Synthesis of micron-sized hollow silica spheres with a novel mesoporous shell of MCF

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Abstract

Micron-sized hollow silica spheres whose shells are made up of mesocellular silica foams (MCFs) have been synthesized by one-pot sol–gel method in benzene/water/P123 emulsion. The material is characterized with SEM, TEM, BET and ^{29}Si MAS NMR. The results show that the MCFs of the unique shell of hollow silica spheres were connected by large windows with a narrow distribution of ~10 nm in diameter, the inner space of the hollow sphere is accessible. And the formation mechanism of the hollow silica spheres is proposed.

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Recently, hollow spherical ceramic materials have attracted much attention due to their potential applications in drug-delivery, adsorption and catalysis [1–3]. Among many types of hollow spheres, those with a mesoporous shell are of significance because the mesopores in the shell will make the large internal void space of the hollow spheres accessible [4]. A number of articles have been published describing the interior templating of mesoporous hollow particles using hard templates [5], vesicles [6] and emulsions [7]. However, the shells of most hollow spheres have a lamellar structure [8], and the size of the mesopores in the shell is small [9] or has a large distribution [10]. These characteristics limit their ability to transport and separate macromolecules. In this paper, we report a one-pot sol–gel/ emulsion approach for the synthesis of micron-sized hollow silica spheres whose shells are made up of MCF. Furthermore, the mesocellular silica foams are connected by large windows with a narrow distribution around 10 nm in diameter. The synthesized hollow silica spheres do not collapse, not even after calcination at 540 °C for 6 h, and have a high specific surface area. These properties make these particles very attractive in applications such as controlled release capsules, artificial cells and separation.

The hollow silica spheres were prepared in the presence of a benzene/poly(ethylene glycol)–block-poly(propylene glycol)–block-poly(ethylene glycol) (P123) emulsion using TEOS as the silica source. In a typical preparation, 1.0 g of P123 was first dissolved in 30.0 mL of deionized water and 4.8 mL of 12 mol/L HCl solution with stirring at the rate
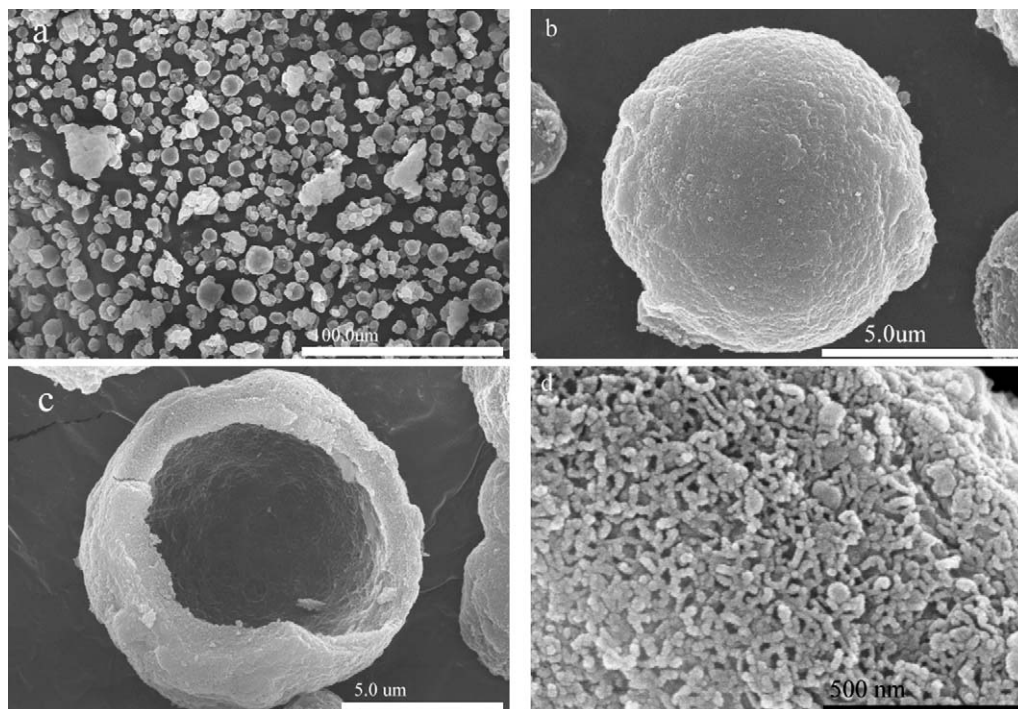
Fig. 1. SEM micrographs of the mesoporous hollow silica spheres. (a) Low magnification SEM of the silica spheres. (b) SEM of a silica sphere of MCF. (c) SEM of a broken hollow silica sphere. (d) SEM of the cross-section surface of the broken hollow silica sphere.

of ~800 rpm at 38 °C, then 1.0 g of benzene was added to the copolymer solution. A milky emulsion formed immediately and was stirred for 3 h. Then 4.1 mL of TEOS was added dropwise into the above solution with stirring for 24 h. After the mixture was aged at 85 °C overnight without stirring, the solid product was recovered. After washing with deionized water, drying and calcination at 540 °C in air, the micron-sized hollow silica spheres were obtained.

