Synthesis of Conducting Mesoporous Materials Implanting Carbon Nanotubes inside Particles

Hyung Ik Lee,[1] Chul Youm,[2] Chanho Pak,[3] Sung Soo Kim,[1] Hyuk Chang,[3] Doyoung Seoung,[3]
Jae-Ho Kim,[2] Young-Uk Kwon,[1] and Ji Man Kim*[1]
[1]*Department of Chemistry and SKKU Advanced Institute of Nano Technology, Sungkyunkwan University, Suwon, 440-746, Korea*
[2]*Department of Molecular Science & Technology, Ajou University, Suwon, 442-749, Korea*
[3]*Energy Laboratory, Samsung Advanced Institute of Technology, P. O. Box 111, Suwon, 440-600, Korea*

(Received February 1, 2006; CL-060141; E-mail: jimankim@skku.edu)

Carbon nanotubes have been successfully implanted inside mesoporous particles as conducting nanowires by one-step synthetic strategy, giving dramatically reduced sheet resistances.

Mesoporous materials are of great interest for a number of applications such as catalysis, adsorption, molecular recognition, sensing, separation, nano template, and so on because of their regular accessible mesopores and high surface areas.[1] Especially, the mesoporous materials have shown many potential applications as a host for sensing molecules and as a photovoltaic material.[2,3] However, the high electrical resistance of the materials is a critical obstacle for the applications requiring electron transfer. This is why copious number of studies to confer the conductivity on porous silica-based materials are being tried.[4]

Our challenge, here, is to create a conductive passage inside the mesoporous inorganic particles without losing significant mesostructural properties such as large pore volume, regular mesopore, and high surface area. We propose a facile synthesis route for carbon nanotube (CNT)-implanted large porous periodic mesoporous silica (PMS) in neutral medium using amphiphilic block copolymer as structure-directing agent. CNT that we adopted as a conducting nanowire is one of the most spotlighted nanomaterials nowadays owing to its unique graphitic and wiry nanostructure and the consequent properties such as abnormal mechanical stability and conductivity.[5]

A typical synthesis for the CNT-implanted PMS material is as follows: First, CNTs (Iljin Nanotech, produced by arc discharge method) were carboxylated by chemical oxidation in a mixture of concentrated sulfuric and nitric acids (3:1 v/v, 98 and 60%) under ultrasonication (Cole-Palmer, 55 kHz) at 25 °C for 4 h. The reaction mixture was filtered with 0.02 µm-pore anodisc (Whatman) and washed with deionized water until the pH of filtrate became nearly neutral (designated as ^{sm}CNT, where "sm" means "surface modified"). In order to synthesize the CNT-implanted PMS materials, 1.8 g of amphiphilic block copolymer, P123 (Aldrich, $EO_{20}PO_{70}EO_{20}$, $M_w = 5800$) was completely dissolved in doubly deionized water at room temperature, and then the ^{sm}CNT was dispersed in the P123 solution under ultrasonication for 1 h. The weight ratios of ^{sm}CNT/(^{sm}CNT + SiO_2) were 0–4.5%. To the browny dark and quasi-transparent ^{sm}CNT-P123 solution, 11.0 g of sodium silicate solution (10 wt % of SiO_2, Na/Si = 2.5) was added. After stirring for 10 min at room temperature, 2.75 g of acetic acid solution (99.8 wt %) was added to the reaction mixture, resulting in the pH around 7 and grey precipitate. The reaction vessel was stirred for more 30 min at room temperature, and subsequently heated to 50 °C and kept at that temperature for 24 h under vigorous stirring. Subsequently, the mixture was aged at 100 °C for 30 h, and slightly ash colored product was collected by suction filtration and dried at room temperature for 24 h. The samples were denoted as PMS-*x*, where the *x* represents the weight ratio of ^{sm}CNT/(^{sm}CNT + SiO_2). The P123 in the PMS-*x* samples was washed using an HCl/EtOH mixture and finally calcined at 370 °C for 3 h. After the calcination, the color of samples was still grey and very homogeneous, indicating that the CNTs were well dispersed and remained in the final PMS materials during the thermal treatment.

XRD patterns in Figure 1 show highly ordered mesostructures of PMS-*x* samples. All the materials, PMS-0, PMS-1, and PMS-4.5, exhibit one well-resolved peak and relatively weak two peaks, which could be indexed as the (100), (110), and (200) of 2-D hexagonal symmetry with lattice parameter of $a = 12.4$, 12.8, and 13.4 nm, respectively. Wide angle XRD patterns in Figure 1 show two kinds of typical peaks arising from amorphous silica frameworks (broad peak around $2\theta = 22°$) and crystalline CNTs (peak centered at 26.5°). As the amount of CNT increases, the peak from CNT starts to appear and become more intense. N_2 sorption analysis reveals the mesoporous structures of the present CNT-implanted PMS materials (see Figure S1 of ESI and Table 1). All the PMS-*x* materials exhibit typical type IV isotherms with BET surface areas in the range of 610–630 m^2/g and total pore volume in the range of 1.56–1.79 cm^3/g. TGA results show the amounts of CNT in the PMS-1 and PMS-4.5 materials are 0.9 and 1.9%, respectively (Table 1). Somewhat lower amount of CNT compared with those initial loading may be due to the decomposition during the calcination.

