Ambient temperature ZrO_2-doped TiO_2 crystalline photocatalysts: Highly efficient powders and films for water depollution

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Abstract

In this paper, several TiO_2 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 consisted in the peptization of the TiO_2 colloid in presence of HNO_3. The corresponding pure TiO_2 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 m^2 g^{-1} vs. 47 m^2 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 TiO_2-ZrO_2 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 ZrO_2 doping increased the degradation efficiency of the pure TiO_2 catalyst due to a better charge separation in the mixed TiO_2-ZrO_2 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 TiO_2 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 TiO_2 and 20 times higher than P25.

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 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 (•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 photoefficiency 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 alkoxides 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]:

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

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 CaF_2 (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 TiO_2 anatase nanoparticles using the following formula [26]:

$$\frac{d_{BET}}{6} = \frac{\frac{1}{\rho_{anatase}}}{S_{BET}} \tag{2}$$

where ρ_{anatase} is the apparent density of TiO_2 anatase estimated to be equal to 3.89×10^3 kg m^{-3} [3, 8].

Optical properties of TiO_2-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 $BaSO_4$ 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 ($E_{g,\mathrm{direct}}$ and $E_{g,\mathrm{indirect}}$). 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 mm^2. 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]:

$$D_{\mathrm{PNPi}}(\%) = \left(1 - \frac{[PNP]_{\mathrm{i}}}{[PNP]_0}\right) * 100 \tag{3}$$

where $[PNP]_{\mathrm{i}}$ represents the residual concentration of PNP at time $t = \mathrm{i}$ 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 x 5 cm x 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 TiO_2 material.

Three suspensions are used for film application: pure TiO_2, TiO_2/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 HNO_3) in order to reach the same concentration as sol-gel colloids. The mixture is placed in ultrasonic bath for 1 h.

For pure TiO_2 and TiO_2/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 TiO_2 in the white painting.

The photocatalytic activity of TiO_2 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 Figure 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 Figure 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, TiO_2/Zr1.4 and TiO_2/Zr2.0 samples are presented in Figure 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 Figure 4 for pure TiO_2 and TiO_2/Zr2.0 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, V_{DR}, are reported in Table 1. These two values are similar for all samples, between 210 and 230 m^2 g^{-1} for S_{BET} and between 0.11 and 0.13 cm^3 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 (Figure 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 $m^2\ g^{-1}$ and 0.03 $cm^3\ g^{-1}$ respectively.

3.5. Optical properties

The normalized Kubelka–Munk function is represented in Figure 5 for pure TiO_2, TiO_2/Zr2.0, 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 Figure 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, Figure 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].

The shift of the absorption towards the visible region enhances the photocatalytic activity under visible light for the pure and doped TiO_2, 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 Figure 6 for pure TiO_2 and TiO_2/Zr2.0. For all doped samples, similar spectra are obtained. On the Ti *2p* spectrum (Figure 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 Ti^{4+} species [10,20,24] and thus TiO_2. 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 TiO_2 [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 (Figure 6c), two peaks are observed for TiO_2/Zr2.0, *i.e.* one centered on 400 eV, as for pure TiO_2, 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 (Figure 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 [10]. This contribution is not taken into account in the latter quantification. For the Zr *3d* spectrum (Figure 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 ZrO_2 material and could be indicative of the production of hybrid TiO_2-ZrO_2 nanoparticles as reported in [24,50,55]. Indeed, TEM micrographs do not show a difference of morphology between pure and Zr-doped TiO_2 samples, indicating that a TiO_2-ZrO_2 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 Figure 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 ZrO_2 seems to be localized rather at the surface of the samples.

3.7. Photocatalytic activity

Experiments under UV-Visible light

The photocatalytic degradation of PNP after 8 h under UV-visible light is presented in Figure 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 TiO_2 to 96% for the highest doping (TiO_2/Zr2.0). In comparison, the commercial Evonik P25 sample degrades 84% of PNP.

The increase of activity under UV-visible light with ZrO_2 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 TiO_2-ZrO_2 oxides. First, regarding the crystallinity (Table 1), the phase distribution estimated with *Profex* software shows that the amorphous fraction is higher for the pure TiO_2 sample. An increase in the amount of crystalline material induces a better photoactivity. Furthermore, when TiO_2 is doped with zirconia, the increased phase fraction is anatase. It is well-known that anatase is the most photoactive phase of TiO_2 materials [26].

