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Synthesis of carbon tubes with mesoporous wall structure using designed silica tubes as templates†

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Hollow silica tubes with mesoporous wall structure were synthesized through the sol–gel reactions of tetraethoxysilane and n-octadecyltrimethoxysilane (TEOS/C18-TMS) on the surface of ammonium *dl*-tartrate crystals. Novel hollow carbon tubes with mesoporous walls and rectangular-shaped channels were fabricated using the silica tubes as templates.

Recently, the development of novel porous materials has attracted great attention, because of their wide-ranging applications in catalysis, adsorption, sensors, and advanced storage materials.[1] Many mesoporous inorganic materials have been synthesized using various surfactants[2] and block copolymers[3] as templates. These mesoporous materials possess well-defined pore structures, extremely high surface areas, and precisely tuned pore sizes. Macroporous materials have been synthesized using latex particles and silica macrospheres as templates.[4] Shinkai and coworkers synthesized various inorganic tubes and fibers through the sol–gel transcription of organic gelators.[5]

Porous carbons have been extensively applied to separation and purification technology.[6] They have been also used as catalytic supports, chromatography columns, and electrode materials for batteries and capacitors. Recently many types of nanoporous carbon materials with uniform and regular pore structures have been produced through templating approaches using various mesoporous and microporous silica materials.[7] These novel mesoporous carbons have been successfully employed as electrodes for electrochemical double-layer capacitors and fuel cells.[8] Recently, our group reported a templating strategy that allows the fabrication of carbon capsules with hollow core/mesoporous shell (HCMS) structures from submicrometer-sized solid core/mesoporous shell (SCMS) silica spheres.[9] In this communication, we report on the synthesis of macroporous carbon tubes with mesoporous wall structure using designed macroporous silica tubes as templates.

In the synthesis, macroporous silica tubes with mesoporous wall structure were used as the template materials and *in-situ* polymerized phenol-resin was used as the carbon source. Macroporous silica tubes were prepared according to the method reported by Nakamura and coworkers with some modifications.[10] Following is a detailed description of the synthetic procedure used for producing the silica tubes. 0.6 g of *dl*-tartaric acid was dissolved in 150 mL of absolute ethanol containing 1.8 mL of water with constant magnetic stirring. Subsequently, 60 mL of ammonium hydroxide was rapidly added and the solution was allowed to stand for 1 day. A mixture solution containing 0.5 mL of tetraethoxysilane (TEOS), 0.2 mL of octadecyltrimethoxysilane (C18-TMS), and 0.16 g of aluminum-tri-*sec*-butoxide was added to the solution dropwise for 1 h with constant stirring. Aluminium was incorporated into the silicate framework to generate strong acid catalytic sites for the polymerization of phenol and formaldehyde. C18-TMS was added to the reaction mixture to generate mesopores in the silica wall. The resulting solution was then left to stand for 3 h. A white powder was retrieved by filtration and was washed with a small amount of water. The powder was calcined at 823 K for 5 h in air to yield aluminosilicate tubes with mesoporous wall structures.

0.47 g of phenol per gram of the aluminosilicate tube template was incorporated into the mesopores by heating at 373 K for 12 h under a static vacuum. The resulting phenol-incorporated mesoporous aluminosilicate tube was reacted with paraformaldehyde (0.3 g) under a static vacuum at 403 K for 24 h inside the mesopores, to yield a phenol-resin/aluminosilicate tube nanocomposite. The nanocomposite was heated at a rate of 1 K min^{-1} up to 433 K. This temperature was maintained for 5 h under nitrogen flowing. The temperature was then ramped up to 1123 K at a rate of 5 K min^{-1}, and this temperature was maintained for 7 h to carbonize the phenol resin inside the mesopores of the aluminosilicate tubes, to obtain carbon/aluminosilicate tube nanocomposite. Dissolution of the aluminosilicate tube templates using 2 N NaOH in a 1 : 1 mixture of EtOH and H_2O generated macroporous carbon tubes with mesoporous wall structures.

The transcription of organic templates into inorganic materials generally occurs by means of electrostatic or hydrogen bonding interaction between the template and the inorganic precursor.[5] The surface of the template contains moieties that can catalyze the formation of the inorganic material. In the current synthesis, the sol–gel polycondensation of tetraethoxysilane (TEOS) and n-octadecyltrimethoxysilane (C18-TMS) of the organic template resulted in the formation of silica–organic template composite fibers. The materials obtained were subjected to calcination in order to remove organic components. Through this procedure, a template that consisted of open-ended hollow silica tubes with mesoporous walls was produced. The formation of the mesoporous structure of the walls can be attributed to the n-octadecyl trimethoxysilane's acting as a porogen in the starting solution.

The scanning electron microscopic (SEM) image of the silica templates, shown in Fig. 1, revealed hollow rectangular-shaped tubes with widths ranging from 500 nm to 2 μm. The pore size distribution data, calculated from the desorption branch of the nitrogen isotherms by the BJH (Barret–Joyner–Halenda) method, showed that the mesopores in the wall were uniform with narrow pore size distribution centered at 3.5 nm (Fig. 3a). The silica tubes exhibited a Brunauer–Emmett–Teller (BET)

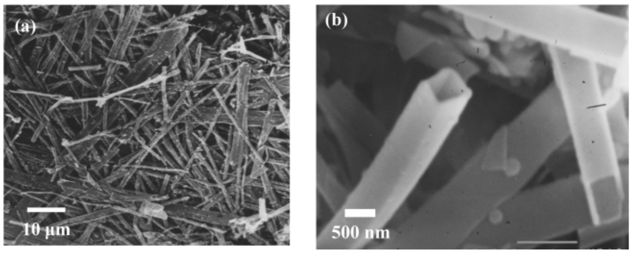

Fig. 1 SEM images of bundles of silica tubes composed of mesoporous walls at low magnification (a), and at high magnification (b). The images were obtained on a JEOL JSM 840-A microscope.

