. The increase of

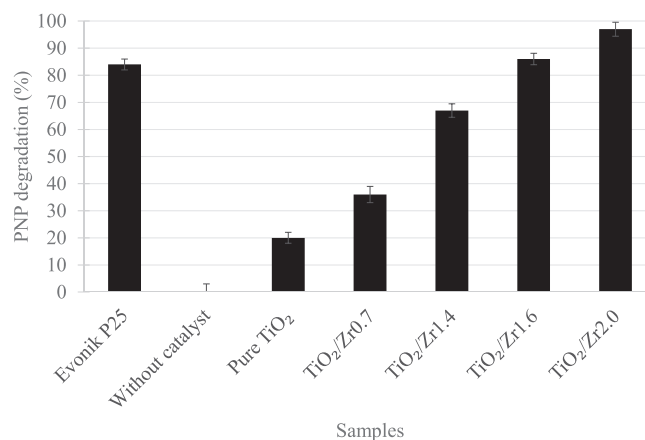


Fig. 7. PNP degradation (%) without catalyst and for all the samples under UV/visible light after 8 h of illumination.

efficiency is thus moderate. In our samples (Fig. 7), the photocatalytic efficiency increases with the amount of zirconia, which is particularly outstanding for 1.6 and 2.0 mol% Zr samples with an activity 5 times higher than the pure TiO_2 sample. The assumption is that the efficiency of charge separation becomes more efficient for higher zirconia contents.

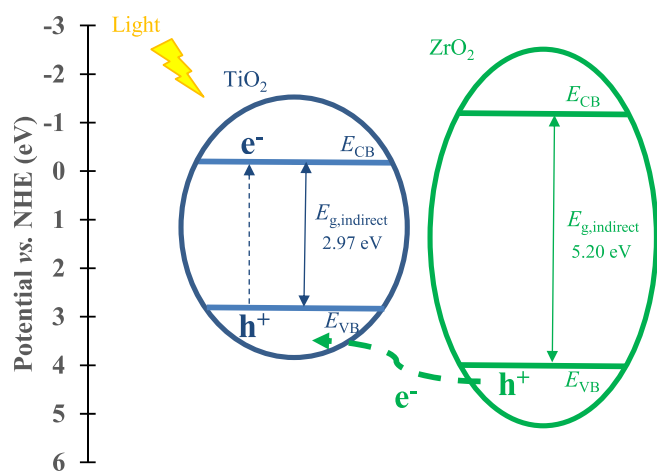


Fig. 8. Mechanism of charge transfer in mixed TiO_2 – ZrO_2 sample. e^- and h^+ correspond to the photogenerated electron and hole, E_{CB} and E_{VB} stand for potentials of conduction and valence band, $E_{g,\text{indirect}}$ corresponds to the indirect band gap.

3.7.2. Experiments under visible light

Under visible light ($\lambda > 390$ nm) and after 24 h of reaction (Fig. 9), the PNP degradation reaches 25% for the pure TiO_2 sample. The doped samples have slightly better activities, reaching a maximum degradation of 38% for the $\text{TiO}_2/\text{Zr}_2.0$ sample. The Evonik P25 degrades only 12% of PNP. Degradation under visible light is less efficient than under UV/Visible light.

The activity under visible light is probably due to the N-doping of the samples with the use of nitric acid for the synthesis [10]. Indeed, Fig. 6c shows that Ti–O–N bonds are most likely present in all samples (pure and doped ones). The photoactivity (Fig. 9) is then greater than that of Evonik P25 which does not contain any trace of nitrogen [59]. Nevertheless, Zr-doping allows an increase of the degradation with the dopant content. This improvement of photoactivity can be explained by the same mechanism (Fig. 8) as explained above for experiments under UV/visible light. Indeed, this mechanism allows a better charge separation and thus a better efficiency. The visible light being less energetic than the UV light, the probability of transfer of photo-generated species could be lower leading to a proportionally lower increase of activity for the doped samples.

3.8. Film characterizations

In order to complete our comparison with Evonik P25 photocatalyst, films are deposited on pre-painted steel starting from P25, pure TiO_2 and $\text{TiO}_2/\text{Zr}_2.0$ samples.