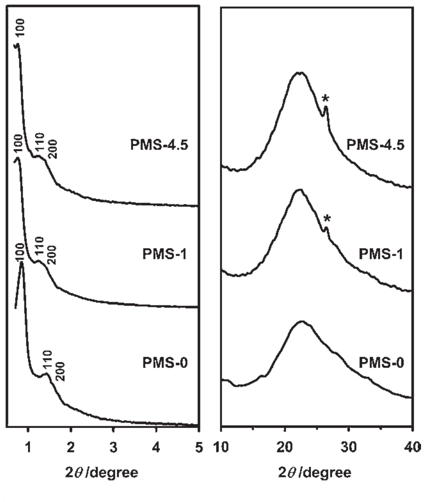

Figure 1. XRD patterns of PMS-*x* materials.

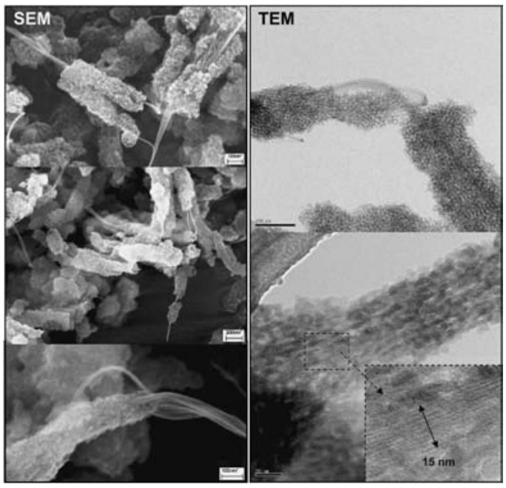

Figure 2. SEM and TEM images of PMS-4.5 material.

The XRD and N_2 sorption results do not give direct evidence whether the PMS-*x* samples are composite material in nanoscale or just a simple mixture of two kinds of the nanomaterials. Figure 2 shows the SEM and TEM images for the PMS-4.5 material, which provide clear evidence of CNT-implanted PMS materials. SEM images in Figure 2 clearly show CNTs embedded within the PMS particles for PMS-4.5 material. In case of PMS-1, some bare PMS particles (without CNTs) are found more often compared with PMS-4.5 from the SEM image. The PMS particles, skewered by CNTs, can be easily found, especially in the PMS-4.5, as expected from the total pore volumes. It seems likely that hydrolyzed silicate species are to self-assemble with the P123 stabilized $^{\mathrm{sm}}$CNT. The detailed structures of PMS-4.5 sample are revealed by TEM images in Figure 2. The TEM images show both ordered mesostructure of PMS and nanostructure of CNT dispersed within the PMS particles. Several nanometer-sized bundles of CNTs are projected from individual PMS particles. The TEM images of CNTs in PMS-4.5 material also confirm that the crystallinity of the $^{\mathrm{sm}}$CNT with about 1-nm diameter is maintained during the surface modification and the synthesis of CNT-implanted PMS materials.

The sheet resistances of CNT-implanted PMS materials are obtained by pressing the samples and subsequent 4-point analysis (Table 1). At the same pressure, the implanting CNT within the PMS particles results in dramatical reduction of resistance of the materials as listed in Table 1. The PMS-1 shows the resistance $73.6\,\mathrm{M\Omega/cm^2}$ at $150\,\mathrm{kg_f/cm^2}$ where the resistance of PMS-0 is almost infinite. Furthermore, PMS-4.5 exhibits about 120-times lower resistance ($0.61\,\mathrm{M\Omega/cm^2}$) than that of PMS-1. The sheet resistance of a physical mixture of PMS-0 and CNT (2 wt % of CNTs), prepared simply by grinding two materials, is also almost infinite under the same conditions, which may be due to the poor dispersion of CNTs.

The present synthesis strategy can be extended to obtain mesoporous materials with various framework compositions such as transition-metal oxides and carbon, where the conducting nanowires, CNTs, are implanted inside the particles. If the CNT-planted PMS materials are used as a template for nanoporous materials via nanoreplication technique,[6] a new CNT-implanted mesoporous materials constructed with various framework composition, can be created after the removal of the silica.

Table 1. Physical properties of PMS-*x* materials

Sample	a^{a}/nm	$S_{\mathrm{BET}}{}^{\mathrm{b}}$ $/\mathrm{m^2\,g^{-1}}$	$V_{\mathrm{tot}}{}^{\mathrm{c}}$ $/\mathrm{cm^3\,g^{-1}}$	Sheet resistance$^{\mathrm{d}}$ $/\mathrm{M\Omega\,cm^{-2}}$
PMS-0	12.4	590	1.56	∞
PMS-1	12.8	625	1.79	73.6
PMS-4.5	13.4	611	1.59	0.61

[a] Calculated from the d_{100} spacing of XRD patterns. [b] Calculated in the range of relative pressure $(p/p_0) = 0.05$–0.20. [c] Measured at $p/p_0 = 0.99$. [d] Measured by 4-point method at $150\,\mathrm{kg_f/cm^2}$.

We are developing the optimum preparation conditions for the CNT-implanted mesoporous materials by the nanoreplication technique. For example, CNT-implanted mesoporous α-Fe_2O_3 materials are shown in Figure S2 in ESI.

In conclusion, implanting the electrically conductive nanowire, CNTs, inside the PMS particle is successfully performed by using surface-modified CNT in the present work. The CNT-implanted PMS particle proves to have a function as electrically conductive wire showing significant enhancement of conductivity and newly endowed potentials for electron transfer related applications without any mesotructural collapse.

Korea Science and Engineering Foundation (KOSEF) is acknowledged for financial support (05M0300-29110).

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Published on the web (Advance View) April 8, 2006; DOI: 10.1246/cl.2006.510