Template Synthesis

DOI: 10.1002/ange.200501556

General Synthetic Route toward Functional Hollow Spheres with Double-Shelled Structures**

*Mu Yang, Jin Ma, Chengliang Zhang,
Zhenzhong Yang,* and Yunfeng Lu**

Hollow spheres and capsules have stimulated great interest because of their potential applications in controlled delivery systems, artificial cells, lightweight fillers, catalysis, and as vessels for confined reactions.[1] Hollow spheres, in particular those with complex core–shell structures, have increasingly attracted interest as a result of their superior properties.[2] For example, a unique plasmon hybridization has been reported on hollow spheres with two concentric metallic nanoshells, thus providing a novel method of tuning resonance frequency by nanostructure engineering.[2a] Polymeric hollow spheres with a movable gold nanoparticle core have also been obtained, which allow the optical sensing of chemicals diffused into the cavity.[2b] In addition, polyelectrolyte capsules with a shell-in-shell structure exhibit an enhanced mechanical strength and preserved permeability.[2d] To date, the synthesis of such complex structures is essentially based on a time-consuming layer-by-layer templating technique, in which layers of desired materials (for example, metals, polymers, and polyelectrolytes) and of sacrificial materials (such as silica) are alternately grown on preformed spheres (for example, silica and polystyrene particles).[2,3]

Herein, we report a one-step approach to the synthesis of hollow spheres with a double-shelled complex structure by using commercial polymer hollow spheres as templates. As shown in Figure 1, a polystyrene hollow sphere containing a thin hydrophilic inner layer and transverse channels of poly(methyl methacrylate)–poly(methacrylic acid) (PMMA–PMA)[2e] is treated with sulfuric acid, and sulfonation takes place in three locations: the exterior shell surface, the interior shell surface, and the transverse channels. This procedure

---

[*] M. Yang, J. Ma, C. Zhang, Prof. Z. Yang
State Key Laboratory of Polymer Physics and Chemistry
Institute of Chemistry, Chinese Academy of Sciences
Beijing 100080 (China)
Fax: (+86) 10-6255-9373
E-mail: yangzz@iccas.ac.cn

Prof. Y. Lu
Department of Chemical and Biomolecular Engineering
Tulane University
New Orleans, LA 70118 (USA)
Fax: (+1) 504-865-6744
E-mail: ylu@tulane.edu

[**] We thank the NSF of China (50573083, 50325313, 20128004, and 90206025), the Chinese Academy of Sciences, and the China Ministry of Science and Technology (KJCX2-SW-H07, 2004-01-09, and 2003CB615600) for financial support.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

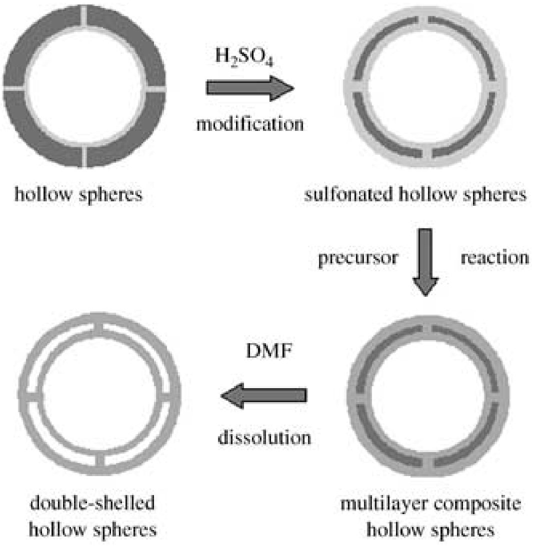

Figure 1. Schematic illustration of the formation of double-shelled hollow spheres.

creates a hollow sphere that contains a hydrophilic inner layer, outer layer, and channels of sulfonated polystyrene gel. Control of the shell thickness of the original polystyrene sphere and the degree of sulfonation allows precise control over the thickness of the hydrophilic sulfonated layers and of the unsulfonated polystyrene middle layer. The sulfonation process produces hydrophilic shells with sulfonic acid ($SO_3^-H^+$) groups that are capable of adsorption or of forming complexes with a large variety of functional components, such as metal ions, metal oxide precursors (for example, titania alkoxides), and basic organic precursors (for example, aniline).[4] Preferential growth of desired materials (such as TiO_2)[4c] within the hydrophilic sulfonated regions followed by removal of the middle polystyrene layer creates various functional composites with a double-shelled structure. This direct approach allows the fabrication of double-shelled functional-composite spheres with controllable shell thickness and shell separation distance.

