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Facile fabrication of double-shelled hollow microspheres *via* double *in situ* miniemulsion polymerization†

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We describe a facile and flexible technique for fabricating double-shelled hybrid hollow microspheres with a controlled void size *via in situ* miniemulsion polymerization. After monomers polymerize the tetraethoxysilane phase is compressed and restricted as a liquid core leading to the formation of a hollow structure and silica shell. Furthermore, magnetic hollow microspheres are obtained conveniently.

The design and controlled fabrication of inorganic–polymer hybrid hollow microspheres have attracted considerable attention due to their giant commercial applications, including encapsulation and controlled release of sensitive materials, such as drugs, cosmetics, and DNA, energy storage and conversion, and catalysis.¹

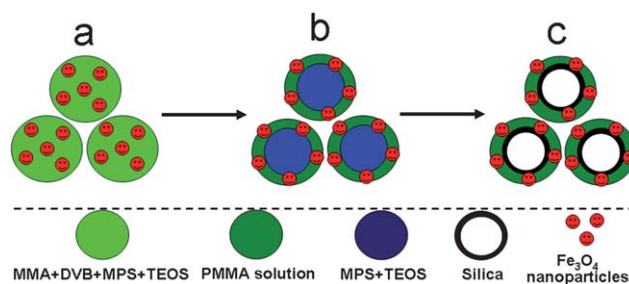
Obviously, the straightforward method to fabricate hollow microsphere is to coat a sacrificial core particle with a shell, and then to remove the core, which is termed as a template method. Various synthetic strategies based on templates have been developed to produce hollow (micro)spheres.² Caruso *et al.*³ had obtained inorganic-hybrid hollow spheres through the colloid templated electrostatic LbL self-assembly followed by removal of the templated core. Recently, Bon *et al.*⁴ prepared TiO₂–polymer hybrid hollow spheres with the size range of 10–50 μm by Pickering emulsion polymerization, which provided a facile one-pot way to obtain hybrid hollow microspheres. Furthermore, inorganic/polymer hollow microspheres have been prepared successfully *via* a double emulsions-templated method by using the *in situ* formed and modified silica particles as Pickering emulsifiers.⁵ However these methods required pre-prepared templating microspheres or/and involved complicated processes. A facile and high throughput method to prepare hybrid hollow microspheres in the nanometer range is still to be resolved.

Miniemulsion polymerization has been proven to be a versatile way to prepare hybrid polymer microspheres.⁶ Owing to the hydrophobic interior of miniemulsion droplets, each submicrometer droplet produces hybrid microspheres with great encapsulation

efficiencies for inorganic particles. Therefore, hybrid polymer microspheres with various morphologies, such as core–shell, raspberry-like, and asymmetric microspheres, have been synthesized successfully *via* miniemulsion polymerization.⁷ Based on our previous work, we have been trying to restrict the oil-soluble tetraethoxysilane (TEOS) as a liquid core when monomers polymerized. However, the compressed TEOS phase tended to be pushed out of miniemulsion droplets, be divided into nanodroplets, or be pushed to one side within the monomer droplets.⁸ As a result, different compression directions of the TEOS phase lead to the formation of hybrid microspheres with various morphologies, such as hollow microspheres, Janus-type microspheres, flower-like nanocomposite micro-particles or raspberry-like nanocomposite microspheres.⁸

Herein, we report a novel approach for the fabrication of hollow microspheres with double-layered shells. By taking full advantage of phase separation between TEOS and the growing polymers, the TEOS phase is compressed and restricted as a liquid core. Hollow microspheres are fabricated by *in situ* hydrolysis–condensation of TEOS under basic conditions and the polymerization of monomers simultaneously using γ-methacryloxy (propyl) trimethoxysilane (MPS) as the functional monomer. Furthermore, magnetic hybrid hollow microspheres could be fabricated by encapsulation of Fe₃O₄ nanoparticles in the polymeric shells.

The formation of double-shelled hybrid hollow microspheres *via* the double *in situ* polymerization technique is displayed in Scheme 1. First of all, methyl methacrylate (MMA), TEOS, divinyl benzene (DVB), and γ-(trimethoxysilyl) propyl methacrylate (MPS) were restricted in miniemulsion microreactor droplets *via* the mini-emulsification process (Scheme 1a). The monomer droplets were



Scheme 1 Illustration for the formation of double-shelled hybrid hollow microspheres by miniemulsion polymerization.

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stabilized by sodium dodecyl sulfate (SDS) and hexadecane (HD). Then, with the polymerization of organic monomers, the naturally different miscibility between the polymer and TEOS resulted in the phase separation, and the TEOS phase was compressed and accumulated to form a liquid core within the initially formed PMMA particles (Scheme 1b).^{7b} After the ammonia was added, silica was generated by *in situ* hydrolysis–condensation of TEOS under basic conditions. Because the volume of TEOS decreased dramatically, the original TEOS phase shrank into a solid shell and led to the formation of a hollow structure (Scheme 1c).

