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Formation of grid-like mesoporous titania film via structural transformation and its surface superhydrophilicity conversion

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ABSTRACT

Thin titania film with accessible and grid-like porosity was formed via structural transformation from a large-pore (~10 nm) 3D hexagonal ($P6_3/mmc$) mesoporous titania thin film. The intermediate 3D hexagonal mesoporous titania thin film (MTF) was synthesized using a tetrabutyl titanate (TBT)–P123–BuOH–HCl system by the combination of dip-coating and evaporation-induced self-assembly (EISA). The MTF calcined at 350 °C exhibited an ordered honeycomb arrangement over the entire top surface and an ABAB stacking sequence in the cross-section. After being calcined at 450 °C, the 3D hexagonal mesostructure was transformed to a grid-like mesostructure with quasi-perpendicular porosity through sintering–diffusion and pore merging along the *c*-axis. The accessibility of this grid-like structure estimated by the adsorption of TIRON (disodium 1,2-dihydroxybenzene, 3,5-disulfonate) was higher than that of intermediate structure. And an interesting finding was that, after structural transformation, the surface wettability changed from hydrophilic to superhydrophilic even without UV irradiation. This phenomenon could be properly explained by the increased accessibility and surface roughness of grid-like structure.

1. Introduction

In recent years, titania has attracted much attention in the field of self-cleaning coatings because of photoinduced superhydrophilicity [1,2]. However, this wettability conversion is always reversed slowly in the dark, which constrains its practical application.

Fortunately, wettability of solid surface with liquids is governed not only by the chemical properties, but also the geometry of the surfaces [3]. It has become the common view that the porous surface structure has some beneficial effects on surface hydrophilicity (e.g., Huang et al. [4] had reported the porosity-driven superhydrophilicity on macroporous titania films). Recently, periodic mesoporous titania thin films (MTFs) with 3D open-pore structure are synthesized by utilizing supramolecular templating methods [5–10], and these materials are actively studied in the self-cleaning fields due to their high surface area and open pores at the surface. However, both 3D cubic [5–8] and 3D hexagonal [9,10] mesoporous structures are formed by stacking of the spherical pores. Neither of them exhibit completely vertical mesochannels, which is the limitation for practical application where diffusion into the pores is required. Therefore, the MTFs with vertically oriented porosity show a high demand for actual applications [11].

To address this issue, efforts were devoted to synthesize the mesoporous films with perpendicular porosity. Yamauchi et al. [12] applied a strong magnetic field of 12 T to construct the 2D hexagonal mesostructured thin films with perpendicularly oriented channels. But even so strong magnetic field was not enough to completely align the vertical channels. Richman et al. [13] provided a route to form vertically oriented pores in honeycomb-structured films by epitaxy on the surface of cubic mesoporous films. However, this method needed repeating coating cycles and a precise lattice match between the hexagonal and cubic films. As the progress goes deeper in this field, development of easy operation and high chemical stability for the synthesis of the vertically oriented mesoporous titania films would have a tendency for practical application.

In order to simplify the synthesis process, much attention still focused on the direct structural transformation from an intermediate 3D mesostructure. Grosso et al. [14,15] reported a vertical grid-like mesostructure through pore merging along the [111] directions of a 3D cubic mesostructure. Similarly, Wu et al. [16] also proposed a mesostructure with vertical pores, derived from a 3D hexagonal mesostructure. In theory, these transformations facilitate the accessibility and mass transport of guest molecules from the surface into the framework of titania. However, so far as we know, no reports have been made on the surface wettability of such MTFs with vertical porosity.

In this study, a synthesis system of tetrabutyl titanate (TBT)–P123–BuOH–HCl is proposed to form the titania films with sub-vertically aligned channel-like porosity. By adjusting the humidity

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during synthesis process, a large-pore 3D hexagonal MTF is produced and transformed into a sub-vertical grid-like structure after special heat treatment. Despite the similarities to the synthesis method of various kinds of mesostructures including 2D hexagonal, 3D hexagonal and 3D cubic reported before [5–10], in our approach, TBT replaces the common titanium sources used in EISA-based system, which is ascribed to its milder reactivity and easier operation for practical application. And the parent alcohol of TBT (n-butanol) can control the reactions better as solvent [17,18] and enlarge the pores as a swelling agent [19]. Meanwhile, it will be shown that accompanied with the structural evolution, the accessibility and surface roughness of MTFs increase. As a result, the surface wettability of the MTF changes from hydrophilic to superhydrophilic even in the dark condition, which might open up the self-cleaning application of titania.

2. Experimental

2.1. Preparation of the sol precursors for dip-coating

All the chemical reagents used in the experiments were obtained from commercial sources without further purification and treatment. Tetrabutyl titanate (TBT) was chemically pure (≥98.0%) and purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Triblock copolymer (PEO_{20}–PPO_{70}–PEO_{20}) Pluronic P123 (Aldrich) was used as templating agent. Typically, 4.1 mL hydrochloric acid (37 wt.%) was added dropwise into 6.5 g tetrabutyl titanate at room temperature (RT) under vigorous stirring. Separately, 1.0 g Pluronic P123 was completely dissolved in 18.15 g n-butanol (BuOH, AR). This solution was slowly added into the HCl/TBT solution under vigorous stirring. The composition of the precursor solutions was confirmed by optimizing as follows (molar ratio): 1 TBT: 0.01 P123: 13 BuOH: 2.6 HCl (37 wt.%). After stirring at room temperature for at least 3 h, the solutions turned into transparent light yellow sol precursors.