Fig. 1(a) shows scanning electron microscopy (SEM) images of the hollow microspheres. It clearly shows that most of the samples are spherical particles with a size distribution of 5–10 μm in diameter, and some small particles aggregate together. From Fig. 1(b) we can see that the particle remains intact and preserves the three-dimensional spherical nature even after calcination at 540 °C for 6 h. From the SEM images of the crushed sphere shown in Fig. 1(c), we can see clearly the internal structure, which indicates the hollow structure of the silica spheres. A closen look shown that the interior surface of the shell has some holes about 500 nm extending to the shell. This indicates that the template making the hollow core structure of the spheres is not a droplet with a smooth exterior surface, but a droplet with smaller spherical particles surrounding the exterior surface. TEM performed on the calcined samples confirms the hollow spherical morphology (Fig. 2(a)) and reveals that the walls have a thickness of 800 nm, which is in agreement with the SEM (Fig. 1(c)).

On the other hand, we found that the inorganic precursors and P123 could be assembled into mesophases, which lead to materials with extremely high porosity and similar to MCF [11]. To understand the morphology of the mesopores in the shell, we carefully observed the cross-section surface of the broken hollow spheres under a SEM. Fig. 1(d) shows that the cross-section surface of the shell is full of holes which are half enclosed. It means that the holes in the shell of the hollow spheres are connected by gaps. In addition, there are some intact vesicles. TEM image of the thin rim of a hollow silica sphere shows that the shell of the hollow sphere is made up of vesicles (Fig. 2(b)). Together with the SEM (Fig. 1(d)), it suggests that the shell of the hollow spheres is made up of mesocellular silica foams which are connected by narrower windows.

Nitrogen sorption measurements strongly support the proposed MCF pore structure of the shell of the hollow spheres. The isotherms (Fig. 3) show large hystereses, which in conjunction with BdB pore size analyses [12], SEM and TEM photographs suggest that the MCF of the shell possess ink-bottle-type pores in which large cells are
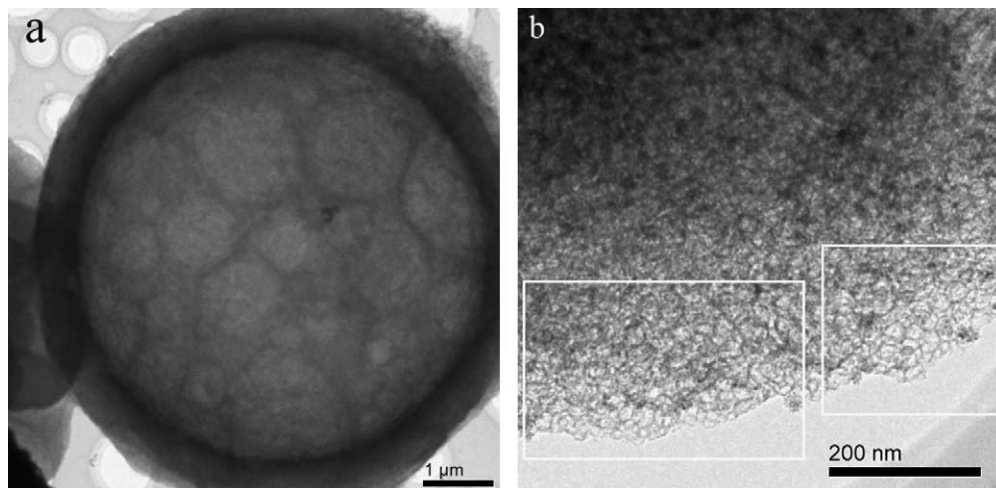
Fig. 2. TEM micrographs of micron-sized hollow silica sphere. (a) TEM of a hollow silica sphere of MCF. (b) TEM of the thin rim of a hollow silica sphere of MCF.
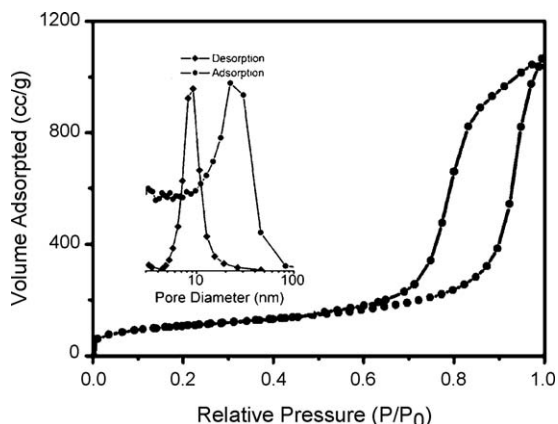