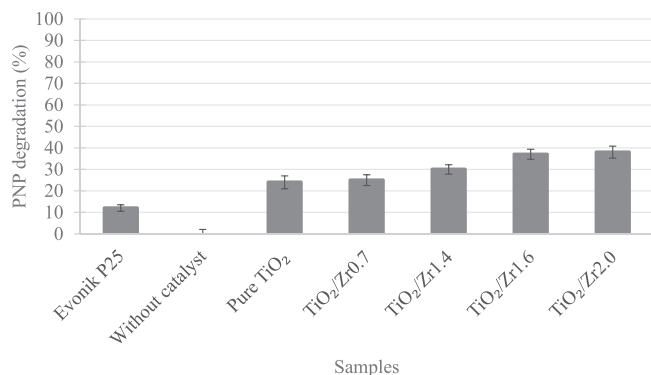


Fig. 9. PNP degradation (%) without catalyst and for all the samples under visible light ($\lambda > 390$ nm) after 24 h of illumination.

As detailed in Section 2.5, the suspensions are deposited on a pre-painted steel substrate by bar-coating. The films are washed with water and dried before characterization in order to ensure that the coating adheres to the substrate. For the sol-gel samples, films are realized with the initial colloids and with the powder dispersed in acidic water. Results are presented only for the dispersed powders, since similar results are obtained with initial colloids.

For both sol-gel samples, the film remains unchanged after washing; a slight iridescence of the surface is observed. On the contrary, the P25 coating is not well anchored to the substrate as determined visually. After the washing step, only some traces (“white zone”) of the coating are observed.

The samples are then measured by GIXRD to assess the presence of the TiO_2 coatings. A measurement of the bare substrate is realized because the white painting on the substrate could contain TiO_2 . The patterns are presented in Fig. 10.

As expected, the bare substrate contains rutile TiO_2 particles (Fig. 10) with well-distinguished peaks. For the P25 film, no difference with the bare substrate is observed, the amount of remaining P25 is probably too low to be detected. Contrarily, for both sol-gel samples, pure TiO_2 and $\text{TiO}_2/\text{Zr}_2.0$, anatase broad peak at 25° is clearly observed. The shape of this peak is similar to the one obtained with the powder (Fig. 1). Indeed, as the crystallites are very small (around 4–6 nm, Table 1), the peaks are broad.

As the GIXRD highlighted the presence of a TiO_2 film, especially for the sol-gel samples of this study, their potential photoactivity is assessed on the degradation of MB under UV-A illumination. The results are presented in Fig. 11.

Dark tests are performed on each type of coating. They show a MB adsorption of maximum 4% (the one illustrated in Fig. 11), which has to be subtracted from the measured percentage in order to obtain the correct MB degradation values. For the P25 film, a slight activity is observed with an absolute degradation around 5% after dark test correction. This weak activity is in agreement with the bad quality of the film produced with the aqueous suspension of Evonik P25. The formation of a more photoactive film with P25 suspension probably needs a more complex protocol of dispersion using dispersing agents [60–64] or surface charging with metallic ions [65].

Contrarily, both pure TiO_2 and $\text{TiO}_2/\text{Zr}_2.0$ samples show high photoactivities for MB degradation (Fig. 11). Again, the zirconia doping enhances the photoactivity of TiO_2 by a factor of 3–4. The easy formation of stable colloids by a simple redispersion of the corresponding powder in acidic water highlights another advantage of our materials compared to Evonik P25.

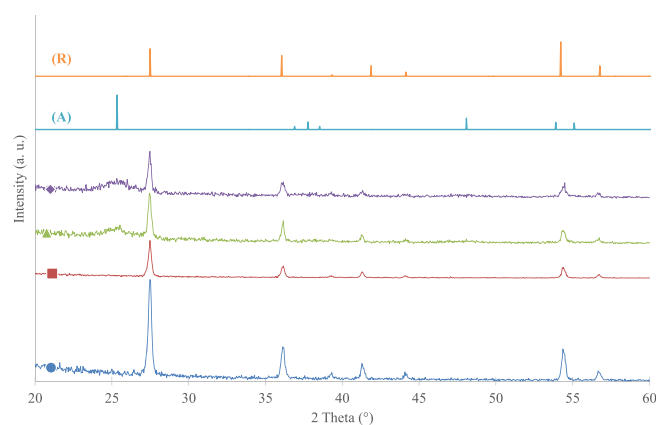


Fig. 10. Grazing Incidence X-Ray diffraction (GIXRD) patterns of films: (●) bare substrate (■) Evonik P25, (▲) pure TiO_2 and (◆) $\text{TiO}_2/\text{Zr}_0.2$. (A) reference pattern of anatase and (R) reference pattern of rutile.

