

PREPARATION OF SILICA TUBULAR NANO-STRUCTURE WITH HIGH SURFACE AREA

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Abstract

Silica nanotubes were simply synthesized through the oxidation pyrolysis of coated and continuous combustion removal of silicon precursor on the surface of carbon nanofibers with prescribed conditions. The inner parts that carbon nanofibers can afford hollow structure to produce silica nanotubes of which the dimension was almost the same with the frame carbon nanofiber. The wall of the resulting silica nanotubes was very thin less than 5 nm. The products showed high surface areas of 450 ~ 800 m²/g which can be controlled by the synthesis conditions. The pore size distribution was of quite homogeneous meso-pores. Various carbon nanofibers are being applied as templates, to generate silica nanotubes of corresponding dimension and shapes.

Introduction

Since the report on carbon nanotubes in 1991 (Iijima, 1991), researches on nano-materials have been boosted under expectation of superior or sometimes novel properties (Remskar, 2004). Various inorganic nanofibers and nanotubes were synthesized through various synthetic routes such as sulfurization, template growth (electrodeposition), solvothermal synthesis, and hydrothermal pyrolysis (Remskar, 2004).

Carbon nanofibers (CNF) can be synthesized in a large amount through a catalytic route, and the CNF structure can be designed by selection of catalysts, carbon sources and synthesis conditions (De Jong, 2000). CNFs are fascinating materials for catalyst supports, electrochemical applications, conductive fillers, etc. CNF is also an excellent candidate as a template to make nanofibers and nanotubes with corresponding dimension and shape (Dai, 1995 and Qiao, 2007), since synthetic routes of the various forms of CNFs have been extensively developed.

Recently, silicon carbide nanofibers were synthesized through the pyrolysis of polycarbomethylsilane (PS) coated platelet carbon nanofibers (PCNF) over 700 °C and burning PCNF under the oxidative atmosphere (Qiao, 2007). CNFs were used as a unique template to govern the shape, crystallinity and morphology of SiC, which had quite high crystallinity in spite of the low synthesis temperature. It was a good example in preparation of functional nano-materials with advanced properties, using CNFs.

In this study, we report an easy preparation of silicon oxide nanotubes through coating of PS on CNFs and successive careful combustion of CNFs from PS-coated CNFs. Several carbon nanofibers with different diameter and morphology were used as a template, to result in silica nanofibers with different structure. Produced silica nanofibers were characterized in the structure, surface area and pore size distribution depending on the synthesis conditions.

Methods

Various carbon nanofibers used in this study were synthesized in the laboratory. Detailed preparation is described in our previous reports (Tanaka, 2004 and Yoon, 2005). Commercially available polycarbomethylsilane ([Si(CH₃)HCH₂]_n) (PS) was used as a precursor (Aldrich). Its softening point and average molecular weight (M_n) were 80 °C and 800, respectively.

Polycarbomethylsilane (PS) of 1 g was dissolved in 100 ml toluene under magnetic stirring and CNF of 5 g was added into the solution with vigorous stirring to disperse CNF in PS solution. The solvent was evaporated to obtain CNF/PS mixture, and the mixture was dried at 80 °C for 5 h in air, to provide PS-coated CNFs.

PS-coated CNF of 0.5 g were heated in the air flow of 200 ml/min at different temperature ranging from 400 to 500°C for prescribed time, to produce white or ivory powder of silica composition.

The oxidation of PS-coated CNFs was tracked by TG to decide the synthetic conditions. The surface area and pore size distribution of the products were evaluated by the nitrogen adsorption. The morphology and structure were observed under scanning electron microscopy (SEM, JSM-6700F) and transmission electron microscopy (TEM, JEM-2100F).

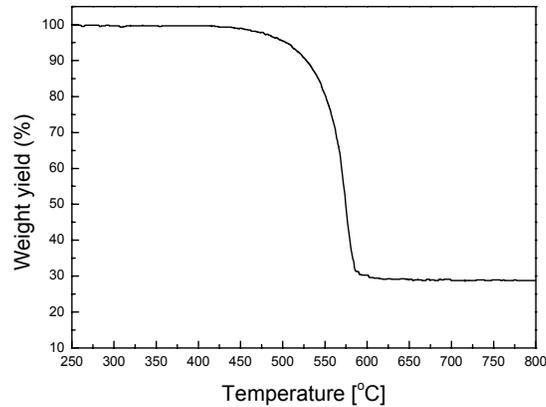


Figure 1. TG profile of PS-coated CNF in air; herringbone CNF with 150 nm diameter was used.

Results and Discussion

Once carbon materials begin to burn, the exothermal reaction will rapidly overheat the system, being uncontrollable. Therefore, the conditions for the mild combustion should be checked. Figure 1 shows a TG profile of PS-coated CNF (PS/CNF = 1/5 w/w) in air. The weight decrease started around 450°C, and then was accelerated around 550°C. The synthesis temperature was selected in the range of 450 ~ 500°C.

PS-coated CNF were heated in air at different temperatures of 450, 470, and 490°C for 8 h, 4 h, and 2 h, respectively, which was estimated through the TG analysis for the complete combustion of CNF. The product was a white powder, and the yield was around 30 wt%. The energy dispersive spectroscopy of the product as prepared showed the O/Si molar ratio 2~3, which means peroxidized silicon or a mixture of silica and incompletely-decomposed siloxane.

