Communication

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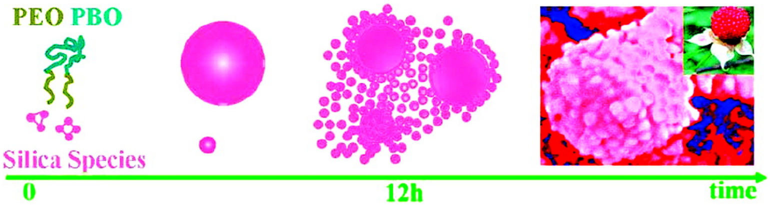

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One Template Synthesis of Raspberry-like Hierarchical Siliceous Hollow Spheres

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Hollow materials with hierarchical pore structures and complex morphologies have attracted much attention for a fundamental interest in biomineralization[1] and their potential applications in catalysis, separation, and controlled release.[2,3] Various templating approaches have been used to synthesize hollow spheres, such as emulsion templating,[2,4,5] colloidal templating,[6] vesicle templating (VT),[3,7] and single crystal templating.[8] However, the synthesis of hierarchical hollow spheres has rarely been reported.[9,10] Recently, Wang et al. synthesized budded mesoporous silica hollow spheres utilizing an emulsion templating system, and a budding mechanism is suggested to interpret the formation of the final structure.[10] To the best of our knowledge, the solution synthesis of hierarchical hollow spheres fabricated by just one template has not been reported so far.

In the present paper, we report the synthesis of raspberry-like hierarchical siliceous hollow spheres (HSHS) through a one-pot, one template approach (Scheme 1). The template used is a block copolymer $EO_{39}BO_{47}EO_{39}$ [commercial product known as B50-6600, Dow Company, EO is poly(ethylene oxide), BO is poly(butylene oxide)], and tetraethyl orthosilicate (TEOS) is employed as a silica source. By carefully adjusting the reaction conditions, both inorganic−organic composite vesicles and micelles are formed simultaneously in the solution. The interaction between colloid spheres with different sizes gives rise to novel HSHS materials with a morphology similar to that of the raspberry.

In a typical synthesis of HSHS, 0.5 g of B50-6600 and 0.852 g of Na_2SO_4 were dissolved in 30 g of pH = 4.7 NaAc−HAc buffer solution [c(NaAc) = c(HAc) = 0.4 M] to form a homogeneous solution under stirring at 40 °C. To this solution was added 2.08 g of TEOS under stirring. The reactant molar ratio of B50-6600/Na_2SO_4/H_2O/TEOS is $7.6 \times 10^{-3}:0.60:1.67 \times 10^{2}:1.0$. After stirring for 5 min, the resultant solution was kept at a static condition for 24 h and then hydrothermally treated at 100 °C for another 24 h. The precipitates were filtered, washed with water three times, and then dried in air. The final product was obtained by calcination at 550 °C for 5 h.

Transmission electron microscopy (TEM) image of calcined raspberry-like HSHS in Figure 1a shows aggregated unilamellar vesicles with diameters of ∼100−200 nm and a wall thickness of ∼10 nm. It is surprising that the surfaces of the large spherical vesicles are not smooth and coated with small “bubbles”. The detailed information of the outer surfaces of large vesicles can be observed at a higher magnification. Figure 1b clearly shows that a big hollow sphere is homogeneously covered with small hollow spheres, resembling the morphology of a raspberry. The diameters of the small hollow spheres are ∼20−25 nm, and the siliceous wall thickness is ∼5 nm.

The N_2 sorption analysis was further employed to observe the pore structure of raspberry-like HSHS. The adsorption branch in Figure 2 shows a major capillary condensation step at relative pressures of ∼0.87−0.91 and another condensation step at $P/P_0 >$ 0.97. A pore size distribution calculated from the adsorption branch by the Barrett−Joyner−Halenda (BJH) method (inset of Figure 2) centered at ∼15 nm is correlated to the cavity of small hollow spheres, and the irregular pore size distribution in the range of 80−150 nm may be associated with the cavity of large vesicles, in accordance with the TEM results. The Brunauer−Emmett−Teller (BET) surface area is 384 m^2/g, and the total pore volume is 1.66 cm^3/g.

Scheme 1. The Formation Process of Raspberry-like HSHS through Self-Assembly of Block Copolymers and Silica Species

It has been observed that the buds on tubular vesicles are the result of a budding process in a multicomponent polymer system.[11] A budding process controlled by kinetic self-assembly is also suggested to explain the formation of budded mesoporous silica hollow spheres.[10] In order to understand the formation mechanism, we studied the influence of reaction time and ionic strength on the self-assembled structure while keeping the other conditions identical to the synthesis of raspberry-like HSHS.

TEM images of the precipitates obtained at 12 h after the addition of TEOS indicate that both small spheres (∼25 nm in diameter) and large vesicles (∼60−200 nm in diameters) coexist in the mixture (Figure 3a,b). However, the small spheres do not adhere to the entire surface of large vesicles at this stage. When the ionic strength is decreased, the HSHS structures (shown in Figure 3c) as well as some tubular structures (indicated by an arrow) are observed. At a higher ionic strength, both aggregated smaller hollow spheres (marked by a black arrow, ∼20−30 in diameter) and foam-like structure with much larger sizes (shown by a white arrow) can be found in the final product (Figure 3d).

