

Synthesis of mesoporous TiO₂ with a crystalline framework

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A thermally stable mesoporous TiO₂ with a crystalline framework and ordered large pores is synthesized using a block copolymer as a structure-directing agent through an N⁰I⁰ assembly pathway, followed by a hydrothermal process.

The synthesis of mesoporous silica with a high surface area and uniform cylindrical mesopores, which was designated as M41S, was first demonstrated in 1992.¹ Since then, the use of surfactants and amphiphilic block copolymers to organize mesoporous structures has been extended to the preparation of non-silica mesoporous metal oxides. Mesoporous MnO₂,² Al₂O₃,^{3,4} TiO₂,^{4,5} Nb₂O₅,^{4,6} Ta₂O₅,^{4,6} ZrO₂,^{4,7} and SnO₂,^{4,8} have been synthesized over the past few years. Among them, mesoporous TiO₂ is most attractive due to its excellent performance in photocatalytic reactions.⁹ It is well known that the effectiveness of titania as a photocatalyst is very sensitive to its crystal phase, particle size and crystallinity, and the mesoporous TiO₂ prepared using phosphate surfactants has low photocatalytic activity because the amorphous titania channel walls afford low quantum yield for photocatalytic reactions.¹⁰ Calcination of the as-synthesized mesoporous TiO₂ at high temperature is essential for the crystallization of titania in the channel wall.⁴ However, damage to the integrity of the mesoporous structure will take place upon calcination at high temperature, thus only mesoporous TiO₂ with amorphous or semicrystallized channel walls have been reported till now. Here we present the first example of mesoporous TiO₂ with crystalline framework, prepared through an N⁰I⁰ assembly pathway using a triblock copolymer as a structure-directing agent and followed by a hydrothermal process.

The mesoporous titania with crystalline framework was prepared as follows: a calculated amount of titanium ethoxide Ti(OC₂H₅)₄ was dissolved in an ethanol solution containing triblock poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (EO₂₀PO₇₀EO₂₀, Aldrich) and a very small amount of CeCl₃ which acts as a stabilizer in the syntheses.¹¹ After stirring for 1 h at ambient temperature, a water–ethanol mixture containing a 20% molar fraction of water was added dropwise. The molar composition of the reaction mixture was: 0.05 Ce³⁺: 1.0 TEOT: 0.02 EO₂₀PO₇₀EO₂₀: 4.0 H₂O: 15.5 C₂H₅OH. The mixture was stirred at ambient temperature for another 48 h. In the hydrothermal process, a large amount of water was added to the resulting solution until the H₂O/TiO₂ molar ratio = 90. Then, the mother liquor containing the precipitate was transferred to a stainless steel autoclave, and heated at 80–180 °C for 24 h. The product obtained was filtered off, washed with distilled water, dried at 100 °C, and finally calcined in air at 350 °C or 500 °C for 4 h. The samples studied are denoted as TiO₂-x-y, where x and y represent the temperatures of hydrothermal aging and calcination, respectively. A mesoporous TiO₂ sample untreated hydrothermally was also prepared for comparison.

Fig. 1 shows the results of wide-angle X-ray diffraction studies performed on a Rigaku D/MAX-IIA diffractometer using Cu-K α radiation of the hydrothermally treated mesoporous titania before and after calcination. No clear diffraction peaks are observed for as-synthesized mesoporous TiO₂ without hydrothermal treatment before calcination. After calcination weak and broad peaks, which can be indexed as the

(101), (004), (200), (105) and (204) reflections of anatase crystalline phase, appear on the pattern, showing that the channel walls are semicrystallized and some anatase nanocrystallites are formed and embedded in the amorphous titania channel walls. In contrast, sharp diffraction peaks of anatase appear on the XRD patterns of samples hydrothermally treated at 80–180 °C even before calcination and the intensity of the peaks increases little after calcination, indicating that the channel walls of the mesoporous oxides can be successfully crystallized at the low hydrothermal treatment temperatures. The crystals in the TiO₂-120-350 and TiO₂-180-350 samples are estimated to be of size 10 and 15 nm, respectively, by applying the Scherrer formula on the (101) diffraction peaks. The degree of crystallization and the anatase crystal size increase as the hydrothermal treatment temperature is increased from 80 to 180 °C. A brookite peak at 31° (2 θ) appears for samples treated at 180 °C. Calcination up to 500 °C does not have significant effects on the diffraction patterns of the samples, showing that the anatase crystal phase is retained at this temperature and no phase transformation has occurred.

Thermogravimetric experiments of the hydrothermally treated samples carried out in flowing air on a Rigaku Thermoflex instrument indicate that there are three endothermic processes in the TG/DTG/DTA curves at 20–120 °C, 120–320 °C and 320–420 °C, corresponding to the release of adsorbed water, block copolymer and structural water, respectively. Therefore, the block copolymer template in this type of mesoporous TiO₂ samples can be completely removed upon calcination in air at 350 °C.

