doi:10.1246/cl.2012.970
Published on the web September 8, 2012

Facile Fabrication of Hybrid Hollow Microspheres via in Situ Pickering Miniemulsion Polymerization

Jianan Zhang,* Jizhi Lin, Bo Wu, Beibei Yang, Mingyuan Wu, Wenlong Yang, Qingyun Wu, and Jianjun Yang
[1]*School of Chemistry and Chemical Engineering, Anhui University, Hefei 230039, P. R. China*
[2]*Anhui Province Key Laboratory of Environment-friendly Polymer Materials, Anhui University, Hefei 230039, P. R. China*

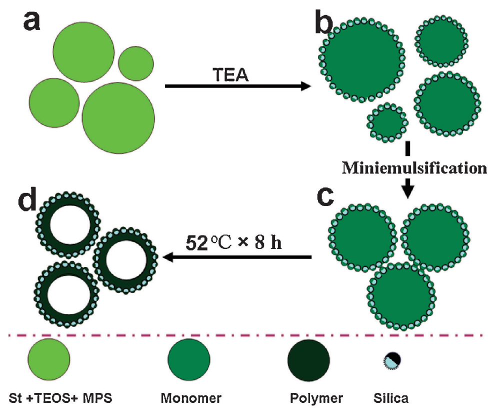
(Received May 1, 2012; CL-120380; E-mail: jianan@mail.ustc.edu.cn)

Hybrid hollow microspheres have been fabricated successfully via miniemulsion polymerization using the in situ formed and modified nanosilica particles as Pickering emulsifier. The hydrolysis and condensation reactions of tetraethoxysilane (TEOS) take place to form nanosilica particles which are then partially modified by oil-soluble 3-(trimethoxysilyl)propyl methacrylate (MPS) at the oil/water interface under basic conditions. After the miniemulsification process, Pickering miniemulsions were stabilized by the in situ nanosilica particles. Hybrid hollow microspheres are obtained with silica nanoparticles closely packed on the surface of polymer microspheres. The results showed that both the weight ratios of TEOS/styrene and MPS/TEOS have great effects on the production of stable Pickering emulsion and then the morphologies of the obtained hybrid microspheres.

In 1907, Pickering observed that stable emulsions of oil and water could be obtained by solid particles, which situate at the oil/water interface forming a dense monolayer minimizing coalescence.[1] Adsorption is typically obtained when the particles are wetted by both liquids or particles are partially modified to introduce a chemical anisotropy making the particles themselves amphiphilic.[2,3] Pickering emulsions provide a straightforward method for the fabrication of hybrid polymer microspheres when the monomer(s) in oil phase polymerize.

Typical Pickering emulsions are obtained by using preprepared solid particles as surfactants to stabilize the oil droplets. Recently Bon prepared a Pickering emulsion using TiO_2 nanoparticles as sole surfactant, and polymer/TiO_2 hybrid hollow spheres were fabricated by taking advantages of phase separation between hexadecane and styrene–divinylbenzene copolymer using hexadecane as the nonsolvent for the polymer.[4] Hollow nanostructural microspheres have been receiving increasing attention from researchers in various disciplines due to giant commercial applications including encapsulation and control release of sensitive materials such as drugs, cosmetics, and DNA, energy storage and conversion, and catalysis.[5] Various synthetic strategies based on templates have been developed to produce hollow (micro)spheres.[6]

We report herein a novel technique to fabricate Pickering miniemulsions stabilized by in situ formed single-component nanosilicas. Silica nanoparticles were formed and modified at the oil/water interface of oil droplets by using tetraethoxysilane as the precursor. Furthermore hybrid hollow microspheres were obtained after the oil phase was polymerized. Compared with other reported methods, our technique is a one-pot synthetic process without any template and can be expected to produce a large quantity of hybrid hollow microspheres for various applications.



Scheme 1. Schematic illustration for the preparation of hybrid microcapsules via in situ Pickering miniemulsion polymerization.

