Template Synthesis of a New Mesostructured Silica from Highly Ordered Mesoporous Carbon Molecular Sieves

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In recent years there has been considerable interest in mesoporous materials. This interest stems mainly from several attractive characteristics that these materials possess including large pore size, high surface area, and periodic arrays of uniform pores.[1] It is believed that such materials hold significant potential for many advanced applications in the areas of catalysis,[2] adsorption,[3] and host−guest chemistry.[4]

Recently, remarkable progress has been made in the synthesis of carbons with periodic ordered structures in the range of micropores (<2 nm), mesopores (2−50 nm), and macropores (>50 nm) using inorganic templates such as zeolites,[5] mesoporous molecular sieves,[6,7] and silica gels.[8] In particular, a new class of mesoporous carbon materials that has attracted great interest has been reported using both cubic[6] and hexagonal[7] silica mesostructures as templates. In these works, a carbon precursor was incorporated into the mesopores of a silica framework to generate a mesoporous carbon templated by the sacrificial silica. It is interesting to note that pore size changes were observed between the silica template and the carbon product, which are due to morphological alterations that occurred during the template replication process. The MCM-48 silica starting template, which has a cubic space-group symmetry of *Ia*3*d*, possesses two non-interconnecting enantiomeric channel systems which are intertwined. During the replication process the pores and walls of the silica host were transformed to the walls and pores, respectively, of the resulting carbon network. However, the resulting mesoporous carbon was not a negative replica of the MCM-48 silica host but rather underwent a phase transition to a new cubic phase.[6] If the mesopores of the new cubic carbon framework were to be infiltrated with a silica source, a mesoporous silica framework would be regenerated, templated by the ordered mesoporous carbon.

In this communication, we report a novel synthesis of a new nanostructured silica with an ordered arrangement of uniform mesopores by nanocasting of a highly ordered mesoporous carbon template, which had itself been prepared from a mesoporous MCM-48 silica host. Particularly, this method using MCM-48 as a starting template offers the possibility of producing new silica materials with periodic nanostructured order not attainable through a conventional surfactant assembly process designed for the synthesis of usual mesoporous silicas. While this work is in preparation,[9] two related works were published which reported the regeneration of a mesoporous silica from a mesoporous carbon (CMK-3) which was a negative replica of SBA-15. The regenerated silica was essentially the starting hexagonal SBA-15 itself, indicating reversible replication between CMK-3 and SBA-15.[10] In this work, the new silica material generated from the mesoporous carbon (CM48T-C) framework was a highly ordered mesoporous silica but distinctly different from the MCM-48 parent silica.

In this work, high-quality silica MCM-48 was prepared based on a modification of the literature procedure.[1b] The newly synthesized MCM-48 was calcined in air to remove the surfactants and the calcined template was denoted as CM48T. Mesoporous carbon was synthesized by infiltration of the template mesopores with divinylbenzene (DVB) and free radical initiator azobisisobutyronitrile (AIBN). The in situ polymerization and carbonization were followed by subsequent template dissolution as reported earlier.[6a] The resulting mesoporous carbon material was then denoted as CM48T-C. To produce a regenerated silica replica, the pores of the carbon template were infiltrated with a silica precursor solution (TEOS). The carbon/silica composite was exposed to HCl vapor to induce hydrolysis and condensa-

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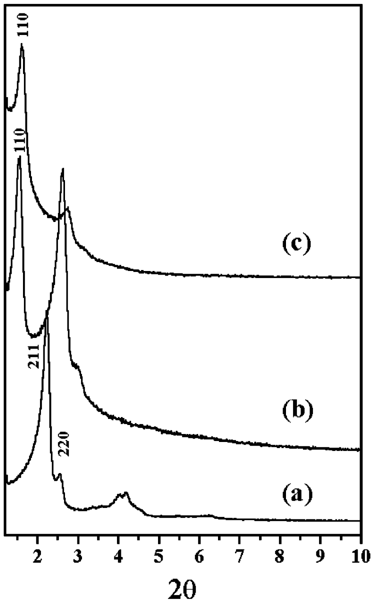

Figure 1. Powder X-ray diffraction patterns using Cu Kα radiation of (a) the CM48T silica host, (b) the corresponding mesoporous carbon, and (c) the HUM-1 silica regenerated from the carbon, respectively.

tion of the silicate precursor. Finally, the carbon/silica composite was heated under oxygen to remove the carbon framework. This regenerated silica replica represents a mesoporous silica structure previously unreported in the literature and it has been given the name HUM-1 (Hannam University Mesostructure-1).

