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Synthesis and photocatalytic properties of highly crystalline and ordered mesoporous TiO_2 thin films

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Highly crystalline and ordered mesoporous TiO_2 thin films have been synthesized by stabilization of the mesostructure with confined carbon; the films exhibit 2.5% photoconversion efficiency for the water photolysis at zero-bias and Xe lamp illumination of 40 mW cm^{-2}.

Ordered mesoporous TiO_2 thin films, made by a self-assembly process,[1] are promising candidates for photocatalysts and optoelectronic applications due to their intrinsic activity, high surface area, and potential low cost.[2] However, the efficiencies of photon-energy conversion realized in practice are still quite low in the ordered material due to the presence of a substantial amorphous component in the framework. Unless the advantages from the mesostructural ordering are demonstrated by the enhanced efficiency of practical devices, commercialization of such mesoporous materials is unlikely. The simultaneous achievement of high crystallinity and high mesoscopic ordering is a major challenge.[3–5] Recently, a crystalline mesoporous TiO_2 thin film has been successfully synthesized using a series of hydrothermal treatments over approximately one month under strictly controlled conditions.[4] The catalytic and photoelectronic properties of these films were not described.

Here we report the significantly enhanced photocatalytic properties of a crystalline and ordered mesoporous TiO_2 thin film, which has been synthesized using a simplified procedure.[6] Carbon materials have been introduced into the porous spaces and act as a "filler" to prevent the pores from collapsing due to the stress induced by TiO_2 crystallization during high temperature (> 500 °C) calcination. Confined carbon can be either back-filled or generated using the structure-directing agents introduced directly during the synthesis. The photoanode properties of those TiO_2 thin films were evaluated for water photolysis and shown to be improved with a zero-bias photoconversion efficiency of 2.5% at an illumination of 40 mW cm^{-2} using a film with both high crystallinity and mesostructural ordering.

The non-crystallized ordered mesoporous TiO_2 thin films with $Im\bar{3}m$ symmetry were synthesized by a one-step sol–gel approach reported elsewhere.[3] Briefly, 3.9 ml of titanium ethoxide was mixed with 2.7 ml HCl (12.1 M) and added into a solution containing 1 g of Pluronic P123 and 12 g of ethanol. The film was deposited by dip-coating. P123 was either removed by calcination at 300 °C for 2 hours or kept as a partial carbon source, and the samples are designated as C–TiO_2 or C–P123–TiO_2, respectively. Furfuryl alcohol was then diffused into either mesoporous or mesostructured TiO_2 as a carbon precursor.[6] Subsequent carbonization and crystallization were carried out under a vacuum at desired temperatures. Carbon was combusted in O_2.†Control samples were prepared at each temperature without carbon treatment. A small-angle XRD peak was present up to 750 °C for each carbon treated sample, as shown in Figs 1A and 1B for the C–P123–TiO_2 and C–TiO_2 films, respectively. Representative data for calcination at 550 °C (curves b and d) and 750 °C (curves a and c) are illustrated.

For C–P123–TiO_2 films, narrow and well-defined small-angle XRD peaks are obtained (Fig. 1A). Two peaks at d = 7.0 nm and d = 6.1 nm are observed at 550 °C, which may arise from the lowered symmetry of the calcined film or different orientations of the mesophase domains. Calcination to 750 °C leads to only a small shift towards smaller d-spacing (d = 5.7 nm), which further demonstrates the robustness of the framework. However, those films do not show evidence of TiO_2 crystallization by wide-angle XRD (Fig. 1C, curves a and b) even at high temperatures. This can be explained by the synthesis method we used. Within the as-made TiO_2/P123 composite, titanium complexes are incorporated into the hydrophilic blocks of the structure-directing agents, therefore, direct carbonization from surfactants may generate carbon species within the TiO_2 matrix and inhibit the growth of anatase nanocrystallites.