We propose a colloidal interaction model to understand the formation of HSHS structure rather than the budding mechanism.[10,11] In a sol system containing two spheres with a diameter of a_1 and a_2, respectively, the repulsive barrier (V, V is the total potential energy including repulsive electrostatic interaction and attractive London−van der Waals force) that stabilizes the sol is greatly dependent on the particle size.[12] For example, V of two large particles ($a_1 = a_2 = 125$ nm), one large and one small particle ($a_1 = 125$ nm, $a_2 = 12.5$ nm), and two small particles ($a_1 = a_2 = 12.5$ nm) is calculated to be 62, 13, and $8kT$ (k is Boltzmann's constant, T is absolute temperature), respectively.[12] Therefore, for a colloidal system containing particles varying in size, small particles may prefer to adhere to large ones.[13] Moreover, compared to the separated aggregation behavior of small or large spheres,

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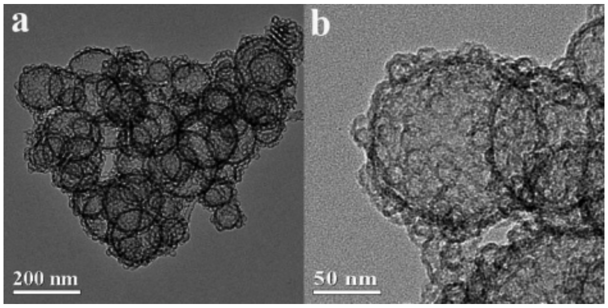

Figure 1. TEM images (a, b) of calcined raspberry-like HSHS.

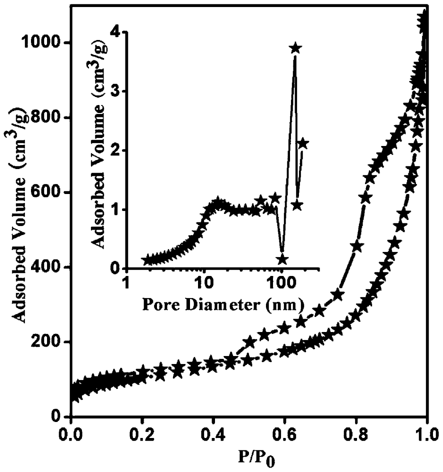

Figure 2. The N_2 sorption isotherm and pore size distribution curve (inset) of calcined raspberry-like HSHS.

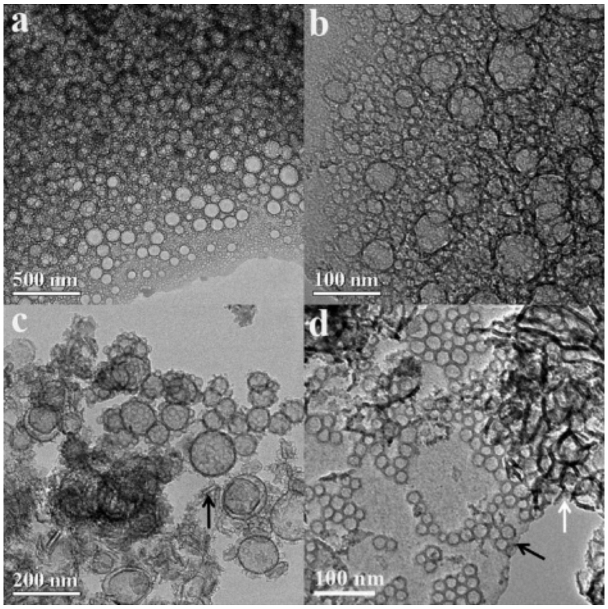

Figure 3. TEM images (a, b) of the sample taken at 12 h after the addition of silica source during the synthesis of raspberry-like HSHS; (c, d) of the final calcined samples synthesized at $c(Na_2SO_4) = 0.0, 0.4$ M, respectively, keeping the other synthesis parameters unchanged compared to the synthesis of raspberry-like HSHS.

the preferred small-coating large structure is further stabilized by an increase in entropy.

In our synthesis system, the starting concentration of block copolymer is quite low (<0.02 g/mL). It is well-known that both micelles and vesicles may form in the dilute solution of surfactants or block copolymers.[14] It is proposed that, in the synthetic condition of HSHS materials, the siliceous species and block copolymer self-assemble simultaneously into composite spherical micelles and vesicles. The colloidal interaction between spheres with different sizes as discussed above and the further calcination process to remove the template give rise to the final HSHS structure with a raspberry morphology.

Our proposed mechanism is further supported by literature reports and our own observations. B50-6600 has been used as a template to synthesize a face-centered cubic (fcc) mesostructure with a cell parameter of 23.6 nm in an acidic condition.[15] Very recently, we have also proposed a hard sphere packing pathway, where an fcc mesostructure is formed by the close packing of condensed spherical composite micelles.[16] In our synthesis, the formation of small spheres should be understood as spherical B50-6600 micelles coated with siliceous species. Moreover, a micelle to tubular micelle and finally vesicle structure transformation has been observed in a previous study at a similar high pH condition.[3] The tubular morphology is also observed in our experiments at a relatively low ionic strength (Figure 3c). Because V is decreased as the ionic strength is increased,[13] the colloidal interaction difference between spheres with different sizes is also decreased, and the fusion of vesicles with similar sizes gives rise to foam-like structures, as shown in Figure 3d.

In general, raspberry-like HSHS materials have been synthesized via a one template process. In this approach, it is crucial to design a system in which micellar and vesicular structures are in one pot and both are pure in morphology. Because there are rich morphologies of micelles (e.g., spherical, rod-like) and vesicles (e.g., uni- and multilamellar, tubules), it is anticipated that more novel materials with complex morphologies and hierarchical pore structures can be designed.

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