

Synthesis of self-standing mesoporous nanocrystalline titania–phosphorus oxide composite films†

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Self-standing, transparent, thick (~90 μm) mesoporous titania–phosphorus oxide composite films containing anatase nanocrystallites were synthesized using the evaporation-induced co-assembly of an amphiphilic triblock copolymer template, titanium tetraethoxide, and phosphorus chloride.

Mesoporous nanocrystalline TiO₂ materials have attracted much attention for their many potential applications, such as in photovoltaic energy conversion, and as photoconductors, photocatalysts, sensors, and heterogeneous catalysts.^{1–3} The processing of mesoporous materials with a controlled macroscopic morphology is a basic prerequisite for applications. Recently, fabrication of mesoporous TiO₂ films has been widely studied because the films have an ideal morphology to improve the efficiency of devices.^{4–6} Further, thick mesoporous TiO₂ films without a substrate (self-standing films) should expand the application window of these materials to new fields in the life sciences, such as implantable drug-release materials.⁷ Very recently, Ostomel *et al.* introduced free-standing 10 μm thick mesoporous TiO₂ films containing anatase nanocrystallites, but their films have poor mesostructural properties ($S_{\text{BET}} = 133 \text{ m}^2 \text{ g}^{-1}$ (the film was calcined at 400 °C)) after removing templates, owing to trans-crystallite growth.⁸ Crystallization of a mesoporous TiO₂ framework is the step that is most necessary to maximize the utility of TiO₂; however, excessive crystallite growth often destroys the mesostructure. Li *et al.*⁹ and Yu *et al.*¹⁰ suggested that a phosphate glass phase prevents nanocrystal growth based on thermal conditions and improves the thermal stability of the mesostructure. The evaporation-induced self-assembly (EISA) process is also an effective procedure for synthesizing well-defined mesoporous materials and for controlling the macroscopic morphology (powder, fibres, monoliths, and films).^{11,12} In this study, we applied both phosphate glass phase and the EISA method to synthesize self-standing mesoporous TiO₂ films in a simple, reproducible way. The TiO₂–P₂O₅ composite films obtained were transparent up to about 90 μm thick, with a surface area up to 330 m² g⁻¹, and a narrow pore-size distribution. High humidity and low temperature during the EISA step promoted the production of transparent, continuous thick films.

In a typical synthesis, 0.6 g of Pluronic P123 (BASF) was dissolved in 6 g of ethanol (EtOH). Stock solutions, which were prepared by mixing 2.1 g of titanium(IV) ethoxide (TTE) and 1.6 g of HCl, were added to this solution. Separately, 0.4 g of phosphorus chloride (PCl₅) was dissolved in 2 g of EtOH, and then added to the stock solution. Titanium tetraisopropoxide (TTIP) can also be used as a metal source; the molar composition was TTIP : PCl₅ : P123 : EtOH : H₂O : HCl = 1 : 0.26 : 0.014 : 23.5 : 7.8 : 2.08 in this case. The reactant solution was stirred for 3 h, transferred to a polystyrene vessel without a cap, and aged at 10 °C–RT, 20–80% RH for 48 h without stirring. Gel films were obtained on evaporating this solvent, and heat-treating the result at 70 °C in air or N₂ for 20 h. The gel films were easily separated from the

vessel after drying and calcined at 400 °C for 8 h in air to remove the template. Removal of the template can be confirmed using Fourier transform infrared (FT-IR) spectrometry¹³ and thermogravimetry–differential thermal analysis (TG–DTA) (Fig. S1 and 2†).

Fig. 1 shows photographs and field emission scanning electron microscopy images (FE-SEM) of as-synthesized and calcined films. The as-synthesized films, which were aged at 15 °C, 80% RH, were transparent, continuous, flexible, plastic-like films (Fig. 1(a)) up to 60 × 30 mm in size with several large cracks, or up to 40 × 10 mm without cracks (Fig. S3†). The films kept their transparency and turned into 85 μm thick glass-like films (Fig. 1(c), (d)), although the films curled owing to the shrinkage that occurred with calcination. The film thickness was controlled by the amount of reactant solution dropped into the polystyrene vessel. The method of Ostomel *et al.*,⁸ which obtained films when the precursor solution crept up the inner wall of a polyethylene vial, was also successfully adapted to a general glass vessel, and the films obtained were transparent and 8 μm thick, Fig. 1(b), which was similar to the results reported by Ostomel *et al.* The transparency and flexibility of the film were affected by the conditions of the EISA process. The films aged at low humidity (20–40% RH) were still transparent, but had a pale white color and were more brittle. Aging for longer than 48 h induced cloudiness in the films. The samples aged at room temperature (RT) without controlling humidity and the samples formed without solvent evaporation both turned into an opaque powder.

