Nanocasting of carbon nanotubes: *in-situ* graphitization of a low-cost mesostructured silica templated by non-ionic surfactant micelles

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The *in-situ* graphitization of an as-made, large pore silica mesostructure templated by nonionic Pluronic 123 surfactant micelles provides a low cost pathway to the nanocasting of linear carbon nanotubes.

Mesostructured silicas have been shown to be useful supports for the metal-catalyzed preparation of carbon nanotubes. The role of the mesostructured silica is to serve as a template for the nanocasting of the metal particles needed for the regulated growth of the carbon nanotubes.[1–3] A related, but non-catalytic, templating process has been reported wherein the surfactant of a micelle-templated silica is transformed directly into carbon nanotubes on the walls of the silica template.[4] Mesostructured silicas also have been used for the nanocasting of completely mesostructured forms of carbon. In this latter application the pores of a three-dimensional cubic,[5] worm-like,[6] hexagonal,[7,8] or foam-like[9] silica are filled with a polymer that is subsequently graphitized at elevated temperature to form a replica of the silica template. However, the isolation of these mesoscopic carbons in pure form requires the dissolution of the silica template. Consequently, the feasibility of utilizing nanocasting processes for the production of bulk quantities of carbon in nanotube and mesostructured forms is dependent in large part on the cost of the silica template and the carbon precursor.

We previously have demonstrated that a structural analog of hexagonal SBA-15 silica, denoted MSU-H silica, can be assembled from sodium silicate under near-neutral pH conditions.[10,11] Ordinarily, the SBA-15 structure type is prepared from silicon alkoxides under strongly acidic reaction conditions.[12,13] The low-cost MSU-H version of SBA-15 was shown to be an attractive template for the nanocasting of a carbon replica, in part, because it retained three-dimensional network of micropore-linked mesopores and the thick framework walls characteristic of the SBA-15 structure type. Moreover, the pore network could be easily replicated using a low-cost carbon source such as sucrose.

The present work reports that MSU-H, in as-made mesostructured form, also can serve as template for the nanocasting of carbon nanotubes. In this process the micellar nonionic surfactant used to template the mesostructure serves as the carbon source for *in situ* graphitization, thus reducing processing time and limiting reagent costs. Moreover, a substantial fraction of the nanocasted carbon is provided in the form of single nanotubes with large pores and a linear morphology.

A mesostructured MSU-H silica–surfactant composite was assembled at 60 °C from a sodium silicate solution (27 wt% SiO_2, 14 wt% NaOH) and the Pluronic P123 triblock copolymer $(EO)_{20}(PO)_{70}(EO)_{20}$.[11] The overall reaction stoichiometry was 1 SiO_2 : 0.011 P123 :0.8 CH_3COOH :0.76 NaOH :230 H_2O and the reaction time was 20 h. As illustrated in Fig. 1, *in situ* carbonization of the surfactant was achieved by heating the as-made mesostructure under flowing nitrogen (10 ml min^{-1}) at 150 °C for 10 h, then ramping the temperature at 2 °C min^{-1} to 800 °C and holding the sample at this temperature for 30 min.

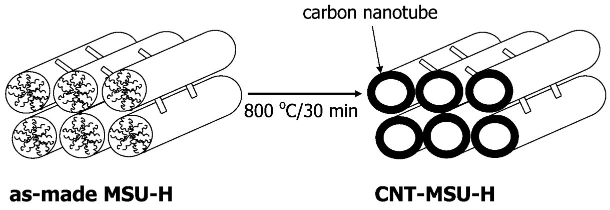

Fig. 1 Formation of a mesostructured CNT-MSU-H carbon–silica composite through *in situ* carbonization of the surfactant porogen in the mesopores of the 3D micropore-mesopore network.

Figure 2A illustrates the powder X-ray diffraction patterns of the resulting CNT-MSU-H composite. Included for comparison is the pattern for the calcined (800 °C) MSU-H silica template. Both mesostructures exhibit resolved *hkl* reflections consistent with two-dimensional hexagonal symmetry and unit cell dimensions of 121 and 125 Å, respectively. Figure 2B illustrates the nitrogen adsorption–desorption isotherms, and Table 1 compares the textural parameters for the two materials. In accord with the presence of a thin coating of carbon on the walls of the silica framework, a relatively small fraction of the total pore volume of the silica framework is occupied by the carbon, and the average pore size of the framework is decreased only slightly.

To confirm that a substantial fraction of the carbon coating the walls of the MSU-H framework is indeed in the form of nanotubes, the silica framework was dissolved in 10% aqueous HF solution. A representative TEM image of the resulting

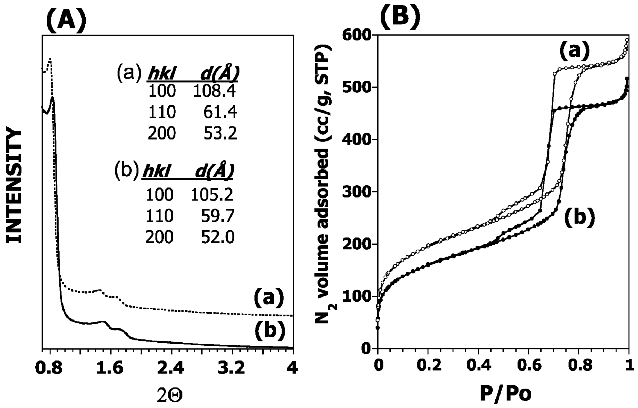

Fig. 2 (A) XRD patterns and (B) N_2 adsorption–desorption isotherms of (a) calcined MSU-H silica and (b) CNT-MSU-H carbon–silica composite.