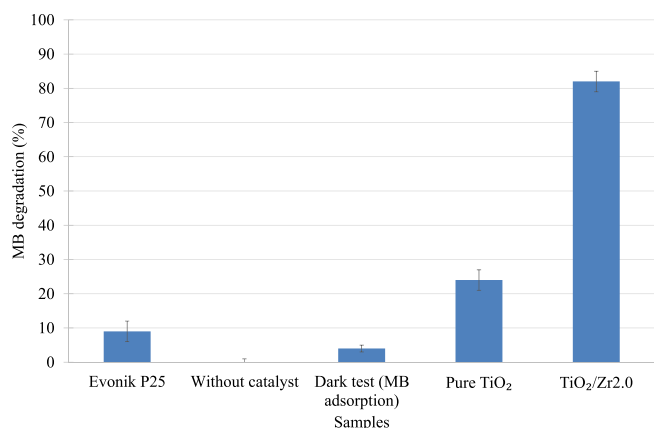


Fig. 11. MB degradation (%) for Evonik P25, pure TiO₂, TiO₂/Zr₂O and without catalyst under UV-A light ($\lambda = 365$ nm) after 17 h of illumination. The adsorption during the dark test is also presented (dark test) and needs to be subtracted from other measurements to evaluate the real MB degradation.

4. Conclusion

In this work, several TiO₂ materials doped with zirconia were synthesized by an easy aqueous sol-gel synthesis at ambient temperature. This method consists in the peptization of the TiO₂ precursor in presence of HNO₃. Four doping concentrations were prepared: 0.7, 1.4, 1.6 and 2.0 mol%. The corresponding pure TiO₂ material was also synthesized for comparison. The physico-chemical properties and the photoactivity of these materials were compared to the well-known Evonik P25 photocatalyst throughout this study.

The physico-chemical characterizations showed that nano-crystalline anatase-brookite particles were produced with sol-gel process. An amorphous fraction is present in each sample decreasing from 50 wt% in pure TiO₂ sample to 20–30 wt% in the doped ones. Higher specific surface areas than P25 were measured for all samples (i.e. around 200 m² g⁻¹ vs. 47 m² g⁻¹). All the samples present visible adsorption compared to P25.

As determined by XPS, all the samples were doped with nitrogen and mixed TiO₂–ZrO₂ oxide materials were obtained when doping with zirconia precursor.

The photoactivity on the powder samples was assessed both under UV/visible and visible illumination. Under UV/visible light, the presence of zirconia improved the efficiency of the PNP degradation. This improvement is suggested to be due to a better charge separation in the mixed semi-conductors TiO₂ and ZrO₂ oxides. In the present experimental conditions, an activity higher than P25 was reached for the highest doping content (i.e. 84% for P25 vs. 96% for TiO₂/Zr₂O). Under visible light, all samples were much better than P25, mainly due to the N-doping allowing photoactivity in visible range. The zirconia also increased the efficiency of the process.

Finally, the possibility to produce films easily with the aqueous suspension of the photocatalyst was assessed on the pure and the most doped material. P25 was also tested as reference material. The results showed that crystalline films were produced with the sol-gel materials, while P25 film had bad adherence. The photoactivity was evaluated on the degradation of methylene blue under UV-A light. The most doped sample highlighted very good MB degradation, i.e. 4 times higher than the pure one and 20 times higher than P25 even if a very low amount of P25 was deposited.

The best sample of this study presented a better activity than P25 in the form of powder as well as film under the three different

sources of illumination used. This sample is prepared with an environmentally-friendly synthesis with a limited use of organic reagents, water as solvent, at ambient temperature and pressure, and without the calcination step usually required for crystallization, whereas P25 is produced by an aerosol process.

Compliance with ethical standards

Conflict of interest

The authors declare that they have no conflicts of interest.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Acknowledgement

S. D. L. thanks the Belgian National Funds for Scientific Research (F.R.S.-FNRS) for her Senior Associate Researcher position. R. G. T. benefits from funding of the Fund for Scientific Research (FNRS) under a Fund for Research Training in Industry and Agriculture (FRIA) grant. The authors also thank the Ministère de la Région Wallonne Direction Générale des Technologies, de la Recherche et de l'Energie (DG06).

