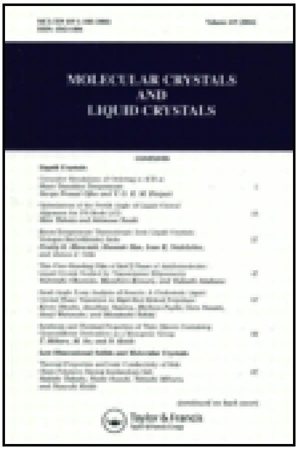

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HYDROTHERMAL SYNTHESIS OF NANO-SIZED IRON OXIDE CRYSTALS IN THE CAVITY OF CARBON NANOTUBES

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Highly crystallized iron oxide nanorods were fabricated by hydrothermal synthesis in the cavity of carbon-coated nanochannels with a diameter of 25 nm. The carbon-coated nanochannels were prepared by uniform carbon coating on the inner walls of the straight nanochannels of an anodic aluminum oxide film. Iron nitrate was loaded in the nanochannels by impregnation method and then subjected to hydrothermal treatment with NaOH aqueous solution in an autoclave. Upon the treatment, the aluminum oxide template was dissolved to leave carbon nanotubes, in which highly crystallized nanorods of α-Fe_2O_3 *were formed. Then, the carbon nanotubes were completely removed by high temperature oxidation and the nanorods were liberated from carbon nanotubes as a result. This study demonstrates that the carbon-coated anodic alumina film can be used as a template even under severe reaction conditions such as hydrothermal treatment.*

Keywords: carbon nanotube; template synthesis; hydrothermal synthesis; α-Fe_2O_3; nano-rod

INTRODUCTION

Recently, many attempts have been made for the fabrication of one-dimensional nano-sized materials using the template technique. Several kinds of materials with straight nanochannel structure are used as templates, e.g., an anodic aluminum oxide film [1,2], a polycarbonate track etched membrane [3] and a nanochannel glass [4]. These template materials suffer from poor chemical stability and therefore it was impossible to employ these templates for the synthesis of nano-sized materials under severe reaction conditions such as hydrothermal treatment.

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We have demonstrated that an anodic aluminum oxide film can be coated with carbon by chemical vapor deposition (CVD) of propylene, where the carbon deposition was uniform and fully covered the whole surface of the film including the inner walls of the nanochannels [5,6]. Such uniform carbon coating must improve the chemical stability of the films, because the carbon deposit will function as a protective layer. The carbon-coated nanochannels in the film, therefore, might be used as a template in hydrothermal treatment.

In this study, we attempt to synthesize highly crystallized iron oxide nanorods by hydrothermal treatment in the cavity of the carbon-coated nanochannels. The crystal structure and morphology of the resultant materials were investigated.

EXPERIMENTAL

An anodic aluminum oxide film was prepared by anodic oxidation of an electropolished aluminum plate at a cell voltage of 20 V in 20 wt.% of H_2SO_4 at 10°C for 2 h. The porosity of the anodic oxide films consisted of parallel and straight channels with a diameter of about 30 nm, and the film thickness was 75 μm. For the uniform carbon coating on the inner walls of the straight nanochannels, the film was subjected to CVD of propylene (1.2% in N_2) at 800°C for 2 h. In order to load the carbon-coated nanochannels with iron salt, the coated films were impregnated with ethanol solution of $Fe(NO_3)_3$ at room temperature and dried under vacuum at 80°C. The loaded films were subjected to hydrothermal treatment with NaOH (0.1 M) solution at 150°C for 24 h in an autoclave. Thereby, iron compound/carbon nanotube composites were obtained as an insoluble fraction. The composites were then heat-treated in O_2 (20% in He) at 600°C for the removal of carbon nanotubes. The synthesis process is illustrated in Figure 1. The microscopic

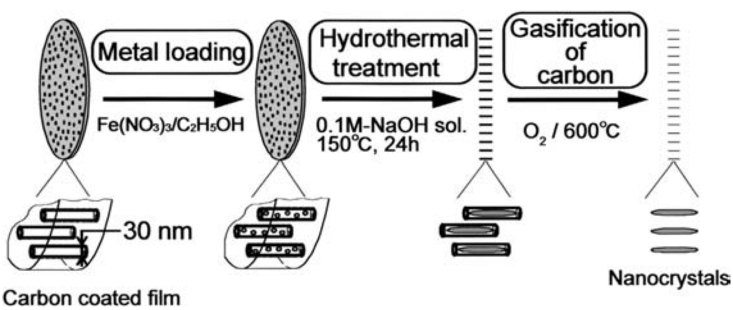

FIGURE 1 Schematic drawing of the synthesis process of nano-sized iron compound.

feature of the iron compounds was studied with a transmission electron microscope (TEM; JEOL, JEM-2010, 200 kV). The crystal structure of the iron compounds was examined by electron diffraction for selected area (SAD) and X-ray diffraction (XRD; Shimadzu XD-D1) techniques.

RESULTS AND DISCUSSION

Figure 2 shows a TEM image of the composites obtained as an insoluble fraction in the hydrothermal treatment. It can be seen that the anodic aluminum oxide films were completely dissolved into NaOH solution under the present conditions, and carbon remains as carbon nanotubes with an inner diameter of 25 nm. In the cavity of carbon nanotubes, many nanorods were observed as dark images. Although some of carbon nanotubes were empty, the others were filled with many nanorods. The diameter of the nanorods was around 25 nm, which is the same as the inner diameter of the carbon nanotubes. The length of the nanorods varies from 50 to a few hundreds nm. The nanorod was identified as α-Fe_2O_3 from the XRD peak position.

