

Preparation of bimodal micro–mesoporous TiO₂ with tailored crystalline properties

David P. Serrano,* Guillermo Calleja, Raúl Sanz and Patricia Pizarro

Department of Chemical, Environmental and Materials Technology, Rey Juan Carlos University, Móstoles (Madrid), Spain. E-mail: d.serrano@escet.urjc.es; Fax: +34 91 664 7490; Tel: +34 91 664 7450

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A new mild crystallization procedure has been applied after a synthesis route in the presence of a non-ionic surfactant, leading to the preparation of bimodal micro–mesoporous TiO₂, with remarkable textural properties and pore walls formed by anatase nanocrystals, which exhibit photocatalytic activity.

Sol–gel synthesis assisted by non-ionic surfactants has been demonstrated to provide mesoporous TiO₂ with high surface area by a N⁰I⁰ assembly mechanism.^{1,2} Nevertheless, the amorphous nature of the pore walls makes these materials non-feasible for many applications, such as electronic devices and photocatalysis, where crystalline titania is required.^{3–5} Traditionally, crystallinity of TiO₂ has been developed by severe treatments, such as calcination and hydrothermal processes, which frequently result in the partial or total collapse of the porous structure.^{2,6,7} Thus, Yue and Gao⁸ recently prepared crystalline mesoporous TiO₂ by a neutral templating route where crystallinity was generated by a hydrothermal post-synthesis treatment. The material so obtained was chemically modified with cerium and presented a surface area at best of 205 m² g⁻¹.

Here we report a new and more controllable method leading to bimodal micro–mesoporous TiO₂ photocatalysts (bm-TiO₂) with high surface area, mesoscopic ordering and crystalline walls. The presence of a bimodal pore distribution can be considered advantageous as the micropores provides the material with a high surface area and may lead to a strong interaction and adsorption of the reactant molecules, while the mesopores are responsible for a fast intraparticle mass transport.

The synthesis method is based on a two-step procedure: i) synthesis of the amorphous porous TiO₂, ii) controlled crystallization of the pore walls by acid treatment. The first step takes place by a neutral templating route^{6,7} using a titanium alkoxide and a non-ionic surfactant as starting materials. This procedure provides mesostructured materials with highly porous properties but with amorphous titania walls. The crystallization of the pore walls is carried out in a second step, through a mild acid treatment, which allows for a controlled phase transition into the anatase form while the high textural properties previously produced are greatly preserved.

In a typical synthesis, Pluronic P-123 (PEO₂₀PPO₇₀PEO₂₀) was dissolved at ambient temperature in 2-propanol containing HCl diluted in water. The mixture was slowly added to a solution of titanium isopropoxide in 2-propanol at 40 °C under continuous stirring, a gel being formed after around 4 h. The molar gel composition was 1.0 Ti(PrO)₄ : 34 C₃H₇O : 0.04 HCl : 3 H₂O : 0.02 P-123. The gel was aged at 40 °C for 16 h, and then vacuum dried and washed with ethanol, at ambient temperature. The solid so obtained was crystallized by treatment with refluxing acid–ethanol mixtures at different compositions (0–5% w/w) during 24 h and, afterwards, it was centrifuged and dried in an opened Petri dish at ambient conditions.

The crystallization step was studied using four inorganic acids in the refluxing treatment: HCl, HNO₃, H₂SO₄ and H₃PO₄. In all cases, the surfactant was efficiently removed from the solid. For 1% acid compositions, the main TiO₂ properties deduced from XRD and nitrogen adsorption–desorption analyses are registered in Table 1. Only HCl and HNO₃ were capable of inducing the phase transformation of the titania walls into pure anatase phase, which is

the most interesting one in applications such as photocatalysis, due to its high photoactivity. The occurrence of strong interactions between titania and sulfuric or phosphoric acid may account for the crystallization inhibition and the low values of surface area and pore volume.