References

- [1] A. Turolla, M. Fumagalli, M. Bestetti, M. Antonelli, Electrophotocatalytic decolorization of an azo dye on TiO₂ self-organized nanotubes in a laboratory scale reactor, *Desalination* 285 (2012) 377–382, <https://doi.org/10.1016/j.desal.2011.10.029>.
- [2] N. Scholz, Setting Criteria on Endocrine Disruptors: Follow-Up to the General Court Judgment, Brief. From Eur. Parliam., 2016, pp. 1–10. [http://www.europarl.europa.eu/RegData/etudes/BRIE/2016/581986/EPRS_BRI\(2016\)581986_EN.pdf](http://www.europarl.europa.eu/RegData/etudes/BRIE/2016/581986/EPRS_BRI(2016)581986_EN.pdf).
- [3] M.A. Oturan, J.J. Aaron, Advanced oxidation processes in water/wastewater treatment: principles and applications. A review, *Crit. Rev. Environ. Sci. Technol.* 44 (2014) 2577–2641, <https://doi.org/10.1080/10643389.2013.829765>.
- [4] J.G. Mahy, S.D. Lambert, G.L.-M. Léonard, A. Zubiaur, P.-Y. Olu, A. Mahmoud, F. Boschini, S.D. Lambert, B. Heinrichs, Towards a large scale aqueous sol-gel synthesis of doped TiO₂: study of various metallic dopings for the photocatalytic degradation of p-nitrophenol, *J. Photochem. Photobiol. A Chem.* 329 (2016) 189–202, <https://doi.org/10.1016/j.jphotochem.2016.06.029>.
- [5] A. Fujishima, K. Hashimoto, T. Watanabe, *TiO₂ Photocatalysis: Fundamentals and Applications*, first ed., BKC Inc., Tokyo, Japan, 1999.
- [6] M. Pelaez, N.T. Nolan, S.C. Pillai, M.K. Seery, P. Falaras, A.G. Kontos, P.S.M. Dunlop, J.W.J. Hamilton, J.A. Byrne, K. O'Shea, M.H. Entezari, D.D. Dionysiou, A review on the visible light active titanium dioxide photocatalysts for environmental applications, *Appl. Catal. B Environ.* 125 (2012) 331–349, <https://doi.org/10.1016/j.apcatb.2012.05.036>.
- [7] A. Di Paola, G. Marcì, L. Palmisano, M. Schiavello, K. Uosaki, S. Ikeda, B. Ohtani, Preparation of polycrystalline TiO₂ photocatalysts impregnated with various transition metal ions: characterization and photocatalytic activity for the degradation of 4-nitrophenol, *J. Phys. Chem. B* 106 (2002) 637–645, <https://doi.org/10.1021/jp013074l>.
- [8] M.R. Espino-Estévez, C. Fernández-Rodríguez, O.M. González-Díaz, J. Araña, J.P. Espinós, J.A. Ortega-Méndez, J.M. Doña-Rodríguez, Effect of TiO₂-Pd and TiO₂-Ag on the photocatalytic oxidation of diclofenac, isoproturon and phenol, *Chem. Eng. J.* 298 (2016) 82–95, <https://doi.org/10.1016/j.cej.2016.04.016>.
- [9] C.J. Bodson, B. Heinrichs, L. Tasseroul, C. Bied, J.G. Mahy, M. Wong Chi Man, S.D. Lambert, Efficient P- and Ag-doped titania for the photocatalytic degradation of waste water organic pollutants, *J. Alloy. Comp.* 682 (2016) 144–153, <https://doi.org/10.1016/j.jallcom.2016.04.295>.
- [10] J.G. Mahy, V. Cerfontaine, D. Poelman, F. Devred, E.M. Gaigneaux, B. Heinrichs, S.D. Lambert, Highly efficient low-temperature N-doped TiO₂ catalysts for visible light photocatalytic applications, *Materials* 11 (2018) 584, <https://doi.org/10.3390/ma11040584>.
- [11] G. Impellizzeri, V. Scuderi, L. Romano, P.M. Sberna, E. Arcadipane, R. Sanz, M. Scuderi, G. Nicotra, M. Bayle, R. Carles, F. Simone, V. Privitera, Fe ion-

