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Preparation of periodically organized mesoporous bicomponent TiO_2 and SnO_2-based thin films by controlling the hydrolytic kinetics of inorganic precursors during EISA process

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ABSTRACT

Highly organized cubic mesoporous TiO_2 and SnO_2 nanocrystalline thin films were reproducibly synthesized via an evaporation-induced self-assembly (EISA) process with a triblock copolymer (Pluronic F127) as the template, by precisely controlling the water content and chelating agent in the initial sol solution as well as by controlling the external relative humidity during the aging step. It has been found that the mesoscopic regularity of the fabricated mesoporous films critically depends on the hydrolytic reactions of inorganic precursors. That is, suppressing the hydrolysis reaction in the initial sol and providing the long-term stability for the sol in the coated film during the aging step are key factors in the formation of highly organized structure. The synthetic strategy was also extended to obtain various TiO_2- and SnO_2-based mixed oxide thin films with tunable composition, including WO_3/TiO_2, SiO_2/TiO_2, Nb_2O_5/SnO_2, by selectively controlling the kinetics of hydrolytic reaction for the additional inorganic precursors. The prepared composite films were crack-free, ultra-highly transparent, and thermally stable.

1. Introduction

As a result of their intrinsic physicochemical properties, high surface area and well-defined pore channel structure, periodically organized mesoporous metal oxide thin films have presented unique advantages in many fields such as adsorption, catalysis, sensor, photoelectrochemical devices, and host–guest chemistry [1–8]. Evaporation induced self-assembly (EISA) process has been developed as a universal synthetic method for mesoporous metal oxide films by coupling the sol–gel process and supramolecular self-assembly. Considerable efforts have been dedicated to the investigations of critical parameters associated with EISA process to understand their effects on the textural properties of resulting mesoporous thin films [9–13].

Recently, Wiesner's group has revealed that the self-assembly is hard to trigger once the sizes of inorganic species exceed the radius of gyration of the surfactants [14]. Typically for widely used Pluronic P123 and F127 micelles, their radii are around 9.8 nm and 12.5 nm, respectively [15,16]. Monitoring the particle sizes in the sol solution is a facile route to understand and control the hydrolysis of multiple metal species in nanosize with a narrow distribution. Stucky's group has demonstrated the feasibility of this characterization method for the mesoporous TiO_2-based materials [17]. Herein we try to extend this methodology to synthesize mesoporous bicomponent TiO_2- and SnO_2-based thin films. In our previous synthetic process for single-component films, the films after spin-coating of initial solution are subjected to aging under humid condition before calcination. Thus the hydrolytic reaction of inorganic precursors occurs at two stages, consisting of the sol formation and aging process. In this study, we investigate the size of particles evolved from the inorganic precursors in these two stages in order to understand and selectively control the hydrolytic kinetics of inorganic precursors and thus to reproducibly synthesize periodically organized mesoporous TiO_2 and SnO_2 thin films. We further developed this approach to elaborate TiO_2 and SnO_2-based mixed oxide thin films with tunable composition, including WO_3/TiO_2, SiO_2/TiO_2, and Nb_2O_5/SnO_2.

2. Experimental section

2.1. Initial sol preparation

All the reagents were purchased from Aldrich unless otherwise stated. For the preparation of bicomponent Ti-based sol, titanium tetraisopropoxide (TTIP) was dissolved and stabilized in an aqueous HCl ethanol solution while vigorously stirring at room temperature. Separately, tungsten(V) pentaethoxide ($W(OEt)_5$, 95%, Gelest), stabilized by 2 equiv. of acetoacetone (AcAc), or tetraethylorthosilicate (TEOS) heat-treated in a mixed solution of HCl, ethanol, and H_2O

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at 60 °C for 2 h, [18] was then added to the sol with vigorous stirring. After being stirred for an additional 10 min, the sol with mixed inorganic species in stoichiometric ratio was added to the Pluronic F127 ethanol solution dropwise. The molar ratio of the final composition in the Ti–M (M = 10% Si or 6% W) sol was as follows: (Ti + M)/F127/HCl/H_2O/ethanol = 1:0.005:1.75–1.85:10:25.

For the Sn-based sol, anhydrous $SnCl_4$ was dissolved in a mixture of ethanol and H_2O with the dissolved F127. Separately, anhydrous $NbCl_5$ was dissolved in concentrated HCl ethanol solution with the 2 equiv. of AcAc. After being stirred for 1 h, two solutions were mixed and obtained a homogeneous colorless solution. The final molar ratio of the Sn–Nb solution was (Sn + Nb)/F127/H_2O/ethanol = (0.94 + 0.06):0.0055:18:30.

2.2. Preparation of mesoporous TiO_2 and SnO_2-based films

Both of the initial sol solutions were stirred for 3–6 h prior to film deposition on a precleaned Pyrex glass by spin coating. The TiO_2-based films were aged for 3 days under a constant relative humidity (RH) of 60%. For the SnO_2-based films, the parameters above were adjusted to 7 days and 80%. The aged films were then annealed at 100 °C for 12 h and finally calcined at 400 °C in air for 2 h at a ramping rate of 1 °C/min.

2.3. Characterization

The particle sizes of the inorganic species in the initial sol were directly measured by a Zetasizer Nano ZS (Malvern Instruments). For the measurement of particle size in the aged films, the suspended samples were prepared by soaking the aged films in anhydrous ethanol with ultrasonication. The concentration of inorganic species in the ethanol soaking solutions was adjusted to 0.02–0.10 mol/L. X-ray diffraction (XRD) patterns for thin films were obtained by using a Rigaku Multiflex diffractometer with a monochromated high-intensity Cu Kα radiation. The mesoporous structure of the synthesized thin films was observed by TEM (Hitachi S-4500 transmission electron microscope operated at 250 kV), and their optical transmissions were recorded using a UV–Visible spectrophotometer (Perkin-Elmer Lambda 40) in a wavelength range of 270–800 nm.