2.2. Preparation of mesoporous thin films

The fresh gel film was deposited onto a previously cleaned glass microscope slide at a controlled pulling rate (20–60 mm/min) by dip-coating. The process was carried out at room temperature (RT). And the relative humidity (RH) was controlled carefully at 90 ± 3% by flowing the wet air into the dip-coater chamber, which was crucial to obtain high-quality 3D hexagonal MTFs. After deposition, the gel films were aged at RT and 60%–80% RH for at least 24 h (see the Supplementary information for the influence of RH). Then, the films were calcined step by step up to desired temperature by 1 °C/min under flowing air. As the first step, the as-synthesized MTFs were gradually heated to 55 °C, 80 °C, 110 °C, and 130 °C, respectively and kept for 1 h. These films were then heated at 350 °C for 3 h to remove the template completely. Finally, the thin films were heated at 450 °C for 1 h to make the mesostructure transform. The special heat-treating process was also crucial to obtain high-quality MTFs (see the Supplementary information for thermal analysis and more details).

2.3. Characterizations

The mesostructures and crystalline phase of the MTFs were deduced, respectively, by small-angle X-ray diffraction (SAXD) and wide-angle X-ray diffraction (WAXD) using a PANalytical X'Pert Pro diffractometer with Cu Kα radiation at 40 kV and 30 mA. The field emission scanning electron microscopy (FESEM, LEO1530) images were obtained on samples prepared by scraping off the thin films onto silicon wafers without coating any metal or carbon. The transmission electron microscopy (TEM, JEOL, JEM-2100) images were obtained on samples prepared by scraping off the thin films onto carbon-film-supported 200 mesh copper grids. Specially, the corresponding selected-area electron diffraction (SAED) patterns were recorded at an instrument camera length of 200 cm. The Raman spectra were measured under ambient conditions using a Renishaw 1000 Raman spectrometer (Renishaw Ltd., UK). The porous structures were analyzed by N_2 adsorption–desorption measurements using a Micromeritics TriStar 3000. Because of the difficulty in collecting enough TiO_2 particles scraped from the films on glass substrates, the samples for adsorption–desorption studies could be prepared as follows: the sol precursors were gelled in an open Petri dish, underwent the same aging and heating process as described above, and finally scraped from the dish. Although the obtained results might not accurately represent the actual structure and morphology of MTFs, it provided valuable information about the structural transformation along heat treatment [20,21]. The pencil hardness was tested for the thin films as follows: the hardness of the pencils ranged from the softest (6B) to the hardest (9H) and the first pencil that scratched the film surface was reported as the hardness of the thin film according to ASTM D 3363-00 [22]. The adhesion tests were conducted in accordance with ASTM D 3359-02 [23] (Test Method B: A lattice with eleven cuts in each direction) using 3 M Scotch 810 tape.

The accessibility of MTFs was evaluated by a TIRON (disodium 1,2-dihydroxybenzene, 3,5-disulfonate) adsorption experiment similar to the reported by Angelome et al. [24]. The calcined MTFs were immersed in a 0.1 M solution of TIRON for 3 h, and then rinsed with amount of deionized water several times to exclude the excess TIRON molecules on the surface. The UV–vis absorbance spectra of the treated films were collected on a Varian Cary 5000 spectrophotometer. For comparison, dense TiO_2 thin films were prepared in the absence of P123 and served as the control samples. The XPS spectra were acquired from a PHI Quantum 2000 spectrometer using monochromated X-rays from an Al Kα source with a take-off angle of 45° from the surface plane. The atomic fractions of oxygen were computed using the attenuation factors provided by the supplier. The static contact angle (CA) was measured with a JC2000A optical contact angle equipment at room temperature without UV irradiation. A droplet was injected on the surface of samples using a 2 μL micro-injector.

3. Results and discussion

3.1. 3D hexagonal mesoporous titania thin films

FESEM was used to directly observe the outer and inner pore configuration on the surface and cross-section of MTFs calcined at 350 °C. The SEM images of the thin films in top and cross-sectional views are presented in Fig. 1a and b. 2D porous structures with different orders are observed in the top and cross-sectional views, indicating that the films have a 3D porous structure. Fig. 1a shows a 6-fold symmetry arrangement on the top surface of the thin films, as viewed along the direction perpendicular to the substrate surface. Fig. 1b shows a hexagonal packed arrangement on the cross-section of the thin films, as viewed from the direction parallel to the substrate surface. These figures indicate that the porous structure of MTFs is 3D hexagonal. In the previous reports on 3D hexagonal MTFs, there were two kinds of space groups, $P6_3/mmc$ [16] and R-3m [9]. If the space group of our thin films is R-3m, the cross section of the 3D hexagonal mesostructure should show an ABCABC stacking sequence (Fig. 1c). However, the cross-section SEM images display an ABAB stacking sequence (Fig. 1b). Consequently, we believe that the space group of the 3D hexagonal mesostructure is $P6_3/mmc$ on the basis of the SEM images. Moreover, the diameter of the pores is ~10 nm, which can be directly measured from the top surface of the thin films (Fig. 1a).

FESEM provided a real-space view of the mesostructure, but did not give average over the entire sample. Small-angle X-ray diffraction (SAXD), in contrast, provided a broad view of the sample. Fig. 2 shows the SAXD patterns of the as-prepared and calcined films, recorded in the θ–2θ scan mode. They all exhibit an intense and narrow first Bragg