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SiO_2/Polymer Hybrid Hollow Microspheres via Double in Situ Miniemulsion Polymerization

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The design and controlled fabrication of inorganic/polymer hybrid microspheres (capsules) have attracted considerable attention.[1−5] These particles not only exhibit special properties of inorganic components but also lead to materials with improved comprehensive properties. Moreover, microspheres of special micro/nanostructures could notably influence the performance of materials.[6,7] For example, inorganic/polymer hybrid hollow spheres could exhibit particular properties and applications, ranging from drug release systems to "containers" for catalytic materials to Pickering emulsifiers.[8−11]

At present, various approaches have been developed to fabricate hybrid microspheres with special morphologies. Caruso et al.[12] had obtained inorganic−hybrid hollow spheres through the colloid templated electrostatic LbL self-assembly followed by removal of the templated core. Bon et al.[13] prepared TiO_2−polymer hybrid hollow spheres with the size range of 10−50 μm by Pickering emulsion polymerization. Armes et al.[14] reported that using commercially available glycerol-functionalized ultrafine silica sol, silica−polymer microspheres with a well-defined "core−shell" morphology were synthesized without surfactant or nonaqueous cosolvents. Miniemulsion polymerization has been proven to be a versatile way to prepare hybrid polymer microspheres.[15] Owing to the hydrophobic internal monomer droplets of miniemulsions, each submicrometer droplet could indeed act as a nanoreactor, which produces hybrid microspheres with great encapsulation efficiencies of inorganic particles. Therefore, hybrid polymer microspheres with various morphologies such as core−shell, raspberry−like, and asymmetric nanocomposite microspheres have been synthesized successfully via the miniemulsion polymerization.[16−18] However, all these methods involved complicated processes or required preprepared inorganic particles. A facile and high throughput method to prepare hybrid hollow microspheres is still to be solved.

Herein, we report a facile approach for the fabrication of SiO_2/polymer hybrid microspheres with various morphologies via the double in situ miniemulsion polymerization.

The formation of silica/polymer microspheres via the double in situ miniemulsion polymerization is displayed in Scheme 1. Monomers of methyl methacrylate (MMA), tetraethoxysilane (TEOS), and γ-(trimethoxysilyl)propyl methacrylate (MPS) were restricted in miniemulsion monomer droplets (Scheme 1a) prepared by a Fluko FM200 homogenizer at 18 000 rpm for 5 min in an ice bath. With the polymerization of organic monomers at 75 °C, the low miscibility between the growing polymer and TEOS resulted in the phase separation. The compressed TEOS was pushed out from the initially formed PMMA particles as

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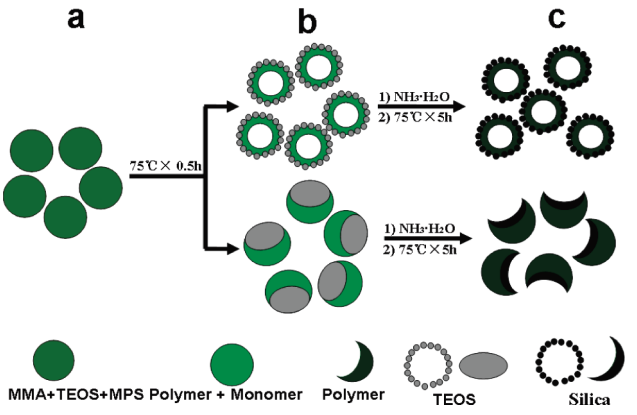
Scheme 1. Schematic Illustration for the Formation of Silica/Polymer Microsphere via Miniemulsion Polymerization[a]



[a] **Hybrid microspheres were prepared by taking full advantage of phase separation between inorganic TEOS and organic polymer.**

nodules at high MPS content[19] or accumulated at one internal side of PMMA particles at low MPS content (Scheme 1b). By the hydrolysis−condensation reactions under basic conditions, TEOS nodules turned into SiO_2 particles and located on the shells of the growing polymer particles or TEOS phase transformed into silica (Scheme 1c). The MPS-modified SiO_2 particles were chemically bonded onto the surfaces of polymer particles, owing to the copolymerization of MPS and MMA.

It is well-known that emulsifier content plays an important role on the stability of miniemulsion polymerization. In our monomer/TEOS system, the emulsifier content also affects the morphologies of hybrid microspheres. A series of polymerizations were carried out to investigate its influences (samples 1, 2, and 3 in Table S1). With a low emulsifier content, the system had a bad stability and hybrid particles were multidispersed because of the aggregation or clustering between the growing particles (Figure S2a). With an increasing emulsifier content, the polymerization stability was enhanced and the obtained hybrid particles had "bowl-type" structure at low MPS content (Figure S2b). When more emulsifier was added, TEOS droplets extruded out from the monomer mixture were stabilized by the excess of emulsifiers in the system, which generated more silica particles in the disperse system (Figure S2c).

