

Transparent Self-Standing Films of Titanium-Containing Nanoporous Silica

Makoto Ogawa,^{*,†,‡} Keita Ikeue,[§] and Masakazu Anpo[§]

PRESTO, Japan Science and Technology Corporation (JST), Department of Earth Sciences, Waseda University, Nishiwaseda 1-6-1, Shinjuku-ku, Tokyo 169-8050, Japan, and Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

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Transparent self-standing films of titanium-containing (Ti/Si ratio of 1/50) silica–surfactant mesostructured materials, having a thickness of ca. 50 μm and a lateral size of a few centimeters, were synthesized by the solvent evaporation method from tetramethoxysilane, vinyltrimethoxysilane, titanium tetraisopropoxide, and octadecyltrimethylammonium chloride. The films were converted to titanium-containing nanoporous silica films by subsequent calcination in air at 550 $^{\circ}\text{C}$, while their highly ordered mesostructures and macroscopic morphology were retained after the surfactant removal. Titanium-containing nanoporous silica films with hexagonal and cubic symmetry were obtained by changing the composition of the starting mixtures. The resulting materials possess a large surface area (ca. 900 m^2/g) as evidenced by nitrogen adsorption/desorption isotherms. The titanium ions exist in the silica network as a tetrahedrally coordinated species. UV irradiation of the titanium-containing nanoporous silica film in the presence of CO_2 and H_2O led to the evolution of CH_4 and CH_3OH , indicating the photocatalytic reactivity of the present material.

Introduction

After the introduction of mesoporous silicas with highly ordered pore arrangements,^{1,2} the synthesis of inorganic–surfactant mesostructured materials has been extensively investigated from both fundamental and practical viewpoints.^{3–5} The processing of the inorganic–surfactant mesostructured materials in a controlled morphology is a basic prerequisite for applications as well as for the preparation of thin films,^{6–15} hollow and hard spheres,^{16–18} and fibers.^{19,20} Films are

an ideal morphology for many applications; however, particular applications of mesoporous silica films have yet to be reported. Possible applications of mesoporous silica films include dielectric coating of semiconductor devices²¹ and hosting photoactive species.^{21,22}

Here, we report the synthesis of self-standing films of titanium-containing nanoporous silicas and their possible application as a photocatalyst. Titanium-containing silicas with a wide variety of microstructures and compositions have been synthesized, and their various properties, such as catalytic and optical, have been extensively investigated.^{23–25} Their photocatalytic property is currently one of the main research topics, and the design of highly transparent photocatalysts is strongly desired.²⁶ On the other hand, the introduction of titanium into mesoporous silica powders has been

* To whom correspondence should be addressed.

† PRESTO, Japan Science and Technology Corp.

‡ Waseda University.

§ Osaka Prefecture University.

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reported previously by direct synthesis and postsynthetic methods.^{27–33}

In the present study, the solvent evaporation method was employed for the synthesis of titanium-containing nanoporous silica films because the ease of the synthetic operations and the homogeneity and transparency of the products make it a promising method.^{6–8} The compositions of the starting mixtures are directly reflected in the compositions of the products in the present synthesis, so that the introduction of titanium was achieved by the addition of titanium tetraisopropoxide into the precursor solution. The materials successfully synthesized in the present study have opened up new opportunities for supramolecular-templated porous solids to such applications as photocatalysts, separators, and nanoreactors for organic reactions.

Experimental Section

Materials. Tetramethoxysilane (abbreviated as TMOS), vinyltrimethoxysilane (VTMOS), octadecyltrimethylammonium chloride (abbreviated as C₁₈TAC), and methanol were purchased from Tokyo Kasei Industries Co. and used without further purification. Titanium tetraisopropoxide (abbreviated as TIP) was purchased from Kanto Chemical Industries Co. and used as received.