Concerning the decrease in aggregate size, it is observed in Table 1 that D_{DLS} decreases when the materials are doped with ZrO_2. 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 TiO_2-ZrO_2 oxide formation, the XPS spectrum (Figure 6d) shows that ZrO_2 doping is well present in the samples with an increased content through the samples. The TEM micrographs (Figure 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 TiO_2 and ZrO_2 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 Figure 8. Indeed, it is possible to calculate the conduction and valence band potentials [55–57] of TiO_2 and ZrO_2 with the estimated band gap (Table 1 and Figure 5) for TiO_2 and the value of 5.2 eV for the ZrO_2 as reported in many studies [19,55,58]. The calculated energy levels for both oxides are represented in Figure 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 (Figure 7), when the doping content is low (TiO_2/Zr0.7), the efficiency of charge separation is quite low due to the low amount of zirconia. The increase of efficiency is thus moderate. In our samples (Figure 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.

Experiments under Visible light

Under visible light (λ > 390 nm) and after 24 h of reaction (Figure 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 TiO_2/Zr2.0 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, Figure 6c shows that Ti-O-N bonds are most likely present in all samples (pure and doped ones). The photoactivity (Figure 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 (Figure 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 TiO_2/Zr2.0 samples.

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 Figure 10.

As expected, the bare substrate contains rutile TiO_2 particles (Figure 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 TiO_2/Zr2.0, anatase broad peak at 25° is clearly observed. The shape of this peak is similar to the one obtained with the powder (Figure 1). Indeed, as the crystallites are very small (around 4-6 nm, Table 1), the peaks are broad.

As the GIXDR 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 Figure 11.

Dark tests are performed on each type of coating. They show a MB adsorption of maximum 4% (the one illustrated in Figure 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 TiO_2/Zr2.0 samples show high photoactivities for MB degradation (Figure 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.

4. Conclusion

In this work, several TiO_2 materials doped with zirconia were synthesized by an easy aqueous sol-gel synthesis at ambient temperature. This method consisted in the peptization of the TiO_2 precursor in presence of HNO_3. Four doping concentrations were prepared: 0.7, 1.4, 1.6 and 2.0 mol%. The corresponding pure TiO_2 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 TiO_2 sample to 20-30 wt% in the doped ones. Higher specific surface areas than P25 were measured for all samples (*i.e.* around 200 m^2 g^{-1} vs. 47 m^2 g^{-1}). All the samples present visible adsorption compared to P25.

As determined by XPS, all the samples were doped with nitrogen and mixed TiO_2-ZrO_2 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 TiO_2 and ZrO_2 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 TiO_2/Zr2.0). 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.

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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.

References

[1] A. Turolla, M. Fumagalli, M. Bestetti, M. Antonelli, Electrophotocatalytic decolorization of an azo dye on TiO_2 self-organized nanotubes in a laboratory scale reactor, Desalination. 285 (2012) 377–382. doi: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) 1–10. 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. doi: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 TiO_2: Study of various metallic dopings for the photocatalytic degradation of p-nitrophenol, J. Photochem. Photobiol. A Chem. 329 (2016) 189-202. doi:10.1016/j.jphotochem.2016.06.029.

[5] A. Fujishima, K. Hashimoto, T. Watanabe, TiO_2 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.

doi: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 TiO_2 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. doi: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 TiO_2–Pd and TiO_2–Ag on the photocatalytic oxidation of diclofenac, isoproturon and phenol, Chem. Eng. J. 298 (2016) 82–95. doi: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. Alloys Compd. 682 (2016) 144-153. doi: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 TiO_2 catalysts for visible light photocatalytic applications, Materials 11 (2018) 584. doi: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 TiO_2 thin film for efficient visible-light photocatalysis, J. Appl. Phys. 116 (2016) 173507. doi:10.1063/1.4901208.

[12] T. Wu, T. Lin, J. Zhao, H. Hidaka, N. Serpone, TiO_2 -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. doi: 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

TiO_2/porphyrin-based composites and photocatalytic studies on methylene blue degradation, Dye. Pigment. 160 (2019) 37–47. doi:10.1016/j.dyepig.2018.07.045.