Fig. 3. N$_2$ adsorption/desorption isotherm of calcined hollow spheres of MCF. The inset is the size distribution of the windows and cells of the MCF.

connected by narrower windows [13]. The sizes of the cells and windows have been determined from the adsorption and desorption branches of the nitrogen sorption isotherms, which are about 23 and 10 nm, respectively (Fig. 3). The cell sizes obtained from nitrogen sorption are similar to the values obtained from the TEM pattern (Fig. 2(b)). Compared to the adsorption branch of a representative MCF [11], the nitrogen sorption isotherm of the hollow silica spheres also shows a clear step of capillary condensation from $p/p_0 = 0.85–1.0$, which is related to the filling of the large cells of the MCF; but it does not reach a plateau, which means that nitrogen molecules continuously condensed in the hollow spheres [14]. It indicates that the inner space of the hollow silica spheres is accessible. Furthermore, the Brunauer–Emmett–Teller (BET) specific surface area and pore volume were 417 m^2 g^{-1} and 1.62 cm^3 g^{-1}, respectively.

The ^{29}Si MAS NMR spectrum (Recorded on a Varian Infinityplus-400 spectrometer at 79.4 MHz, using 7.5 mm rotors with the samples spun at 4 kHz, $\pi/4$ pulse width of 1.9 μs, 300 s recycle delay and 120 scans.) shows that the majority of silicon coordination states are Q^4 (−112 ppm, 79.1%) and Q^3 (−103 ppm, 19.4%). This is surprising as it points to a relatively high degree of cross-linking, thereby suggesting a rather effective condensation during the precipitation reaction under 85 °C (Fig. 4).

In benzene/water systems, a PEO–PPO–PEO triblock copolymer concentrates at the benzene/water interface as emulsifier to stabilize the benzene/water emulsion droplets [15]. Optical microscopy revealed the formation of an emulsion of spherical droplets with diameters of approximately 10 μm. From the dimensions of the aggregates, the
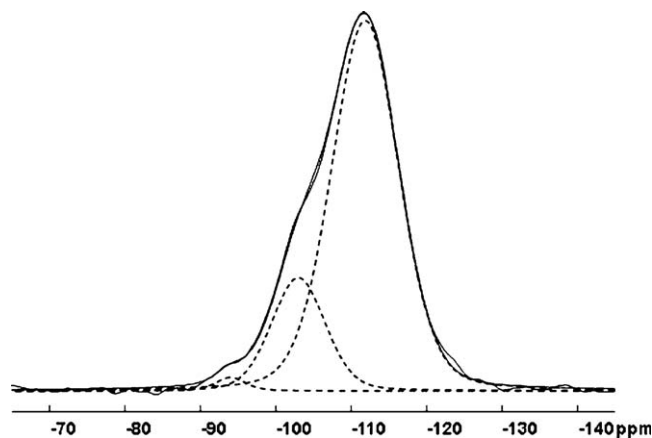
Fig. 4. ^{29}Si MAS NMR spectrum of as-made micron-sized hollow silica spheres.

molecular structure of the polymer and the polymer/benzene ratio, it can be approximated that these aggregates consist of benzene droplets with a diameter of ∼8 μm surrounded by a microemulsion of benzene/P123 droplet shell. This can be proven by the hollow structure of the spheres and the holes in the interior shell of the hollow silica spheres (Fig. 1(c)). To further prove this, we increased the benzene to P123 ratio in the synthesis process, and obtained a more hierarchical micron-sized hollow silica sphere, whose shell was made up of smaller hollow spheres (see SI). It also suggests that the formation of these hollow silica spheres is directed by the structure and dimensions of the aggregates of benzene/P123.

We propose that the addition of benzene to the solution of P123 leads to two results: (1) Part of the benzene added to the P123 solution leads to a microemulsion, and produces uniform little droplets of benzene/P123 in water whose size determines the cell size of the mesocellular silica foams of the shell. (2) Another part of the benzene added to the P123 solution produces larger droplets of benzene surrounded by the microemulsion of benzene/P123 droplets shell. The size of the larger droplet of benzene determines the size of the hollow core of the spheres. Subsequently added tetraethoxysilane (TEOS) may hydrolyze at the surface of the uniform benzene/P123 droplets of the shell and then polymerize to give a MCF shell of the hollow silica spheres, and the larger droplet of benzene leads to the hollow structure of the spheres.

In summary, a very facile method for the preparation of micron-sized hollow silica spheres with a novel mesoporous shell of MCF has been described. The unique MCF shell makes the micron-sized hollow silica spheres potentially useful in applications like encapsulation, delivery, controlled release and separation technology.

Acknowledgments

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