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Hollow Zeolite Capsules: A Novel Approach for Fabrication and Guest Encapsulation

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Hollow capsules have recently attracted much attention because their unusual properties may find wide potential applications in chemistry, biotechnology, and materials science.[1−8] Currently, a typical method for their preparation relies on the template-assisted synthesis by which hollow capsules comprising a variety of materials such as polymers,[2] metals,[3] ceramics,[4,5] and composites[6] have been successfully prepared to date. In addition, an important aspect about hollow capsules is their functionalization normally achieved by encapsulating guest species, which would endow them with diverse properties.[7,8] So far, most studies about guest encapsulation have focused on organic hollow capsules, inside which guest species can be encapsulated through a number of strategies.[7] Inorganic hollow capsules possess many advantages such as higher mechanical and thermal stabilities over their organic counterpart; however, until very recently, few studies have dealt with their guest encapsulation[8] and the choice of the guest species has been limited, probably because of the lack of versatile encapsulating strategies.

Zeolites are the ideal building blocks to construct hollow capsules because they may introduce the uniform micropores on the shell, which would be beneficial for shape-selective catalysis and components delivery. Several groups have prepared the hollow zeolite capsules through the multistep assembly of nanozeolite onto the polymer spheres to form a core−shell structure[5] (or with the further growth in a synthesis gel[5d]), followed by calcination to remove the template cores. However, the preparation of hollow zeolite capsules with functionalized interiors has not been reported. Here, we describe a novel approach that allows for the fabrication of hollow capsules with homogeneous and dense zeolitic shells and, most importantly, readily functionalized interiors achieved by the prespecified encapsulated species. This preparation process was fulfilled through the vapor-phase transport (VPT) treatment[9] of the nanozeolite

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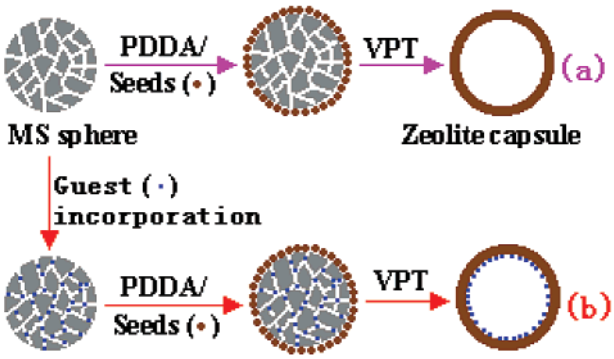

Figure 1. Schematic illustration for the fabrication of hollow (a) and guest encapsulated (b) zeolite capsules.

(seeds) coated mesoporous silica (MS) spheres, which were preformed by the electrostatic assembly technique[5] (Figure 1). Under the effect of the amine vapor during VPT treatment, the seeds on the surface grew up by consuming the silica "nutrition" in the MS cores, and the hollow spherical shells built of grown zeolite crystals were formed upon the complete digestion of the MS spheres (Figure 1a). It is also worth noting that the utility of pore-containing MS template made the guest encapsulation much easier. The desired guests, especially inorganic species, which had been pre-incorporated in the mesopores of the MS template could be entrapped inside the generated capsule along with digestion of the silica in the MS core (Figure 1b); thus, hollow zeolite capsules with functionalized interiors could be easily fabricated by this strategy.

The scanning electron microscopy (SEM) images of the original MS spheres (prepared as in the literature[10]) and the monolayer silicalite-1 seeds (≈60 nm, prepared as in the literature[11]) coated MS spheres[12] are shown in Figure 2a,b, respectively. Precoating MS spheres with a layer of seeds is the premise for the successful preparation of hollow capsules because, without seeding, no transformation of the MS cores could be observed by this approach. After VPT treatment of the seeded MS spheres,[13] almost all of the products (>90%) presented the discrete and intact spherical morphology, and the original spherical zeolite seeds on the MS surface grew to quadrate-shaped crystals with sizes of 100−200 nm (Figure 2c). Transmission electron microscopy (TEM) demonstrated their hollow structure with a homogeneous shell thickness of ca. 200 nm (Figure 2d), indicating that the MS cores had been completely consumed during the growth of the zeolitic shells. The intact spherical morphology of the hollow capsules was well-

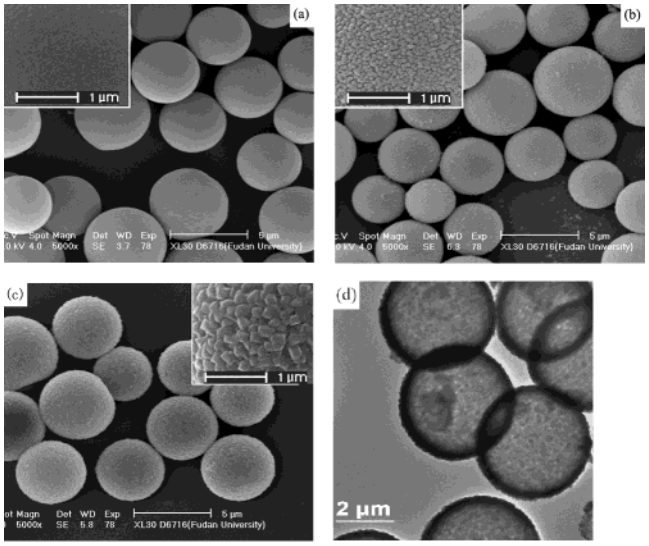

Figure 2. SEM images of (a) the original MS spheres, (b) monolayer seeds coated MS spheres, and (c) hollow zeolite capsules. The insets show the corresponding blowup SEM images of one sphere surface. (d) TEM image of the same sample shown in (c).