Porosity of the samples treated with both HCl and HNO₃ are quite similar with high surface areas. By variation of the acid concentration in the crystallization step, bm-TiO₂ materials with surface area up to 260 m² g⁻¹ have been obtained. As an example, Fig. 1 illustrates the nitrogen adsorption–desorption analysis of a bm-TiO₂ sample crystallized using 1% HCl. The isotherm is apparently of type IV, typical of mesoporous materials, although with a remarkable adsorption at low relative pressures, suggesting the presence also of micropores. This result is confirmed by the pore size distribution, which exhibits a clear bimodal porosity. The inset of Fig. 1 illustrates the pore size distribution derived for one of the HCl-extracted samples by applying the DFT-Plus software using the Harkins and Jura thickness model. In this figure two families of pores, with sizes centered at 1.4 and 2.9 nm, respectively, are discernible. The DFT-Plus method provides also the relative contribution of both types of porosity to the overall surface area, with values of 146 and 100 m² g⁻¹ for the micropore and mesopore surface area, respectively.

The presence of micropores has been also detected in silica-based mesostructured materials, such as SBA-15, prepared using block copolymers as surfactants.⁹ A similar reason may be also considered for explaining the bm-TiO₂ microporosity, although the

Table 1 Properties of bm-TiO₂ after different acid–ethanol treatments

Acid	S _{BET} /m ² g ⁻¹	V _{pore} /cm ³ g ⁻¹	Phase	D _{crystal} /nm
HCl	246	0.136	Anatase	5.2
HNO ₃	213	0.108	Anatase	6.2
H ₃ PO ₄	65	0.032	Amorphous	—
H ₂ SO ₄	89	0.070	Amorphous	—

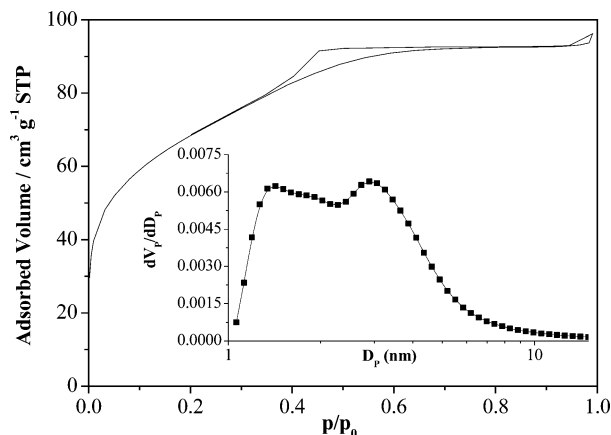


Fig. 1 N₂ adsorption–desorption isotherm and pore size distribution of bm-TiO₂ after treatment with 1% HCl/EtOH.

possible formation and/or enhancement of the microporosity during the crystallization treatment cannot be discarded.

Fig. 2 shows a typical wide-angle X-ray diffraction pattern of a crystalline bm-TiO₂. The main diffraction peak related to the anatase phase (25.3°) is clearly observed while no signals corresponding to the other allotropic titania phases (rutile and brookite) are detected. The average size of the anatase crystallites was calculated from the width of the main diffraction peak (101), by applying the Scherrer equation, confirming that the materials are formed by anatase nanocrystals with sizes around 5–6 nm. Crystallite dimensions provided by HCl treatment were found to be slightly smaller than those attained when HNO₃ was used (Table 1). These sizes can perfectly match within the pore walls of the inorganic TiO₂ framework allowing the porous structure to be preserved after crystallization.

TEM images of bm-TiO₂ treated with 5% HCl–EtOH are presented in Fig. 3. At short range, a mesoscopic ordering is observed in Fig. 3A. This result is in agreement with the broad peak present in the low-angle diffraction pattern, as shown in the inset of Fig. 2, which is typical of mesostructured solids prepared from surfactant-containing synthesis mixtures. Higher magnifications (not shown here) reveal that the pore walls are constituted of anatase crystallites whose dimensions are very close to those calculated from XRD data. Moreover, dark field images (CDF) indicate that these anatase entities possess very regular dimensions and are uniformly distributed in the material (Fig. 3B).

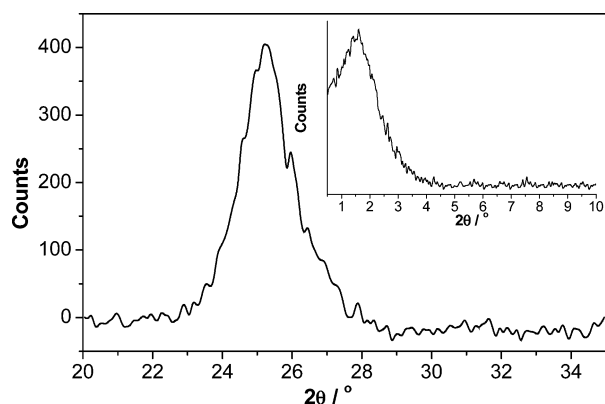


Fig. 2 XRD pattern of bm-TiO₂ after treatment with 5% HCl/EtOH.