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† Electronic supplementary information (ESI) available: TEM image of a carbon tube showing disordered mesoporous walls. See http://www.rsc.org/suppdata/cc/b2/b212336c/

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surface area of 457 $m^2 g^{-1}$ and a total pore volume of 0.49 $cm^3 g^{-1}$.

The dissolution of the silica tube template from the carbon–silica composites resulted in the generation of hollow rectangular-shaped carbon tubes with mesoporous walls. The elemental analysis of the carbon tubes revealed that silica templates were successfully removed (C, 89.3%; H, 1.74%; N, 0.45%). The SEM images of the carbon tubes (Fig. 2) show that their lengths ranges from 5 μm to 1 cm and their width from 500 nm to 2 μm. The tubes are rectangular shaped channels. The TEM image of a single carbon tube with an extremely small width of 100 nm shows the presence of randomly distributed mesopores of ~4.0 nm in the wall (ESI†). Typical nitrogen adsorption–desorption isotherms at 77 K for carbon tubes and their corresponding pore size distributions are shown in Fig. 3b. The pore size distribution data calculated from the desorption branch of the nitrogen isotherms by the BJH method showed that the wall pores of the carbon tubes are uniform with a narrow pore size distribution centered at 4 nm, which matches very well with the TEM data. The specific surface area of the carbon tubes was found to be 307 $m^2 g^{-1}$ from nitrogen BET adsorption measurements. The total pore volume was 0.44 $cm^3 g^{-1}$. The very similar structure of both the template and the carbon tube suggests that phenol-resin formation and the subsequent carbonization process did not occur inside the main hollow tubes of the silica templates, but rather that these processes proceeded inside the mesoporous pores in the wall of the aluminosilicate templates. Phenol vapor can be incorporated into mesoporous pores in the walls of the templates at low vapor pressure. However, phenol cannot infiltrate into the hollow tube of the templates, because a very high vapor pressure is required for incorporating phenol into large sub-micrometer sized tubes.

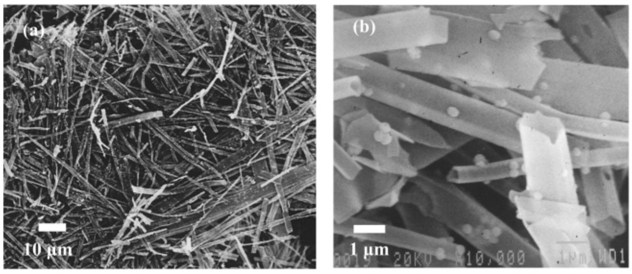
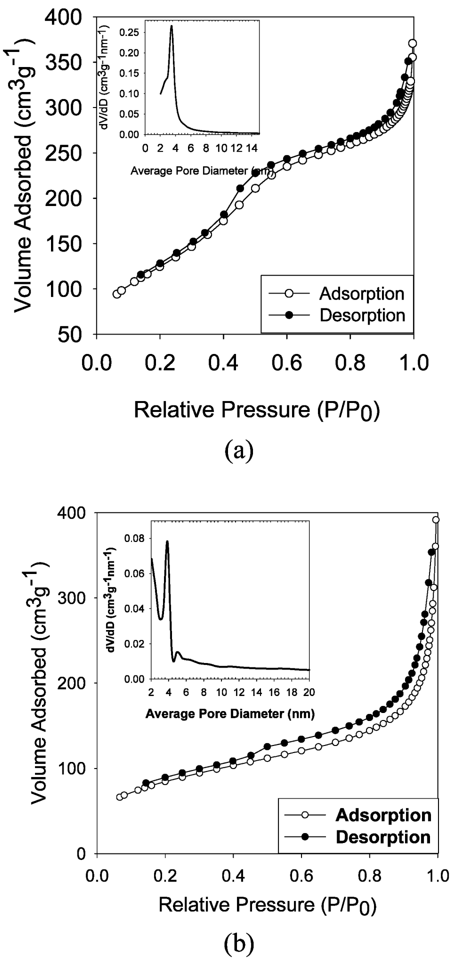


Fig. 2 SEM images of bundles of carbon tubes composed of mesoporous walls at low magnification (a), and at high magnification (b). The images were obtained on a JEOL JSM 840-A microscope.



(a)

(b)

Fig. 3 N_2 adsorption–desorption isotherms and the corresponding pore size distributions (insets) of silica tubes (a) and carbon tubes (b).

In conclusion, we fabricated hollow silica tubes with mesoporous walls and rectangular-shaped channels through the sol–gel reaction of tetraethoxysilane and n-octadecyltrimethoxysilane on ammonium *dl*-tartrate self-assembles. Carbon tubes with mesoporous walls were synthesized using the silica tubes as templates. The structure of the carbon tubes was an exact replica of the silica tube templates. This carbon material is expected to have a wide range of applications, including catalysts, adsorbents, sensors, electrode materials, and advanced storage materials. The presence of a macro-cavity in the carbon tubes facilitates the bidirectional diffusion of reactants to both interior and exterior surfaces of the tubes.

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