For C–TiO_2 samples, weaker and broader small-angle XRD peaks are observed (Fig. 1B), which suggests partial destruction of the long-range meso-ordering due to less effective filling by carbon. The peaks are present at a lower d-spacing (4.5 nm and 4.0 nm for 550 °C and 750 °C, respectively) due to large shrinkage along the direction normal to the film surface upon template removal. A reference XRD pattern from the starting material is

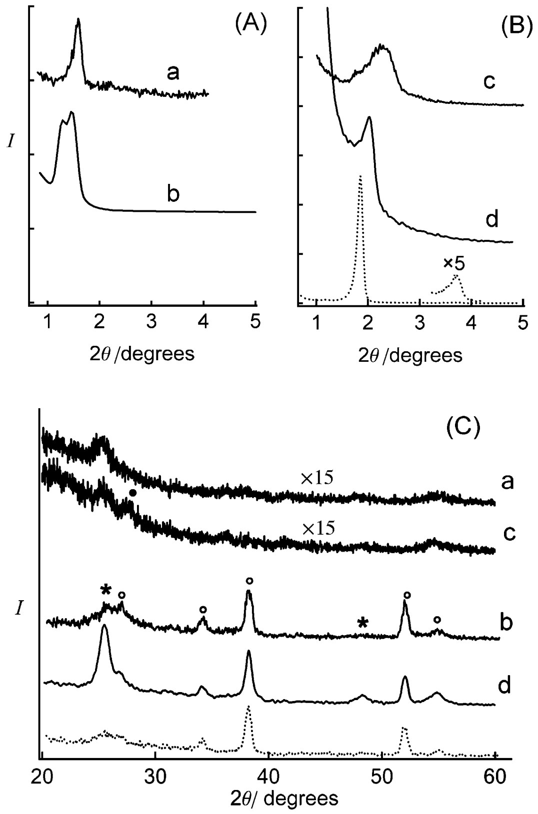

Fig. 1 Small-angle XRD patterns of (A) C–P123–TiO_2 thin films and (B) C–TiO_2 thin films crystallized at (a, c) 750 °C and (b, d) 550 °C. (C) Corresponding wide-angle XRD patterns. Data from starting mesoporous TiO_2 (template removed at 300 °C) were plotted (dotted line) as a reference. Diffraction peaks marked with circles (○) were from conducting substrates (SnO_2:F); peaks marked with asterisks (*) were from anatase. Substrates used for 750 °C calcinations were quartz, and therefore no circles were marked. The peak labelled with a solid circle was from rutile. The X-ray source is Cu Kα.

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shown in Fig. 1 (dotted line) for comparison. In contrast to C–P123–TiO_2, the XRD data of this set of C–TiO_2 films show significantly enhanced intensities for the anatase phase in the range of 400 °C to 550 °C (curve d, Fig. 1C). The intensities of the anatase peaks of C–TiO_2 gradually decrease above 550 °C and are followed by the appearance of a rutile peak at 750 °C (curve c, Fig. 1C).[4,7] Transmission electron microscopy (TEM) was used to further characterize the structure. Images from a C–TiO_2 sample crystallized at 550 °C (same sample as shown in Fig. 1, curve d) are shown in Fig. 2. The low-magnification TEM image shown in Fig. 2 (left) clearly confirms the presence of the mesostructural ordering of the film. The particle sizes are 5–10 nm in size and are consistent with the calculated result, 7.8 nm, from the XRD data (Fig. 1C, curve d) by applying the Scherrer equation. The high-resolution TEM image shown in Fig. 2 (right) was recorded from the same region. The anatase lattice fringes were present throughout the wall structure indicating high crystallinity. The anatase phase is also confirmed by analyzing the electron diffraction (ED) pattern (Fig. 2, inset).

