



# Influence of the surface-to-bulk defects ratio of ZnO and TiO<sub>2</sub> on their UV-mediated photocatalytic activity



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## ARTICLE INFO

### Article history:

Received 22 September 2016

Received in revised form 2 December 2016

Accepted 7 December 2016

Available online 8 December 2016

### Keywords:

Photocatalysis

Zinc oxide

Surface defects

Bulk defects

Nanoparticles

## ABSTRACT

Developing rational routes for nanoparticle synthesis with high photocatalytic (PC) efficiency is a mature field of research with yet unresolved issues. The presence of surface and bulk defects in the crystal structure is crucial as these exert different effect on the PC efficiency. However, understanding how the relative bulk-to-surface defects influence the PC activity is still missing. Mechanical activation (ball-milling) of ZnO nanoparticles is employed in this study as it provides a means to introduce lattice defects in a controlled way. The activated nano-powders were fully explored using techniques probing structure and optical properties. Notably, the defect density exhibits non-monotonic behavior against milling conditions. This unexpected behavior is interpreted by considering – the frequently overlooked fact – that various defect-probing techniques have different penetration depths into the particle volume; hence, each technique provides specific information on the relative bulk-to-surface defect ratio. Ball-milling appears to introduce mainly bulk defects as revealed by Raman scattering and X-ray diffraction. The kinetics of the PC activity on the degradation of methylene blue (MB) in water is in very good correlation with the defect density. Qualitative different results are obtained for TiO<sub>2</sub> nanoparticles where ball-milling engenders phase-transformation effects on the crystal lattice (phase transition and partial amorphization), while the PC activity in the MB degradation decreases also systematically with milling time. The current study provides some new insights into the issue of more reliable estimation of the bulk-to-surface defects ratio and their role on the PC activity of ZnO and TiO<sub>2</sub>.

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## 1. Introduction

The development of pure and modified photo-catalytically active nanomaterials, with potential use for water purification and disinfection, has been extensively studied for the degradation of most kinds of persistent organic pollutants, such as dyes, pesticides, chlorinated solvents and detergents, under UV, visible and solar irradiation [1–6]. Among the metal oxides used, TiO<sub>2</sub> has attracted most of the interest, whereas ZnO emerges over the last years as a very promising photocatalytic (PC) material for wastewater treatment, exhibiting even better photocatalytic activity than TiO<sub>2</sub> [7] attributed to its much higher electron mobility i.e. at least two orders of magnitude larger than that of TiO<sub>2</sub> [8]. However, both ZnO

and TiO<sub>2</sub> exhibit moderate charge separation and quick recombination of photo-generated charge carriers, which leads to low reaction photoefficiency [9]. To alleviate this problem as well as to activate these semiconductors to solar irradiation, many efforts have been focused on the enhancement of the PC activity of TiO<sub>2</sub> and ZnO by increasing their visible light absorption; this has mostly been based on changing the electronic structure of the semiconductor [10–15]. On another front, certain studies have focused on the influence of structure defects on the PC efficiency of these oxides whose structure has been modified by changing particle shape and size, surface defects, etc. [16]. As defects play a key role in the fundamental phenomena involved in photocatalysis, particular emphasis has been placed on discriminating the effect of bulk and surface defects [17]. Surface defects have a twofold role serving as (i) charge carrier traps; hence, deteriorating PC activity and (ii) adsorption sites for the pollutant improving electron-hole separation. On the contrary, bulk defects serve only as charge carriers recombination sites [18]. Many studies revealed that surface oxygen vacancies created

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by several methods (e.g. high temperature quenching, hydrogen thermal treatment, sonochemical process, etc.) [19–21] induced visible light absorption and enhanced the PC performance of TiO<sub>2</sub> [22,23] and ZnO [24,25]. However, contradictory results have been reported regarding the effect of bulk defects on the PC activity [26–28].

As defects play a dominant role of the lifetime and recombination rate of the photo-excited carriers, and taking into account that various kinds of defects exist in TiO<sub>2</sub> and ZnO such as oxygen vacancies, zinc/titanium interstitials, zinc vacancies and oxygen interstitials [29–31], it is challenging to understand how the type and concentration of defects affects the material PC performance. Furthermore, a thorough systematic comparison between the structural defects of TiO<sub>2</sub> and ZnO and their effect on the photocatalytic activity under UV irradiation is still lacking.

In this article we present a detailed investigation on the influence of defects, induced by high energy ball milling, on the PC activity of commercially available ZnO and TiO<sub>2</sub> (Degussa P25) nanoparticles. The PC activity was evaluated by the degradation of methylene blue (MB) from aqueous solutions in a lab-scale photocatalytic reactor under a UV light irradiation. The photocatalytic nanoparticles were characterized by a number of techniques such as SEM, XRD, Raman, UV–vis absorption, N<sub>2</sub> adsorption, PL and photoelectron spectroscopies (XPS/UPS). These techniques were employed in order to obtain information about the morphology (shape, size and aspect ratio), structure (crystal lattice, crystallinity and defects), other physicochemical properties (optical bandgap, photoluminescence, etc.) and surface chemistry of the photocatalytic materials. The combination of this information with the PC kinetics will shed light on the role of defects to the different PC activity between TiO<sub>2</sub> and ZnO.

