Communication

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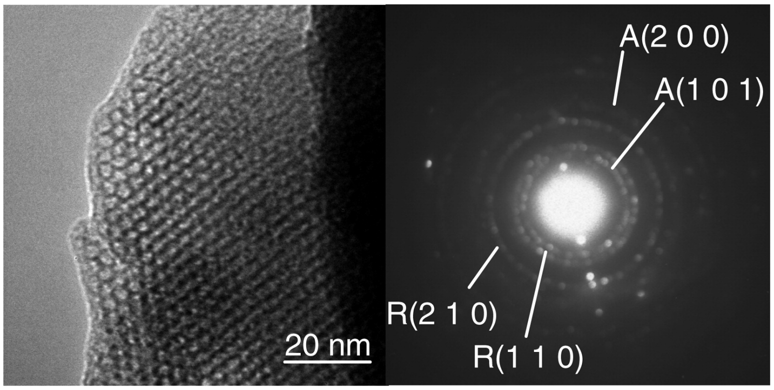

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Direct Synthesis of Mesoporous Titania Particles Having a Crystalline Wall

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Mesoporous materials[1−6] prepared by sol−gel reaction using surfactant lyotropic liquid crystal as the reaction template have gathered considerable attention because of their application to catalyst and separation technology. However, the wall of these materials is normally amorphous, and under heat treatment, crystallization results in collapse of the uniform mesoporous structure. Titania (titanium dioxide) has been widely used as a photocatalyst for the removal of hazardous organic substances[7,8] and as an electrode material for dye-sensitized solar cells[9,10] due to its strong oxidizing and reducing ability under UV light irradiation. Two of the most important factors affecting the photocatalytic activity of titania are its specific surface area and crystallinity. If mesoporous titania could be prepared with an anatase crystalline wall, it would be a useful material applicable to high performance photocatalyst and wet-type solar cells. In this study, we demonstrate a novel *direct* method for preparing *crystallized* mesoporous titania using a low-temperature crystallization technique[11] in the presence of cationic surfactant.

We have recently demonstrated that mesoporous titania with an amorphous wall can be prepared by sol−gel reaction of titanium oxysulfate sulfuric acid hydrate ($TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$) in the presence of the cationic surfactant cetyltrimethylammonium bromide ($C_{16}TAB$) at room temperature (molar ratio of $C_{16}TAB:TiOSO_4 = 1:12$).[12] In the present study, we have succeeded in synthesizing crystallized mesoporous titania. Sol−gel reaction of $TiOSO_4$ in the presence of $C_{16}TAB$ was optimized for various temperatures, reaction times, and $C_{16}TAB:TiOSO_4$ molar ratios. After stirring the mixed solution for 24 h, the obtained particles were filtered, washed with ultrapure water, and dried at 393 K for 10 h.

The photocatalytic activity of mesoporous titania calcinated at 723 K for 2 h was determined by time-course measurements of the concentration of 2-propanol in a quartz cell under UV light irradiation (intensity $= 0.5$ mW/cm^2) using a gas chromatograph (GC-8A, Shimadzu Co.). The column, filler, and detector used were a 3 m long glass column, Sorbitol (GL Science, KK), and a hydrogen flame ionization detector, respectively. The light irradiating apparatus and light source were a UV fiber spot irradiator (San-Ei Supercure 203S, San-Ei Electric) and a 200 W mercury−xenon lamp, respectively. 2-Propanol does not undergo autoxidation by UV light irradiation and heating and is selectively oxidized to form acetone through photocatalytic reaction on the titania surface.[13]

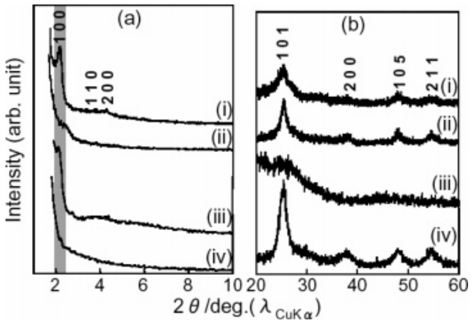

Figure 1. (a) Low- and (b) wide-angle X-ray diffraction patterns of titania particles (i and iii) before and (ii and iv) after calcination at 723 K for 2 h synthesized at 333 K (i and ii) and at room temperature (iii and iv).

Figure 1a shows the low-angle X-ray diffraction patterns of titania particles synthesized by stirring aqueous mixtures of 3000 mM $TiOSO_4$ and 60 mM $C_{16}TAB$ for 24 h at (i) 333 K ($TiOSO_4$:$C_{16}TAB = 50:1$ in molar ratio) and (iii) room temperature ($TiOSO_4$:$C_{16}TAB$ is 12:1 in molar ratio; this ratio was the optimized condition for room temperature synthesis). The diffraction patterns for both samples had three diffraction peaks at around $2\theta = 2.2$, 3.8, and 4.2° assigned to the hexagonal mesoporous structure. The distance between pores estimated using Bragg's equation was 40 Å, and the regularity of the pore size was better for the sample prepared at 333 K (i). This distance was almost the same as those previously reported for mesoporous silica and titania of hexagonal structure.[12,14]

Figure 1b shows the wide-angle diffraction patterns of the same titania samples. The XRD pattern of the particles synthesized at 333 K had three at peaks around $2\theta = 25$, 48, and 55° assigned to anatase-type titania, while the XRD pattern of those synthesized at room temperature had no peaks. The samples synthesized at 333 K are considered to be mesoporous titania particles with an anatase crystalline wall.

