Synthesis of Siliceous Hollow Spheres with Ultra Large Mesopore Wall Structures by Reverse Emulsion Templating

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By using reverse emulsion templating, siliceous hollow spheres with ultra large mesopore wall structures (~50 nm in pore diameter, ~200 nm in wall thickness) have been synthesized with a high surface area (674 m^2/g) and pore volume (1.25 cm^3/g).

Ordered porous materials with controlled morphology may have potential uses in storage and release, confined-space catalysis, separation, chromatography and large biomolecular-release systems.[1–3] Mesoporous molecular sieves with well-defined pore sizes of 2–40 nm are now accessible either by direct surfactant templating or microemulsion templating.[4–6] For ordered macroporous materials with pore sizes larger than 50 nm, emulsions,[7] mono-disperse polymer latex spheres[8] or silica particles[9] are utilized as colloidal templates. However, materials with pore size at the boundary of meso-macro scale have been difficult to obtain by using surfactant templating method. Moreover, unlike mesoporous materials that can be designed in various morphologies, current strategies for obtaining macroporous materials result in no feature on morphology (usually films on substrates). By using normal oil-in-water emulsions stabilized by ionic surfactants, S. Schacht et al. have reported the synthesis of hollow spheres with relatively small diameter mesopores.[10] Here we extend previous work from water-rich phases to oil-rich phases. Siliceous hollow spheres (1–4 μm) with ultra large mesopore wall structures (50 nm) have been synthesized by the combination of reverse emulsion chemistry and sol-gel chemistry in the presence of amphiphlic block copolymers.

The siliceous hollow spheres were prepared in water-in-oil emulsion system in the presence of poly(ethylene oxide)-*b*-poly(butylene oxide)-*b*-poly(ethylene oxide) (PEO-PBO-PEO) block copolymers. In a typical synthesis procedure, 0.5 g (0.074 mmol) of triblock copolymer $EO_{39}BO_{47}EO_{39}$ was first dissolved in 5 g of 2M HCl (10 mmol), then the solution was added slowly to 20 g (167 mmol) of 1,3,5-trimethylbenene (TMB) under stirring with constant rate of ~200 RPM to make a water-in-oil emulsion. Emulsion drops with a relatively good dispersion were obtained[11] and the property of the reverse emulsion drops is confirmed by Bancroft's rule. To the milky emulsion solution, 2.08 g (10 mmol) tetraethyl orthosilica (TEOS) was added with stirring, the final composition was 0.0074/16.7/1.0/27.8/1.0 $EO_{39}BO_{47}EO_{39}$/TMB/TEOS/H_2O/HCl (molar ratio). After stirring for 24 h at room temperature (RT), white powders were recovered by centrifugation, washed with ethanol and dried in air at RT. In order to remove the organic species, the calcination was carried out in an oven by slowly increasing the temperature from RT to 550 °C in 4 h and heating at 550 °C for 6 h in air.

Scanning electron microscopy (SEM) photographs reveal that calcined samples prepared in the TMB/water system consist entirely of spherical particles with a size distribution of 1–4 μm in diameter (Figure 1(a)). SEM measurements show that the diameter of the spheres is shrinked about 20% after calcinations. Moreover, these spheres are indeed hollow at high magnifications for the same batch of samples (Figure 1(b)). In order to depict the structure of the walls, the transmission electron micrograph (TEM) images of the calcined samples in ultra thin sections were examined. The hollow spherical morphology is clearly confirmed (Figure 1(c)), the wall of the calcined hollow spheres is ~200 nm in thickness. Surprisingly, the wall consists of uniform and hexagonally ordered ultra large mesopores (Figure 1(c) and Figure 1(d)). The mesopores are ~50 nm in diameter and possess strut-like silica arrays which are ~10 nm in diameter. Since the section for TEM observation is ~80 nm in thickness, one can obviously look into the pore structure and observe another layer (Figure 1(d)).

The N_2 adsorption-desorption isotherm (Figure 2) of the calcined siliceous hollow spheres prepared by reverse emulsion templating shows a steep increasing at relative pressure $0.8 < P/P_o < 1$, suggesting that the hollow spheres have very large pores. An ultra large mesopore with a mean size of 50 nm calculated from