- implanted TiO₂ thin film for efficient visible-light photocatalysis, *J. Appl. Phys.* 116 (2016) 173507, <https://doi.org/10.1063/1.4901208>.
- [12] T. Wu, T. Lin, J. Zhao, H. Hidaka, N. Serpone, TiO₂-assisted photodegradation of dyes. 9. Photooxidation of a squarylium cyanine dye in aqueous dispersions under visible light irradiation, *Environ. Sci. Technol.* 33 (1999) 1379–1387, <https://doi.org/10.1021/es980923i>.
 - [13] K.S. Min, R.S. Kumar, J.H. Lee, K.S. Kim, S.G. Lee, Y.-A. Son, Synthesis of new TiO₂/porphyrin-based composites and photocatalytic studies on methylene blue degradation, *Dyes Pigments* 160 (2019) 37–47, <https://doi.org/10.1016/j.dyepig.2018.07.045>.
 - [14] J.G. Mahy, C.A. Paez, C. Carcel, C. Bied, A.S. Tatton, C. Dambon, B. Heinrichs, S.D. Lambert, Porphyrin-based hybrid silica-titania as a visible-light photocatalyst, *J. Photochem. Photobiol. A Chem.* 373 (2019) 66–76, <https://doi.org/10.1016/j.jphotochem.2019.01.001>.
 - [15] G.L.-M. Léonard, C.A. Paez, A.E. Ramírez, J.G. Mahy, B. Heinrichs, Interactions between Zn²⁺ or ZnO with TiO₂ to produce an efficient photocatalytic, superhydrophilic and aesthetic glass, *J. Photochem. Photobiol. A Chem.* 350 (2018) 32–43, <https://doi.org/10.1016/j.jphotochem.2017.09.036>.
 - [16] J.J. Reinoso, C.M. Alvarez Docio, V.Z. Ramírez, J.F. Fernández Lozano, Hierarchical nano ZnO-micro TiO₂ composites: high UV protection yield lowering photodegradation in sunscreens, *Ceram. Int.* 44 (2018) 2827–2834, <https://doi.org/10.1016/j.ceramint.2017.11.028>.
 - [17] Q. Tian, W. Wei, J. Dai, Q. Sun, J. Zhuang, Y. Zheng, P. Liu, M. Fan, L. Chen, Porous core-shell Ti_xSn_{1-x}O₂ solid solutions with broad-light response: one-pot synthesis and ultrahigh photooxidation performance, *Appl. Catal. B Environ.* 244 (2019) 45–55, <https://doi.org/10.1016/j.apcatb.2018.11.045>.
 - [18] M. Wu, D.Y.C. Leung, Y. Zhang, H. Huang, R. Xie, W. Szeto, F. Li, Toluene degradation over Mn-TiO₂/CeO₂ composite catalyst under vacuum ultraviolet (VUV) irradiation, *Chem. Eng. Sci.* 195 (2019) 985–994, <https://doi.org/10.1016/j.ces.2018.10.044>.
 - [19] J. Lang, L. Matějová, I. Troppová, L. Čapek, J. Endres, S. Daniš, Novel synthesis of Zr_xTi_{1-x}O_n mixed oxides using titanyl sulphate and pressurized hot and supercritical fluids, and their photocatalytic comparison with sol-gel prepared equivalents, *Mater. Res. Bull.* 95 (2017) 95–103, <https://doi.org/10.1016/j.materresbull.2017.07.023>.
 - [20] K. Maver, U.L. Štangar, U. Černigoj, S. Gross, R. Cerc Korošec, Low-temperature synthesis and characterization of TiO₂ and TiO₂-ZrO₂ photocatalytically active thin films, *Photochem. Photobiol. Sci.* 8 (2009) 657–662, <https://doi.org/10.1039/b817475j>.
 - [21] S. Ranjbar, K. Saberyan, F. Parsayan, A new process for preparation of Zr doped TiO₂ nanopowders using APCVS method, *Mater. Chem. Phys.* 214 (2018) 337–344, <https://doi.org/10.1016/j.matchemphys.2018.04.119>.
 - [22] 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. Gen.* 333 (2007) 264–271, <https://doi.org/10.1016/j.apcata.2007.09.026>.
 - [23] M.R. Mohammadi, D.J. Fray, Synthesis and characterisation of nanosized TiO₂-ZrO₂ binary system prepared by an aqueous sol-gel process: physical and sensing properties, *Sensor. Actuator. B Chem.* 155 (2011) 568–576, <https://doi.org/10.1016/j.snb.2011.01.009>.
 - [24] T.V.L. Thejaswini, D. Prabhakaran, M.A. Maheswari, Synthesis of mesoporous worm-like ZrO₂-TiO₂ monoliths and their photocatalytic applications towards organic dye degradation, *J. Photochem. Photobiol. A Chem.* 344 (2017) 212–222, <https://doi.org/10.1016/j.jphotochem.2017.05.015>.
 - [25] N. Todorova, T. Giannakopoulou, S. Karapati, D. Petridis, T. Vaimakis, C. Trapalis, Composite TiO₂/clays materials for photocatalytic NO_x oxidation, *Appl. Surf. Sci.* 319 (2014) 113–120, <https://doi.org/10.1016/j.apsusc.2014.07.020>.