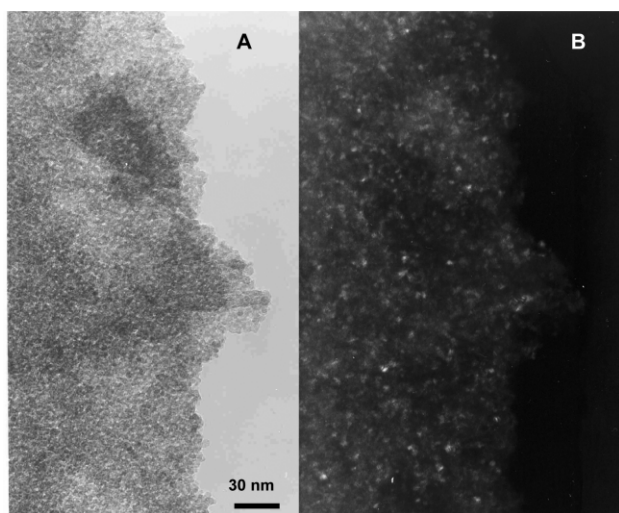


Fig. 3 TEM images of bm-TiO₂ treated with 5% HCl/EtOH: A) bright field and B) dark field.

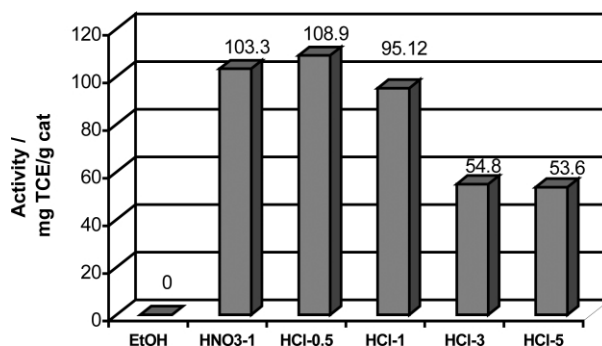


Fig. 4 Photocatalytic activity of bm-TiO₂ catalysts prepared from different acid treatments (the x axis indicates the acid type and concentration used in the preparation of each sample).

Finally, the photocatalytic properties of bm-TiO₂ materials have been tested in the oxidation with air of trichloroethylene (TCE) in water. The reaction system consisted of a medium-pressure Hg lamp immersed into the center of a 1.2 L batch reactor, where 60 ppm of TCE and 0.1 g of catalyst per litre of the organochlorinated water were put into contact. By measuring the TCE remaining into the reactor and the chloride ions liberated from the photooxidation reaction, the evolution of the process was followed during 4 h. Carbon dioxide, water and HCl were obtained as main products of the TCE degradation. Fig. 4 summarizes the activity obtained in the TCE photocatalytic degradation over bm-TiO₂ samples prepared by different acid treatments. The surface area of the HCl-extracted samples increased in the range 216–260 m² g⁻¹ with the HCl concentration, whereas a slight decrease was observed in the crystal size (from 6.9 to 5.0 nm). For comparison, bm-TiO₂ treated only with ethanol was also tested, no activity being observed due to the amorphous nature of the TiO₂ in this sample. In contrast, both HCl and HNO₃ treatments provided highly active photocatalysts. The higher degradation rate was detected for the bm-TiO₂ treated with 0.5% of HCl, probably due to a right balance of high surface area and crystalline properties.

In conclusion, the method here reported leads to the preparation of bm-TiO₂ materials having a singular combination of textural and crystalline properties. To the best of our knowledge, we are pioneers in applying a mild procedure, based on an acid treatment, for the controlled crystallization of mesostructured TiO₂. This approach provides well crystallized materials consisting of anatase nanocrystals located within the mesopore walls, exhibiting high surface area and a bimodal micro-meso pore size distribution. Moreover, these crystallized materials have been demonstrated to be active for the photocatalytic oxidation of trichloroethylene in the aqueous phase.

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