Sample Preparation. Titanium-containing nanoporous silica films were synthesized in a way similar to that of the method described previously for the synthesis of self-standing nanoporous silica film.³⁴ A typical synthetic procedure for the self-standing films is as follows: 0.98 g of TMOS, 0.32 g of VTMOS, 0.05 g of TIP, 0.38 g of C₁₈TAC, and 0.1 g of methanol [(TMOS + VTMOS):TIP:C₁₈TAC:methanol = 1:¹/₅₀:¹/₈:¹/₂₅ and TMOS:VTMOS = 7:1] were mixed by magnetic stirring, and the mixture was allowed to react under acidic conditions (by the addition of 0.1 mL of 1 M HCl) for 10 min at room temperature. To hydrolyze the alkoxides, deionized water was added to the mixture. The amount of water was varied to control the mesostructures of the products. Then, the resulting solution was deposited on a poly(ethylene) film and dried in air at 60 °C for 1 day to remove the solvent and to complete condensation of the alkoxides. The dried films could then be peeled off from the substrate, yielding flexible, self-standing, transparent films. As mentioned in our previous papers,^{6–8} rapid evaporation of the solvents before gelation is very important to obtain highly ordered mesostructured materials. The trifunctional organoalkoxysilane, VTMOS, suppressed the gelation to give self-standing films with a thickness of several tens of microns.⁹ The as-synthesized films were calcined in air at 550 °C for 5 h with a heating rate of 5 °C min⁻¹ in order to remove surfactants and obtain porous films.

Characterization. X-ray diffraction (XRD) patterns were obtained on a RAD IB diffractometer (Rigaku) using monochromatic Cu K α radiation operated at 30 kV and 30 mA. The self-standing films were placed on a glass substrate for the

XRD measurements. Scanning electron micrographs (SEMs) were obtained on a Hitachi S-2840N scanning electron microscope. The samples were cut in air to see the cross section of the film. Transmission electron micrographs of the films were obtained on a Hitachi H8100 transmission electron microscope (TEM) with an accelerating voltage of 200 kV. For the TEM observation, the samples were crushed into a powder, and the powder was deposited on a carbon-coated grid. Infrared spectra were obtained on a Shimadzu FT-8200PC Fourier transform infrared spectrometer. Thermogravimetric–differential thermal analysis (TG–DTA) curves were obtained on a Rigaku TAS-2000 instrument with a heating rate of 10 °C min⁻¹ and α -alumina as the standard. The nitrogen adsorption/desorption isotherms of the calcined films were measured at 77 K on a Belsorp 28 instrument (Bell Japan Inc.). The sample was cut into small pieces (less than 5 mm) to put into the sample folder. Prior to the measurements, the samples were dried at 200 °C under vacuum for 3 h. The X-ray absorption fine structure (XAFS) spectra (XANES and EXAFS) were measured at the BL-9A facility of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba, Japan. Si(111) double crystals were used to monochromatize the X-rays from the 2.5 GeV electron storage ring. The Ti K-edge absorption spectra were recorded in the transmission mode or fluorescence mode at 295 K. The normalized spectra were obtained by a procedure described in previous literature,³⁵ and Fourier transformation was performed on k^3 -weighted EXAFS oscillations in the range of 3–10 Å. The curve fitting of the EXAFS data was carried out by employing the iterative nonlinear least-squares method and the empirical backscattering parameter sets extracted from the shell features of titanium compounds.

Results and Discussion

As reported for the siliceous films,³⁴ titanium-containing silica–surfactant mesostructured materials were obtained as transparent self-standing films with a thickness of ca. 50 μ m and a lateral size of a few centimeters. A photograph and a SEM image of the as-synthesized product are shown in Figures 1a and 2, respectively, as typical examples.

