

Using the effects of pH and moisture to synthesize highly organized mesoporous titania thin films†

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Received (in Cambridge, UK) 24th March 2004, Accepted 7th May 2004

First published as an Advance Article on the web 1st June 2004

Highly ordered mesoporous titania films were synthesized within a short time period by controlling the pH of sols and moisture exposure of as-prepared films.

Synthetic processes of surfactant-templated mesoporous materials¹ have been focused on developing frameworks to control an ordered array of structures *via* supramolecular assemblies within the range of 2–50 nm. Among the non-siliceous mesostructured transition-metal oxides, mesoporous TiO₂ film is one of the most interesting materials due to the useful applications associated with its electronic and optic properties such as solar cells, lithium batteries, and electrochromic devices.^{2–5} Highly ordered mesoporous TiO₂ films have been rarely prepared by hydrolysis of TiCl₄ in the presence of amphiphilic block copolymers or surfactants.^{6,7} TiCl₄ was chosen as the inorganic precursor, an ethanol–water solution as the reaction medium, and the films were prepared by dip-coating on glass or silicon substrates. Synthesis conditions such as composition, concentration, type of template, surface charge conditions, pH, and annealing temperature are factors well recognized to determine morphologies of mesoporous materials.^{6–10} In this study, we report the effects of pH and moisture exposure of as-prepared films. By controlling the pH of the sols and the moisture exposure of the film, highly organized mesoporous TiO₂ films could be synthesized reproducibly in a short time.

Well-organized mesoporous TiO₂ films are obtained as follows. The sol is prepared with a molar ratio of 1 TiCl₄ (Aldrich, 99.9%) : 44.6 EtOH (Merck, 99.9%) : 0.0645 polyoxyethylene(20) cetyl ether (Brij 58, Aldrich). The prepared sol is evaporated in a 40 °C oven for 1 hour to remove HCl produced during the reaction. Some ethanol is also evaporated (less than 5%), but the sol is not aged further. Then, the sol is deposited on the Si-wafer or ITO glass by spin-coating (3000 rpm for 10 s), and the film is aged at different RH (relative humidity) for 10 h. Finally, the film is calcined at 150 °C for 2 h and at 300 °C for 4–8 h, raising the temperature at a rate of 2 °C min⁻¹. For a low-temperature treatment, a two-step process was applied. The first step implies the thermal desorption of ethanol and the soft condensation (*i.e.* resulting in a partially or incompletely condensed state)¹¹ at 150 °C. Then residues, surfactant template and extra ethanol, are calcined, and the network condensation occurs at 300 °C (see ESI†).

The pH of the mixed sol is about –1.4, which is too acid to form a well-organized structure. Under extremely high acid conditions (pH < –1.0), the interaction between protonated surfactant headgroups and positively ionized inorganic species becomes weaker. So, the weak organization of surfactants and inorganic species may be collapsed easily during the calcination process. However, suitable acid conditions lead to a periodic organization because this hinders the rapid formation of a dense inorganic network which causes a poorly organized structure.^{6,7} The pHs of the sols to obtain well-defined structures range from –0.7 to –0.5, and the optimal pH is near –0.6. Here, evaporation within 1 hour brings the pH of the sol to an optimum.

The X-ray diffraction (XRD) patterns were obtained on a Rigaku D/max-RC (30 kV, 60 mA) using CuK_α radiation. Fig. 1 shows the low angle XRD patterns of calcined mesoporous TiO₂ films prepared by spin-coating on the Si-wafer and exposing the films to RH of 60% (a), 70% (b), 80% (c), and 85% (d) for 10 hours before calcination. The inset shows the low angle XRD patterns of as-prepared films before calcination. In the case of as-prepared films, similar peak positions and peak areas appeared regardless of procedure, but it is found that the patterns of calcined films are very sensitive to the conditions of moisture exposure. Well-organized structures are obtained at about 70% to 80% RH, and especially near 80%, the sharpest XRD peak appears. Above 80%, however, the ordered structure is collapsed and destroyed.

Fig. 2 shows the low angle XRD patterns of calcined TiO₂ films spin-coated on the Si-wafer and exposed at 80% during 0 h (a), 5 h (b), 10 h (c), 15 h (d), 20 h (e), 25 h (f), and 48 h (g). TiO₂ film prepared with no moisture exposure (a) shows one reflection peak at 2θ = 3.73 with a very weak intensity. However, the peak intensity abruptly increases with increase of exposure time. The XRD patterns of TiO₂ film exposed for 10 hours (c) shows a very well-defined intense and sharp single Bragg peak with a characteristic *d*-spacing of 2.7 nm, suggesting that a long-range order exists in the film. The Bragg diffraction becomes less intense after 15 hour exposure (d), and finally disappears after 48 hour (g).

These experiments indicate that the formation and stability of a mesophase are strongly affected by moisture exposure, and that a mesophase network is mainly formed on the substrate by hydrolytic condensation after spin-coating. When using non-aqueous solvents (*i.e.*, ethanol), a non-hydrolytic condensation path can run in parallel with the hydrolytic condensation, low quantities of water being provided by moisture or impurities.⁶ The effects of two different condensation paths can be estimated by comparison of

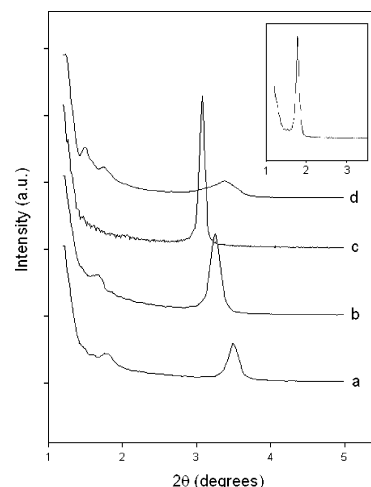


Fig. 1 XRD patterns of calcined mesoporous titania films prepared by spin-coating on the Si-wafer and exposing the films to RH of 60% (a), 70% (b), 80% (c), and 85% (d) for 10 hours before calcination. Inset shows an XRD pattern of an as-prepared film.