To characterize both the mesostructural order and crystalline phase of the self-standing films obtained, small angle X-ray diffraction (SAXRD) and wide-angle X-ray diffraction (WAXRD) measurements were carried out (Cu–Kα radiation). The SAXRD trace of the as-synthesized films (Fig. 2A(a)) shows three peaks with $d = 92, 54, \text{ and } 45 \text{ \AA}$. These diffraction peaks can be indexed as the (100), (110), and (200) reflections, respectively, from the diffraction planes that are typically observed in the hexagonal symmetry. After

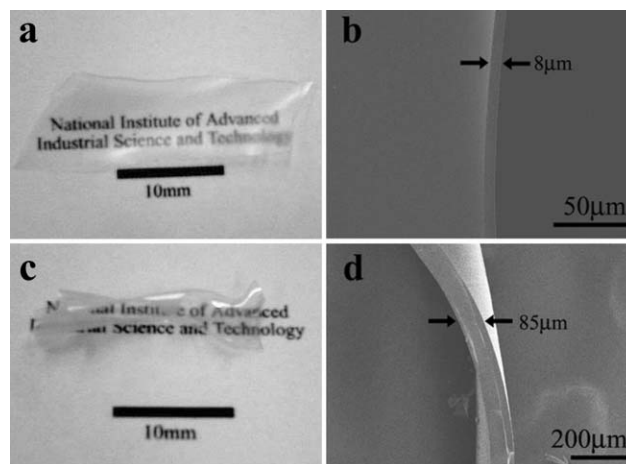


Fig. 1 Photographs and SEM images of self-standing meso-TiO₂–P₂O₅ films after drying at 70 °C (a) and calcination at 400 °C (b–d).

† Electronic supplementary information (ESI) available: FT-IR spectra (Fig. S1), TG–DTA trace (Fig. S2) and optical images (Fig. S3) of self-standing thick films of TiO₂–P₂O₅. See <http://www.rsc.org/suppdata/cc/b4/12396d/>

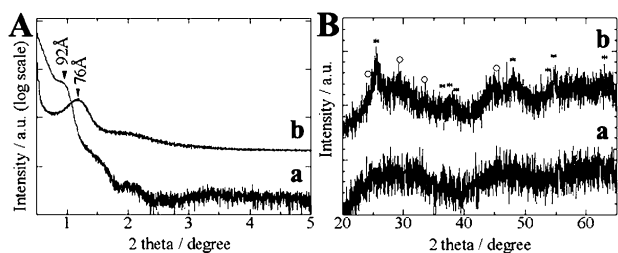


Fig. 2 SAXRD (A) and WAXRD (B) patterns obtained from meso-TiO₂-P₂O₅ thick films before (a) and after (b) calcination. *Anatase patterns, ○ P₂O₅ patterns.

calcination at 400 °C, the diffraction peaks appear at higher angles with $d = 76$ and 44 Å, which can be assigned as the (100) and (110) reflections, respectively, associated with a hexagonal structure (Fig. 2A(b)). Although only two diffraction peaks remained after calcination, owing to a decrease in the long-range order, these SAXRD results provide evidence for the formation of thermally stable self-standing mesoporous TiO₂-P₂O₅ films with a hexagonal-like structure. The crystallization of the framework of mesoporous TiO₂ is particularly important for applying these films in devices that utilize their semiconducting properties, such as in electrodes and photocatalysts. The WAXRD patterns (Fig. 2B(a-b)) clearly show the presence of nanocrystalline anatase (JCPDS No. 211272) and amorphous TiO₂ in the calcined samples (b) with several extra diffraction peaks from P₂O₅ (JCPDS No. 231302). The mean crystallite size of TiO₂ calculated from the (101) diffraction peak of anatase using the Scherrer equation was 24 Å. The XRD patterns of mesoporous TiO₂ films, which were synthesized under the same conditions, show a very sharp diffraction peak of nanocrystalline anatase. Similarly, the calculated average crystallite size is 140 Å without an ordered mesostructure. These results prove the crystallite size-controlling effect of the glass P₂O₅ phase. The broad absorption bands at 800, 1120, and 1290 cm⁻¹ in the FT-IR spectra confirmed the existence of a glass P₂O₅ phase (Fig. S1(b-c)).¹⁴

