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Morphological control of TiO_2 anatase nanoparticles: What is the good surface property to obtain efficient photocatalysts?

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ABSTRACT

The richness of titanium dioxide sol–gel syntheses described in literature provided a set of four different morphologies of pure anatase nanoparticles to study the impact of the exposed surfaces on the photocatalytic efficiency of the corresponding material. The selection of the experimental parameters such as the temperature, the heating method or organic additives allowed the synthesis of pure anatase materials with significantly different shapes. A thorough microscopic study of these particles gave the exposed crystallographic faces. The photocatalytic activity of the different materials was estimated following the degradation of the rhodamine B dye under UV-light and significantly different behaviors were observed. In the applied photodegradation conditions, two samples were shown to be more efficient than the reference photocatalyst P25. The rationalization of these results was done through the study of the oxide surface properties, using FT-IR spectroscopy with pyridine as a surface probe and the EPR analysis of photogenerated radicals under UV light. The most efficient photocatalyst for rhodamine B degradation was found to be the morphology presenting the stronger acidic surface sites.

1. Introduction

TiO_2 (titania) is a key industrial material used in a large span of application and more specifically, it is widely studied for its photoelectronic properties [1–4]. The anatase metastable phase is generally proposed as the most efficient polymorph for applications such as dye sensitized solar cells [5] and photocatalysis [6,7]. Thanks to the expression of relatively low energy surfaces, anatase is actually the most stable TiO_2 structure for small nanometric size [8] and can be prepared using various low temperature syntheses methods [1]. An impressive number of different experimental conditions gave rise to a whole zoology of nanoparticles morphologies from classical truncated square bipyramids, to rods, needles, cubes, squares plates, belts or even hollow rods. Most of them were evaluated in terms of photocatalytic efficiency more or less accurately sometimes using different pollutants and different experimental degradation conditions. Yet in many studies, a clear correlation between the morphology and the photocatalytic efficiency is not given. This is most of the time due to the difficulties obtaining well defined surface and consequently to the absence of its careful description. For instance, in the specific case of anatase nanoplatelets exposing mainly {0 0 1} faces it is still not completely clear whether the good activity is due to the presence of the high energy surface itself or to the fluoride leftovers on that surface due to the preparation method [9]. Moreover, the comparison of different anatase morphologies whose photocatalytic efficiencies are described in different articles is very often impossible due to the large differences in the photocatalysis procedure. Overall, the

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influence of the exposed crystallographic faces, and thus the influence of the particles morphology, on the photocatalytic properties remains unclear [10].

The photocatalytic degradation of a pollutant is a multi-step process in which the structural characteristics of the materials may impact differently. Indeed, electrons and holes must first be efficiently photogenerated within the bulk material and migrate to the surface where they are likely to react. The anatase structure is efficient in producing those charge carriers but their surface or bulk recombination and their surface trapping may depend on the crystalline quality and the particles shape [11]. In a second step, surface reactions involving those charge carriers may proceed directly with the pollutant very close to the surface or with intermediate molecules such as water or solubilized oxygen to yield active radicals that are prone to degrade pollutants near to the surface. Again, the relative reactivity of the exposed surfaces impacts the global efficiency of the photocatalytic material.

The aim of the present study is to provide a detailed correlation between the photocatalytic efficiency of different anatase morphologies on the same photocatalytic test and their surface characteristics. Sol–gel syntheses [12,13] were used to prepare pure anatase nanoparticles with a good structural and morphological control. The focus was led on particles synthesized in water as reacting medium. The rhodamine B degradation was chosen as photocatalytic test in the present study since it is easy to handle and commonly used in the literature as a tracer dye. In addition, it may involve direct surface reactions. The photocatalytic efficiencies of the different TiO_2 morphologies for that specific pollutant may either be correlated to their ability to avoid recombination of photogenerated charge carriers, to produce active surface radicals or to directly transfer holes on the adsorbed dye. On that last point the adsorption efficiency may be understood in terms of the interaction of Lewis/Brønsted surface acidic sites with the corresponding basic sites of the dye.

In order to elucidate the real impact of morphology, a fine characterization of four anatase particles morphologies was achieved using high-resolution transmission electron microscopy analyses. The photocatalytic efficiencies of the selected samples for the degradation of the rhodamine B dye under UV light are presented. The surface reactivity was studied by a surface study by *in situ* Fourier transformation spectroscopy (FT-IR) using pyridine as basic probe and trough electronic paramagnetic resonance (EPR) for the detection of photogenerated radicals. The influence of the surface properties on the degradation of rhodamine B is rationalized.