[14] J.G. Mahy, C.A. Paez, C. Carcel, C. Bied, A.S. Tatton, C. Damblon, B. Heinrichs, S. D. Lambert, Porphyrin-based hybrid silica-titania as a visible-light photocatalyst, J. Photochem. Photobiol. A Chem. 373 (2019) 66–76. doi:10.1016/j.jphotochem.2019.01.001.

[15] G.L.-M. Léonard, C.A. Pàez, A.E. Ramírez, J.G. Mahy, B. Heinrichs, Interactions between Zn^{2+} or ZnO with TiO_2 to produce an efficient photocatalytic, superhydrophilic and aesthetic glass, J. Photochem. Photobiol. A Chem. 350 (2018) 32-43. doi:10.1016/j.jphotochem.2017.09.036.

[16] J.J. Reinosa, C.M. Álvarez Docio, V.Z. Ramírez, J.F. Fernández Lozano, Hierarchical nano ZnO-micro TiO_2 composites : High UV protection yield lowering photodegradation in sunscreens, Ceram. Int. 44 (2018) 2827–2834. doi: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 $Ti_xSn_{1-x}O_2$ solid solutions with broad-light response: One-pot synthesis and ultrahigh photooxidation performance, Appl. Catal. B Environ. 244 (2019) 45–55. doi: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-TiO_2/CeO_2 composite catalyst under vacuum ultraviolet (VUV) irradiation, Chem. Eng. Sci. 195 (2019) 985–994. doi: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. doi: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 TiO_2 and TiO_2-ZrO_2 photocatalytically active thin films, Photochem. Photobiol. Sci. 8 (2009) 657–662. doi:10.1039/b817475j.

[21] S. Ranjbar, K. Saberyan, F. Parsayan, A new process for preparation of Zr doped TiO_2 nanopowders using APCVS method, Mater. Chem. Phys. 214 (2018) 337–344. doi:10.1016/j.matchemphys.2018.04.119.

[22] B. Neppolian, Q. Wang, H. Yamashita, H. Choi, Synthesis and characterization of ZrO_2-TiO_2 binary oxide semiconductor nanoparticles: Application and interparticle electron transfer process, Appl. Catal. A Gen. 333 (2007) 264–271. doi:10.1016/j.apcata.2007.09.026.

[23] M.R. Mohammadi, D.J. Fray, Synthesis and characterisation of nanosized TiO_2-ZrO_2 binary system prepared by an aqueous sol-gel process: Physical and sensing properties, Sensors Actuators, B Chem. 155 (2011) 568–576. doi:10.1016/j.snb.2011.01.009.

[24] T.V.L. Thejaswini, D. Prabhakaran, M.A. Maheswari, Synthesis of mesoporous worm-like ZrO_2–TiO_2 monoliths and their photocatalytic applications towards organic dye degradation, J. Photochem. Photobiol. A Chem. 344 (2017) 212–222. doi:10.1016/j.jphotochem.2017.05.015.

[25] N. Todorova, T. Giannakopoulou, S. Karapati, D. Petridis, T. Vaimakis, C. Trapalis, Composite TiO_2 / clays materials for photocatalytic NOx oxidation, Appl. Surf. Sci. 319 (2014) 113–120. doi:10.1016/j.apsusc.2014.07.020.

[26] C.M. Malengreaux, S. Douven, D. Poelman, B. Heinrichs, J.R. Bartlett, An ambient temperature aqueous sol–gel processing of efficient nanocrystalline doped TiO_2-based photocatalysts for the degradation of organic pollutants, J. Sol-Gel Sci. Technol. 71 (2014) 557–570. doi: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, ChemistrySelect. 3 (2018) 10915–10924. doi: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 TiO_2 for photocatalytic discoloration of Reactive Red 120 dye in aqueous solution, Desalin. Water Treat. 136 (2018) 413–421. doi:10.5004/dwt.2018.23118.

[29] T. Ohno, K. Sarukawa, K. Tokieda, M. Matsumura, Morphology of a TiO_2 Photocatalyst (Degussa, P-25) Consisting of Anatase and Rutile Crystalline Phases, J. Catal. 203 (2001) 82–86. doi: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. doi: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. doi: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 TiO_2 surface-exposed nanoparticle (TiO_2-SEN) thin plastic films, J. Photochem. Photobiol. A Chem. 369 (2019) 142–149. doi:10.1016/j.jphotochem.2018.10.025.