Depending on the synthetic conditions such as the amount of water added, films with different mesostructures were obtained. When the water/Si ratio in the precursor solution was below 2/3, the XRD patterns of the products showed a single diffraction peak (d value of 3.5 nm) with a second-order reflection. Figure 3a shows the X-ray diffraction pattern of the as-synthesized film prepared at a water/Si ratio of 1/3 as a typical example. The TEM image of the product (Figure 4a) shows the hexagonal pore arrangement. Because the films are thought to be composed of cylindrical surfactant aggregates oriented parallel to the film plane, (110) and (210) reflections of the hexagonal phase were absent in the X-ray diffraction pattern^{7,10,13} (Figure 3a). If compared with the previously reported self-standing nanoporous silica films which are composed of disordered nanopores as revealed by the TEM observations,³⁴ the present titanium-containing materials possessed highly ordered mesostructures. The controlled amounts of water in the starting mixture are thought to contribute to the formation of highly ordered mesostructures, because the rapid solvent evaporation is known to be a dominant factor in the present synthesis.^{6,7}

On the other hand, the XRD patterns of the films prepared at a water/Si ratio of 4/3 showed diffraction

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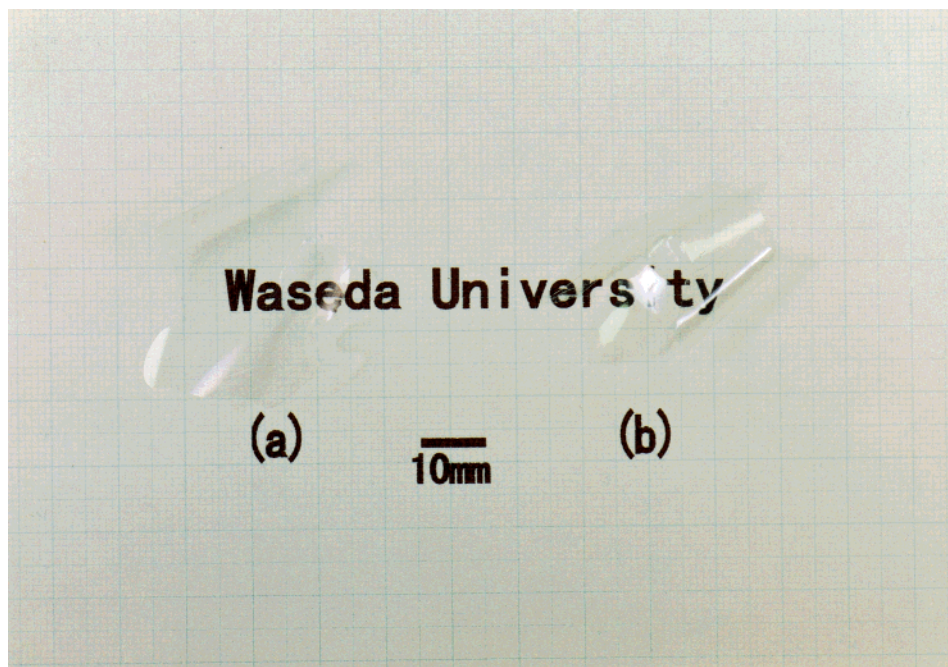


Figure 1. Photographs of the titanium-containing nanoporous silica self-standing film prepared at a water/Si ratio of 1/3 (a) before and (b) after the calcination.

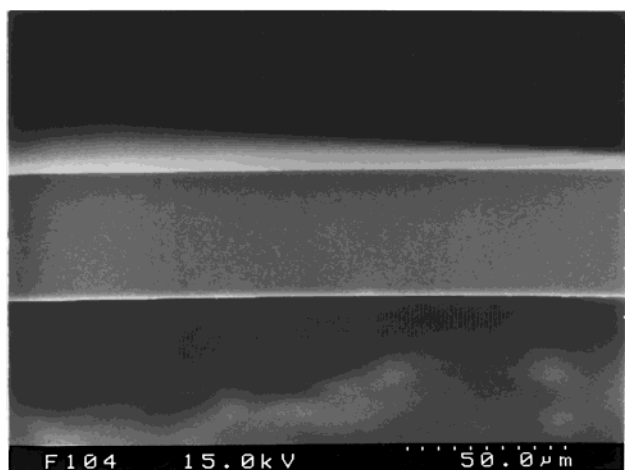


Figure 2. SEM of the self-standing film of the titanium-containing silica-surfactant mesostructures material prepared at a water/Si ratio of 1/3.