The schematic procedure for the preparation of hybrid hollow microspheres via in situ Pickering miniemulsion polymerization is shown in Scheme 1. The pre-emulsions were prepared first under magnetic stirring by using the mixtures of styrene (St), tetraethoxysilane (TEOS), hexadecane (HD), 2,2′-azobis(2,4-dimethylvaleronitrile) (ABVN), and 3-(trimethoxysilyl)propyl methacrylate (MPS) as the oil phase, and water as the water phase (Scheme 1a). After the added triethylamine (TEA) diffuses to the oil/water interface, nanosilica particles were formed in situ through the hydrolysis-condensation of TEOS under basic conditions. Then the nanosilica particles were partially modified by MPS showing amphiphilic properties and located on the surfaces of monomers droplets (Scheme 1b). Miniemulsions were obtained subsequently by high-speed shearing via a Fluko FM200 homogenizer (Scheme 1c). Hollow microspheres are fabricated with silica particles closely packed on their surface after the polymerization is completed (Scheme 1d).

In order to identify the formation and surface modification of silica particles at the interface of oil droplets, controlled experiments were carried out. Silica nanoparticles were withdrawn for characterization before the polymerization of organic monomer in the step c of Scheme 1. The results from FT-IR spectrum (see Supporting Information; SI, Figures S1a and S1b[10]) confirmed that silica nanoparticles were synthesized and modified by MPS at the interfaces. Since it remains difficult to directly evaluate wettability of the modified silica particles,[7] we investigated their dispersibility in water/toluene medium.[8] The dried modified silica particles were added in water/toluene and then thoroughly sonificated. The modified silica particles in the toluene phase spontaneously moved to the water/toluene interface, and the water phase became clear gradually from the bottom of the test-tube. These results indicated that silica particles were

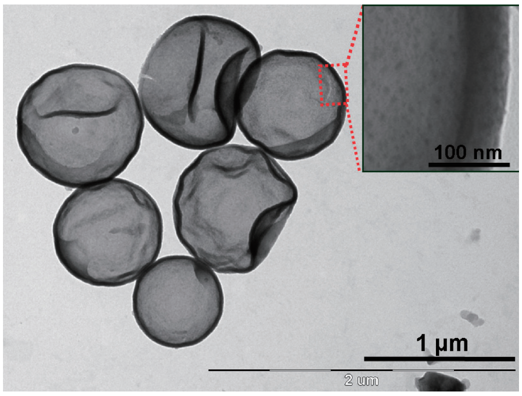


Figure 1. TEM images showing the morphology of hybrid hollow microspheres. The weight ratio of St/TEOS/MPS/HD/PSt is 10.0/12.0/1.2/0.8/0.2 (Sample **5** shown in Table S1[10]).

partially modified by MPS and had amphiphilic properties. Because MPS and TEOS are oil-soluble, the functionalization of silica mainly occurred at the O/W interface. The amphiphilic properties of silica particles made it possible to obtain stable emulsions. Without addition of any surfactant, we believe that miniemulsions were stabilized by the in situ formed silica particles via forming a dense monolayer at the outer interface.[9]

As shown in Figure 1, hybrid microspheres have a hollow-structured morphology. EDX elemental analysis was employed to check the composition of the as-prepared microspheres scanned by X-ray beam (Figure S2[10]). The results confirmed that the hollow microspheres consist of silica and polymer. The existence of nanosilica particles on the surface of hollow microspheres was confirmed by the HRTEM image. As shown in the inset of Figure 1, solid silica particles could be observed, and the size is about 10 nm in diameter. The obtained hybrid hollow microspheres have an average size mainly between 600 and 800 nm (Figure 2). The formation of a hollow morphology is caused by the phase separation of copolymers inside the droplets. The polystyrene undergoes phase separation at the interface to form a shell on the soft template (hexadecane) due to the diffusion of ethanol into the aqueous phase, which came from the hydrolysis and condensation reactions of TEOS.

We also investigated the effects of the ratios of silica content to monomer content (TEOS/St) and modifier content to silica content (MPS/TEOS) on the production of stable Pickering emulsion and then morphologies of the obtained hybrid microspheres. With 15 wt % or more MPS relative to TEOS in the formulation or less TEOS relative to monomer, the Pickering emulsions were unstable and the obtained hollow microspheres thus were deformable and had an irregular morphology. The unstable Pickering miniemulsions and the aggregation and coalescence during polymerization process led to the polydisperse particles in size (TEM images shown in Figures S3 and S4[10]).