Figure 3(a) shows an α-Fe_2O_3 nanorod with a length of 700 nm. The SAD pattern and the lattice fringe taken from this nanorod are shown in Fig. 3(b) and (c), respectively. The diffraction pattern appears not as a ring but as spots, indicating high crystalline nature of the α-Fe_2O_3 nanorod. This is confirmed by a high-resolution TEM image in which the lattice fringes in the nanorod are clearly observed. The regular spacing of the observed lattice planes was about 0.27 nm, which is consistent with the d spacing of (104) of α-Fe_2O_3. In many other nanorods, similar lattice fringes were also observed. In the carbon-coated nanochannels, crystal growth of α-Fe_2O_3 during the

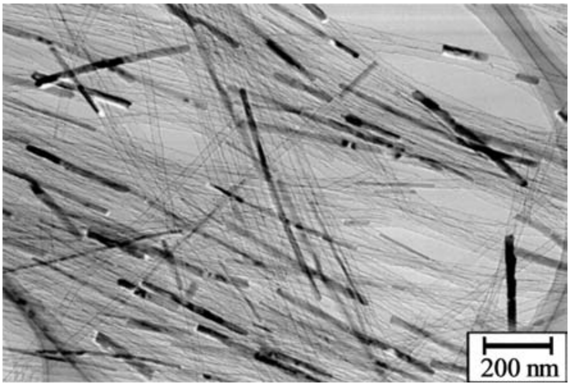

FIGURE 2 TEM image of α-Fe_2O_3/carbon nanotube composites after the hydrothermal treatment.

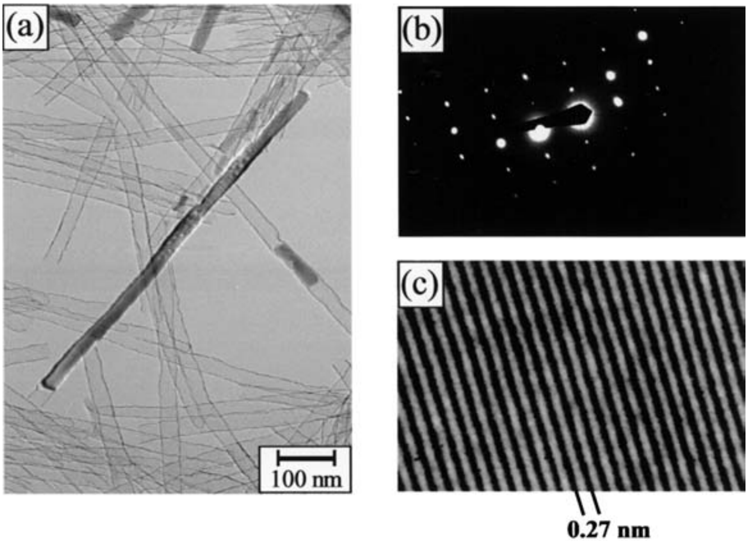

FIGURE 3 TEM image (a), SAD pattern (b) and lattice fringe (c) of an α-Fe_2O_3 nanorod in the cavity of carbon nanotube.

hydrothermal treatment was suppressed by the carbon walls and thereby crystallized nanorods are formed in the carbon nanotubes. Thus, the nano-channels of the carbon coated template could be utilized as a reaction field for the hydrothermal reaction, producing one dimensional nano-materials.

After the gasification of the carbon nanotubes, the resultant substances were only α-Fe_2O_3 nanorods. This finding suggests that the nanorods could completely be liberated from carbon nanotubes by the gasification. The TEM image of the α-Fe_2O_3 nanorods obtained after the gasification is shown in Figure 4. The size of individual nanorods in the TEM image was almost the same as that observed in the carbon nanotubes before the gasification process. Furthermore, the high crystalline nature of α-Fe_2O_3 nanorod after the gasification were confirmed by the presence of the sharp XRD peaks and sharp spots in the SAD patterns.

CONCLUSIONS

Highly crystallized α-Fe_2O_3 nanorods were synthesized by the hydrothermal reaction in the cavity of carbon nanotubes prepared in anodic aluminum oxide templates. The size of the nanorods is almost the same as the inner diameter (25 nm) of the carbon nanotubes and the length is around a few

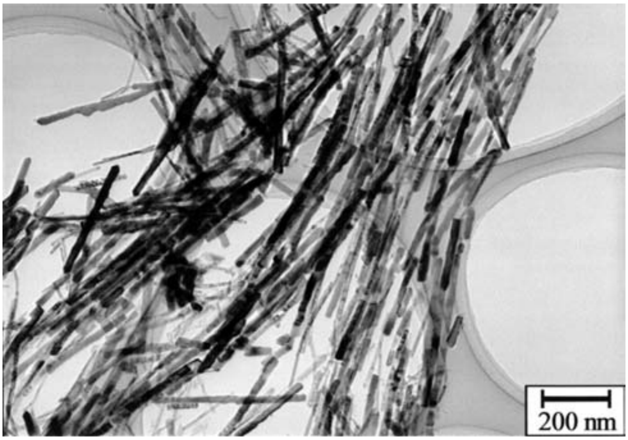

FIGURE 4 TEM image of α-Fe_2O_3 nanorods liberated from carbon nanotubes by O_2 gasification at 600°C.

hundred nm. The formation of such nanorods indicates that the nanochannels in anodic aluminum oxide films, which were uniformly coated with carbon, can be used as a reaction space for the hydrothermal synthesis. The α-Fe_2O_3 nanorods were liberated from the carbon nanotubes by O_2 gasification without changing the shape and the high crystalline nature.

The use of carbon-coated alumina film as a template enables us for the first time to apply hydrothermal synthesis method to template-based preparation of nano-sized materials. This technique would be used for the synthesis of other types of highly crystallized metal oxide nanorods.

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