Figure 2 shows scanning electron micrography (SEM) and transmission electron micrography (TEM) images of unsulfonated spheres, sulfonated spheres, and the resultant double-shelled titania spheres. The unsulfonated hollow spheres (Figure 2a) have an average diameter of 500 nm and a smooth, uniform shell of thickness 80 nm. Sulfonation at 40 °C for 0.5, 2, and 4 h results in sulfonated hollow-sphere templates denoted as S1, S2, and S3, respectively. Compared to the unsulfonated spheres, the S1 spheres (Figure 2b) show a significantly thickened shell (from 80 to 125 nm), a decreased cavity diameter (from 340 to 260 nm), and a slightly deformed spherical shape, which indicate the effective sulfonation and gel formation on both exterior and interior shell surfaces. The appearance of the sulfonic and sulfonyl peaks in the FTIR spectrum further confirms the sulfonation (see Supporting Information). Elemental analysis showed that the S1 spheres contain 2.5 wt% of sulfur atoms. An increase in the sulfonation time to 2 h (sample S2) increased the amount of sulfur to 6.1 wt% and resulted in a thinner unsulfonated polystyrene middle layer, which indicates a higher degree of sulfonation. An excess degree of sulfonation may completely consume the entire polystyrene middle layer, and cause collapse of the structure upon drying. Indeed, the S3 spheres were easily deformed and lost their spherical contour after freeze-drying (see Supporting Information).

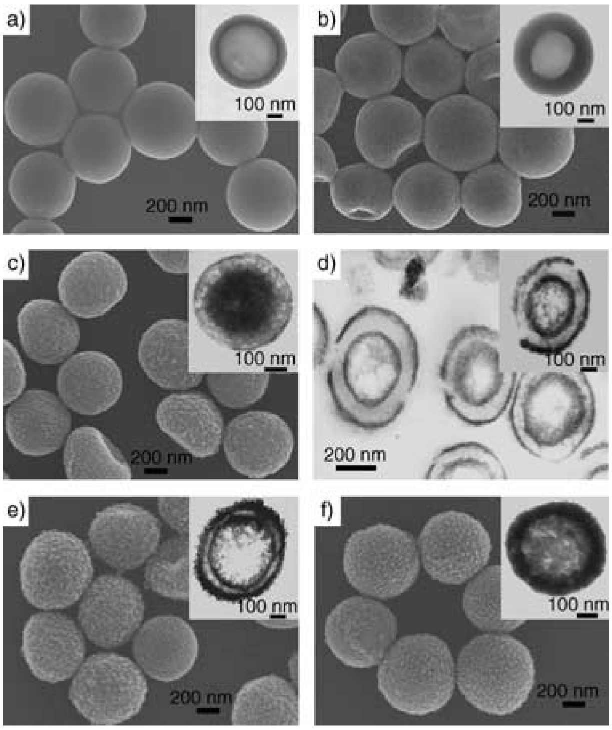

Figure 2. Morphologies of representative templates and titania hollow spheres. a) SEM and TEM (inset) images of unsulfonated polymer hollow-sphere templates. b) SEM and TEM (inset) images of the sulfonated S1 templates. c) SEM image of titania composite hollow spheres templated by S1; the inset shows a TEM image of the corresponding double-shelled titania hollow spheres after treatment with DMF. d) Cross-sectional TEM images of ultramicrotomed titania hollow spheres before and after (inset) treatment with DMF. e) SEM image of titania composite hollow spheres templated by S2; the inset shows a cross-sectional TEM image of the composite hollow spheres after treatment with DMF. f) SEM image of titania composite hollow spheres templated by S3; the inset shows a TEM image of the corresponding titania hollow spheres after treatment with DMF.

We have previously found that tetrabutyl titanate (TBT) can favorably undergo a sol–gel process within sulfonated polystyrene gel to form titania.[4c] The same reactions can be applied to the sulfonated hollow spheres. Figure 2c and d shows the resultant titania spheres produced with S1 as the template. The spheres are approximately 500 nm in diameter (Figure 2c) with a similar morphology to that of the S1 template (Figure 2b). The removal of the polystyrene templates, which was confirmed by the weakening of the characteristic peaks of polystyrene in the FTIR spectrum, creates the double-shelled, concentric titania hollow spheres shown in the TEM image (Figure 2c, inset). The thickness of the shells is around 25 nm and the distance between the shells is around 75 nm, although the contour of the inner shell is somewhat unclearly defined (Figure 2d). The use of sulfonated templates with a higher degree of sulfonation results in hollow titania spheres with an increased diameter and decreased shell-to-shell distance. For example, the S2-templated titania hollow spheres show an average diameter of 580 nm, a reduced shell-to-shell distance of approximately 30 nm, and a thicker shell of 50 nm (Figure 2 e). The use of the S3 template results in 630-nm single-shelled titania hollow spheres (Figure 2 f). These results demonstrate the efficiency of controlling the morphology of the double-shelled structure by simply tuning the degree of sulfonation. As a control experiment, titania spheres were prepared by using the unsulfonated hollow spheres as templates. Titania was formed only within the hydrophilic inner layer[2e] and not on the exterior surface, which indicates the key role of sulfonation in the formation of such double-shelled structures.