Table 1 Properties of the CNT-MSU-H composite and the MSU-H silica template

Sample	*d* spacing/ nm	Pore size[a]/ nm	Wall thinkness[b]/ nm	S_{BET}/ m^2g^{-1}	Total pore volume/ cm^3g^{-1}
MSU-H	10.8	8.6	4.1	691	0.86
CNT-MSU-H	10.5	8.0	3.9	567	0.74

[a] BJH pore size calculated from the adsorption branch of the nitrogen isotherm. [b] Determined from the difference between the unit cell parameter (a_o = $(2/\sqrt{3})d_{100}$) and the framework pore size.

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carbon is shown in Fig. 3. Individual thin-walled tubes with diameters compatible with the framework pore size estimated by nitrogen adsorption are clearly evident.

Thermogravimetric analysis of the CNT–silica composite indicated that about 25% of the P123 surfactant was converted to carbon under the above graphitization conditions. The loss of carbon through volatile product formation may explain why the nanocasting process generates single nanotubes primarily on the walls of the mesopores and not a replica of the mesostructure. Apparently, the amount of surfactant that is graphitized in the cross linking micropores of the silica framework is not sufficient to provide a replica.

In a recently reported related study[4] carbon nanotubes also have been observed to form on the walls of as-made MCM-41 and MCM-48 silica under graphitization conditions analogous to those used in the present study. The surfactant serving as the nanotube precursor was the cetyltrimethyl ammonium ion in the case of MCM-41, and a mixture of this onium ion surfactant and the secondary nonionic surfactant Triton X-100 in the case of MCM-48. The nanotubes reported in the present work were formed exclusively from an oxygenated nonionic surfactant. More importantly, the use of a large pore silica as the nanocasting template affords a much higher fraction of single tubes with a linear morphology. In addition, the tubes made by the present nanocasting process have substantially larger diameters in the range 8–11 nm, as judged by TEM, which is in reasonable agreement with the average pore size of the nanocasting agent determined by N_2 adsorption (*c.f.*, Table 1). In contrast to this latter result, the tubes formed through MCM-41 and MCM-48 nanocasting are smaller in diameter (5–6 nm) and typically bent, especially in the case of MCM-48 nanocasting.

The limited polymerization of furfuryl alcohol in the framework pores of SBA-15 has been observed to form ordered hexagonal arrays of carbon nanotubes.[14] The long range ordering suggests that the tubes are linked by carbon filaments formed through the graphitization of the alcohol in the micropores connecting the mesopores of the silica template. The analogous ordering of nanotubes is not observed for the *in situ* surfactant carbonization process reported in the present work, perhaps, because the polyethylene oxide segments of the P123 surfactant that initially occupy the micropores of the template are not graphitized in the thermal decomposition process. This would cause the carbon nanotubes to be formed primarily from the polypropylene oxide segments that occupy the mesoporous channels and account for the formation of individual nanotubes.

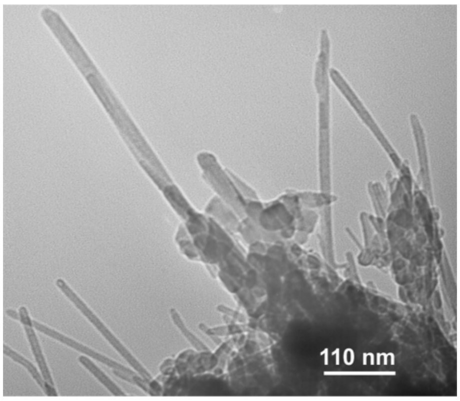

Fig. 3 TEM image of templated carbon nanotubes obtained after dissolving the silica component of the CNT-MSU-H composite in 10% HF.

Finally, we note that CNT-MSU-H composite mesostructure shows promise as a trapping agent for the removal of organic pollutants from water. Whereas the hydrophilic nature of mesostructured silicas limits the uptake of organic adsorbates from aqueous environments, the carbon-coated walls of the composite composition should have a much lower polarity. To confirm this, we investigated the relative adsorption properties of CNT-MSU-H and MSU-H toward the EPA priority pollutant 3,5-dichrophenol in aqueous solution. Equilibrating both mesostructures in a 100 μmol L^{-1} 3,5-dichlorophenol resulted in the uptake of 1.2 μmol g^{-1} by the CNT-MSU-H composite and < 0.01 μmol g^{-1} for MSU-H silica. That is, the adsorption capacity of the CNT-MSU-H carbon–silica composite was at least 100 times higher than that of MSU-H silica.

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