The composition of hollow microspheres was analyzed by thermogravimetric analyses (TGA) in air, which identified the formation and content of silica. The SiO_2 content from TGA in the hybrid microspheres was about 16.8 wt % (Figure 3), which is consistent with the value of theoretical calculation.

We have successfully prepared organic–inorganic hybrid hollow microspheres via a Pickering miniemulsion polymerization. This straightforward template-free method comprises in situ formation and modification of SiO_2 nanoparticles at the interface of oil droplets dispersed in water, miniemulsification, and polymerization of the oil phase. Such hybrid hollow microspheres may find applications as carriers for drug release systems, encapsulation of cosmetics and DNA, and catalyst supports.

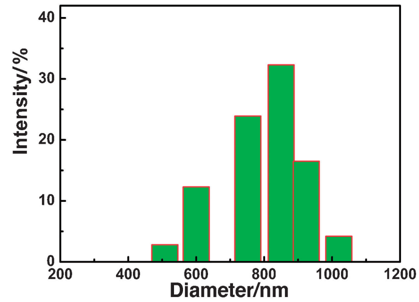


Figure 2. Size distribution of the hybrid hollow microspheres.

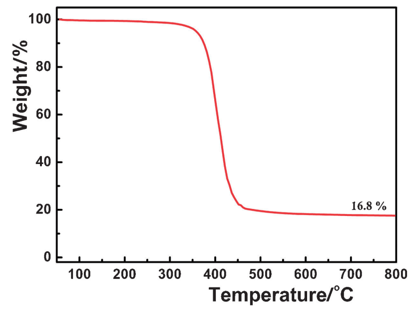


Figure 3. TGA curve of hybrid hollow microspheres.

This work was supported by the Anhui Provincial Natural Science Foundation (No. 11040606M59), the National Natural Science Foundation of China (Nos. 21044006 and 51173001), the Doctoral Scientific Research Startup Fund (No. 33190129), the Student Research Training Program (No. 20110032), and the 211 Project of Anhui University of China.

References and Notes

1 S. U. Pickering, *J. Chem. Soc., Trans.* **1907**, *91*, 2001.
2 B. P. Binks, P. D. I. Fletcher, *Langmuir* **2001**, *17*, 4708.
3 L.-P. Xu, S. Pradhan, S. Chen, *Langmuir* **2007**, *23*, 8544.
4 T. Chen, P. J. Colver, S. A. F. Bon, *Adv. Mater.* **2007**, *19*, 2286.
5 a) H. Tamber, P. Johansen, H. P. Merkle, B. Gander, *Adv. Drug Delivery Rev.* **2005**, *57*, 357. b) K. An, T. Hyeon, *Nano Today* **2009**, *4*, 359. c) Y. Zhao, L. Jiang, *Adv. Mater.* **2009**, *21*, 3621.
6 a) X. W. Lou, L. A. Archer, Z. Yang, *Adv. Mater.* **2008**, *20*, 3987. b) J. Zhang, J. Yang, Q. Wu, M. Wu, N. Liu, Z. Jin, Y. Wang, *Macromolecules* **2010**, *43*, 1188.
7 S. Sacanna, W. K. Kegel, A. P. Philipse, *Phys. Rev. Lett.* **2007**, *98*, 158301.
8 a) J. Zhang, X. Ge, M. Wang, J. Yang, Q. Wu, M. Wu, N. Liu, Z. Jin, *Chem. Commun.* **2010**, *46*, 4318. b) J. Zhang, M. Wu, Q. Wu, J. Yang, N. Liu, Z. Jin, *Chem. Lett.* **2010**, *39*, 206.
9 Y. K. Takahara, S. Ikeda, S. Ishino, K. Tachi, K. Ikeue, T. Sakata, T. Hasegawa, H. Mori, M. Matsumura, B. Ohtani, *J. Am. Chem. Soc.* **2005**, *127*, 6271.
10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.