Figure 1 shows the powder X-ray diffraction (XRD) patterns for (a) the calcined silica host template, CM48T, (b) the mesoporous carbon, CM48T-C, and (c) the resulting silica replica, HUM-1. The CM48T shows an intense (211) XRD signal at $2\theta = 2.35°$ whereas two intense signals at $2\theta = 1.62°$ and 2.70° with almost equal signal intensities were observed for the CM48T-C. The new (110) signal at $2\theta = 1.62°$, which is visible in the mesoporous carbon but not seen in the silica host, was the result of the phase transition of the cubic MCM-48 with the $Ia3d$ space group to a new cubic phase with $I4_1/a$.[11] This phase transition has been attributed to a change in the relative position of the enantiomeric pair of the two nonintersecting mesopore channels filled with carbon. This change is thought to have occurred for the sake of energy minimization during the course of the removal of the silica framework. The regenerated HUM-1 silica shows an XRD pattern with two signals slightly shifted to $2\theta = 1.64°$ and 2.74° but with a second signal being much weaker compared with that of CM48T-C. The XRD pattern of the HUM-1 indicates a long-range structural order characteristic of silica materials with periodically ordered mesopores, but represents a new structure never before seen in mesoporous silicates. The generation of the new silica mesostructure may be triggered by the symmetry changes observed in the parent mesoporus carbon, CM48T-C. Signal intensities were estimated by integrating the area under the signals of the 2θ in the range of 1.2°−7.0°. The areas of HUM-1 silica were more than 90% of those of CM48T, indicating the continuity of template integrity despite the serial replication processes. On the basis of its XRD pattern being quite different from that of CM48T, the HUM-1 is thought to have a new cubic phase different from the symmetry of the original mesoporous MCM-48 silica host.

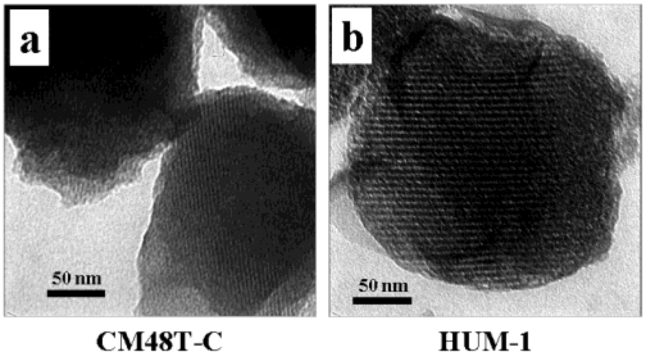

Figure 2. Transmission electron microscopy (TEM) images of (a) CM48T-C and (b) corresponding HUM-1 silica.

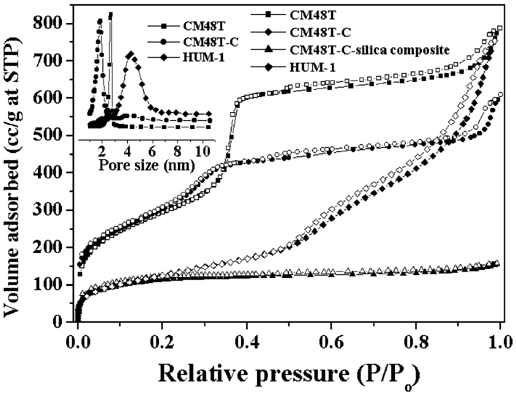

Figure 3. N_2 adsorption (filled line) and desorption (unfilled line) isotherms of CM48T, CM48T-C, corresponding carbon−silica composite, and HUM-1. (Insert) The corresponding pore size distribution curves calculated from the adsorption branch of the nitrogen isotherm by the BJH method. The isotherms were measured at 77 K on a Micromeritics ASAP 2000 gas adsorption analyzer after the silicas and carbons were degassed at 423 K to 20 μTorr for 4−6 h.

Figure 2 shows transmission electron microscopy (TEM) images for CM48T-C and HUM-1. The HUM-1 silica clearly exhibits periodic highly ordered nanoporous networks with evenly spaced pores and walls much like CM48T-C, indicating a well-developed long-range order consistent with the XRD results.