† Electronic supplementary information (ESI) available: TG-DTA curve of the mixed sol, prepared with a molar ratio of 1 TiCl₄: 44.6 EtOH : 0.0645 Brij 58. See <http://www.rsc.org/suppdata/cc/b4/b404409f/>

XRD peaks in Fig. 2a) and c). The inset of Fig. 2 shows the low angle XRD patterns of as-prepared (a) and calcined (b) TiO₂ films spin-coated on the Si-wafer and prepared at optimal exposure, aging 10 hours at RH of 80%. As shown, there are differences between as-prepared and calcined TiO₂ films. First, the *d*-spacing decreases from 4.9 nm to 2.7 nm due to a contraction of the structure, often observed after removal of surfactants, and further condensation of inorganic networks.⁶ Second, the diffraction patterns of films become slightly less intense after calcination. In TiO₂ films prepared by previous methods, there is a considerable reduction of peak intensity and sharpness after the heat treatment, which is related to a local collapse of structure. In this study, however, the control of acidity and moisture exposure of the film could prevent the collapse of the structure during heat treatment.

When sols are deposited on the other substrates (*i.e.*, ITO glass), the optimal conditions for well-organized structures may not remain the same because the surface properties affect the formation of mesophases. When the film is spin-coated on ITO glass, the optimal moisture exposure of an as-prepared film is about 2 hours at 57%, but above 60%, structural collapse and aggregation of the coated material are observed. Since the surface of ITO glass is less hydrophilic than that of the Si-wafer, the surface of ITO glass is less wettable with the sols. Under moisture exposure, penetrated moisture spreads well at the interface of the Si-wafer and titania, and this well-dispersed water (gas phase) is provided for hydrolytic condensation. For ITO glass, however, penetrated moisture cannot easily spread, and is condensed to liquid water at the interface. This condensed water can collapse the mesostructure. Therefore, it is believed that the less hydrophilic substrate is more sensitive to the humidity, and the structure collapses at relatively low RH. The effects of surface properties, which influence the formation of mesophase, are now being studied.

Fig. 3 shows the transmission electron micrograph (TEM) images of calcined TiO₂ films spin-coated on the Si-wafer and

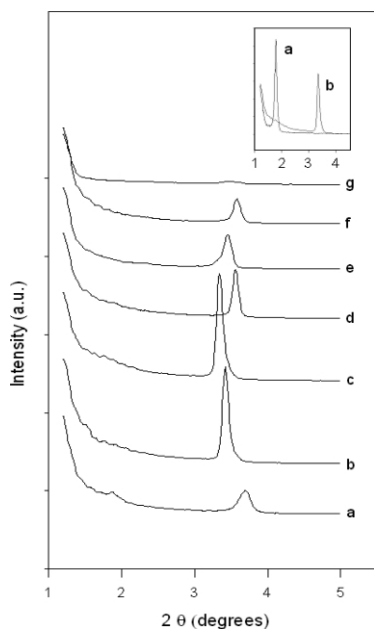


Fig. 2 XRD patterns of calcined titania films spin-coated on the Si-wafer and exposed to RH of 80% for 0 h (a), 5 h (b), 10 h (c), 15 h (d), 20 h (e), 25 h (f), and 48 h (g). Inset shows the XRD patterns of as-prepared (a) and calcined (b) titania films, aged 10 hours at RH of 80%.

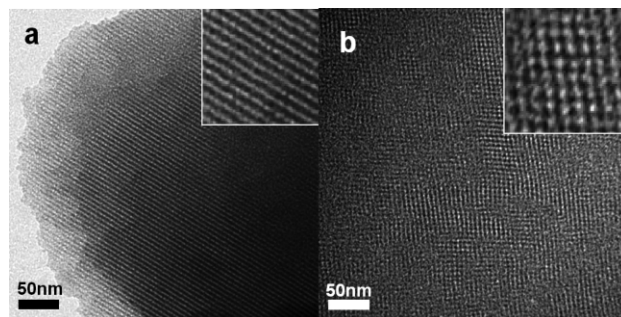


Fig. 3 TEM images of calcined mesoporous titania films spin-coated on the Si-wafer and prepared at optimal moisture exposure. (Philips CM200, operated at 200 kV). The image plane of (a) is parallel to the long axis of pore cylinders and that of (b) is vertical to the long axis.

prepared at optimal moisture exposure, aging 10 hours at RH of 80%; image plane of a) is parallel to the long axis of the pore cylinders and that of b) is vertical to the long axis. In most TEM images, repeated straight lines can be observed whose length is longer than the film thickness, and an image like Fig. 3b) is rarely observed because cylindrical pores are aligned parallel to the surface of the substrate. Well-ordered cylindrical pore structures are observed, which can be indexed in a pseudo 2D centered-rectangular structure (*c2m*). By the effect of contraction during calcination, the 2D hexagonal structure (*p6m*) of the template is modified into the pseudo 2D centered-rectangular structure (*c2m*) of the pores.⁶

In summary, the highly organized mesoporous TiO₂ films were synthesized within a short time period by controlling the pH of sols and the moisture exposure, and the formation of mesoporous films was significantly influenced by the penetration or wetting of moisture on or near the interface. The structures of surfactant-assisted calcined thin films were reformed from the as-prepared structures during the heat treatment.

This work was supported by the Brain Korea 21 Project and the Center of Ultramicrochemical Process Systems.

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