Synthesis and Structural Characterization of Hollow Hexagonal Cylinder Co–SiO_2 Composites Prepared in a Micelle Solution

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Novel submicron scale composites with hollow hexagonal cylinder structures were prepared by hydrolysis of tetraethyl orthosilicate in a micelle solution composed of polyoxyethylene ($n = 15$) cetyl ether/cyclohexane/water containing Co–N_2H_4 compound nanoparticles.

In recent years, there have been many reports on the preparation of materials with unique structures. Some examples of materials with unique structures include nanoparticles with anisotropic structures such as rods,[1–3] tetrapods,[4–6] and mesoporous materials such as MCM-41.[7] Materials with an anisotropic structure have superior function to conventional materials for the application in a variety fields such as optics,[1,6] photochemistry,[2] and magnetics[3] because of the specific physical and chemical properties that arise from their structures. Therefore, the development of preparation methods of materials with new structures is required.

We produced a silica composite with a new structure—a hollow hexagonal cylinder with the submicron scale—by the hydrolysis and polycondensation of silicon alkoxide in a micelle solution containing nanoparticles of cobalt compounds. In this work, the structural characteristics and formation mechanism of these hollow hexagonal cylinder materials are described.

Cobalt–silica composites were prepared as follows. First 4.5 mL of aqueous $Co(NO_3)_2 \cdot 6H_2O$ solution with concentrations of 0.14 mol/L was added into 50 mL of 0.50 mol/L polyoxyethylene ($n = 15$) cetyl ether (C-15) solution in cyclohexane to prepare the reversed micelle solution. The water-to-surfactant molar ratios were 10. In order to form some cobalt compounds 0.24 mL of aqueous ammonia and 0.50 mL of hydrazine monohydrate were added to the reversed micelle solution at 323 K. Into the solution containing Co compound nanoparticles, 9.0 g of tetraethyl orthosilicate (TEOS) as a silica source, 15 mL of triethylamine as a base catalyst to promote TEOS hydrolysis were added followed by the hydrolysis and polycondensation of TEOS in the reversed micelle solution. The precipitates thus obtained were thoroughly washed with 2-propanol and dried overnight at 353 K. The dried samples were characterized by transmission electron microscopy (TEM), electron beam tomography (3D-TEM), X-ray fluorescence spectroscopy (XRF), and powder X-ray diffractometry (XRD).

TEM micrographs of the prepared samples are shown in Figure 1. Figure 1a shows the presence of rectangular materials and small particles with diameters of ca. 20 nm. The rectangular materials had a high aspect ratio; i.e., the short side length was

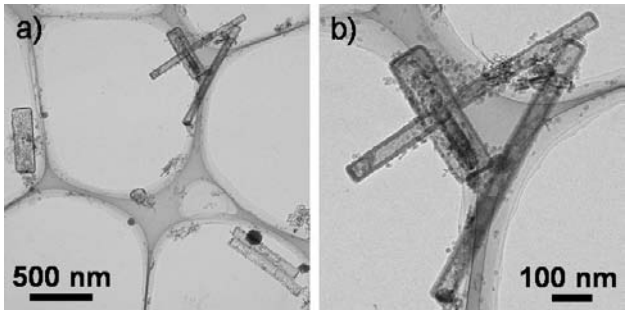

Figure 1. a) TEM image of the nanoparticles prepared in a micelle solution and b) its closed-up TEM image.

60 to 200 nm and the long one was 500 to 1000 nm. Figure 1b shows a close-up TEM photograph of Figure 1a. The fringes of the rectangular materials observed in Figure 1b were darker than those of the other parts, and the width of the fringe was ca. 15 nm. Generally, a rectangular material with a high aspect ratio and dark fringes observed by TEM usually has a hollow cylinder stereostructure. In Figure 1b, all the fringes of the rectangular materials were dark. Accordingly, the structure of the rectangular materials shown in Figure 1 would be hollow cylinder.

The stereostructure of the materials could not be determined only from their TEM micrographs. Thus, the prepared materials were observed by 3D-TEM. Figure 2a shows the rendering image of the materials in Figure 1a. It was found that the material seen in Figure 2a is hexagonal cylinder because a long rod-like material and hexagon base surfaces of the materials were observed. The hexagonal cylinder had the width of ca. 120 nm and length of ca. 960 nm, and these sizes were similar to those of the rectangular materials in Figure 1a. Figure 2b shows the same rendering image as Figure 2a but without surface coloring. The image suggests a hollow structure of the cylinder material. Thus, a cross-sectional view of the hexagonal cylinder by 3D-TEM is shown in Figure 2c. It was noteworthy that the hexagonal cylinder materials had hollow structure. The wall thickness of the hexagonal cylinder was ca. 15 nm, which matches the width of the dark fringes of the rectangular materials shown in Figure 1a. From these results, we concluded that the materials with hollow hexagonal cylinder structure could be prepared by hydrolysis of TEOS in the reversed micelle solution composed of a C-15/cyclohexane /water containing Co compound particles. Synthesis of these large and long hollow hexagonal cylinder materials has not been reported yet.