2. Experimental

All chemicals were analytic grade reagents used without further purification (the oleic acid from Sigma is at $90\%_w$ purity). As a reference, P25 nanoparticles from Evonik were used as received.

2.1. Syntheses

2.1.1. $A\mu W$

The synthesis is reported in details in one of our previous work [14]. A Ti^{4+} stock solution ($[Ti^{IV}] = 1.0\,mol\,L^{-1}$) was prepared by dilution of the $TiCl_4$ precursor in a HCl ($3\,mol\,L^{-1}$) solution. Then, 30 mL of the stock solution were introduced into 100 mL of Milli-Q water; the pH of the solution was set to 6 with sodium hydroxide and the volume of the sample was completed to 300 mL with water. A white precipitate immediately appeared and aliquots of this suspension were transferred to Teflon cups, sealed in autoclaves and placed at 200 °C in a microwave oven (Synthos3000, Anton Paar) for 2 h.

2.1.2. AGlu

The synthesis adapted from the procedure reported by Durupthy et al. is similar to the previous one [15] except that 1.98 g of glutamic acid (GA) was introduced under stirring into the reacting medium in order to obtain a [GA]/[Ti] ratio of 0.5 and the pH of the solution was then set to 4. A white precipitate immediately appeared and aliquots of this suspension were heated in a closed glass vessel at 120 °C in an oven for 48 h.

2.1.3. ARods

The synthesis of TiO_2 nanorods was adapted from Sugimoto [16]. Titanium isopropoxide (TIPO, 6.9 mL) was mixed with triethanolamine (TEOA, 6.7 mL) under stirring in a closed flask and the volume was completed to 30 mL with deionized water. Then, 1.4 mL of ethylenediamine was added. The measured pH was close to 10. Finally, water was added under stirring to complete the volume to 100 mL. A first aging-step, leading to the formation of a gel, was carried out by heating the closed flasks in an oven at 100 °C for 24 h. The resulting gel was poured into Teflon-lined autoclaves for a second aging step at 140 °C for 72 h.

2.1.4. ACubes

The synthesis of anatase cube-shaped nanoparticles was adapted from Sugimoto [16] TIPO (21.0 mL) was mixed with TEOA (20.3 mL) under stirring and the resulting solution was completed to 150 mL with water. 2.8 g of oleic acid previously added in 50 mL of water was mixed with the 150 mL of stock solution under constant stirring. A further addition of 50 mL of water was then supplied. The pH of the solution was found to be close to 10.5 and was adjusted if necessary to this value with $HClO_4$ or NaOH solutions. Finally, water was added up to a volume of 300 mL. A first aging-step, leading to gel formation, was carried out by heating the closed flask in an oven at 100 °C for 24 h. The resulting gel was poured into Teflon-lined autoclaves for a second aging-step at 140 °C for 72 h.

The resultant precipitates of the whole as-synthesized oxide materials were collected by centrifugation, washed first with water, then with nitric acid ($3\,mol\,L^{-1}$) and one last time with water. The obtained powders were then centrifuged and dried under a dry airflow overnight. All the centrifugation steps are performed at 29 000 RCF during 20 min.

2.2. Characterization

2.2.1. X-ray diffraction (XRD) measurements

The phase and crystallite size analyses of TiO_2 powders were performed with a Bruker D8 X-ray diffractometer operating in the Brag–Brentano reflection mode equipped with a nickel filter to select the Cu-$K\alpha$ radiation. The data were collected in the $2\theta = 10–70°$ range with 0.05° steps. Pattern analyses were performed using EVA software (Bruker AXS) and the ICDD DD View PDF-4 + 2009 RDB base (PDF number 00-021-1272 for anatase, 00-021-1276 for rutile and 04-007-0758 for brookite). The proportions of the different TiO_2 polymorphs were assessed from the relative areas of the anatase (1 0 1), brookite (1 2 1) and rutile (1 1 0) diffraction lines obtained after diagram deconvolution and according to the procedure reported in Pottier et al. [17]. For average size of anatase nanoparticles, (1 0 1), (0 0 4) and (2 0 0) diffraction lines were exploited as reported elsewere [14]. In terms of particle size measurements, the evaluated error is ±0.5 nm

2.2.2. Transmission electron microscopy

The morphology and mean particle size of the samples were analysed by transmission electron microscopy (TEM) using a Tecnai spirit G2 apparatus operating at 120 kV (LaB_6). High resolution TEM (HRTEM) was performed at 200 kV on a Jeol–Jem 2011HR apparatus