COMMUNICATION

ChemComm
www.rsc.org/chemcomm

# Synthesis of stable hollow silica microspheres with mesoporous shell in nonionic W/O emulsion

**Wenjiang Li, Xiaoxiang Sha, Wenjun Dong and Zichen Wang***
*Department of Chemistry, Jilin University, Changchun, 130023 China. E-mail: wangzc@mail.jlu.edu.cn*

*Received (in Cambridge, UK) 26th June 2002, Accepted 27th August 2002*
*First published as an Advance Article on the web 24th September 2002*

**Stable hollow silica microspheres were synthesized by a sol–gel method in nonionic W/O emulsion; the mesoporous shell wall of the spheres could have potential applications as controlled release capsules for drugs, dyes, cosmetics and inks, artificial cells, catalysts, and fillers.**

Inorganic–organic hybrid materials with hierarchal morphologies have become one of the pursued areas because of their potential applications in functional materials and smart systems. A number of papers have described the formation of hollow spherical materials, and several of them are on silica materials.[1] So far, most of the systems reported were based on nozzle reactor approaches, sol–gel/emulsion technologies, and self-assembly processes.[2] Recently layer-by-layer self-assembly of preformed nanoparticles onto colloid particles to form hollow spheres has also attracted considerable attention, and many hollow particles with various diameters and wall thickness have been fabricated for a variety of inorganic materials, such as silica, iron oxide, titania, zeolite, clay, and inorganic-hetero-composites.[3,4] However, these porous materials usually are unstable, and hence limited in their applications. In this communication, we report a method to synthesize stable hollow silica microspheres by a sol–gel process of tetraethyl orthosilicate (TEOS) in nonionic W/O emulsion containing kerosene, sorbitan monooleate (Span 80, $C_{24}H_{44}O_6$), and water. The method includes the following steps: (1) prehydrolysis of TEOS; (2) self-assembly of the silicon source with the surfactant. The microspheres synthesized show no agglomeration and do not collapse even after calcination at 700 °C for 8 h. Furthermore the shell of the hollow sphere is mesoporous with pore size in the nm range. The shell is thermally stable and has high specific surface area. These characteristics make it potentially useful in applications like controlled release capsules for drugs, dyes, cosmetics and inks, artificial cells, catalysts, and fillers.

It is well known that emulsion chemistry can be used to control the macroscale topology of silica and other metal oxides.[5,6] The present procedure to prepare the hollow silica microspheres is as follows: TEOS was firstly dissolved in ethanol, and then distilled water and nitric acid were added to promote hydrolyzing of the TEOS. The molar composition of this mixture $TEOS:H_2O:HNO_3:EtOH$ was 1:4:0.01:3. The mixture was vigorously stirred for 30 min at 50 °C. Then the TEOS molecules became water-soluble in the presence of the acid catalyst. The mixed solution began to be changed into a viscous sol, and was poured into a 200 ml Telflon beaker containing 26.1 g kerosene and 7.9 g nonionic surfactant (sorbitan monooleate). The resulting synthetic system was agitated by using a homogenizer at a rate of 500 rpm at 80 °C to form W/O emulsion solution. Complex structured (core–shell) droplets were then formed after gelation (about 1 h) and inorganic–organic microspheres with core-shell structure were precipitated at the bottom of beaker. These spheres were filtrated, washed with hexane, acetone and water, and dried for 3 h at 100 °C. The dispersed spheres with hollow structure were obtained after the organic ‘oil’ and surfactant were removed by calcination at 700 °C for 8 h. The prehydrolysis process was a crucial step, without which it was impossible to produce hollow silica microspheres.

Fig. 1 shows scanning electron microscopy (SEM) (JEOL-6300F) images of the hollow microspheres. It is worth noting that the spheres remain intact and preserve the three-dimensional spherical nature of particles even after calcination (Fig. 1(a)). From the SEM images of the crushed spheres shown in Fig. 1(b,c), we can see clearly the smooth internal structure (this indicates that the silica spheres are of hollow structure). This