The synthesized double-shelled titania hollow spheres are strong enough to survive calcination at 450 °C in air, which removes the polymer and generates titania crystalline phases. In contrast to the dissolution of polystyrene by *N*,*N*-dimethylformamide (DMF), calcination leads to a significant volume contraction. For example, the diameter of the S1-templated titania spheres contracts from 500 to 400 nm (see Figure 3 a and Supporting Information). The inner shell, in particular, contracts remarkably and becomes a movable inner hollow sphere. High-resolution TEM analysis indicates that the nanoparticles in both the shell layers have a crystalline order and form almost fully crystallized inorganic frameworks (see Supporting Information). Increasing the amount of titania in the composite helps to stabilize the double-shelled structure. For example, thermogravimetric analysis (TGA) shows that titania/S1 and titania/S2 composite spheres contain 24.3 and 37.1 wt % titania, respectively. As a result, the S2-templated titania spheres maintain the concentric double-shelled structure after calcination (Figure 3 b and Supporting Information). X-ray diffraction (XRD) studies show that the calcined titania is composed of anatase (Figure 4 a). The average particle size calculated using Scherrer's formula is about 11.4 nm, consistent with the TEM result. A higher calcination temperature (for example, 600 °C) results in a dominant rutile phase with a small amount of the anatase phase (see Figure 4 b and Supporting Information; the calculated average particle size is 32.0 nm) and also deterioration of the spherical structure (see Supporting Information).

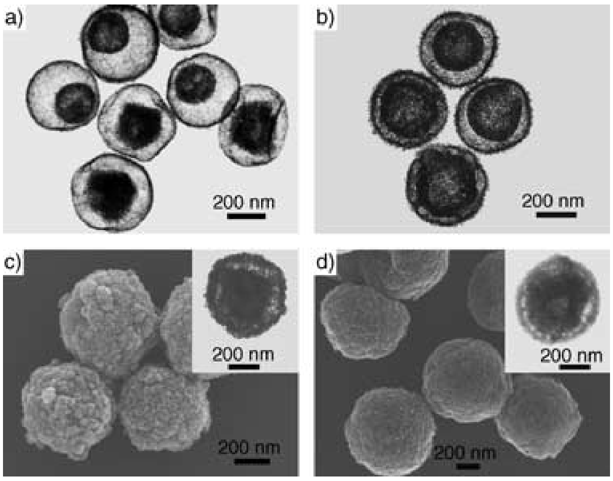

Figure 3. Morphologies of representative double-shelled crystalline metal oxides and conducting polymer hollow spheres. a, b) TEM images of titania hollow spheres templated by S1 and S2, respectively, followed by template removal by calcination at 450 °C in air to form anatase. c) SEM image of double-shelled Fe_3O_4 hollow spheres templated by S2. d) SEM image of double-shelled polyaniline hollow spheres templated by S2. The insets in (c) and (d) show TEM images of the spheres after treatment with DMF.

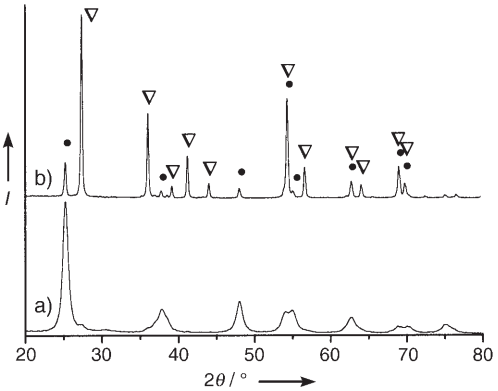

Figure 4. X-ray powder diffraction spectra of TiO_2 hollow spheres calcined at a) 450 and b) 600 °C for 2 h in air (rutile ▽; anatase ●).