3. Results and discussion

During the preparation of pure Ti-sol and aging process for the coated sol, TTIP is stabilized by the added HCl aqueous solution without precipitation, while it is hydrolyzed and the sol–gel reaction is progressed by the simultaneously introduced H_2O. Hence, the concentration of HCl and H_2O in the Ti-sol should be optimized. Fig. 1a shows the colloidal particle sizes of Ti species in the initial Ti-sol solution and in the films during the aging process with various molar ratios (R_m) of TTIP/HCl/H_2O. It was found that, when R_m was 1/1.75/10, the particle size of Ti-species was maintained around 3.6–4.2 nm during the whole aging period (Fig. 1b). Small-angle XRD pattern (Fig. 1c) showed a sharp and intense diffraction peak in the 2θ range of 1.0–1.2°. Upon calcination, highly organized grid-like cubic mesoporous structure with anatase nanocrystallites was obtained, as revealed by TEM analysis. When R_m was 1/1.75/20, the particle size of Ti-species in the sol solution was increased steadily upon aging under humid condition. Finally, the particles grew up to 13.5 nm, which seems to be larger than the gyration radius of F127. Correspondingly, small-angle XRD pattern did not show any diffraction peak indicating the absence of long-range ordering, suggesting that the Ti precursor is rapidly hydrolyzed in early EISA process before the self-assembly of triblock copolymer, due to high content of water. Upon calcination, highly crystallized particulate films were formed. On the other hand, when R_m was 1/0.8/5, Ti-species remained in very small sizes in the initial sol solution, due to relatively

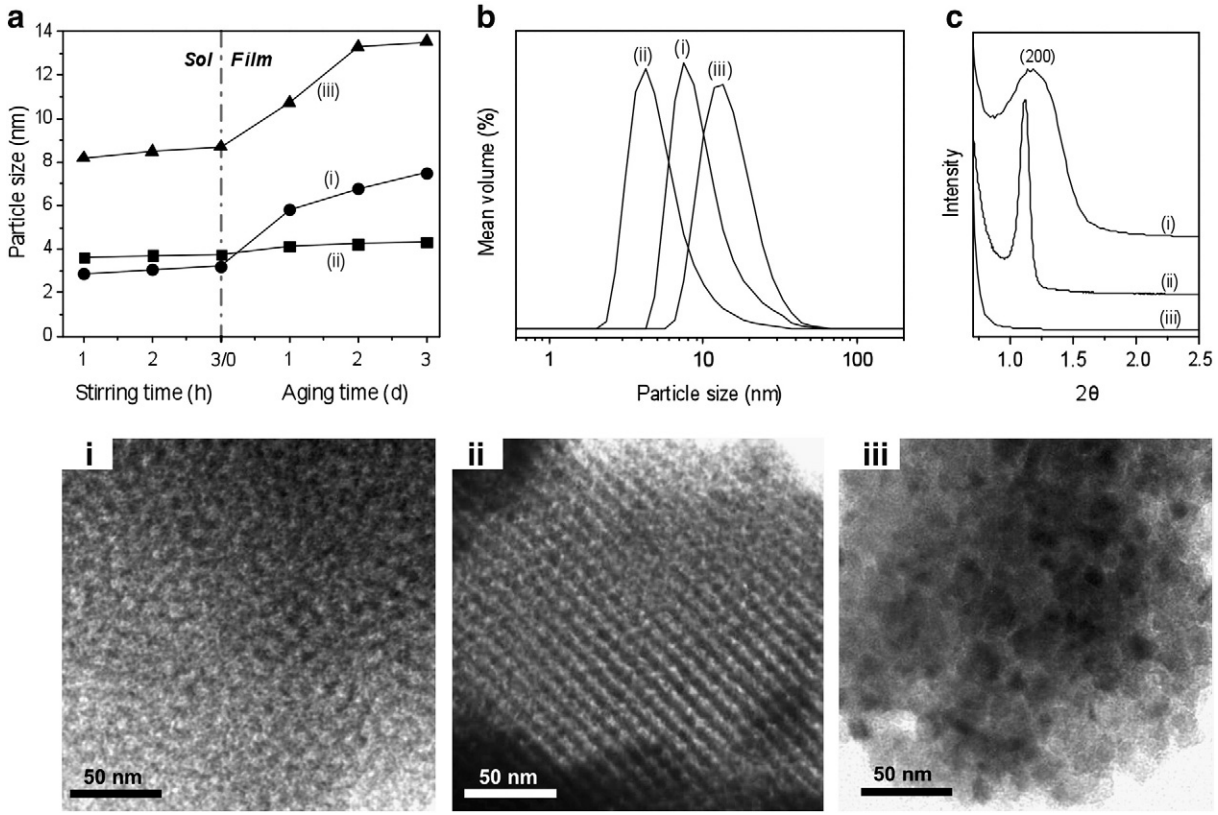

Fig. 1. Time evolution of particle sizes (a) and final size distributions (b) of Ti species in the initial sol solution and aging films derived from different molar ratio of Ti/HCl/H_2O: (i) 1/0.8/5; (ii) 1/1.75/10; (iii) 1/1.75/20; small-angle XRD patterns (c) for corresponding films annealed at 150 °C; and TEM images (below) for their resultant TiO_2 films calcined at 400 °C.