Transmission electron micrographs of the TiO₂-120-350 sample recorded on a Philips CM 200 FEG Microscope (Fig. 2) shows that the pore channel walls are not totally continuous and the mesostructure is spotted with a few micro-domains of less ordered worm-like pore symmetry. Selected-area electron diffraction patterns (Fig. 2 inset) recorded on the same sample

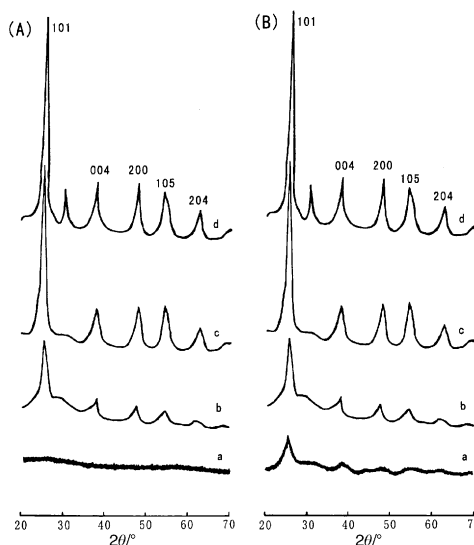


Fig. 1 XRD patterns of mesoporous TiO₂ before (A) and after (B) calcination. (a) TiO₂; (b) TiO₂-80-350; (c) TiO₂-120-350; (d) TiO₂-180-350.

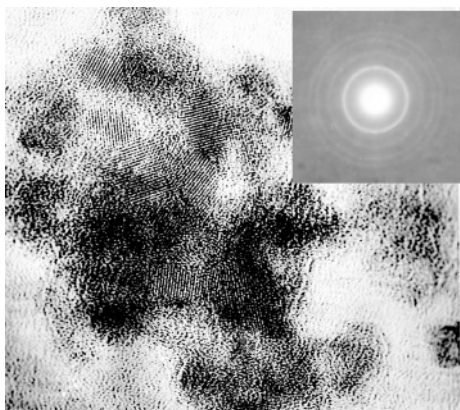


Fig. 2 TEM image and selected-area electron diffraction pattern (inset) of the TiO₂-120-350 sample

confirm that the channel walls are comprised of nanocrystalline anatase displaying characteristic diffuse electron diffraction rings.

Fig. 3 illustrates the N₂ adsorption/desorption isotherms of the TiO₂-120-350 sample measured using a Micromeritics ASAP 2000 system. A large H1-type hysteresis loop at high relative pressure is observed, which is related to the capillary condensation associated with large pore channels. BJH analysis of the desorption isotherm is shown in Fig. 3 (inset). The narrow gaussian pore size distribution curve implies that the material has very regular pore channels in the mesoporous region. The textural properties of all the hydrothermally treated samples are listed in Table 1 along with the data of the untreated samples. The pore size and volume of the hydrothermally treated samples are significantly greater than those of the untreated sample, whereas their specific surface areas are slightly lowered. The dramatic increase in pore size of the samples shows that the mesoporous TiO₂ could be restructured under hydrothermal treatment in the presence of the block copolymer template. The

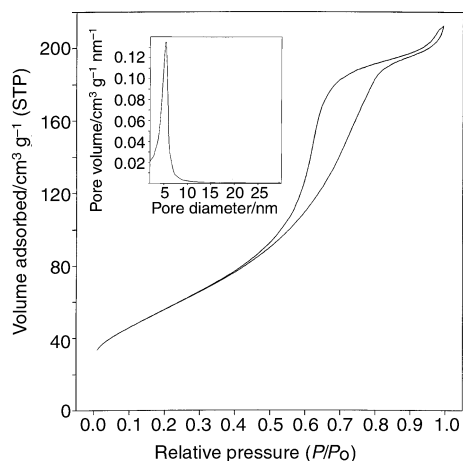


Fig. 3 N₂ adsorption/desorption isotherm and BJH pore size distribution plot (inset) of the TiO₂-120-350 sample at 77 K.

Table 1 Textural properties of mesoporous TiO₂ samples

Sample	Aging temperature/ °C	Calcination temperature/ °C	BET surface area/m ² g ⁻¹	Pore diameter/ nm	Pore volume/ cm ³ g ⁻¹
TiO ₂ -80-350	80	350	201	4.4	0.271
TiO ₂ -80-500	80	500	150	5.2	0.249
TiO ₂ -120-350	120	350	204	5.5	0.315
TiO ₂ -120-500	120	500	157	6.2	0.302
TiO ₂ -180-350	180	350	159	7.0	0.366
TiO ₂ -180-500	180	500	134	8.0	0.336
TiO ₂	none	350	242	2.2	0.156
TiO ₂	none	500	191	2.0	0.130

pore sizes of TiO₂-180-350 and TiO₂-180-500 reach 7.0 and 8.0 nm, respectively, which are the largest reported for mesoporous titania until now.⁴ The mesoporous TiO₂ materials with crystalline framework retain their structural integrity and mesoporosity when calcined at 500 °C.

This work shows that mesoporous TiO₂ materials with anatase crystalline framework can be successfully prepared using a templating procedure followed by hydrothermal treatment and calcination. Amorphous titania in the channel walls of the mesoporous structure is crystallized at low hydrothermal temperature without sacrificing porosity and pore regularity, and the template is removed at a relatively low calcination temperature to ensure the materials against structure degradation. The crystalline framework, high specific surface area, large pore size and high thermal stability of these new materials are expected to afford better activity toward photocatalytic reactions, in particular those concerned with bulky molecules and high space velocity.

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