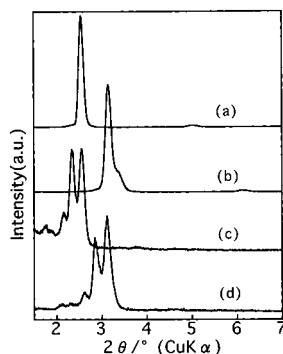


Figure 3. XRD patterns of the as-synthesized self-standing films prepared at water/Si ratios of 1/3 (a) and 4/3 (c). Traces b and d correspond to the calcined a and c, respectively.

peaks ascribable to a cubic symmetry. Figure 3c shows the XRD pattern of the product prepared at 4/3 (water/Si). The formation of the cubic mesostructure was confirmed by the TEMs (Figure 4b,c). Thus, self-stand-

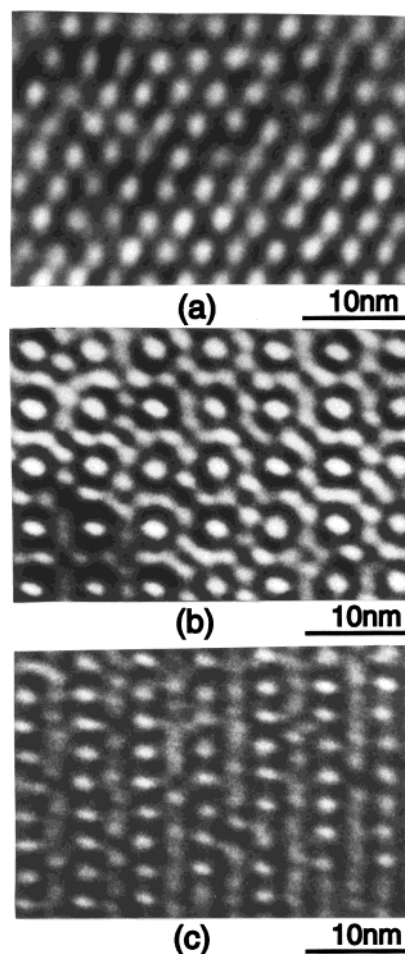


Figure 4. TEMs of the products: (a) the film prepared at a water/Si ratio of 1/3; (b and c) the film prepared at a water/Si ratio of 4/3.

ing films with two different mesostructures were successfully synthesized, and the mesostructures were controlled by the experimental conditions. It is known

that different phases could be obtained depending on the synthesis conditions, principally the silica/surfactant ratios in the starting solution.^{3,12} In the present system, the added amount of water controlled the mesostructures. When the water/Si ratios were 4/3 and 2, mesostructured materials with a cubic symmetry were obtained. On the other hand, hexagonal mesostructured materials formed when the water/Si ratios were 2/3 and 1/2. It is thought that the added water may affect the condensation of the siloxanes to vary the effective volume ratios of the silica/surfactant. Further increases and decreases of the water/Si ratios may cause the precipitation of titanium oxides and insufficient polymerization of alkoxysilanes, respectively.

The TG curves of the products showed weight losses at around 300–400 °C which accompanied exothermic peaks in the corresponding DTA curves. Because the reaction was the oxidative decomposition of the surfactant as well as that of the vinyl group of VTMO, it seemed possible that the films were transformed into porous silica. Accordingly, the as-synthesized films were calcined in air at 550 °C for 3 h in order to remove the surfactant. The surfactant removal by the calcination was seen by the IR spectra of the calcined products, where absorption bands ascribable to the surfactant were absent. The infrared (IR) spectra of the calcined products showed that vinyl groups from VTMO were also completely decomposed during the calcination. The calcined films were continuous and crack-free as evidenced by SEM observation. Figure 1b shows a typical example of the calcined film. To leave vinyl groups in the resulting nanoporous silica films, the surfactant extraction from the as-synthesized products was attempted by using ethanol and water as solvents. However, the removal of surfactant resulted in the complete loss of the mesostructures. Thus, at the present stage, the thermal decomposition of the surfactant is the best way for surfactant removal.

