A Simple Route for Preparing Radiolarian-like Mesoporous Silica from Water–Diethyl Ether Binary Solvent System

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An interesting radiolarian-like silica sphere has been prepared from a water–diethyl ether binary solvent system, which is characterized by SEM, TEM, XRD, and adsorption experiments. The results indicate its particular morphology and hierarchical structure, i.e., hollow interior and a crust wherein two types of mesopores with radial orientation are located. This silica product embodies a novel morphosynthesis involving unstable water–oil interface.

In recent years, mesoporous materials with hollow interior have attracted increasing attention because of their potential applications in adsorption,[1] catalysis,[2,3] and drug delivery.[4] As one of the main strategies for preparing hollow morphologies, using surfactant (-assisted) aggregates, for example, micro-emulsion,[5] and vesicles,[6] has resulted in various mesoporous oxides with hollow interior, including macro-cellular mesoporous silica foams,[7] hollow silica spheres with multi-lamellar shells,[8] microspheres with sponge-like morphology or hollow interior,[9] and vesicles.[10] All these morphologies and structures involve relatively stable curved interfaces where condensation of silicate species takes place.

Investigation on the self-assembly at dynamically unstable curved interface of oil–water is quite rare, but very intriguing.[11] For instance, Oliver[12] used tetraethyl glycol as a co-surfactant for constructing an interesting radiolarian-like meso-lamellar aluminophosphate that exemplifies pattern formation on curved surface. Considering that organic solvents may play various roles on morphogenesis, besides the co-surfactant role, we choose an organic solvent of low boiling point, diethyl ether, as a co-solvent which may result in unstable interface with diethyl ether gasification under proper conditions and consequently may produce novel silica morphologies. Herein we describe a synthetic route based on water–diethyl ether binary solvent system, the structure of product, i.e., a novel radiolarian-like mesoporous silica sphere.

In a typical synthesis, 2 mL of aqueous ammonia (28%, A.R.) was mixed with 278 mL of distilled water, and then 2 g of hexadecyltrimethylammonium bromide (CTAB) (99%, A.R.) was dissolved in the solution by steadily heating to 323 K. After the solution became homogeneous and was cooled to room temperature, 200 mL of diethyl ether was added into the mixture. In order to enlarge interface area of oil–water, vigorous stirring was necessary all through the reaction. Then, 10 g of tetraethylorthosilicate (TEOS) was subsequently added into the reaction system. The mixture was stirred for 24 h. Finally the precipitate was filtered, washed with distilled water, dried at ambient temperature, and calcined in air for 5 h at 823 K.

Figure 1 shows the spherical morphology of the calcined sample observed using scanning electron microscope (SEM). Figure 1a reveals that the diameter of the spheres ranges from 0.4 to 1.3 µm with the mean value of 0.7 µm. High magnification SEM image (Figure 1b) indicates that the representative sphere is characteristic of radiolarian-like morphology. Namely, the surface of the sphere is fully constituted by pores and walls of homogenous thickness. Figure 1b shows that the pore diameter is about 50 nm.

The nitrogen adsorption–desorption isotherms and the corresponding BJH (Barrett–Joyner–Halenda) pore-size distribution plot for the calcined sample are shown in Figure 2 (Brunauer–Emmett–Teller (BET) analysis was performed to

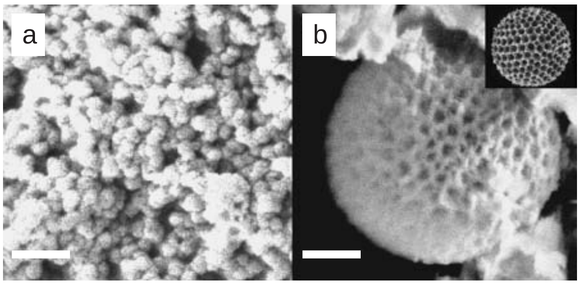

Figure 1. SEM images of the calcined sample showing the morphology of sphere. (a) Overview morphology of the bulky spherical silica. Scale bar: 2 µm; (b) High magnification SEM image of one sphere exhibiting the radiolarian-like morphology. Scale bar: 290 nm. The inset image shows the silica skeleton of a radiolarian.