Calcination was conducted to remove the $C_{16}TAB$ template from the obtained mesoporous titania particles. Figure 1 (ii) shows the XRD patterns of the particles after calcination at 723 K for 2 h. The XRD patterns of particles synthesized at room temperature are also shown in Figure 1 (iii) before and (iv) after calcination. Though the regularity of the hexagonal pore structure has deteriorated, the particles synthesized at 333 K maintained their hexagonal structure even after removal of the surfactant by calcination at 723 K for 2 h, as seen in the low-angle XRD pattern (Figure 1a (ii)), while the titania particles with an amorphous wall lost their mesoporous structure upon crystallization (iv).

A BET nitrogen adsorption−desorption isotherm was measured for the mesoporous titania particles after calcination (Figure 1 (ii)). The adsorption and desorption isotherm is characteristic of a mesoporous solid and shows a hysteresis phenomenon that suggests the presence of cylindrical pores. Estimation of the specific surface area of the obtained crystalline mesoporous titania particles gave a high value of 262.25 m^2/g.

Figure 2 shows the (a) TEM image and (b) electron diffraction (ED) pattern of particles prepared at 333 K and calcinated at 723 K for 2 h. This sample kept a uniform honeycomb structure even after calcination, and the ED pattern shows that the wall of the honeycomb structure is made of a mixture of anatase- and rutile-type crystal structures. These results confirmed that the wall of the mesoporous powders synthesized at 333 K has an anatase framework.

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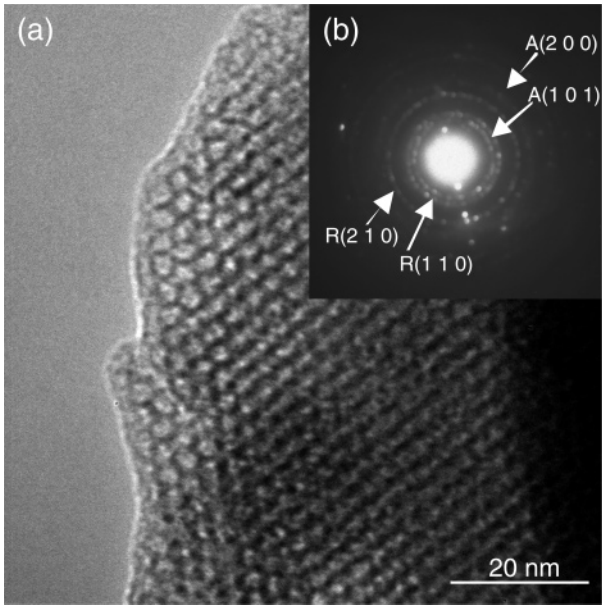

Figure 2. (a) Transmission electron microscopy (TEM) image and (b) electron diffraction (ED) pattern of titania particles prepared by stirring at 333 K for 24 h (C_{16}TAB:$TiOSO_4$ = 1:50) followed by calcination at 723 K for 2 h. A and R represent ED patterns assigned to anatase- and rutile-type titania, respectively.

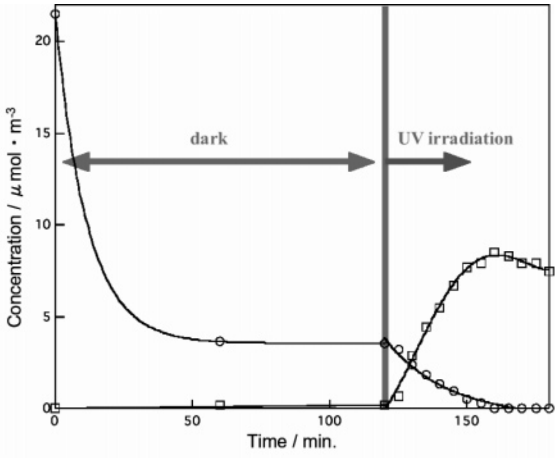

Figure 3. Changes in the concentrations of 2-propanol and acetone under UV light irradiation. Open circles (○) and squares (□) represent the concentrations of 2-propanol and acetone, respectively.

Figure 3 shows the time-course changes in concentration of 2-propanol (○) and acetone (□). Although the cell was placed in the dark for 120 min, the concentration of 2-propanol initially decreased due to its adsorption onto the mesoporous titania particles, which as mentioned have a high specific surface area. Under UV light irradiation, the concentration of 2-propanol decreased and acetone was generated. The results suggest that the obtained mesoporous material thus prepared has good adsorbability as well as photocatalytic activity.

The direct synthesis of mesoporous materials with a crystalline wall has been considered to be difficult for several reasons. One major reason is that phase transformation from amorphous to crystalline by heat treatment or UV light irradiation usually induces the collapse of mesopores because the wall is too thin to retain the three-dimensional mesoporous structure during crystallization. Recently, some mesoporous materials with crystalline structure have been prepared by initial strengthening of the porous structure through depositing another material on the inside surface of the mesopore and then calcining the sample to cause its crystallization. Direct synthesis of crystalline mesoporous titania without any supports requires deposition of very fine titania crystalline particles on the nanoscale surface of surfactant molecular assemblies. When the crystallization rate of, and the wall formation rate around, the surfactant molecular assemblies used as templates are balanced (at 333 K for the present case), mesoporous titania particles with a crystalline wall can be prepared. The combination of a $TiOSO_4$ precursor and a C_{16}TAB template with quaternary ammonium ion affects the formation rate of anatase crystal nuclei at the surface of the assemblies. Optimization of the composition of these two components and the temperature enables us to obtain anatase crystalline particles while maintaining the hexagonal pore structure.

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