Transmission electron microscopy (TEM) images and selected-area electron diffraction (SAED) patterns support the SAXRD and WAXRD results. A well-defined hexagonal structure is readily observed in the as-synthesized thick films (Fig. 3(a)). TiO₂-P₂O₅ films calcined at 400 °C had wormhole-like or short-range hexagonal structures, as expected (Fig. 3(b)). The pore size estimated from TEM was 46 Å. SAED patterns of the calcined films show several weak Debye-Scherrer rings and spots corresponding to the reflection of anatase, which reveal that the films possess anatase nanocrystallites (Fig. 3(b) (inset)), while the as-synthesized films are composed of amorphous TiO₂ (Fig. 3(a) (inset)).

Fig. 4 shows the nitrogen adsorption-desorption isotherms and pore size distribution calculated using the Dollimore-Heal algorithm from the desorption branch for mesoporous TiO₂-P₂O₅ films. The films calcined at 400 °C show a type-IV isotherm,

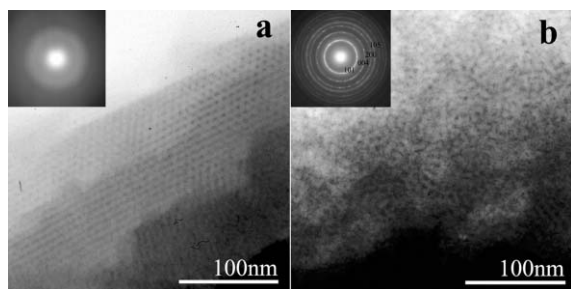


Fig. 3 TEM images and SAED patterns (inset) of self-standing meso-TiO₂-P₂O₅ thick films before (a) and after (b) calcination.

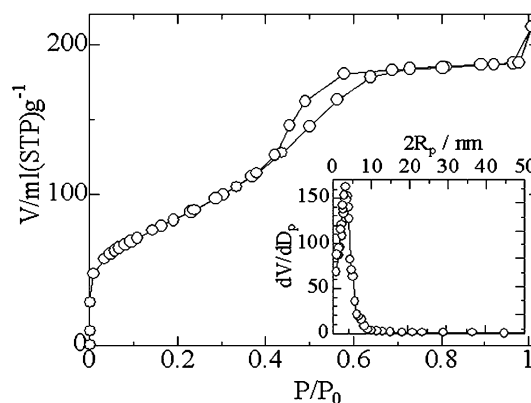


Fig. 4 BET nitrogen adsorption and desorption isotherms and pore size distribution plot (inset) for a self-standing meso-TiO₂-P₂O₅ film.

which is representative of mesoporous solids. The specific surface area of the films is about 330 m² g⁻¹ using the Brunauer-Emmett-Teller method. The pore diameter of the TiO₂-P₂O₅ films was 43 Å, with a very sharp pore size distribution (inset). The surface area of the self-standing mesoporous TiO₂-P₂O₅ films is larger than that of the previously reported free-standing (alternatively known as self-standing) mesoporous TiO₂ films.⁸ The mesostructural properties, which were confirmed from the XRD and TEM results, were also improved by adding a phosphorous phase. Thicker films, up to 90 μm thick, can be obtained using the EISA process. Mesoporous TiO₂ films with a greater surface area, more uniform pore morphologies, and nanocrystallites are essential for the maximum utilization of these materials.⁶

This is the first report of the synthesis of self-standing, transparent, thick mesoporous nanocrystalline TiO₂-P₂O₅ films using a glass P₂O₅ phase and EISA process. We hope that this simple, reproducible synthetic method can be adopted for the preparation of various self-standing mesoporous transition metal oxides, which have excellent potential for applications involving devices and biomaterials. More detailed structural investigation of mesoporous TiO₂-P₂O₅ films, and studies of their optical, electrical, and *in vivo* properties are now in progress.

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