The TiO_2 thin films were characterized as photoanodes by measuring the zero-bias photocurrent for water photolysis using a xenon lamp.[8]‡Efficiencies of photon-to-chemical energy conversion are summarized in Fig. 3.§It is known that crystal phase, crystallinity, particle size, surface states and surface area affect photocatalytic properties.[2] As shown in Fig. 3, at low calcination temperatures (400 °C) where crystallization-induced stresses are not sufficient to destroy the mesoporous framework, all C–TiO_2, C–P123–TiO_2 and control samples display comparable photocatalytic activities. Significant differences arise at higher calcination temperatures. At 500 °C, the highest efficiency of 2.5% was obtained from C–TiO_2. This value is 4 times higher than that of a control sample that has comparable crystallinity and 10 times higher than that of C–P123–TiO_2 which has a similar pore structure. This clearly demonstrates the added advantages of mesostructural ordering on the photocatalytic properties of TiO_2, which can be attributed to the large accessible surface areas presented in the ordered sample. As shown in Figs 3a and 3b, efficiencies from both C–TiO_2 (Fig. 3a) and the control samples (Fig. 3b) increase until 500 °C and drop, which is consistent with the trend of the crystallinity. Significantly lower values were observed for C–P123–TiO_2 (Fig. 3c) primarily due to the amorphous nature of the framework.

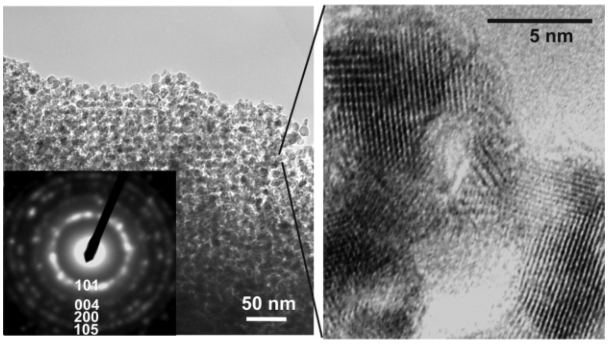

Fig. 2 TEM images of a TiO_2 thin film crystallized at 550 °C with pure post-induced carbon as the confining material. The zoom-in image is also shown on the right. The inset is a selected area electron diffraction pattern (SAED) indexed as the anatase phase.

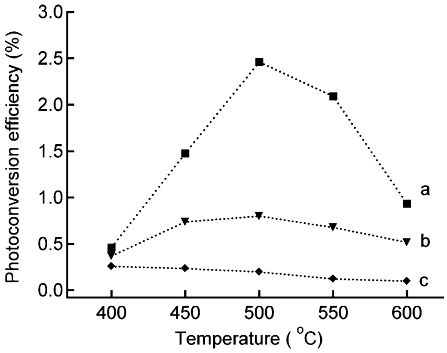

Fig. 3 Photoconversion efficiencies of (a) C–TiO_2, (b) control and (c) C–P123–TiO_2 samples at zero-bias and illumination of 40 mW cm^{-2}. Film thickness was 250–300 nm.

In summary, highly crystalline, mesoporous anatase thin films have been synthesized using carbon inclusion to stabilize the framework during thermal crystallization. The benefit of mesostructural ordering on the photocatalytic properties of the film has been demonstrated. In order to achieve high photon-conversion efficiency, both high crystallinity and accessible ordered mesoscopic structure are essential; however, the influence of crystallinity on the photocatalytic properties is greater than that of mesoporous ordering. The improved efficiency and potentially low-cost synthesis suggest that this material might be practically useful as a photocatalyst.

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Notes and references

† The carbon filling and crystallization processes were as follows: furfuryl alcohol vapor was polymerized and accumulated into the TiO_2 or TiO_2/P123 films at 200 °C for 6 hours in argon. The brown film was carbonized and crystallized at a target temperature (3 °C min^{-1}) for 5 hours under a vacuum. The black film (amorphous carbon) was then heated to 400 °C (1 °C min^{-1}) in O_2 for 30 min to remove the carbon.

‡ TiO_2 thin film deposited on a transparent conducting glass substrate (SnO_2:F) was used as a photoanode in an electrochemical cell with a meshed Pt counter electrode and 0.1 M sodium acetate as an electrolyte. Illumination was provided by a chopped (0.5 Hz) 1000 W xenon light source. Intensity was measured to be 40 mW cm^{-2} due to the energy loss in the optical path.

§ Efficiency was calculated by the following equation: efficiency = (j_{ph} × E^{o}_{st})/I_{in} where j_{ph} and E^{o}_{st} are the zero-bias photocurrent and standard reversible potential of the water splitting reaction, which is 1.23V. I_{in} is the incident light intensity.

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