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Effect of ball-milling and Fe-/Al-doping on the structural aspect and visible light photocatalytic activity of TiO2 towards *Escherichia coli* bacteria abatement

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ABSTRACT

Escherichia coli abatement was studied in liquid phase under visible light in the presence of two commercial titania photocatalysts, and of Fe- and Al-doped titania samples prepared by high energy ball-milling. The two commercial titania photocatalysts, Aeroxide P25 (Evonik industries) exhibiting both rutile and anatase structures and MPT625 (Ishihara Sangyo Kaisha), a Fe-, Al-, P- and S-doped titania exhibiting only the rutile phase, are active suggesting that neither the structure nor the doping is the driving parameter. Although the MPT625 UV–visible spectrum is shifted towards the visible domain with respect to the P25 one, the effect on bacteria is not increased. On the other hand, the ball milled iron-doped P25 samples exhibit low activities in bacteria abatement under visible light due to charge recombinations unfavorable to catalysis as shown by photoluminescence measurements. While doping elements are in interstitial positions within the rutile structure in MPT625 sample, they are located at the surface in ball milled samples and in isolated octahedral units according to ^{57}Fe Mössbauer spectrometry. The location of doping elements at the surface is suggested to be responsible for the sample cytotoxicity observed in the dark.

1. Introduction

The photocatalytic activity of titanium dioxide (TiO_2) has given rise to many studies in view of fundamental understanding and practical applications in the fields of environment and sustainable energy production [1,2]. Amongst the used semiconductors, TiO_2 still remains the most attractive and efficient one, due to a high photocatalytic efficiency in UV range, suitably located valence and conduction bands allowing surface redox reactions to occur, a high quantum yield, a high stability towards photocorrosion and chemicals, a water insolubility, a low toxicity and cost-effectiveness. Applications of TiO_2 photocatalysis to life science gave rise to many researches in the field of disinfection of water, air or surfaces by oxidation photocatalysis. Even if the mechanism is known to imply the attack of the bacteria by Reactive Oxygen Species causing damages to the bacterial cell such as lipid peroxidation, protein degradation and DNA damage and consequently leading to cell death, the molecular mechanisms of the photocatalytic killing of bacteria remain still unclear and are a matter of debate [3].

Titania crystallizes mainly under rutile, anatase, or brookite structures. In addition, an intermediate phase called TiO_2 II and isomorphous to α-PbO_2 was already encountered when anatase transforms into rutile under high energy ball milling [4,5]. Anatase is well-known to be more active in photocatalysis under UV light than the rutile allotropic form. However, commercial Aeroxide TiO_2 P25 (Degussa–Evonik), with an anatase to rutile ratio equal to four and prepared through the chloride technology is nowadays considered as the *de-facto* standard reference, even if the reason of its high activity level still remains a matter of debate [6].

However, due to the TiO_2 wide band-gap, *i.e.* 3.23 eV for anatase, the activation is restricted to the UV range, so that only few percents of solar energy can be used. Therefore, many strategy approaches have been investigated in the last decades for synthesizing photocatalytic materials active under visible light. [7] Metallic (*e.g.* chromium [8], nickel [9], vanadium [10], iron [11], cobalt [12], ruthenium [13], platinum [14]) or non-metallic ions (*e.g.* nitrogen, [15,16] carbon [17] or sulfur [18]) were introduced at a few percent or so as doping elements, *i.e.* by adopting the solid state chemistry terminology for doping aspects.

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Various synthesis techniques were used, including mechanical mixing or high energy ball milling [19], sol–gel or hydrothermal routes [20–23], MOCVD, [24] solid-state reactions [25], and ion implantation [26]. Amongst investigated methods, doped titania powders, synthesized by heat treatment of pre-ground reactants, have been found to display very interesting photocatalytic properties under UV and visible light [19]. Indeed the mechanical activation step is often reported to allow ensuring a good contact between reactants and favors the formation of homogeneous nanosized materials at lower temperature [4].

But, the cationic doping efficiency on the visible-light photoactivity of TiO_2-based materials remains till now a matter of debate and contradictory results have been obtained [27]. Choi et al. underlined that the wide-variability in reported impact on visible light activity – and the associated controversy in evidencing the net effects of metal-ion dopants – could notably result from the large variety of specific preparation methods and of experimental conditions used to quantify activity, as well as from the broad array of chemical reactions used to assess photoactivity over a large range of wavelengths greater than 400 nm [28]. They recently reported that the cationic doping of TiO_2 influences the anatase to rutile ratio, in most of the cases by lowering the anatase to rutile transformation temperature – even the reverse phenomenon was also scarcely observed – and that the fraction of rutile depends on the doping level. Whereas no correlation between the effectiveness of a single doping metal on this phase transformation and its valence state or its ionic radius was directly drawn, with in most of the cases no incorporation of cations into the TiO_2 lattice and a preferential location in the near surface region, the authors have linked the rutile content to the visible light activity measured in both Methylene Blue and phenol degradation, as well as in the iodide oxidation. Other conflicting results have been recently published on the correlation between the crystalline structure and bacteria degradation [29,30]. In that context, the present study aims at determining the efficiency of ball-milled Fe- and/or Al-doped titania powders towards the abatement in liquid phase under visible-light illumination, of Gram-negative *Escherichia coli* model bacteria – commonly used as an indicator of water fecal contamination – , and at comparing these home-made powders to commercially available doped or undoped TiO_2 products. High energy ball-milling has the advantage to be an easy-using and low-cost method that allows ten or so grams to be homogeneously produced. Stoechiometric ratios of iron and aluminum chlorides have been mixed with TiO_2 in order to get Fe and Al at.% in a few percent range. The location of iron and aluminum and the iron environment will be determined by using XPS and Mössbauer spectrometry, and linked to the photocatalytic results and toxicity.