In our research, we found that MPS content had a great impact on the morphologies of hybrid microspheres. With the polymerization of monomer, phase separation occurred spontaneously due to the naturally different miscibility of TEOS and polymer. MPS here acting as a solubilizer enhanced the compatibility between TEOS and the growing polymer particles. Therefore, MPS content played a critical role on the morphologies of hybrid particles. Figures 1, 2, and 3 show the effects of MPS content on the morphologies of hybrid microspheres at a given content of SDS with 0.15 g. When no MPS was added, hybrid particles had a "bowl-type" structure as shown in Figure 1a,b. From the magnified images in Figure 1c,d, no silica particles were found. For the formation of "bowl-type" particles, shortly after the polymerization of MMA monomer, TEOS phase was compressed and moved to accumulate at one internal side of the initially formed PMMA particles. After the formation of SiO_2, the volume of TEOS decreased dramatically (up to 70% of the original TEOS volume), which led to the

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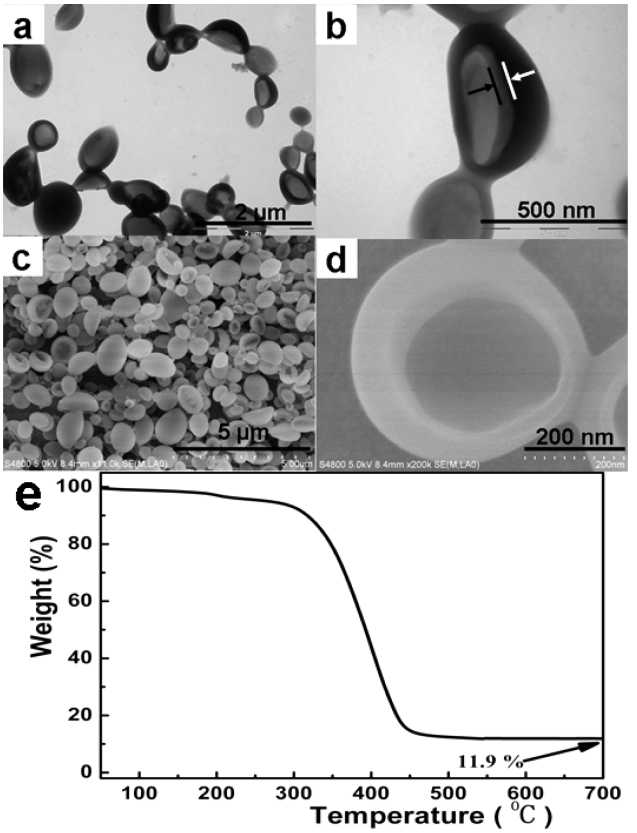

Figure 1. (a−d) Morphologies of hybrid microspheres with mass ratio of MMA/TEOS/MPS/SDS = 14/6/0/0.15: TEM of (a) low-magnification and (b) magnified images; SEM of (c) low-magnification and (d) magnified images. (e) TGA curve for SiO_2/PMMA hybrid microspheres.

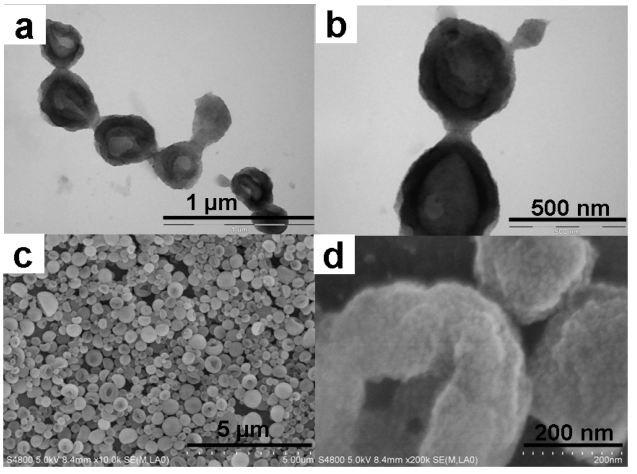

Figure 2. Morphology of hybrid hollow microspheres with mass ratio of MMA/TEOS/MPS/SDS = 14/6/0.3/0.15: TEM of (a) low-magnification and (b) magnified images; SEM of (c) low-magnification image and (d) magnified image showing a broken microsphere.

original TEOS phase constracted and collapsed as the arrows in Figure 1b pointed to. Then, "bowl-type" hybrid particles formed with the bottom of the bowl consisting of PMMA. The SiO_2 content in the hybrid particles was consistent with the value of theoretic calculation from the thermogravimetric analyses (TGA) result (Figure 1e).