Nitrogen adsorption/desorption isotherms measured at 77 K and their corresponding pore size distribution for the CM48T silica host, the mesoporous carbon, the corresponding carbon−silica composite, and the resulting HUM-1 silica, respectively, are shown in Figure 3. Except for the carbon−silica composite, the measured isotherms are characteristic of mesoporous solids and they can be classified as type-IV isotherms according to the IUPAC nomenclature.[12] An almost flat sorption isotherm was observed for the carbon/silica composite, indicating much lowered pore volume and surface area. The carbon/silica composites have about 58−63 wt %

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Table 1. Structural Parameters of the Silica M48T Host, the Corresponding Mesoporous Carbon, and the Regenerated Silica Replica Prepared in This Work

sample name	*d* spacing (nm)	unit cell parameter, a_0[a] (nm)	BET surface area (m^2/g)	total pore volume (mL/g)	pore size[b] (nm)
CM48T	3.76[c]	9.21	1082	1.21	2.78
CM48T-C	5.46[d]	7.72	1100	0.94	1.88
HUM-1[e]	5.38[d]	7.61	472	1.25	4.21

[a] XRD unit cell parameter (a_0) equal to $6^{1/2} \times d(211)$ for the CM48T, $2^{1/2} \times d(110)$ for the CM48T-C and HUM-1 silica, respectively.[15] [b] Maximum value of the BJH pore size distribution peak calculated from the adsorption branch of the N_2 isotherm. [c] $d(211)$. [d] $d(110)$. [e] The structural parameters of the HUM-1 silica were determined based on the structural symmetry of its corresponding carbon template.

for SiO_2 and 37−42 wt % for carbon as determined by TG analysis. This gives silica-filling ratios of around 75−83% into the mesopores of the carbon when compared with the amount of the silica calculated from the pore volume of the carbon and the amorphous silica density of 2.2 g/cm^3.[13] This is consistent with some mesopore volume observed in the carbon/silica composites, which is about 20% of that of CM48T-C. The filling ratios are much higher than 60−70% observed in the previous work.[10b] and may indicate a high degree of fidelity in replication. BET surface area was determined for the HUM-1 silica and found to be about 472 m^2/g, which is nearly a half of what was found for CM48T or CM48T-C. The total pore volume was found to be 1.25 mL/g for HUM-1, which is about the same as that of the original CM48T silica host. It is important to note that the isotherm profile of the HUM-1 silica is quite different from those of either the corresponding carbon template or the original silica host. The pore size distribution data calculated from the adsorption branches using the BJH (Barrett−Joyner−Halenda) method showed a pore size distribution centered at 4.2 nm for the resulting HUM-1 silica, which is much larger than those centered at 2.8 and 1.9 nm for the calcined mesoporous silica CM48T host and for the corresponding CM48T-C, respectively. This unexpectedly large pore size is particularly interesting when compared to the pore size of 2.8 nm and the wall thickness of ~1.3 nm[14] that was determined for CM48T. The structural parameters for these materials are summarized in Table 1.

On the basis of the results of the XRD patterns, the TEM images, and the adsorption isotherms, the regenerated mesoporous HUM-1 silica is significantly different from either the corresponding mesoporous carbon or the original silica host. This demonstrates that a totally new mesoporous silica structure with a uniformly large pore size has been generated. The increase in pore size that occurred in going from the original silica host to the HUM-1 silica is intriguing and we would like to offer a tentative explanation. It is likely that the mesopore channels of CM48T with their 2.8-nm pore size would have generated carbon walls, which were only about 2.0 nm in diameter due to the shrinkage that would have occurred during carbonization of the in situ formed polymer. Unit cell size also would have decreased for the same reason. The two enantiomeric carbon channels (each about 2.0 nm in diameter) may have moved closer together as the partitioning silica wall was dissolved during the formation of CM48T-C. Then the large 4.2-nm pores would have been generated in the HUM-1 silica as the two carbon channels now situated close together were removed during the oxidation process used to form HUM-1. Then, the two noninterconnecting enantiomeric channel systems embedded in the starting MCM-48 framework may be no longer found in the HUM-1. Further studies with high-resolution TEM and electron crystallography are needed to better understand the three-dimensional structural characteristics of the HUM-1 silica.

In summary, it has been found that the regenerated HUM-1 is a cubic mesoporous silica that is distinctly different from the original MCM-48 silica and represents a previously unreported new mesoporous silica material. The HUM-1 does not possess the two noninterconnecting enantiomeric channel systems found in the starting MCM-48 framework. The HUM-1 silica shows highly periodic nanosturctured order and three-dimensionally interconnected uniform pore arrays as confirmed by XRD, TEM, and sorption studies. This new mesoporous silicate was prepared by a cyclic serial replication process and it may not be possible to make this material using the conventional surfactant assembly methods currently employed for the synthesis of mesoporous silicates. Thus, we believe that this method is likely to be a valuable complement to the existing methods for the fabrication of new mesoporous silicas. Furthermore, the HUM-1 that was generated in this work may itself be able to be used as a template to regenerate a subsequent generation nanostructured carbon replica. These new materials will in turn lead to many future studies on their characterizations and advanced applications.

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