[33] L. Tasseroul, C.A. Páez, S.D. Lambert, D. Eskenazi, B. Heinrichs, Photocatalytic decomposition of hydrogen peroxide over nanoparticles of TiO_2 and Ni(II)-porphyrin-doped TiO_2: A relationship between activity and porphyrin anchoring mode, Appl.

Catal. B Environ. 182 (2016) 405–413. doi: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. doi:10.1016/j.micromeso.2014.06.009.

[35] K.S.W. Sing, J. Rouquerol, 3 Characterization of Solid Catalysts, Handb. Heterog. Catal. 438 (1997) 428–582. doi: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. doi: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. doi: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. doi:10.1007/s10971-016-4020-5.

[40] P. Kubelka, F. Munk, Ein Beitrag zur Optik der Farban striche, 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. doi:10.1364/JOSA.38.000448.

[42] C.M. Malengreaux, S.L. Pirard, G. Léonard, J.G. Mahy, M. Herlitschke, B. Klobes, B. Heinrichs, J. R. Bartlett, Study of the photocatalytic activity of Fe^{3+}, Cr^{3+}, $La^{3+}$and Eu^{3+}single-doped and co-doped TiO_2 catalysts produced by aqueous sol-gel processing, J. Alloys Compd. 691 (2017) 726-738. doi:10.1016/j.jallcom.2016.08.211.

[43] C.E. Bryson, Surface potential control in XPS, Surf. Sci. 189/190 (1987) 50–58. doi: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. doi:10.1103/PhysRevB.5.4709.

[45] C.A. Páez, D.Y. Liquet, C. Calberg, S.D. Lambert, I. Willems, A. Germeau, J. P. Pirard, B. Heinrichs, Study of photocatalytic decomposition of hydrogen peroxide over ramsdellite-MnO_2 by O2-pressure monitoring, Catal. Commun. 15 (2011) 132–136. doi: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 TiO_2 powder, J. Sol-Gel Sci. Technol. 87 (2018) 568–583. doi:10.1007/s10971-018-4751-6.

[47] B.L. Bischoff, M.A. Anderson, Peptization Process in the Sol-Gel Preparation of Porous Anatase (TiO_2), Chem. Mater. 7 (1995) 1772–1778. doi:10.1021/cm00058a004.

[48] S. Mahshid, M. Askari, M.S. Ghamsari, Synthesis of TiO_2 nanoparticles by hydrolysis and peptization of titanium isopropoxide solution, J. Mater. Process. Technol. 189 (2007) 296–300. doi: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 TiO_2 coating for volatile organic compound (VOC) air remediation, AIMS Mater. Sci. 5 (2018) 945–956. doi:10.3934/matersci.2018.5.945.

[50] M. Li, X. Li, G. Jiang, G. He, Hierarchically macro – mesoporous ZrO_2–TiO_2 composites with enhanced photocatalytic activity, Ceram. Int. 41 (2015) 5749–5757. doi: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, TiO_2 doping by hydroxyurea at the nucleation stage: towards a new photocatalyst in the visible spectral range, Phys. Chem. Chem. Phys. 12 (2010) 11325-11334. doi:10.1039/B923548E.

[52] C. Bittencourt, M. Rutar, P. Umek, A. Mrzel, K. Vozel, D. Arcon, K. Henzler, P. Krüger, P. Guttmann, Molecular nitrogen in N-doped TiO_2 nanoribbons, RSC Adv. 5 (2015) 23350–23356. doi:10.1039/C4RA14410D.

[53] A. Mbiri, D.H. Taffa, E. Gatebe, M. Wark, Zirconium doped mesoporous TiO_2 multilayer thin films : Influence of the zirconium content on the photodegradation of organic pollutants, Catal. Today. 328 (2019) 71-78. doi: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. doi: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 TiO_2/ZrO_2 composites toward enhanced photocatalytic degradation of Rhodamine B, J. Colloid Interface Sci. 541 (2019) 18–29. doi: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. doi: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. doi: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. doi: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 $TiO_{2-x}N_x$ Photocatalysts and Their Transformation at the Nanoscale, J. Phys. Chem. B. 108 (2004) 1230–1240. doi: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. doi: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. doi: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. doi: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. doi: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. doi: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. doi:10.1146/annurev.matsci.29.1.327.