 - [26] C.M. Malengreux, S. Douven, D. Poelman, B. Heinrichs, J.R. Bartlett, An ambient temperature aqueous sol-gel processing of efficient nanocrystalline doped TiO₂-based photocatalysts for the degradation of organic pollutants, *J. Sol. Gel Sci. Technol.* 71 (2014) 557–570, <https://doi.org/10.1007/s10971-014-3405-6>.
 - [27] A. Romeiro, M.E. Azenha, M. Canle, V.H.N. Rodrigues, J.P. Da Silva, H.D. Burrows, Titanium dioxide nanoparticle photocatalysed degradation of ibuprofen and naproxen in water: competing hydroxyl radical attack and oxidative decarboxylation by semiconductor holes, *Chemistry* 3 (2018) 10915–10924, <https://doi.org/10.1002/slct.201801953>.
 - [28] A.P. Mbouopda, E. Acayanka, S. Nzali, G.Y. Kamgang, E.B. Njoyim Tamungang, S. Laminsi, D. Richard, Comparative study of plasma-synthesized and commercial-P25 TiO₂ for photocatalytic discoloration of Reactive Red 120 dye in aqueous solution, *Desalin. Water Treat.* 136 (2018) 413–421, <https://doi.org/10.5004/dwt.2018.23118>.
 - [29] T. Ohno, K. Sarukawa, K. Tokieda, M. Matsumura, Morphology of a TiO₂ photocatalyst (Degussa, P-25) consisting of anatase and rutile crystalline phases, *J. Catal.* 203 (2001) 82–86, <https://doi.org/10.1006/jcat.2001.3316>.
 - [30] B. Ohtani, O.O. Prieto-Mahaney, D. Li, R. Abe, What is Degussa (Evonic) P25? Crystalline composition analysis, reconstruction from isolated pure particles and photocatalytic activity test, *J. Photochem. Photobiol. A Chem.* 216 (2010) 179–182, <https://doi.org/10.1016/j.jphotochem.2010.07.024>.
 - [31] M. Janus, A.W. Morawski, New method of improving photocatalytic activity of commercial Degussa P25 for azo dyes decomposition, *Appl. Catal. B Environ.* 75 (2007) 118–123, <https://doi.org/10.1016/j.apcatb.2007.04.003>.
 - [32] A. McNeill, N. Wells, Y. Xu, X. Li, S.E.J. Bell, A. Mills, Production and testing of novel photocatalytic TiO₂ surface-exposed nanoparticle (TiO₂-SEN) thin plastic films, *J. Photochem. Photobiol. A Chem.* 369 (2019) 142–149, <https://doi.org/10.1016/j.jphotochem.2018.10.025>.
 - [33] L. Tasseroul, C.A. Paez, S.D. Lambert, D. Eskenazi, B. Heinrichs, Photocatalytic decomposition of hydrogen peroxide over nanoparticles of TiO₂ and Ni(II)-porphyrin-doped TiO₂: a relationship between activity and porphyrin anchoring mode, *Appl. Catal. B Environ.* 182 (2016) 405–413, <https://doi.org/10.1016/j.apcatb.2015.09.042>.
 - [34] J.G. Mahy, L. Tasseroul, A. Zubiaur, J. Geens, M. Brisbois, M. Herlitschke, B. Heinrichs, S.D. Lambert, Highly dispersed iron xerogel catalysts for p-nitrophenol degradation by photo-Fenton effects, *Microporous Mesoporous Mater.* 197 (2014) 164–173, <https://doi.org/10.1016/j.micromeso.2014.06.009>.
 - [35] J.C.W. Sing, J. Rouquerol, 3 characterization of solid catalysts, *Handb. Heterog. Catal.* 438 (1997) 428–582, <https://doi.org/10.1002/9783527619474.ch3a>.
 - [36] N. Doebelin, R. Kleeberg, Profex: a graphical user interface for the Rietveld refinement program BGMN, *J. Appl. Crystallogr.* 48 (2015) 1573–1580, <https://doi.org/10.1107/S1600576715014685>.
 - [37] I.C. Madsen, R.J. Finney, R.C.A. Flann, M.T. Frost, B.W. Wilson, Quantitative analysis of high-alumina refractories using X-ray powder diffraction data and the Rietveld method, *J. Am. Ceram. Soc.* 74 (1991) 619–624, <https://doi.org/10.1111/j.1151-2916.1991.tb04069.x>.
 - [38] A. Lecloux, Exploitation des isothermes d'adsorption et de désorption d'azote pour l'étude de la texture des solides poreux, *Mémoires Société R. Des Sci. Liège.* (1971) 169–209.
 - [39] J.G. Mahy, G.L.-M. Léonard, S. Pirard, D. Wicky, A. Daniel, C. Archambeau, B. Heinrichs, Aqueous sol-gel synthesis and film deposition methods for the large-scale manufacture of coated steel with self-cleaning properties, *J. Sol. Gel Sci. Technol.* 81 (2017) 27–35, <https://doi.org/10.1007/s10971-016-4020-5>.