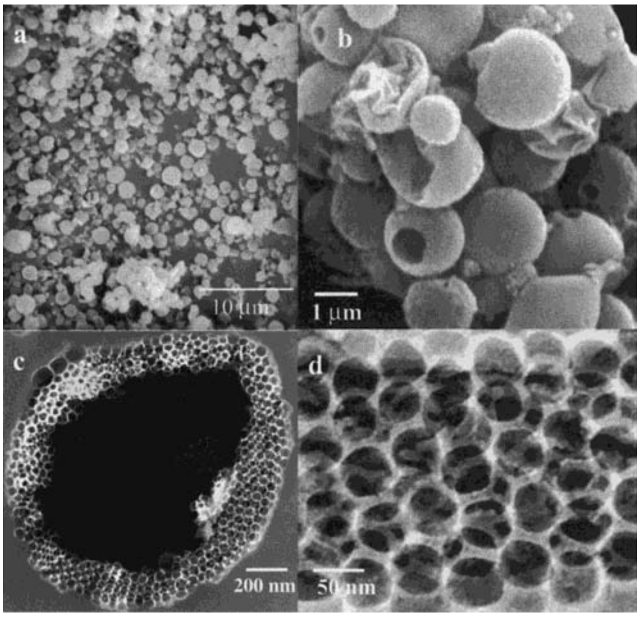

Figure 1. (a, b) SEM (Hitachi S-520) images of calcined siliceous hollow spheres synthesized by reverse emulsion tempelating, (a) at low magnigication, (b) at high magnification. (c, d) TEM (Philips CM120, 100 kV) images of hollow spheres, (c) at small magnification recorded along the cross-section to show a single calcined hollw sphere, (d) at high magnification to reveal the ultra large mesoporous wall structures. For TEM measurements, the ground samples embedded in epoxy resin were cut in ultrathin sections (~80 nm). The contrast of TEM images has been inverted and the silica networks appear light.

Broekhoff-de Boer (BdB) model[12] is observed (inset of Figure 2), which correlates well with the hexagonal ring diameter and is in agreement with that measured from TEM images. The calcined hollow spheres synthesized in water/TMB systems have a surface area of 674 m^2/g and a pore volume of 1.25 cm^3/g.

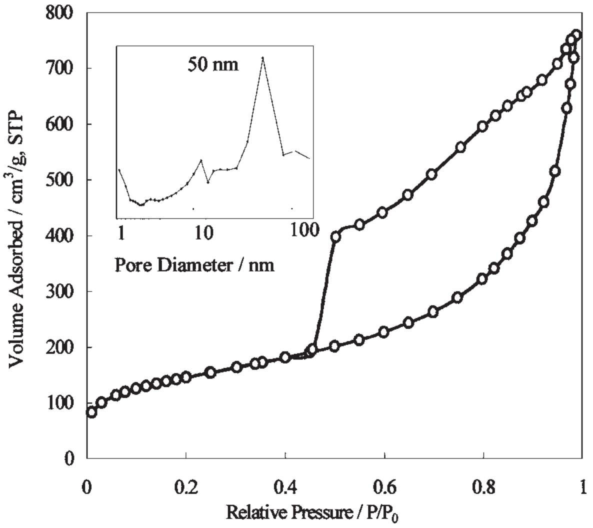

Figure 2. Nitrogen adsorption-desorption isotherm curves and pore size distribution curves (inset) of calcined siliceous hollow spheres prepared by using triblock copolymer $EO_{39}BO_{47}EO_{39}$ and reverse emulsion templating. N_2 adsorption measurements were performed at 77 K using a Micromeritics ASAP 2000 analyzer.

We postulate that the hollow spheres are formed by a reverse emulsion templating pathway. In water/TMB systems, block copolymer surfactants can stabilize the water-in-oil emulsion droplets. Due to the small polarity of the polyoxybutylene hydrophobe, block copolymer surfactants tend to dissolve in oil rather than in water. At the water/oil interface, we presume that there is a transition layer of microemulsions stabilized by PEO-PBO-PEO block copolymer surfactants, thus the ultra large mesoporous wall structures are most likely formed through a mechanism similar to that of mesostructured cellular foams (MCFs).[6] After drying and removing the block copolymers, the hollow spheres with ultra large mesopore wall structures are obtained.

The choice of proper surfactants is the key to the successful synthesis of hollow spheres with ultra large mesopore wall structures by this reverse emulsion templating method. Previously we reported the synthesis of highly ordered mesoporous materials obtained by di- and tri-block copolymers with PBO moieties.[13] Compared to the commonly used Pluronic block copolymers with poly (propylene oxide) (PPO) hydrophobes, the interfacial tensions of PEO-PBO-PEO is much smaller, while the contrast of solubility between oil and water for PEO-PBO-PEO is larger.[14] The reverse water-in-oil emulsion is therefore better stabilized by using PEO-PBO-PEO block copolymers rather than PEO-PPO-PEO block copolymers or ionic surfactants such as CTAB. The size of mesopore within hollow spheres (50 nm) is larger than that reported for MCFs (24–40 nm), this can be explained also by the fact that PBO segments are more hydrophobic than PPO segments, thus the PBO moiety may contain more amount of TMB than the PPO part does. The hollow sphere assembly is also different both in mechanism and in wall structures than that obtained using ionic surfactants,[10] where the macrostructure is formed via a oil-in-water emulsion pathway and the small diameter mesoporous silica wall structures are obtained through normal micellar assembly.