In order to testify the formation mechanism of miniemulsion polymerization, we investigated the size distributions of miniemulsion droplets and the nanocomposite microspheres, respectively. As Fig. 1 displays, the particle size distributions of the polymerized miniemulsions (Fig. 1b) were close to those of the corresponding monomer droplets prior to polymerization (Fig. 1a). Thus, nucleation occurs primarily within the monomer droplets, which were stabilized against coalescence and diffusional degradation.⁹ It should be noted that there existed an optimum SDS content for the polymerization stability (Fig. S1, S2, and S3†). Furthermore, without the addition of polystyrene as co-stabilizer, the miniemulsion polymerization became unstable. Morphology of polymer particles prepared without the addition of polystyrene further confirmed that there existed coalescence and diffusional degradation, although the polymer particles showed a hollow structure (Fig. S4†).

For our present miniemulsion system, the compatibility of inorganic TEOS and the growing polymer should play a great role in the phase separation process and then in the final morphology of microspheres. MPS, here acting as a solubilizer, enhanced the compatibility between TEOS and the growing polymer particles. The addition of MPS has a great effect on the morphologies of the resulting composite particles. Without MPS in the miniemulsion droplets, the TEOS phase was compressed and moved to accumulate at one internal side of the initially formed PMMA particles. After the formation of silica, up to 70% of the original TEOS volume turned into ethanol and “bowl-type” hybrid particles formed, with the bottom of the bowl consisting of PMMA (Fig. S5†).^{8a} When the content of MPS increased, the compatibility between TEOS and PMMA/MMA solution enhanced. The compressed TEOS phase was divided into small droplets, which were extruded out and settled on the shells of the growing polymer particles. Hybrid hollow microspheres with silica particles on the shells were obtained after TEOS nodules were transformed into silica particles (Fig. S6 and S7†). The detailed schematic formation was illustrated in Scheme S1.† The

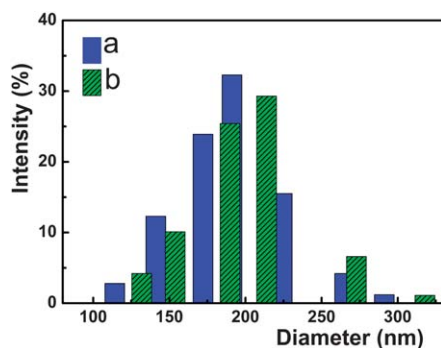


Fig. 1 Size distributions of the miniemulsion droplets (a) and the hybrid hollow microspheres (b).

characterization results confirmed that silica was formed *in situ* from TEOS during the polymerization of monomers (Fig. S8†).

However, we further found that the addition of DVB in the formulation affected the compression and extruding direction of the TEOS phase when the monomers polymerized. As shown in Fig. 2a, composite microspheres with a hollow structure were obtained. Compared with the above experiments carried out in the absence of DVB, the polymerization rate of organic monomers became faster. The great differences in the miscibility of polymer and TEOS resulted in phase separation, and the compressed direction of the TEOS phase was quite different. The compressed TEOS phase accumulated to form a liquid core within the initially formed PMMA particles. Therefore, after the added TEA dispersed and permeated into the polymer microspheres, silica nucleated and grew into a thin shell adhering to the polymer shell. From the inset of Fig. 2a, it could be seen clearly that hollow microspheres had double-layered shells with silica as the inner layer and polymer as the outer layer, respectively. As estimated from the inset of Fig. 2a, the diameter ratio of void/microsphere was approximately 1/2.

Then a series of controlled experiments was carried out at the same synthetic conditions to investigate the role of TEOS content on the void size of hollow microspheres. With more TEOS added in the miniemulsion monomer droplets, the voids of hollow microspheres should become larger, and the thickness ratio of silica/polymer shells would increase. As expected, when the weight ratio of MMA/TEOS increased from 14/6 to 14/8 (g g^{-1}), hybrid microspheres retained the double-shelled hollow structure with a larger volume of void as shown in Fig. 2b. The diameter ratio of void/microsphere increased from 1/2 to approximately 4/5 (estimated from the inset of Fig. 2b).

Furthermore, we continued to carry out experiments with a lower content of TEOS and expected to obtain hollow microspheres with

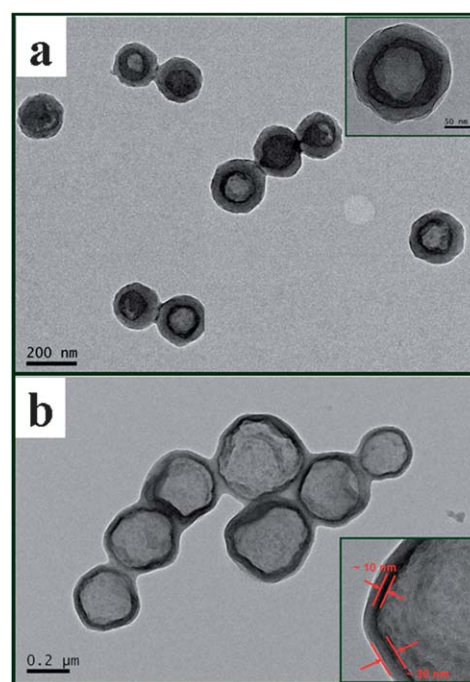


Fig. 2 TEM images of silica–polymer hybrid hollow microspheres prepared with weight ratios of MMA/DVB/TEOS/MPS/HD/PSt of 14.0/1.4/6.0/1.8/0.8/0.2 (a) and of 14.0/1.4/8.0/2.4/0.8/0.2 (b) (typical high-magnification shown in inset).