retained after sonication (HF frequency = 50 kHz, 120 W, 10 min) or calcination (in air, 600 °C, 6 h) treatment, implying the good mechanical and thermal stability of the products. The transformation of MS spheres to hollow zeolite capsules was also confirmed by X-ray diffraction (XRD). The flat baseline and the high-intensity MFI diffraction peaks[14] shown in the XRD pattern of the products suggested the highly crystallized shells and the disappearance of the amorphous MS cores. Analyses of the alkaline solution at the bottom of autoclave after VPT treatment demonstrated that almost no silica species were dissolved in it, suggesting that most of the MS sphere had been converted to the zeolitic shell. MS spheres worked as the active silica source whose silica species were drawn and subsequently transformed into zeolite crystals on the shell under the induction of the seeds in the mixed vapor of amine and water.

In addition to providing a "nutrition pool" for zeolitic shells growth, notably, MS spheres also have the ability to entrap components inside their abundant mesopores[15−18] so that hollow zeolite capsules with selectively functionalized interiors could be readily fabricated using the desired species embedded MS spheres as the template. Here, we choose iron oxide (Fe_2O_3) as an example. The Fe_2O_3-containing MS templates were prepared through the wet impregnation technique,[15,19] and the following seeds coating and VPT treatment steps were carried out in the same way as those for the MS spheres

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(12) The as-synthesized MS spheres (3−6 μm) were modified by one layer of cationic poly(diallyldimethylammonium chloride) (PDDA, Aldrich). The negatively charged silicalite-1 seeds were then deposited onto the PDDA-modified MS spheres through electrostatic attraction. After the removal of the unbound seeds by washing with 0.01 M NH_4-OH, the seeded MS spheres were dried in air at 100 °C for 2 h.
(13) In a typical synthesis, 0.1 g of the dried seeded MS spheres was dispersed on a porous stainless steel plate which was placed horizontally in the upper part of a stainless steel autoclave, and a liquid mixture of 3 mL of triethylamine, 0.1 mL of ethylenediamine, and 0.5 mL of H_2O was injected into the bottom of the autoclave. The autoclave was then enclosed and heated in an oven at 140 °C for 2 days.
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(19) Typically, 0.1 g of MS spheres was impregnated in a solution of 1.6 M iron(III) nitrate (3.0 mL) under stirring at room temperature overnight. After being washed with deionized water, the product was dried in an oven at 100 °C for 2 h and then heated in air at 400 °C for 4 h. The loading content of Fe_2O_3 can be controlled through the number of impregnation/calcination cycles.

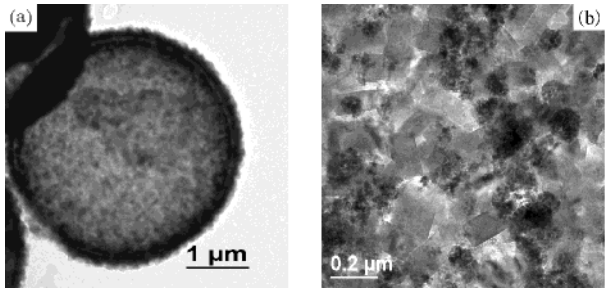

Figure 3. TEM images of (a) the Fe_2O_3-encapsulated zeolite capsules and (b) the entrapped Fe_2O_3 nanoparticles on the inner shell of a broken Fe_2O_3-encapsulated capsule.

without Fe_2O_3. Figure 3a shows a TEM image of Fe_2O_3-encapsulated capsules prepared from the MS spheres with a 10 wt % Fe content. The still generated hollow structure and the homogeneous shell indicated that the embedded metal oxide had no notable influence on the transformation of MS cores. Figure 3b shows a TEM image of the inner shell of a broken capsule. Besides the well-intergrown zeolite crystals, we could clearly observe darker clusters of Fe_2O_3 nanoparticles whose size was ≈13 nm, close to the pore size of MS spheres.[10] The significant difference of the Fe signals in the energy-dispersive spectra (EDS) between the inner and outer capsule shell further confirmed that most of the Fe_2O_3 had indeed been encapsulated inside the capsules.

To summarize, we have demonstrated a new strategy involving the transformation of nanosilicalite-1 seeded MS spheres by VPT treatment to fabricate hollow zeolite capsules whose interiors can be functionalized by the encapsulated guests. The MS spheres provide not only a template but also a silica source for capsule shells formation and a transport medium for guest encapsulation. Although only Fe_2O_3 was demonstrated in this paper, we believe this novel encapsulation scheme should be extendable to a broad range of species such as metals,[16] semiconductors,[17] carbon,[18] or even multiple components which can be easily incorporated in mesoporous materials. This novel type of hollow capsules is expected to be very useful in catalysis, adsorption, and components delivery as promising microreactors, owing to their unique zeolitic shells and selectively functionalized interiors.

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Supporting Information Available: Preparation and characterization of MS spheres, SEM images of the broken hollow capsules, XRD patterns, and EDS (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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