With more MPS in the formulation, the boundary area between organic and inorganic phase increased accordingly. With the polymerization of MMA, the viscosity of PMMA/MMA

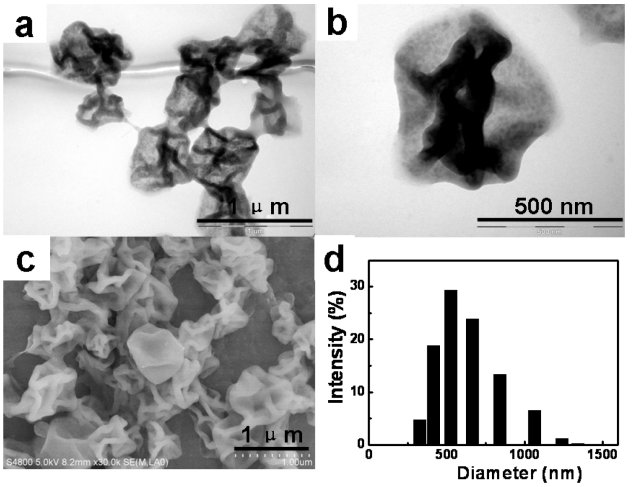

Figure 3. (a−c) Morphology of hybrid hollow microspheres with mass ratio of MMA/TEOS/MPS/SDS = 14/6/1.2/0.15: TEM of (a) low-magnification and (b) magnified images; SEM of low-magnification image (c). (d) Size distribution of hybrid hollow microspheres.

solution increased greatly and the compressed TEOS phase was divided into small droplets. TEOS nodules were pushed out from the initially formed PMMA particles, which left voids in the internal part of polymer particles. The voids consistuted the interal hollow structure after the polymerization of MMA was completed and TEOS nodules turned into silica particles under basic conditions. Hybrid hollow microspheres were obtained with silica particles chemiscally bonded onto the shells. As shown in Figure 2a,b, hybrid microspheres with a collapsed hollow structure were obtained. Silica nanoparticles with size of about 20 nm were on the outer shells of microspheres as shown in Figure 2d. It is understandable that when the MPS content continued to increase again, the compressed TEOS phase with the same volume would be divided into more droplets of smaller volume. Therefore, silica nanoparticles with smaller size would form on the shells of hybrid microspheres. As expected, the hybrid microspheres remained the hollow structure as shown in Figure 3a, and smaller silica particles of about 15 nm were obtained as the magnified image shown in Figure 3b. The size of the as-prepared hollow microspheres was mainly in the range of 500−900 nm as shown in Figure 3c,d.

In conclusion, a facile and effective approach has been developed to prepare hybrid hollow/bowl-type SiO_2/PMMA microspheres via the double in situ miniemulsion polymerization by taking full advantage of phase separation. The as-prepared hybrid microspheres would find applications in catalysis, cosmetics, and drug delivery. The approach can be applied to prepare hybrid particles from other organic monomers.

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Supporting Information Available: Detailed experimental part, TEM images of SiO_2/PMMA hybrid microspheres prepared with different SDS amounts, and typical FTIR spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Giulio, M.; Aldo, P.; Marco, S.; Ezio, A.; Elisa, Z.; Elena, F. *Polymer* **2005**, *46*, 2872–2879.

(2) Watanabe, M.; Tamai, T. *Langmuir* **2007**, *23*, 3062–3066.
(3) Watanabe, M.; Tamai, T. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 4736–4742.
(4) Reynolds, C. H.; Annan, N.; Beshah, K.; Huber, J. H.; Shaber, S. H.; Lenkinski, R. E.; Wortman, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 8940–8945.
(5) Davies, R.; Schurr, G. A.; Meenan, P.; Nelson, R. D.; Bergna, H. E.; Brevett, C. A. S.; Goldbaum, R. H. *Adv. Mater.* **1998**, *10*, 1264–1270.
(6) Fujii, S.; Armes, S. P. *Adv. Mater.* **2005**, *17*, 1014–1018.
(7) Zhao, Y.; Jiang, L. *Adv. Mater.* **2009**, *21*, 1–18.
(8) Fujii, S.; Armes, S. P.; Binks, B. P.; Murakami, R. *Langmuir* **2006**, *22*, 6818–6825.
(9) Liu, Y. L.; Hsu, C. Y.; Wang, M. L.; Chen, H. S. *Nanotechnology* **2003**, *14*, 813–819.
(10) Liu, Y. L.; Hsu, C. Y.; Su, Y. H.; Lai, J. Y. *Biomacromolecules* **2005**, *6*, 368–373.
(11) Su, Y. H.; Liu, Y. L.; Sun, Y. M.; Lai, J. Y.; Wang, D. M.; Gao, Y.; Liu, B. J.; Guiver, M. D. *J. Membr. Sci.* **2007**, *296*, 21–28.
(12) Frank, C.; Caruso, R. A.; MÖhwald, H. *Science* **1998**, *282*, 1111–1114.
(13) Chen, T.; Colver, P. J.; Bon, S. A. F. *Adv. Mater.* **2007**, *19*, 2286–2289.
(14) Schmid, A.; Tonnar, J.; Armes, S. P. *Adv. Mater.* **2008**, *20*, 3331–3336.
(15) Landfester, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 4488–4507.
(16) Zhou, J.; Zhang, S. W.; Qiao, X. G.; Li, X. Q.; Wu, L. M. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 3202–3209.
(17) Qiao, X. G.; Chen, M.; Zhou, J.; Wu, L. M. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1028–1037.
(18) Qiang, W. L.; Wang, Y. L.; He, P.; Xu, H.; Gu, H. C.; Shi, D. L. *Langmuir* **2008**, *24*, 606–608.
(19) Lu, W.; Chen, M.; Wu, L. M. *J. Colloid Interface Sci.* **2008**, *328*, 98–102.