The unique template structure combined with the complexation capability of the sulfonic acid groups within the sulfonated layers allows this synthesis approach to be generalized for the production of a large variety of double-shelled composite spheres. For example, double-shelled composite hollow spheres containing crystalline Fe_3O_4 nanoparticles can be fabricated, based on the complex of iron ions and sulfonic acid groups. Figure 3 c shows SEM and TEM (inset) images of the Fe_3O_4 nanoparticle composite spheres prepared with S2 as the template. The composite spheres contain 57 wt % of Fe_3O_4 nanoparticles of diameter 10–15 nm, as deduced from TGA and TEM studies. The positions and relative intensities of all the XRD diffraction peaks (see Supporting Information) are well-matched with those of magnetite (JCPDS card 19-0629). Thus, it can be concluded that magnetite dominates the nanoparticles. The crystallographic form was further verified by its color change from the dark brown of the as-prepared sample to red, which corresponds to maghemite, upon oxidation at 100 °C for 4 h. The average particle size calculated from the XRD data is 11.0 nm. Such crystalline nanoparticles show superparamagnetic behavior at room temperature (see Supporting Information). Similarly, by utilizing acid–base interactions, aniline monomer can favorably be adsorbed within the sulfonated layer. Subsequent polymerization leads to the formation of conductive double-shelled polyaniline composite spheres. Figure 3 d shows the SEM and TEM (inset) images of the polyaniline composite spheres prepared with S2 as the template; the spheres have a smooth surface with well-retained spherical contour. Compared with the easily deformed single-shelled polyaniline hollow spheres,[4d] the double-shelled structure effectively enhances the mechanical stability of the hollow spheres, which is similar to the previous reports of double-shelled polyelectrolyte capsules.[2c,d] As revealed by the FTIR spectrum (see Supporting Information), the resultant polyaniline (36.8 wt% of the composite, estimated from elemental analysis) was doped in situ with the sulfonated polystyrene and formed the emeraldine salt,[5] which resulted in an appreciable conductivity of $6\times 10^{-3}\,\mathrm{S\,cm^{-1}}$. Studies aimed at a detailed understanding and possible applications of such functional spheres are in progress.

In conclusion, we have demonstrated a one-step method for the synthesis of double-shelled composite hollow spheres by using sulfonated hollow spheres as templates. Controlled sulfonation allows the synthesis of templates with tunable thickness of the sulfonated outer layer, sulfonated inner layer, and unsulfonated middle layer. The sulfonation process gives layers with sulfonic acid groups that allow the formation of a wide variety of functional composites. This research provides a novel and efficient approach to the synthesis of various double-shelled functional spheres for many important applications.

Experimental Section

Sulfonated hollow-sphere templates: Freeze-dried polymer hollow spheres[2e] (Rhom & Haas Company) were immersed in concentrated sulfuric acid. Sulfonation at 40 °C for 0.5, 2, and 4 h resulted in the sulfonated hollow-sphere templates denoted as S1, S2, and S3, respectively. The sulfonated spheres were thoroughly rinsed with water and ethanol.

Titania hollow spheres: Freeze-dried sulfonated templates (0.1 g) were immersed in tetrabutyl titanate (TBT)/ethanol (1:1 v/v, 5 mL) for 24 h. After centrifugation and rinsing with ethanol, the resultant materials were transferred to a closed vessel containing ethanol (5 mL) at ambient temperature. Water (5 mL) was then added to the dispersion with stirring, and the sol–gel process was allowed to proceed for 4 h. Double-shelled titania hollow spheres were obtained after centrifugation, rinsing with ethanol, and template removal by dissolution in DMF or calcination at 450 °C for 2 h in air.

Magnetite hollow spheres: Freeze-dried S2 (0.1 g) was immersed in ammonium hydroxide (10 M, 5 mL) for 12 h before transfer to a solution containing water (10 mL). Aqueous ferrous chloride/ferric chloride (1:2 M, 0.6 mL) was then added dropwise with stirring under a nitrogen atmosphere.[6] Magnetite hollow spheres were obtained after the polymer was dissolved with DMF and collected by a magnet (see Supporting Information). The collected spheres could be readily redispersed by ultrasonication.

Polyaniline hollow spheres: Freeze-dried S2 (0.1 g) was dispersed in water (10 mL) containing monomeric aniline (0.1 g) with stirring. After 2 h, aqueous ferric chloride (1 M, 0.5 mL) was added to initiate oxidative polymerization at room temperature for 24 h. Polyaniline hollow spheres were obtained after centrifugation and treatment with DMF to dissolve the polystyrene.

Characterization: The structure and morphology of the spheres were characterized by TEM (JEOL 100CX instrument operated at 100 kV) and SEM (Hitachi S-4300 instrument operated at an accelerating voltage of 15 kV). TEM samples were prepared by dispersing the spheres from dilute ethanol dispersions onto carbon-coated copper grids or by the ultramicrotoming technique. The ultramicrotomed samples were prepared by embedding the spheres in resin and ultramicrotoming to form 30–50-nm-thick slices with a Leica ultracut UCT ultramicrotome at room temperature. The SEM samples were prepared by vacuum sputtering of Pt onto the dried samples at ambient temperature.