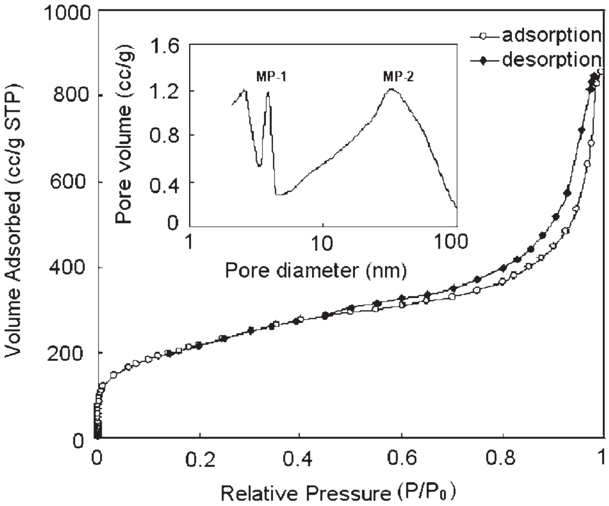

Figure 2. N_2 sorption isotherms collected at 77 K for a calcined sample. The insert picture is the BJH pore size distribution plot calculated from the desorption branch. (The pore volume is determined from the data of dV/dlog (D)).

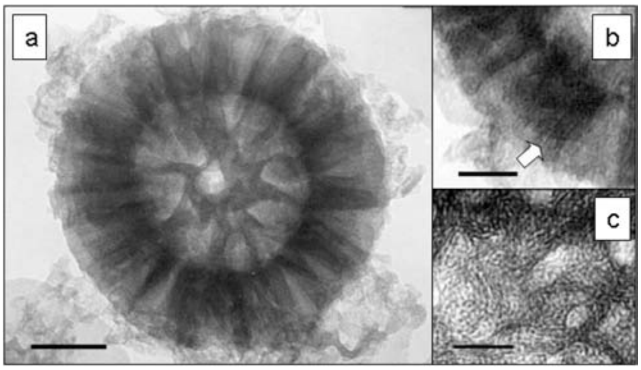

Figure 3. TEM images of the calcined silica sphere: (a) the circle-shaped projection of one sphere. Scale bar: 100 nm. (b) HRTEM reveals that the bundle-like pattern is composed of radial streaks with the oriented periodic distance of 4 nm. Scale bar: 60 nm. (c) the selective district HRTEM on the center of circle-shaped projection of sphere in Figure 3a. Scale bar: 60 nm.

determine the specific surface area; the specific pore distribution was obtained by the BJH method). The isotherms can be categorized as the type IV[13] with a distinct H4 hysteresis loop observed in the range from 0.45 to 1.0 P/P_0, indicating that the pore structure of the sample is similar to that of the vesicle-like silica.[10,14] The sample exhibits the high BET specific surface area of 803 m^2/g. The BJH analysis reveals a bi-modal pore-size distribution (inset picture) with a sharp peak at 3 nm (here, the mesopore denoted as MP-1), and a broad hump centered at 34 nm (here, the mesopore detonated as MP-2).

The representative transmission electron microscope image (Figure 3a) shows that the circle-shaped projection of one silica sphere with a much brighter contrast at the central zone encircled by the relatively dark peripheral zone that is composed of radially oriented bundle-like patterns. The apparent change in contrast between the two zones probably originates from a hollow structure possessing cavity with diameter of about 490 nm and crust with thickness of about 120 nm. Otherwise, the projection of a solid sphere may exhibit relatively dark contrast at the central zone. High resolution TEM (Figure 3b) reveals that the radially oriented bundle-like pattern in Figure 3a is composed of parallel streaks with radial orientation and the periodic distance of 4 nm. The selective district TEM (Figure 3c) on the center of circle-shaped projection of sphere in Figure 3a, i.e., a projection of the wall of sphere along the radial direction, displays disordered stripes.