In conclusion, hollow spheres with ultra large mesopore wall structures have been synthesized by using reverse emulsion templating in the presence of PEO-PBO-PEO block copolymers. Our synthetic pathway provides an important example of a well ordered, ultra large mesopore material with designed morphology. Moreover, this technique is convenient for incorporating water-soluble materials including nanoparticles into the core of the hollow spheres, the large pore size of the wall is suitable for the storage, release and transportation of large biomolecules.

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References and Notes

1 J. Y. Ying, C. P. Mehnert, and M. S. Wong, *Angew. Chem., Int. Ed.*, **38**, 56 (1999).

2 K. Kageyama, J. Tamazawa, and T. Aida, *Science*, **285**, 2113 (1999).

3 Y. J. Han, G. D. Stucky, and A. Butler, *J. Am. Chem. Soc.*, **121**, 9897 (1999).

4 a) C. T. Kresga, M. E. Leonowicz, W. J. Roth, J. C. Vartali, and J. S. Beck, *Nature*, **359**, 710 (1992). b) J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, and J. L. Schlenker, *J. Am. Chem. Soc.*, **114**, 10834 (1992).

5 a) D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, and G. D. Stucky, *Science*, **279**, 548 (1998). b) D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, and G. D. Stucky, *J. Am. Chem. Soc.*, **120**, 6024 (1998).

6 a) P. Schmidt-Winkel, W. W. Lukens, Jr., D. Zhao, P. Yang, B. F. Chmelka, and G. D. Stucky, *J. Am. Chem. Soc.*, **11**, 795 (1999). b) P. Schmidt-Winkel, W. W. Lukens, Jr., P. Yang, D. I. Margolese, J. S. Lettow, J. Y. Ying, and G. D. Stucky, *Chem. Mater.*, **12**, 686 (2000). c) J. S. Lettow, Y. J. Han, P. Schmidt-Winkeo, P. Yang, D. Zhao, G. D. Stucky, and J. Y. Ying, *Langmuir*, **16**, 8291 (2000).

7 a) A. Imhof and D. J. Pine, *Nature*, **389**, 948 (1997). b) A. Imhof and D. J. Pine, *Adv. Mater.*, **10**, 697 (1998).

8 a) O. D. Velev, T. A. Jede, R. F. Lobo, and A. M. Lenhoff, *Chem. Mater.*, **10**, 3597 (1998). b) B. T. Holland, C. F. Blanford, and A. Stein, *Science*, **281**, 538 (1998). c) F. Caruso, R. A. Caruso, and H. Möhwald, *Science*, **282**, 1111 (1998). d) J. E. G. J. Wijnhoven, and W. L. Vos, *Science*, **281**, 802 (1998). e) S. H. Park and Y. Xia, *Chem. Mater.*, **10**, 1745 (1998).

9 a) S. I. Matsushita, T. Miwa, D. A. Tryk, and A. Fujishima, *Langmuir*, **14**, 6441 (1998). b) A. A. Zakhidov, R. H. Baughman, A. Lqbal, C. Cui, I. Khayrullin, S. O. Dantas, J. Marti, and V. G. Ralchenko, *Science*, **282**, 897 (1998). c) S. A. Johnson, P. J. Ollivier, and T. E. Mallouk, *Science*, **283**, 963 (1999).

10 S. Schacht, Q Huo, G. Voigt-Martin, G. D. Stucky, and F. Schüth. *Science*, **273**, 768 (1996).

11 Emulsion drops were obtained by the following procedure: treat the result emulsion with sonication for 30 minutes, centrifuge at slow speed, and fractionate from different part of the emulsion. Such procedures were repeated 4 times. The resultant emulsion is monitored by optical microscopy.

12 W. W. Luckens, Jr., P. Schmidt-Winkel, D. Zhao, J. Feng, and G. D. Stucky, *Langmuir*, **15**, 5403 (1999).

13 a) C. Yu, Y. Yu, and D. Zhao, *Chem. Commun.*, **2000**, 575. b) Y. Yu, C. Yu, Z. Yu, and D. Zhao, *Chem Lett.*, **2000**, 504.

14 V. M. Nace, *J. Am. Oil. Chem. Soc.*, **73**(1), 1 (1996).