FTIR spectroscopy was performed using a Bruker Equinox 55 spectrometer with the samples pressed into KBr pellets. X-ray powder diffractometry (Rigaku D/max-2500) was used to characterize the crystalline phases of the materials. A Perkin-Elmer TGA 7 apparatus was used to determine the inorganic content of the composite spheres. Elemental analysis was carried out with a Flash EA-1112 apparatus. A vibrating-sample magnetometer (VSM JDM-13) was used to characterize the magnetic properties of the magnetite composite spheres. Conductivity measurements were performed on pieces of compressed dry powder by using a standard four-probe method at room temperature.[4d]

Received: May 7, 2005
Revised: July 1, 2005

Keywords: nanostructures · polymers · sol–gel processes · template synthesis · titanium

[1] a) F. Caruso, *Chem. Eur. J.* **2000**, *6*, 413; b) F. Caruso, *Adv. Mater.* **2001**, *13*, 11; c) F. Caruso, R. A. Caruso, H. Möhwald, *Science* **1998**, *282*, 1111; d) D. L. Wilcox, M. Berg, T. Bernat, D. Kelleman, J. K. Cochran, *Hollow and Solid Spheres and Microspheres: Science and Technology Associated with Their Fabrication and Application, Vol. 372*, Materials Research Society Proceedings, Pittsburgh, **1994**.

[2] a) E. Pordan, C. Radloff, N. J. Halas, P. Nordlander, *Science* **2003**, *302*, 419; b) K. Kamata, Y. Lu, Y. N. Xia, *J. Am. Chem. Soc.* **2003**, *125*, 2384; c) Z. F. Dai, L. Dähne, H. Möhwald, B. Tiersch, *Angew. Chem.* **2002**, *114*, 4191; *Angew. Chem. Int. Ed.* **2002**, *41*, 4019; d) Z. F. Dai, H. Möhwald, B. Tiersch, L. Dähne, *Langmuir* **2002**, *18*, 9533; e) M. Yang, J. Ma, Z. W. Niu, H. F. Xu, Z. K. Meng, Y. F. Lu, Z. B. Hu, Z. Z. Yang, *Adv. Funct. Mater.* **2005**, *15*, 1523.

[3] a) K. Zhang, X. H. Zhang, H. T. Chen, L. L. Zheng, J. H. Zhang, B. Yang, *Langmuir* **2004**, *20*, 11312; b) M. Kim, K. Sohn, H. B. Na, T. Hyeon, *Nano Lett.* **2002**, *2*, 1383; c) J. Y. Kim, S. B. Yoon, J.- S. Yu, *Chem. Commun.* **2003**, 790; d) A. G. Dong, N. Ren, W. L. Yang, Y. J. Wang, Y. H. Zhang, D. J. Wang, J. H. Hu, Z. Gao, Y. Tang, *Adv. Funct. Mater.* **2003**, *13*, 943.

[4] a) R. F. Ziolo, E. P. Giannelis, B. A. Weinstein, M. P. O'Horo, B. N. Ganguly, V. Mehrotra, M. W. Russell, D. R. Huffman, *Science* **1992**, *257*, 219; b) M. Breulmann, S. A. Davis, S. Mann, H. P. Hentze, M. Antonietti, *Adv. Mater.* **2000**, *12*, 502; c) Z. Z. Yang, Z. W. Niu, Y. F. Lu, Z. B. Hu, C. C. Han, *Angew. Chem.* **2003**, *115*, 1987; *Angew. Chem. Int. Ed.* **2003**, *42*, 1943; d) Z. W. Niu, Z. Z. Yang, Z. B. Hu, Y. F. Lu, C. C. Han, *Adv. Funct. Mater.* **2003**, *13*, 949.

[5] a) Z. X. Wei, M. X. Wan, *Adv. Mater.* **2002**, *14*, 1314; b) A. L. Briseno, S. Han, I. E. Rauda, F. M. Zhou, *Langmuir* **2004**, *20*, 219; c) S. A. Chen, H. T. Lee, *Macromolecules* **1995**, *28*, 2858.

[6] a) Y. S. Kang, S. Risbud, J. F. Rabolt, P. Stroeve, *Chem. Mater.* **1996**, *8*, 2209; b) L. A. Harris, J. D. Goff, A. Y. Carmichael, J. S. Riffle, J. J. Harburn, J. G. St. Pierre, M. Saunders, *Chem. Mater.* **2003**, *15*, 1367.