The XRD patterns of the calcined films are shown in Figure 3b,d. Sharp diffraction peaks were observed in the XRD patterns of the calcined films, showing that the ordered mesostructures (both hexagonal and cubic) were retained even after the removal of surfactant. The repeat distance decreased by calcination because of the removal of surfactant and the condensation of the SiOH groups. For the hexagonal films, the $d(100)$ value decreased to 2.8 nm (Figure 3b). The d values of the calcined cubic silica-surfactant film were 3.36, 3.10, and 2.81 nm (Figure 3d).

Nitrogen adsorption/desorption isotherms of the calcined films are shown in Figures 5 and 6. The isotherms showed that the Brunauer-Emmett-Teller (BET) surface area of the hexagonal and cubic films was ca. 900 m² g⁻¹. The average pore sizes were estimated from the Horváth-Kawazoe plot³⁶ derived from the isotherms to be 1.9 and 1.8 nm for the products with the hexagonal and cubic mesostructures, respectively. Thus, the successful formation of self-standing titanium-containing nanoporous silica films with large BET surface areas and highly ordered pore arrangements was confirmed. Although the synthesis and applications of titanium-containing mesoporous silica powders have already been

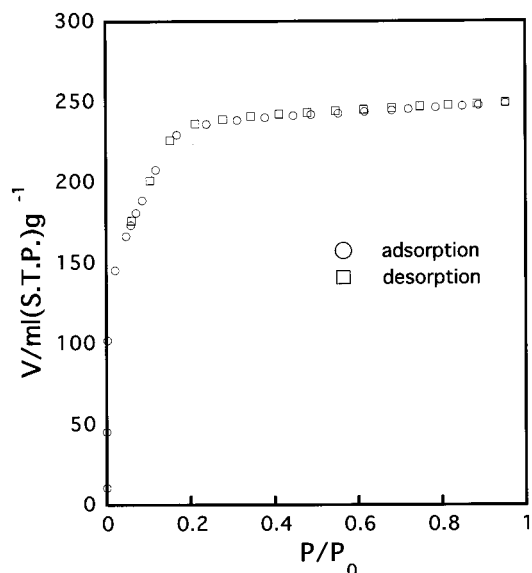


Figure 5. Nitrogen adsorption/desorption isotherms of the titanium-containing nanoporous silica film prepared at a water/Si ratio of 1/3.

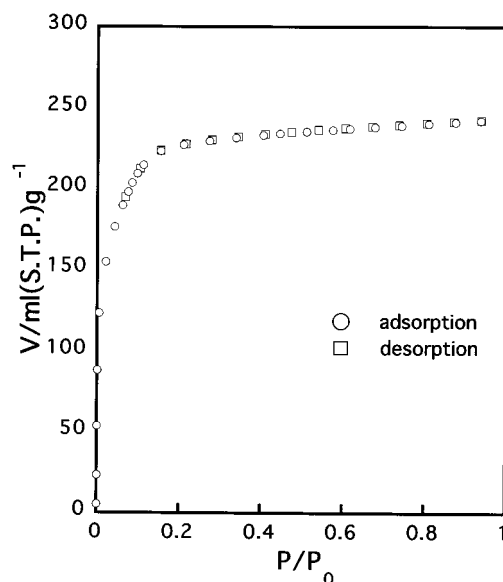


Figure 6. Nitrogen adsorption/desorption isotherms of the titanium-containing nanoporous silica film prepared at a water/Si ratio of 4/3.

documented,^{27–33} this is the first successful synthesis of titanium-containing nanoporous silica films.