Figure 2 shows electron micrographs of CNF used as the template and the produced silicon oxide. The original CNF used has the herringbone structure with 80 ~ 300 nm diameters, which was synthesized from ethylene over a Ni-Cu alloy catalyst. Some coiled or helical forms were mixed (Fig. 2a) and high resolution TEM showed the graphene alignment angled to the fiber axis, indicating the herringbone structure (Fig. 2b). The produced silicon oxide (Fig. 2c) was found to exactly copy the original fiber. The coiled form and surface roughness of CNFs appear almost unchanged in the silicon oxide nanotube. It has tubular structure, and the wall is so thin around 5 nm that the electron transmitted easily to give a clean image as shown in Fig. 2c. Most of nanotubes are independent although some parts are fused.

Figure 3 shows the adsorption isotherms of silicon oxide nanotubes prepared at different temperatures of 450,

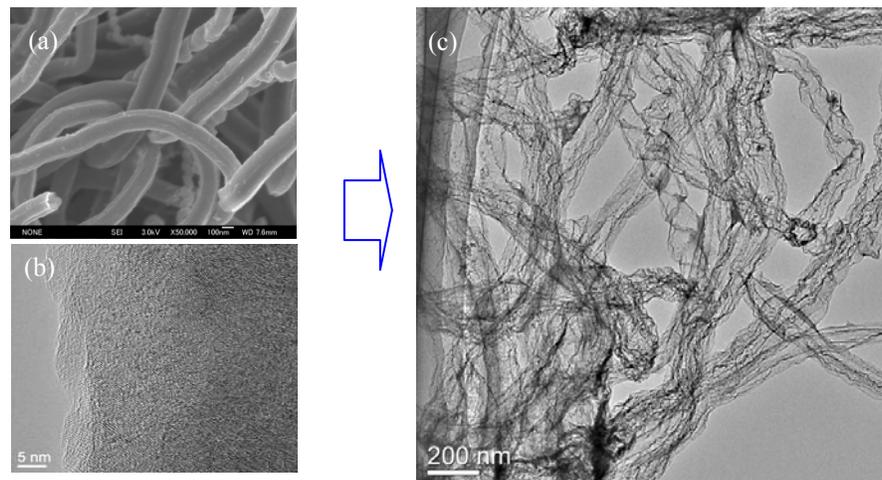


Figure 2. Electron micrographs of CNF used as the template (a, SEM and b, TEM) and the produced silicon oxide nanotubes (c, TEM).

470, and 490°C. The surface area of products showed high values of 470 ~ 860 m²/g, and increased according to increase of the synthesis temperature (Fig. 3). Particular hysteresis loops at P/P0 0.45 ~0.9 were found in the adsorption-desorption isotherms, and mesopores as well as micropores appears to have increased together as the temperature increased. The pore size distribution calculated by a NLDFT method occurred at the mesoporous range of several nanometers, and interestingly the pore size became more uniform at higher synthesis temperature (Data not shown). Such a high surface area of silicon oxide nanotube appear to be ascribed to the unique nano-structure as shown Fig. 2 and pores which might be formed by combustion of CNF as well as decomposition of PS coated on CNF like a thin film. However, formation of pores, especially relating to the temperature dependency should be more examined in details.

Conclusions

Silicon oxide nanotubes have been successfully synthesized using a polysilane precursor and CNF as a template. The nanotubes, which copied the template CNF, has thin wall of around 5 nm and high surface area with unique nano-sized pores. CNFs with various structures are now being applied as a template to synthesize various silicon oxide nanotubes with the corresponding dimension and shape. The present products are expected to be useful as precursors of nano-structured silicon compounds, catalyst supports, etc.

Acknowledgements

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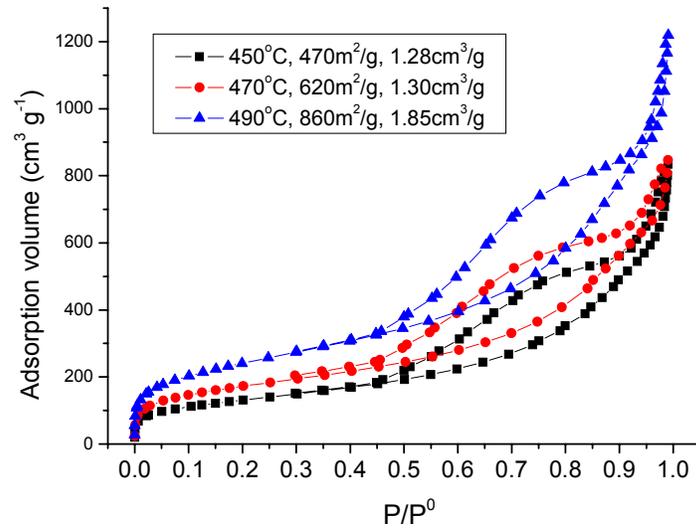


Figure 3. Nitrogen adsorption-desorption isotherms of silicon oxide nanotubes prepared at 450, 470, and 490°C. The BET surface area and maximum pore volume are shown in the legend.