 - [40] P. Kubelka, F. Munk, Ein Beitrag zur Optik der Farbanstriche, *Z. Tech. Phys.* 12 (1931) 593–601.
 - [41] P. Kubelka, New contributions to the optics of intensely light-scattering materials, *J. Opt. Soc. Am.* 38 (1948) 448–457, <https://doi.org/10.1364/JOSA.38.000448>.
 - [42] C.M. Malengreux, S.L. Pirard, G. Léonard, J.G. Mahy, M. Herlitschke, B. Klobes, B. Heinrichs, J.R. Bartlett, Study of the photocatalytic activity of Fe³⁺, Cr³⁺, La³⁺ and Eu³⁺ single-doped and co-doped TiO₂ catalysts produced by aqueous sol-gel processing, *J. Alloy. Comp.* 691 (2017) 726–738, <https://doi.org/10.1016/j.jallcom.2016.08.211>.
 - [43] C.E. Bryson, Surface potential control in XPS, *Surf. Sci.* 189/190 (1987) 50–58, [https://doi.org/10.1016/S0039-6028\(87\)80414-4](https://doi.org/10.1016/S0039-6028(87)80414-4).
 - [44] D.A. Shirley, High-resolution X-ray photoemission spectrum of the valence bands of gold, *Phys. Rev. B* 5 (1972) 4709–4714, <https://doi.org/10.1103/PhysRevB.5.4709>.
 - [45] C.A. Paez, D.Y. Lique, C. Calberg, S.D. Lambert, I. Willems, A. Germeau, J.P. Pirard, B. Heinrichs, Study of photocatalytic decomposition of hydrogen peroxide over ramsdellite-MnO₂ by O₂-pressure monitoring, *Catal. Commun.* 15 (2011) 132–136, <https://doi.org/10.1016/j.catcom.2011.08.025>.
 - [46] J.G. Mahy, F. Deschamps, V. Collard, C. Jérôme, J. Bartlett, S.D. Lambert, B. Heinrichs, Acid acting as redispersing agent to form stable colloids from photoactive crystalline aqueous sol-gel TiO₂ powder, *J. Sol. Gel Sci. Technol.* 87 (2018) 568–583, <https://doi.org/10.1007/s10971-018-4751-6>.
 - [47] B.L. Bischoff, M.A. Anderson, Peptization process in the sol-gel preparation of porous anatase (TiO₂), *Chem. Mater.* 7 (1995) 1772–1778, <https://doi.org/10.1021/cm00058a004>.
 - [48] S. Mahshid, M. Askari, M.S. Ghamsari, Synthesis of TiO₂ nanoparticles by hydrolysis and peptization of titanium isopropoxide solution, *J. Mater. Process. Technol.* 189 (2007) 296–300, <https://doi.org/10.1016/j.jmatprotec.2007.01.040>.
 - [49] J.G. Mahy, S.D. Lambert, J. Geens, A. Daniel, D. Wicky, C. Archambeau, B. Heinrichs, Large scale production of photocatalytic TiO₂ coating for volatile organic compound (VOC) air remediation, *AIMS Mater. Sci.* 5 (2018) 945–956, <https://doi.org/10.3934/matricsci.2018.5.945>.
 - [50] M. Li, X. Li, G. Jiang, G. He, Hierarchically macro – mesoporous ZrO₂-TiO₂ composites with enhanced photocatalytic activity, *Ceram. Int.* 41 (2015) 5749–5757, <https://doi.org/10.1016/j.ceramint.2014.12.161>.
 - [51] R. Azouani, S. Tieng, K. Chhor, J.F. Bocquet, P. Eloy, E.M. Gaigneaux, K. Klementiev, A.V. Kanaev, TiO₂ doping by hydroxyurea at the nucleation stage: towards a new photocatalyst in the visible spectral range, *Phys. Chem. Chem. Phys.* 12 (2010) 11325–11334, <https://doi.org/10.1039/B923548E>.
 - [52] C. Bittencourt, M. Rutar, P. Umek, A. Mrzel, K. Vozel, D. Arcon, K. Henzler, P. Krüger, P. Guttman, Molecular nitrogen in N-doped TiO₂ nanoribbons, *RSC Adv.* 5 (2015) 23350–23356, <https://doi.org/10.1039/C4RA14410D>.
 - [53] A. Mbiri, D.H. Taffa, E. Gatebe, M. Mark, Zirconium doped mesoporous TiO₂ multilayer thin films: influence of the zirconium content on the photo-degradation of organic pollutants, *Catal. Today* 328 (2019) 71–78, <https://doi.org/10.1016/j.cattod.2019.01.043>.
 - [54] J. Qian, Q. Hu, X. Hou, F. Qian, L. Dong, B. Li, Study of different Ti/Zr ratios on the physicochemical properties and catalytic activities for CuO/Ti-Zr-O composites, *Ind. Eng. Chem. Res.* 57 (2018) 12792–12800, <https://doi.org/10.1021/acs.iecr.8b02674>.
 - [55] J. Tian, Q. Shao, J. Zhao, D. Pan, M. Dong, C. Jia, T. Ding, Microwave solvothermal carboxymethyl chitosan templated synthesis of TiO₂/ZrO₂ composites toward enhanced photocatalytic degradation of Rhodamine B,