2. Experimental

Commercially available TiO_2 MPT625, Ishihara Sangyo Kaisha (ISK, Japan) and Aeroxide TiO_2 P25 standard reference from Degussa–Evonik (Germany) photocatalytic materials, labeled MPT625 and P25 respectively, were used in this study. Chemical analysis by X-ray fluorescence of MPT625 sample revealed that it contains Fe: 0.28 at.%, Al: 6.6 at.%, S: 0.23 at.% and P: 0.19 at.%. Anhydrous $FeCl_3$ and $AlCl_3 \cdot 6H_2O$ from Prolabo were used as metallic precursors for cationic modifications of TiO_2.

2.1. Preparation of doped P25 powders by high energy ball-milling

TiO_2 P25 and metallic precursors (iron and/or aluminum chlorides) were mechanically activated by high energy ball-milling in a planetary ball mill (Fritsch Pulverisette 5). The disk and vials' rotation speed was around 360 rpm. The vial volume was approximately 400 cm^3, and fifteen 20 mm diameter balls were used. Vials and balls are made of 100C6 steel. The powder to ball weight ratio was 1/20. The grinding was performed for 30 min in order to avoid the contamination by stainless steel grinding tools and to ensure a sufficient mixing [3]. After milling, the samples were annealed in air at 500 °C for 3 h. The residual chlorides were removed by washing in distilled water. The iron and/or aluminum ratios in the starting mixture are listed in Table 1.

Depending on the atomic content of the precursor doping mixture, ball milled doped TiO_2 samples were labeled as P25b30 (metal free without annealing), P25b30r500 (metal-free with annealing), P25Fe1b30 (1 at.% Fe without annealing), P25Fe05b30r500 and P25Fe1b30r500 (0.5 at.% and 1 at.% Fe, respectively with annealing), P25Alb30r500 (6.15 at.% Al with annealing) and P25AlFeb30r500 (6.15 at.% Al and 0.26 at.% Fe with annealing).

The sample composition was analyzed by ICP-AES after dissolution in an HCl–HNO_3 mixture (Table 1). The amounts of iron are slightly higher than expected due to a low contamination by stainless steel balls during the ball milling and taking into account the standard deviation on chemical analyses of such low iron amount. Furthermore, as seen in the following, no metallic iron is detected by Mössbauer spectroscopy confirming thus that the contamination by grinding tools is very low.

2.2. Powder characterization

The various phases were identified from X-ray diffraction (XRD) patterns recorded with a Bruker D8 diffractometer using Cu $K_{\alpha 1}$ radiation at 0.15406 nm. The XRD patterns were analyzed using the Fullprof (2007) program, based on the Rietveld structure refinement method, which compares a calculated X-ray pattern to the recorded one, allowing for the determination of the weight fractions of the various phases in the investigated powder and of the grain sizes [31].

The specific surface areas were determined by BET-N_2 adsorption at LN_2 temperature. The particle sizes were derived from the relation $\phi(\text{nm}) = 6000 / \mu S$, in which ϕ is the particle diameter, μ is the density and S is the specific surface. The Zeta potential was calculated from the electrophoretic mobility according to the Huckel law which considers that the radius of the particles is small compared to the thickness of the electric double layer. The electrophoretic mobility of the nanoparticles was measured with a Malvern Zetasizer (NanoZS).

^{57}Fe Mössbauer spectra were recorded at 300 K in transmission geometry with a spectrometer operating in the conventional acceleration mode using a ^{57}Co source diffused into a Rh matrix. The sample consists of crushed powder with very low Fe content (highly lower than typically 5 mg/cm^2). It is therefore important to emphasize that the Fe content in the Al window has been previously tested and found to be extremely much smaller than that of the present sample, preventing some misinterpretations of the hyperfine structure. Velocity calibrations were made using an α-Fe foil at 300 K. The hyperfine parameter values were refined using a least-square fitting unpublished MOSFIT program by means of quadrupolar and magnetic components based on lorentzian lines. The isomer shift values are quoted to that of α-Fe at 300 K.

Table 1
Chemical composition of the starting mixture used for ball-milling of commercial P25 as well as chemical composition of raw and ball-milled samples obtained by ICP-AES analysis. P25b30r500, P25Fe05b30r500, P25Fe1b30r500, P25AlFeb30r500 and P25Alb30r500 were submitted to a grinding of 30 min and an annealing in air at 500 °C for 3 h.

	% in the starting mixture		Analysis			
	Fe (at.%)	Al (at.%)	Fe (at.%)	Al (at.%)	S	P
P25	–	–	–	–		
MPT625	–	–	0.26 (2)	6.15 (7)	0.21 (3)	0.18 (3)
P25b30r500	–	–	0.10 (7)	–	–	–
P25Fe05b30r500	0.5	0	0.50 (7)	–	–	–
P25Fe1b30r500	1	–	1.50 (7)	–	–	–
P25AlFeb30r500	0.26	6.15	1.29 (7)	6.2 (2)	–	–
P25Alb30r500	–	6.15	1.10 (7)	6.2 (2)	–	–