## 2. Experimental section

### 2.1. Materials preparation

Commercial ZnO (Alfa Aesar, 99.8% purity) and TiO<sub>2</sub> (Degussa P25) powders were mechanically ground using a planetary milling instrument (Fritsch, model Pulverisette 7) operating at 400 rpm. Three different milling times were selected and the resulted activated nanopowders will be henceforth labeled as ZnO-0, ZnO-30, ZnO-60, and ZnO-180 for the 0, 30, 60, and 180 min milling time, respectively. Correspondingly, Degussa P25 TiO<sub>2</sub> powders were milled for the same times, hence following the labeling TiO<sub>2</sub>-0, TiO<sub>2</sub>-30, TiO<sub>2</sub>-60, and TiO<sub>2</sub>-300. The ball-to-mass ratio is 2:1, using 4 g of ZnO each time and 4:1 for TiO<sub>2</sub> using 1 g of TiO<sub>2</sub>.

### 2.2. Morphological and optical characterization

The morphology of the ZnO and TiO<sub>2</sub> powders was characterized by field-emission scanning electron microscopy FE-SEM (Zeiss SUPRA 35VP-FEG) operating at 5 keV. Changes brought about in the crystal structure and particle size of the milled powders were examined by X-ray diffraction (XRD) using a Bruker D8 Advanced instrument operating with Ni-filtered CuK $\alpha$ 1 radiation ( $\lambda = 0.154059$  nm). The optical properties and hence the defect density of the nanostructures were investigated with the aid of photoluminescence spectroscopy (Hitachi F2500) employing a Xenon lamp operating at 325 nm as the excitation source. A narrow band-pass filter centered at 325 nm with full-width at half height of  $\sim 10$  nm was used to improve the quality of the excitation light. Raman spectra were excited by a He-Cd laser operating at 441.6 nm. Backscattered light (through a microscope objective 50 $\times$ ) was analyzed by a single monochromator (Labram HR800, Jobin-Yvon) and detected by a liquid-nitrogen cooled CCD detector. The specific

surface area of the samples was measured with a N<sub>2</sub> adsorption analyzer (Micromeritics Gemini) by using the Brunauer–Emmett–Teller (BET) method.

### 2.3. Photoelectron spectroscopies

The surface analysis studies were performed in a UHV chamber ( $P < 10^{-9}$  mbar) equipped with a SPECS LHS-10 (EA10) hemispherical electron analyzer. The XPS measurements were carried out at room temperature using un-monochromatized AlK $\alpha$  radiation under conditions optimized for maximum signal (constant  $\Delta E$  mode with pass energy of 36 eV giving a full width at half maximum (FWHM) of 0.9 eV for the Au 4f $_{7/2}$  peak). The analyzed area was an ellipsoid with dimensions  $2.5 \times 4.5$  mm<sup>2</sup>. The XPS core level spectra were analyzed using a fitting routine, which allows the decomposition of each spectrum into individual mixed Gaussian-Lorentzian components after a Shirley background subtraction. The samples were in powder form and pressed into pellets. Wide Scans were recorded for all samples, while the core level peaks that were recorded were: Zn2p $_{3/2}$ , C1s, O1s, and Zn Auger peak. The wide scans were recorded with pass energy of 97 eV. Errors in quantitative data are found in the range of  $\sim 10\%$  (peak areas), while the accuracy for BEs assignments is  $\sim 0.1$  eV. The binding energy reference for the electrostatic charging due to X-ray irradiation was the C1s at 284.8 eV from the superficial carbon contamination. The surface charging in all samples was  $\sim 1$  eV. The Ultra Violet Photoelectron Spectroscopy (UPS) studies were performed using HeI irradiation with  $h\nu = 21.22$  eV produced by a UV source (model UVS 10/35). During UPS measurements the analyzer was working at the Constant Retarding Ratio (CRR) mode, with CRR = 10. A bias of  $-12.29$  V was applied to the sample in order to avoid interference of the spectrometer threshold in the UPS spectra. The high and low binding energy and highest cutoff positions were assigned by fitting straight lines on the high and low energy cutoffs of the spectra and determining their intersections with the binding energy axis. Regarding measurement errors it should be noted that an error of  $\pm 0.05$  eV is assigned to the absolute values for work function. In order to avoid charging effects due to the high intensity of the UV irradiation, the powders were dispersed in 3D water and drop-casted on indium tin oxide (ITO)-coated glass. The ITO substrates were previously subjected to oxygen plasma treatment (RF = 10.5 W, 20 min) to improve surface wetting and the coating homogeneity.

### 2.4. Photocatalytic activity experiments

The PC activity of the P25 TiO<sub>2</sub>, pristine ZnO, ball-milled TiO<sub>2</sub> and ZnO samples was evaluated by the degradation of methylene blue in drinking water (MB, 1 mg L<sup>-1</sup>) under UV light irradiation. All experiments were conducted in a PC reactor consisting of a cylindrical glass tube with double walls for water recirculation acting as thermostating jacket, whereas dry air was injected upwards at a constant flow rate (0.2 L min<sup>-1</sup>) through the wastewater. The UV light source (8 W, 365 nm) was inserted inside a quartz cylinder, which was placed in the center of the glass tube. In each test, 40 mg of photocatalyst was dispersed in 200 mL of MB solution. The aqueous solution was sonicated for 1 h in the dark and then stirred for 1 h to establish adsorption-desorption equilibrium between MB and photocatalyst before being irradiated. During the experiment, several solution samples (2 mL) were collected at various PC treatment times, centrifuged for 15 min at 13,000 rpm (Thermo Scientific, Heraeus Megafuge 16) and then analyzed in a UV–vis spectrophotometer (Hitachi, U-3000) to determine the concentration of MB from its characteristic adsorption peak at 663 nm [32]. The MB photodegradation rate was defined as  $C/C_0$ , where  $C_0$  and  $C$  are the MB concentrations before and after irradiation, respec-

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