- J. Colloid Interface Sci. 541 (2019) 18–29, <https://doi.org/10.1016/j.jcis.2019.01.069>.
- [56] L. Renuka, K.S. Anantharaju, Y.S. Vidya, H.P. Nagaswarupa, S.C. Prashantha, S.C. Sharma, H. Nagabhushana, G.P. Darshan, A simple combustion method for the synthesis of multi-functional ZrO_2/CuO nanocomposites: excellent performance as Sunlight photocatalysts and enhanced latent fingerprint detection, *Appl. Catal. B Environ.* 210 (2017) 97–115, <https://doi.org/10.1016/j.apcatb.2017.03.055>.
- [57] Y. Xu, M.A.A. Schoonen, The absolute energy positions of conduction and valence bands of selected semiconducting minerals, *Am. Mineral.* 85 (2000) 543–556, <https://doi.org/10.2138/am-2000-0416>.
- [58] H. Jiang, R.I. Gomez-abal, P. Rinke, M. Scheffler, Electronic band structure of zirconia and hafnia polymorphs from the GW perspective, *Phys. Rev. B* 81 (2010) 1–9, <https://doi.org/10.1103/PhysRevB.81.085119>.
- [59] J.L. Gole, J.D. Stout, C. Burda, Y. Lou, X. Chen, Highly efficient formation of visible light tunable $\text{TiO}_{2-x}\text{N}_x$ photocatalysts and their transformation at the nanoscale, *J. Phys. Chem. B* 108 (2004) 1230–1240, <https://doi.org/10.1021/jp030843n>.
- [60] A. Kohut, S. Ranjan, A. Voronov, W. Peukert, V. Tokarev, O. Bednarska, O. Gevus, S. Voronov, Design of a new invertible polymer coating on a solid surface and its effect on dispersion colloidal stability, *Langmuir* 22 (2006) 6498–6506, <https://doi.org/10.1021/la060162u>.
- [61] I. Zhitomirsky, A. Petric, Electrophoretic deposition of electrolyte materials for solid oxide fuel cells, *J. Mater. Sci.* 39 (2004) 825–831, <https://doi.org/10.1023/B:JMSC.0000012910.70526.61>.
- [62] B. Ferrari, S. González, R. Moreno, C. Baudín, Multilayer coatings with improved reliability produced by aqueous electrophoretic deposition, *J. Eur. Ceram. Soc.* 26 (2006) 27–36, <https://doi.org/10.1016/j.jeurceramsoc.2004.10.018>.
- [63] M. Feng, C. Gu, C. Bao, X. Chen, H. Yan, Z. Shi, X. Liu, Q. Lin, Synthesis of a benzyl-grafted alginate derivative and its effect on the colloidal stability of nanosized titanium dioxide aqueous suspensions for Pickering emulsions, *RSC Adv.* 8 (2018) 34397–34407, <https://doi.org/10.1039/C8RA04300K>.
- [64] J.S. Gebauer, V. Mackert, S. Ognjanović, M. Winterer, Tailoring metal oxide nanoparticle dispersions for inkjet printing, *J. Colloid Interface Sci.* 526 (2018) 400–409, <https://doi.org/10.1016/j.jcis.2018.05.006>.
- [65] O.O. Van der Biest, L.J. Vandeperre, Electrophoretic deposition of materials, *Annu. Rev. Mater. Sci.* 29 (1999) 327–352, <https://doi.org/10.1146/annurev.matsci.29.1.327>.