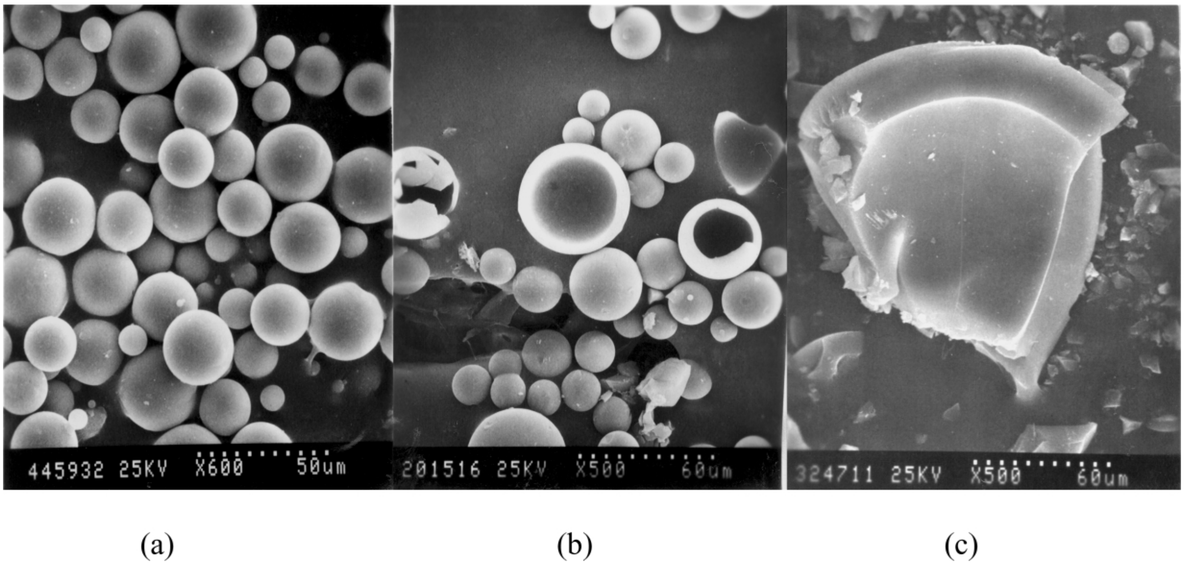
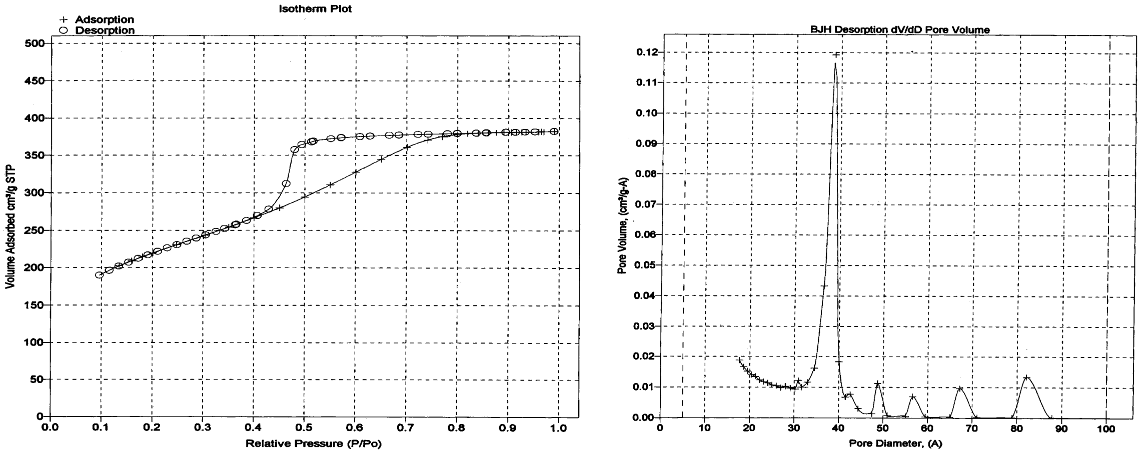


**Fig. 1** SEM images of the hollow microspheres after calcination at 700 °C (a) and crushed hollow silica spherical particles (b, c).

DOI: 10.1039/b206020e



(A) (B)

**Fig. 2** (A) Adsorption–desorption isotherm of nitrogen at 77 K for calcined samples, (B) shows the BJH pore size distribution calculated from the desorption branch of the isotherm.

could be the result of rapid gelation of silica pieces in the water surrounding the oil droplets. Moreover, the kerosene phase outside the water region also provided a complete isolation condition, which avoided the agglomeration among spheres.