UV-vis absorption, photoluminescence, and XAFS investigation clarified the nature of the titanium site in the nanoporous silica films. In the UV-vis absorption and photoluminescence spectra, the absorption (at around 250 nm) and photoluminescence (at 490 nm) attributed to the charge-transfer absorption process and the reverse radiative decay process on the tetrahedrally coordinated titanium oxides were observed.^{31,32} The XANES spectrum at the Ti K-edge shows several well-defined preedge peaks which are related to the states of the titanium atom. The Ti K-edge XANES spectra (Figure 7a and 7b) of the hexagonal (7a) and cubic (7b) titanium-containing nanoporous silica films prepared at water/Si ratios of 1/3 and 4/3 exhibit an intense single preedge peak, indicating that the titanium oxide species has a tetrahedral coordination in the nanoporous silica

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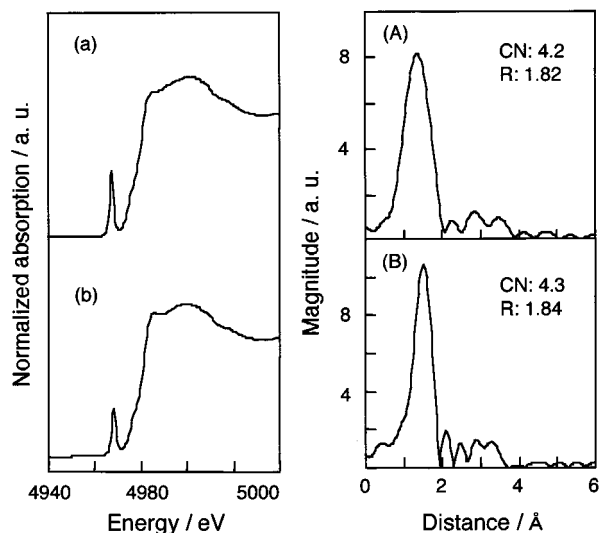


Figure 7. XANES (a and b) and Fourier transform of EXAFS (A and B) spectra of the titanium-containing nanoporous silica prepared at water/Si ratios of 1/3 (a and A) and 4/3 (b and B). The coordination numbers (CN) of titanium are 4.2 and 4.3 for the hexagonal and cubic films, respectively. The atomic distances (R) are determined to be 1.82 (hexagonal) and 1.84 Å (cubic).

film.^{24,27,32} Figure 7A and 7B shows the FT-EXAFS spectra of the same products. From the results of the curve-fitting analysis of EXAFS, it was determined that the coordination numbers (CN) of titanium are 4.2 and 4.3 for the hexagonal and cubic films, respectively. The atomic distances (R) are determined to be 1.82 and 1.84 Å for the hexagonal and cubic films, respectively. All of these results indicate the presence of an isolated tetrahedrally coordinated titanium oxide species in the silica framework.

To show the photocatalytic activity of the titanium-containing nanoporous silica film, preliminary studies on the photocatalytic reduction of CO_2 with H_2O were carried out. UV irradiation of the hexagonal titanium-containing nanoporous silica film in the presence of CO_2

and H_2O led to the evolution of CH_4 and CH_3OH , indicating high selectivity for the formation of CH_3OH , showing the characteristic reactivity of the charge-transfer excited complexes of the tetrahedrally coordinated titanium oxide species.

Titanium-containing mesoporous silicas were synthesized, and the loaded titanium was found to affect the catalytic properties as well as the photochemical reactions of the adsorbed species.^{27–33} On the other hand, sol–gel-processed silica–titania mixed oxides can be applied for optical devices such as graded refractive index optics.²⁴ The titanium-containing nanoporous silica films successfully synthesized in the present study show significant potential for applications in such fields. The synthesis of titanium-containing nanoporous silica films with variable chemical compositions was found to be possible, and their properties and microstructures are currently under investigation.

Conclusions

Transparent self-standing films of titanium-containing (Ti/Si ratio of 1/50) nanoporous silica with a thickness of ca. 50 μm and a lateral size of a few centimeters were synthesized from TMOS, VTMOs, TIP, and $\text{C}_{18}\text{-TAC}$ by the solvent evaporation method and subsequent calcination in air. The titanium-containing nanoporous silica films possess periodic pore arrangements with hexagonal and cubic symmetries, and the mesostructures were controlled by the composition of the starting mixtures. The resulting materials possess a large BET surface area (ca. 900 m^2/g). The titanium ion exists in the silica network as a tetrahedrally coordinated species.

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