Combining with the adsorption data, the pore on the surface observed by SEM corresponds to the MP-1 mesopore; the projection of channels of the MP-2 mesopore observed by TEM shows the radial streak. Furthermore, Figure 3c indicates that the MP-2 mesopore is a worm-like one.

The calcined sample was monitored using small-angle X-ray scattering (SAXS). The SAXS pattern of the sample exhibits a broad peak at around 2.2° consistent with a mesoporous structure that lacks of long-range order,[5,9] which also substantiates the worm-like mesoporous structure observed in Figure 3c.

The two types of mesoporous structures embody self-assembly characteristic of two different length scales: (i) diameter (about 3 nm) of MP-1 is similar to that (about 3 nm) of MCM-41 directly templated by CTAB;[15] (ii) diameter (about 34 nm) of MP-2 approaches the upper limit (50 nm) for mesopore. At present stage, there is no definite mechanism on the formation of this structure. We suppose that the MP-2 may be the trace of radial diethyl ether current escaping through the crust, because there has not been report on preparing radially oriented mesopore structure using micro-emulsion template.

Hierarchical morphology of mesophase over different length scales has caused considerable attention in material science, due to their potential applications in gradient function materials, large-molecule catalysis, and so on.[16,17] The radiolarian-like silica reported here presents not only a method for inorganic materials of different length scales, but also a potential carrier for the control on mass transfer, such as drug delivery, based on its hollow interior and radial mesoporous channels.[4]

To sum up, the mesoporous silica sphere with hollow interior and radiolarian-like crust could be obtained via a convenient procedure. It provides an example for constructing hierarchical porous materials probably involving dynamic self-assembly at the unstable interface.

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References

1 A. Dabrowski, *Adv. Colloid Interface*, **93**, 135 (2001).

2 R. Hoppe, A. Ortlam, J. Rathousky, G. SchulzEkloff, and A. Zukal, *Microporous Mater.*, **8**, 267 (1997).

3 A. Corma, *Chem. Rev.*, **97**, 2373 (1997).

4 B. Munoz, A. Ramila, J. Perez-Pariente, I. Diaz, and M. Vallet-Regi, *Chem. Mater.*, **15**, 500 (2003).

5 D. Walsh, J. D. Hopwood, and S. Mann, *Science*, **264**, 1576 (1994).

6 S. S. Kim, W. Z. Zhang, and T. J. Pinnavaia, *Science*, **282**, 1302 (1998).

7 S. A. Bagshaw, *Chem. Commun.*, **1999**, 767.

8 Q. Y. Sun, P. J. Kooyman, J. G. Grossmann, P. H. H. Bomans, P. M. Frederik, P. C. M. M. Magusin, T. P. M. Beelen, R. A. van Santen, and N. A. J. M. Sommerdijk, *Adv. Mater.*, **15**, 1097 (2003).

9 E. Muthusamy, D. Walsh, and S. Mann, *Adv. Mater.*, **14**, 969 (2002).

10 P. T. Tanev, Y. Liang, and T. J. Pinnavaia, *J. Am. Chem. Soc.*, **119**, 8616 (1997).

11 H. P. Lin, Y. R. Cheng, and C. Y. Mou, *Chem. Mater.*, **10**, 3772 (1998).

12 S. Oliver, A. Kuperman, N. Coombs, A. Lough, and G. A. Ozin, *Nature*, **378**, 47 (1995).

13 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierrotti, J. Rouquerol, and T. Siemieniewska, *Pure Appl. Chem.*, **57**, 603 (1985).

14 D. H. W. Hubert, M. Jung, P. M. Frederik, P. H. H. Bomans, J. Meuldijk, and A. L. German, *Adv. Mater.*, **12**, 1286 (2000).

15 Q. Cai, Z. S. Luo, W. Q. Pang, Y. W. Fan, X. H. Chen, and F. Z. Cui, *Chem. Mater.*, **13**, 258 (2001).

16 S. Mann and G. A. Ozin, *Nature*, **382**, 313 (1996).

17 C. Z. Yu, J. Fan, B. Z. Tian, and D. Y. Zhao, *Chem. Mater.*, **16**, 889 (2004).

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