On the other hand, we found the inorganic precursors and nonionic surfactant could be assembled into mesophases, which leads to materials with extremely high porosities but less order similar to MSU-x.[7] The porosity of the shell was investigated using nitrogen adsorption–desorption isotherms. As exemplified in Fig. 2, nitrogen absorption isotherms at 77 K for the hollow spheres showed a typical IV isotherm. Typical values for the specific surface area according to the BET method, and the average pore diameter according to BJH calculated from nitrogen isotherms are 875.3 $m^2 g^{-1}$ and 35.7 nm, respectively[8] (Micromeritics ASAP2000). Fig. 3 shows a TEM image of the pore structure of the shells cut from the as-made spheres. It is clear that the pores of shells are mesoporous with random orientations similar to that of the phases made with neutral surfactant with mono-sized pore distribution described by Tanev and Pinnavia[9] and disordered mesoporous silica material by using surfactant in presence of organic salts by Ryoo *et al.*[10] It was suggested that hydrogen bonds between the surfactants and the precursors direct the formation of the mesostructures in the interface of emulsion.[9] For mesoscale structures, this approach generally works well, provided that there is sufficient chemical and interfacial complimentarity between the organic and inorganic components. Small angle X-ray diffraction (XRD) patterns of as-made spheres before and after calcinations didn't exhibit the (100) basal peak and other reflection peaks corresponding to a hexagonal structure consistent with the above TEM image. Furthermore, the results suggest that crystallization did not occur and the mesopore provided a pathway by which liquid could be removed from the hollow spheres during the drying stage, thus keeping the hollow spheres intact.

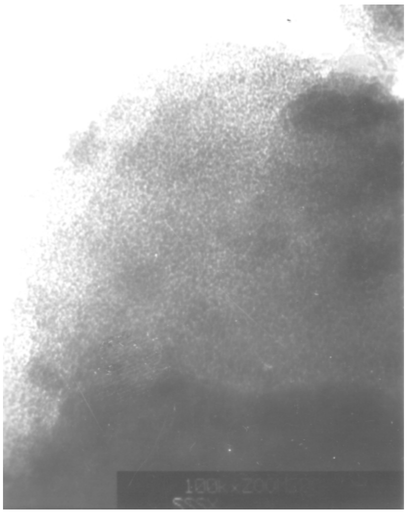


**Fig. 3** TEM image of a crashed calcined spherical particle.

A new method for the preparation of thermally stable hollow silica microspheres has been described using a sol–gel/emulation technology. Owing to their large specific area, stability and surface permeability, the hollow spheres can be used possibly in catalysis, separation technology, and optic electronics. Although the mechanism of the formation of the hollow microspheres is not clear and is still under investigation, this work presents an easy method to control the microstructure during the synthesis of materials. The present approach may also be applied to synthesize analogues of other oxide composition such as Ti–Si, Ai–Si and Zr–Si eta hollow microspheres.

We thank Dr W. Y. Tam at Physics Department, Hong Kong University of Science & Technology for useful suggestions, and thank Dr Sailing He at State Key Laboratory for Modern Optical Instrumentation, Center for Optical and Electromagnetic Research, Zhejiang University for useful discussions.

## Notes and references

1 P. T. Tanev, M. Chibwe and T. J. Pinnavaia, *Nature*, 1994, **368**, 321; Y. N. Jun, D. M. Dabbs, I. A. Aksay and S. Erramilli, *Langmuir*, 1994, **10**, 3377.
2 P. D. Yang, D. Y. Zhao, B. F. Chmelka and G. D. Stucky, *Chem. Mater.*, 1998, **10**, 1033; H. Ringsdorf, B. Schlarb and J. Venzmer, *Angew. Chem., Int. Ed. Engl.*, 1998, **27**, 113.
3 B. Mdischer, Y.-Y. Won, D. S. Ege, J. C.-M. Lee, F. S. Bates, D. E. Discher and D. A. Hammer, *Science*, 1999, **284**, 1143; M. S. Wendland and S. C. Zimmerman, *J. Am. Chem. Soc.*, 1999, **121**, 1389.
4 F. Caruso, X. Shi, R. A. Caruso and A. Susha, *Adv. Mater.*, 2001, **13**, 740; B. Bourlinos, M. A. Karakassides and D. Petridis, *Chem. Commun.*, 2001, 1518; F. Caruso, M. Spasova, A. Susha, M. Giersig and R. A. Caruso, *Chem. Mater.*, 2001, **13**, 109.
5 A. Imhof and D. J. Pine, *Nature*, 1997, **389**, 948.
6 Q. Huo, J. Feng, F. Schuth and G. D. Stucky, *Chem. Mater.*, 1997, **9**, 14.
7 K. Osseo-Asare and F. Arriagada, *J. Colloid. Surf.*, 1990, **50**, 321.
8 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniewska, *Pure Appl. Chem.*, 1985, **57**, 603.
9 P. Tanev and T. Pinnavia, *Science*, 1995, **269**, 1242.
10 R. Ryoo, J. Kim, C.H Shin and J.Y. Lee, *11th International Zeolite Conference*, Seoul, Korea, 1996.