Preparation of Mixed Oxide Nanotubes by Precursor-accumulation on Carbon Nanofiber Templates

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Various mixed oxide nanotubes, such as perovskite-type compounds, ferrites, and silica-based mixed oxides, could be synthesized using carbon nanofibers as templates. Carbon nanofibers are effective templates for preparing mixed oxide nanotubes because they are easily coated with mixed oxide by the accumulation of precursors on their surface.

Synthesis of nanoscale materials with various shapes and elements is one of the main issues for nanotechnology, and a lot of nanotubes, nanowires, and nanoparticles have been prepared. Oxide nanotubes have been synthesized through the template method.[1,2] Porous anodic alumina,[3] organogels,[4] carbon nanotubes,[5] and crystalline nanowires[6] have been used as templates. In general, oxide nanotubes are prepared by the coating of templates with oxide through sol–gel process (i.e., hydrolysis and polycondensation of precursors), followed by the removal of templates. The advantage of template method for nanotube synthesis is that their shapes can be controlled by the shapes of templates.[7–9]

It is well known that mixed oxides have the attractive physical and chemical property. For example, perovskite-type compounds show specific ionic conductivity, superconductivity, ferroelectricity, and catalytic activity. Therefore, mixed oxide nanotubes are expected to be useful nanoscale materials. However, there have been few investigations of the preparation of mixed oxide nanotubes.[10–12] The main reason would be the difficulty in coating of templates with mixed oxide. To prepare mixed oxide nanotubes through sol–gel process, simultaneous deposition of two oxides on the templates is needed. However, this is difficult, because the hydrolysis rates of precursors (i.e., deposition rate of oxides) are not equal. In the present paper, the general and simple preparation of mixed oxide nanotubes is demonstrated. We have already reported the synthesis of single oxide nanotubes by using carbon nanofibers as templates.[9] Carbon nanofibers were easily coated with various oxides through the adsorption of precursors on the surface of them. If carbon nanofibers can be coated with mixed oxide by using two precursors, mixed oxide nanotubes would be formed.

First, the preparation of SiO_2–Al_2O_3 and SiO_2–TiO_2 nanotubes was examined. It is well known that they are useful catalysts because of their acidic property. Preparation processes of nanotubes are described below. Carbon nanofibers used as templates in the present study are VGCFs (vapor grown carbon fibers, Showa Denko Co.). VGCFs were placed in a suction filtering unit (Buchner funnel with filter paper), and precursors diluted with CCl_4 ($SiCl_4$ and $Al(O^{sec}Bu)_3$ in CCl_4 (Si/Al = 30, 500 mM as Si), or $SiCl_4$ and $Ti(O^{n}Bu)_4$ in CCl_4 (Si/Ti = 30, 500 mM as Si)) were dropped into VGCF templates. Immediately, precursor solution infiltrated into the space of the fibrous structure. Excess precursor solution was removed by filtration. Obtained samples were dried with the air flow at 293 K. By this drying process, CCl_4 present in the space of the fibrous structure was vaporized. The remained precursors were adsorbed on the surface of the templates. The precursor adsorbed on the templates was immediately hydrolyzed by the water vapor in air. Consequently, the carbon nanofiber templates were covered with a thin oxides and hydroxides. This coating process was repeated 20 times. Finally, the VGCF templates were removed by the calcination in air at 1023 K for 4 h.

Figure 1a shows a TEM image of VGCF templates. The shape of VGCF was straight, and most of their diameters were ranged 100–200 nm. Figures 1b and 1c show TEM images of SiO_2–Al_2O_3 and SiO_2–TiO_2 nanotubes, respectively. The TEM images strongly suggested that the shapes of the nanotubes were similar to those of the VGCF templates; that is, the nanotubes were straight and their inner diameters were ranged ca. 100–200 nm. Their wall thickness was ca. 10–20 nm. As far as we know, this is the first preparation of SiO_2–Al_2O_3 and SiO_2–TiO_2 nanotubes. EDX analysis indicated that Si/Al and Si/Ti ratios were 8–10, but these ratios were much lower than those of raw solutions. This would result from the vaporization of some $SiCl_4$ during drying process at 293 K, because the boiling point of $SiCl_4$ (331 K) is lower than those of $Al(O^{sec}Bu)_3$ (473–479 K at 40 kPa) and $Ti(O^{n}Bu)_4$ (583–587 K). Therefore, Si/Al and Si/Ti ratios of the nanotubes decrease from those of raw solutions.

As described above, ferrites and perovskite-type compounds are attractive materials in various fields. There are a lot of ferrites and perovskite-type compounds, but preparations of oxide nanotubes with their structures are few.[10–12] In the present study, the preparation of $NiFe_2O_4$ and $CoFe_2O_4$ nanotubes as spinel ferrites, and $LaMnO_3$ nanotubes as a perovskite-type compound was examined. Metal nitrates were used as precursors for the preparation of ferrite and perovskite-type compound

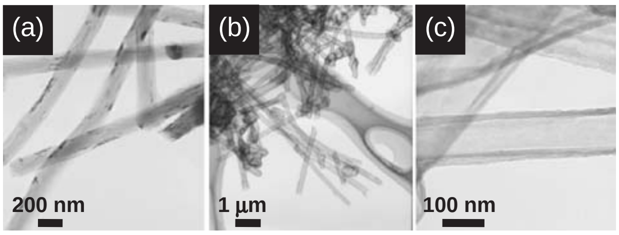

Figure 1. (a) TEM images of VGCF, (b) SiO_2–Al_2O_3 nanotubes, and (c) SiO_2–TiO_2 nanotubes.