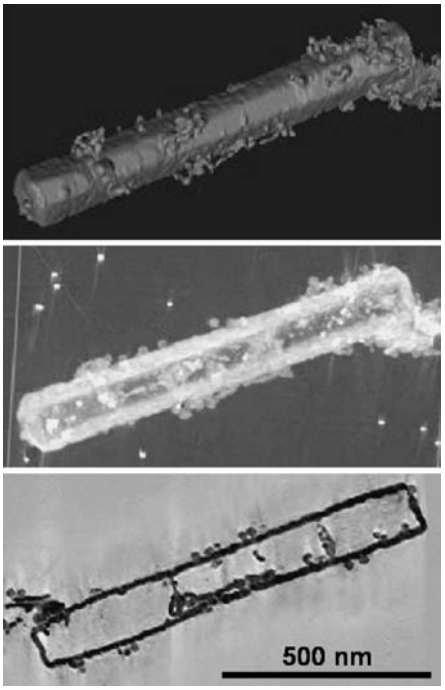

Figure 2. a) 3D-TEM image, b) 3D-TEM image without surface coloring, and c) cross-sectional image of the sample which is the same one that in Figure 1.

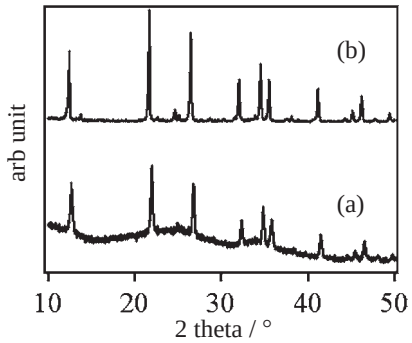

Figure 3. XRD spectra of a) the sample which is the same one that in Figure 1 and b) the reference sample prepared by injecting hydrazine monohydrate into an aqueous Co solution.

Next the composition of the hollow hexagonal cylinder materials was examined. Figure 3 shows XRD patterns of a) the sample which is the same one that in Figures 1 and 2 and b) a reference sample. The reference sample was a Co–N_2H_4 compound precipites obtained by injecting hydrazine monohydrate into an aqueous $Co(NO_3)_2 \cdot 6H_2O$ solution. In Figure 3a, several sharp peaks and a broad peak were observed. The broad peak at $2\theta = 24^\circ$ could be assigned to amorphous silica. The several sharp peaks coincided with those of the reference samples. The sample shown in Figures 1 and 2 was also characterized by XRF. The XRF analysis indicated that the existence of Co and Si atoms, and the molar ratio of Co to Si was 1:2. From these results, the sample shown in Figures 1 and 2 contained both amorphous silica and Co compound particles. Subsequently, the sample shown in Figures 1 and 2 was washed with aqueous HNO_3 to remove Co species. The sample was immersed in a sufficient amount of 0.1 mol/L aqueous HNO_3 solution for 1 h and then washed with distilled water. XRF spectra of the sample after the acid treatment showed that any Co species were not contained in the sample. In TEM micrograph of the sample after the acid treatment, hollow hexagonal cylinder materials were kept in spite of the removal of Co compounds. However, some hexagonal cylinders were divided into a few pieces. It is considered that the hollow hexagonal cylinder material was composed of amorphous silica and a small amount of Co–N_2H_4 compound.

In order to examine the role of Co species for the formation of hollow hexagonal cylinder materials, another sample was prepared under the same conditions but without cobalt cations. In this case, a hexagonal cylinder structure was not obtained but several structures such as a small sphere and a thin sheet were formed. This result strongly suggests that Co species were contained in the hollow hexagonal cylinder material and played an important role in the formation of the hexagonal cylinder structure.

Submicronsize amorphous materials with unique structures are usually prepared by using templates. In this work, the hollow hexagonal cylinder materials were prepared in the micelle solution; therefore, the micelles would work as a template for the formation of the materials. The shape of the micelle was examined by static light scattering method (SLS) because the micelle size was larger than the wavelength of visible light. The morphology and size of the micelle were estimated by fitting a scattering intensity curve with Fournet equation[8] (see Supporting Information). The results indicated the presence of rod-like micelles with diameter of 2.3 μm and length of 10 μm. The rod-like micelle is significantly larger than the size of the obtained hexagonal cylinder materials. Thus, the micelles measured in SLS would be aggregates or bundles of rod-like micelles which work as a template for the formation of the hexagonal cylinder. This assumption is reasonable because the interface of a single micelle is extremely soft and the template effect is generally not manifested. On the other hand, a small amount of Co compounds existed in the hexagonal cylinder materials but were necessary for the formation of the hexagonal cylinders. Accordingly, Co compounds were considered to adsorb in the vicinity of the micelle interface, acting to promote the generation of silica nuclei at the interface. However, further investigation is necessary.

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