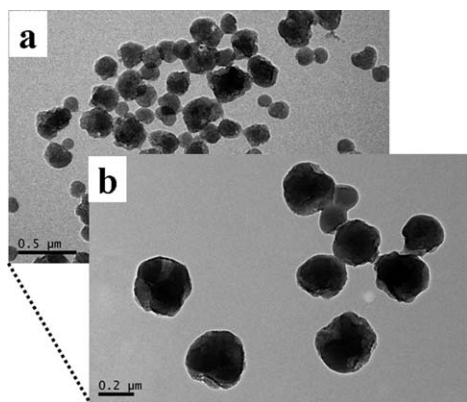


Fig. 3 TEM images of hybrid microspheres prepared with weight ratios of MMA/DVB/TEOS/MPS/HD/PS_t of 14.0/1.4/2.0/1.2/0.8/0.2 (a) and of 14.0/1.4/4.0/1.2/0.8/0.2 (b), respectively.

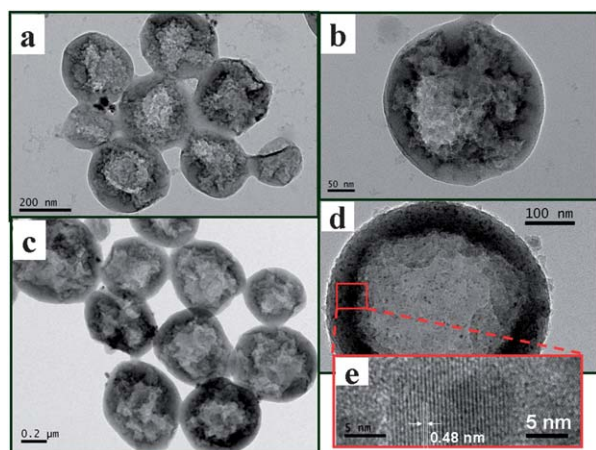


Fig. 4 TEM images of magnetic hybrid hollow microspheres prepared with different ratios of MMA/DVB/TEOS/MPS/HD/PS_t/Fe₃O₄. (a): MMA/DVB/TEOS/MPS/HD/PS_t/Fe₃O₄ = 14.0/1.4/6.0/1.2/0.8/0.2/2.0; (b): partial high-magnification image of (a); (c): MMA/DVB/TEOS/MPS/HD/PS_t/Fe₃O₄ = 14.0/1.4/6.0/1.2/0.8/0.2/1.0; (d): partial high-magnification image of (c); (e): HRTEM analysis of the magnetic nanoparticles embedded in a hollow microsphere of (d).

relatively smaller voids. However, when the weight ratios of MMA/TEOS were 14/4 and 14/2 (g g^{-1}), the as-prepared hybrid microspheres did not show a hollow structure. As shown in Fig. 3a and b, composite microspheres have a nonspherical morphology. The collapsed structure of hybrid microspheres may come from the contraction of the polymer phase during the polymerization (Fig. S9 and S10†).

Due to the hydrophobic internal environment of miniemulsion droplets, hybrid microspheres can be fabricated successfully by facile encapsulation of various inorganic particles. By adding MPS modified magnetic nanoparticles to the oil phase, we prepared hybrid hollow microspheres with magnetic nanoparticles embedded in the

polymer shells. As shown in Fig. 4, the as-prepared composite microspheres showed a hollow structure at different magnetic particles contents (Fig. 4a and c). Fe₃O₄ contents of the magnetic hollow microspheres were 5.7% and 11.9%, respectively (Fig. S11†). Magnetic Fe₃O₄ nanoparticles could be seen clearly from the corresponding magnified pictures (Fig. 4b and d). The HRTEM image shows that the nanoparticles were structurally uniform with an interplanar spacing of about 0.48 nm, which corresponds to the (111) lattice plane of the cubic Fe₃O₄ (0.483 nm) (Fig. 4e) as indicated by atomic lattice fringes.¹⁰

In summary, the facile fabrication of double-shelled hollow microspheres is reported *via* the double *in situ* miniemulsion polymerization method by taking full advantage of phase separation between TEOS and polymer during the polymerization of monomers. The voids of hollow microspheres could be easily tuned by controlling the weight ratio of monomer and TEOS. Magnetic hollow microspheres were fabricated successfully by adding hydrophobic Fe₃O₄ nanoparticles in the oil phase, which could find applications in controlled release areas, energy storage and conversion, and catalysis.

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