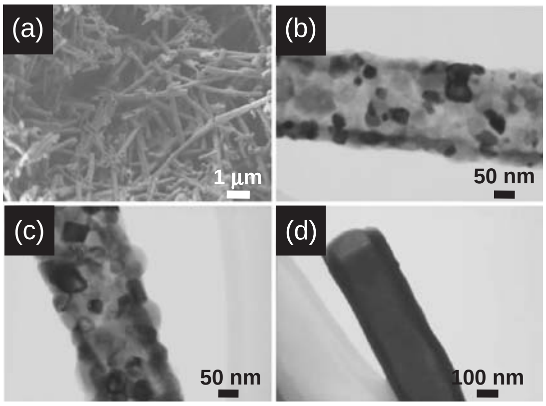

Figure 2. (a) SEM image of $NiFe_2O_4$ nanotubes. TEM images of (b) $NiFe_2O_4$ nanotubes, (c) $CoFe_2O_4$ nanotubes, and (d) $LaMnO_3$ nanotubes.

oxide nanotubes. The utilization of metal nitrates as precursors is desirable from viewpoint of cost, handling, and availability. Used raw materials are as follows: $La(NO_3)_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Mn(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and $Co(NO_3)_2 \cdot 6H_2O$. Ethanol solutions of corresponding two metal nitrates (Fe/Ni and Fe/Co = 2, Mn/La = 1, the concentration of metals = 0.6 M) were prepared, and mixed oxide nanotubes were prepared with the similar experimental procedures as mentioned in the silica-based mixed oxide nanotube synthesis. In the preparation of ferrite and perovskite-type compound nanotubes, drying process, the number of coating process and combustion temperature of VGCF were different. Samples were dried in the air at 573 K to remove ethanol and decompose nitrates into oxides, and coating process was repeated 10 times. VGCFs were removed at 873 K in the air. Formed nanotubes were observed by SEM and TEM measurements. A SEM image shows that formed $NiFe_2O_4$ had fibrous structure (Figure 2a). TEM images of obtained $NiFe_2O_4$, $CoFe_2O_4$, and $LaMnO_3$ indicated that they had nanotubular structures (Figures 2b–2d). When the number of coating process was low, the shapes of formed oxides were not nanotubes, but nanofibers without tubular structures. For $NiFe_2O_4$ and $CoFe_2O_4$ nanotubes, crystallites with size of several ten nanometers consisted their walls, while clear crystallites were not observed in the walls of $LaMnO_3$ nanotubes. EDX analyses of these nanotubes showed that Fe/Ni, Fe/Co, and Mn/La ratio were ca. 2, 2, and 1, respectively. In addition, elemental analysis of the walls of nanotubes by EDX mounted on TEM showed that Fe/Ni, Fe/Co, and Mn/La ratios were almost same as those of raw solutions.

To investigate crystal structure of nanotubes, X-ray diffraction (XRD) patterns were measured. In the XRD patterns of SiO_2–Al_2O_3 and SiO_2–TiO_2 nanotubes, diffraction lines due to Al_2O_3 or TiO_2 were not observed, and a broad peak between 20 and 40° due to the amorphous structure was confirmed. The mullite phase between Al_2O_3 and SiO_2 was not confirmed in the XRD patterns. This result indicates that Al or Ti atoms are present in SiO_2 matrix with amorphous structure randomly dispersed. Figure 3 shows XRD patterns of $NiFe_2O_4$, $CoFe_2O_4$, and $LaMnO_3$ nanotubes. Diffraction lines due to spinel ferrite structure and rhombohedral perovskite structure were observed in the XRD patterns of them. Therefore, it is clear that these nanotubes are composed of corresponding ferrite and perovskite-type structures. The average crystallite sizes of mixed metal oxides calculated using Scherrer's equation are 29.4 nm for $NiFe_2O_4$, 33.5 nm for $CoFe_2O_4$, and 22.1 nm for $LaMnO_3$. In addition, specific surface areas of nanotubes were estimated through N_2 adsorption at liquid N_2 temperature. Specific surface areas of $NiFe_2O_4$, $CoFe_2O_4$, and $LaMnO_3$ nanotubes are 12.0, 8.2, and 12.9 m^2/g, respectively.

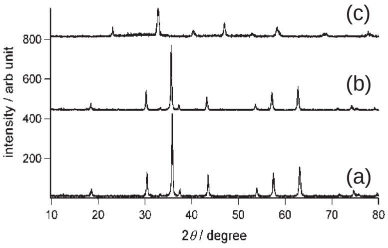

Figure 3. XRD patterns of (a) $NiFe_2O_4$ nanotubes, (b) $CoFe_2O_4$ nanotubes, and (c) $LaMnO_3$ nanotubes.

VGCF templates were removed through oxidation reaction with oxygen. This removal process was examined by thermogravimetric analyses (shown in Supporting Information).[14] Coating mixed oxides except SiO_2–Al_2O_3 catalyzed the reaction between VGCF and oxygen. In particular, $LaMnO_3$ was most effective catalyst for the combustion of VGCF templates. The starting temperature of VGCF combustion was decreased from ca. 900 to ca. 600 K by the coating of $LaMnO_3$. It was possible that $LaMnO_3$ catalyzed the combustion of VGCF dramatically because $LaMnO_3$ shows high activity for the oxidation of carbons and hydrocarbons.[13]

In summary, mixed oxide nanotubes can be prepared by using carbon nanofibers as templates. Carbon nanofibers are coated with mixed oxide by the accumulation of precursors on carbon nanofibers. The formation of various types of nanotubes indicates that our synthesis method is suitable for the preparation of mixed oxide nanotubes.

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14 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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