

# Porous polystyrene microspheres having dimpled surface structures prepared within micellar assemblies of amphiphilic silica particles in water

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**Production of porous polystyrene microspheres having dimpled surface structures was demonstrated using amphiphilic and hydrophobic silica particles as structure-directing agents.**

Since the discovery of mesoporous silicates based on amphiphilic supramolecular templates,<sup>1</sup> the use of surfactant molecules to organize mesoporous or macroporous oxides has been investigated over a wide range of conditions.<sup>2</sup> Self-assembly of colloidal suspensions provides another versatile approach to the fabrication of macroporous oxides,<sup>3</sup> metals,<sup>4</sup> polymers,<sup>5</sup> and carbons,<sup>6</sup> with potential applications in catalysis, sensors, optical devices, and host materials for organic and inorganic substances. The advantages of these template-directed methods are their size tunability of pores and the simple procedure including immersion or impregnation of desired precursors onto the templates and subsequent removal of the templates.

Recently, we have found that amphiphilic silica particles, which were prepared by a partial modification of their surfaces with an alkylsilylation agent, form a micellar assembly similar to molecular surfactants to solubilize hydrophobic polystyrene (PS).<sup>7</sup> The micellar assembly, moreover, resulted in the formation of spherical PS particles with several semispherical dimples imprinting morphologies of silica shells on their surfaces after removal of the silica particles with aqueous HF solution. These findings indicate the possibility of using amphiphilic silica particles as a template or a host material for syntheses of various kinds of spherical particles.

Based on this idea, we propose here a novel template-directed method for fabrication of porous PS microspheres with a “golf ball-like” dimpled surface structure using monodispersed silica particles having two different surface properties: one has an amphiphilic surface and the other has a hydrophobic surface. The strategy is based on the formation of a micellar assembly of amphiphilic silica particles to solubilize PS and hydrophobic silica particles. We expected that the amphiphilic particles would act as a template to form spherical materials with a dimpled surface and

that the hydrophobic ones would act as a template to form meso- and/or macro-porous structures.

Spherical monodispersed silica particles (SiO<sub>2</sub>) with sizes of 50 nm, 250 nm and 400 nm in diameter were prepared by Stöber's method.<sup>8</sup> Amphiphilic SiO<sub>2</sub> particles with external surface partially covered with alkylsilane (w/o-SiO<sub>2</sub>) were prepared by a previously reported procedure.<sup>7,9</sup> To 50 cm<sup>3</sup> of toluene containing 2.5 mmol of *n*-octadecyltrimethoxysilane, 2.5 g of SiO<sub>2</sub> particles (250 nm or 400 nm) thoroughly mixed with 12 wt% of water was added and the suspension was shaken for 2 min at room temperature. After the addition of triethylamine (2.5 mmol), the suspension was further shaken for 10 min at room temperature. Then the solid was collected by centrifugation, washed twice with ethanol, and dried at 383 K for 2 h under vacuum. SEM observation of the as-obtained w/o-SiO<sub>2</sub> particles, their remaining hydrophilic surfaces having had been selectively modified with colloidal gold particles, revealed that each particle has an asymmetric surface structure; one side of the surface is hydrophilic and the other is hydrophobic.<sup>7</sup> Modified silica particles with external surfaces fully covered with alkylsilane (o-SiO<sub>2</sub> (50 nm or 250 nm)) were also prepared without mixing water in the first step of the above-described procedure for preparation of w/o-SiO<sub>2</sub>.

A composite of PS and o-SiO<sub>2</sub> (core)-w/o-SiO<sub>2</sub> (shell), the precursor of porous PS microspheres, was synthesized as follows. In 1.5 cm<sup>3</sup> of toluene containing 0.25 g of PS (Wako, Mw = 200 000), 0.05 g of w/o-SiO<sub>2</sub> or 0.2 g of o-SiO<sub>2</sub> was suspended by sonication for a few minutes in an ice bath. Then the two suspensions of w/o-SiO<sub>2</sub> and o-SiO<sub>2</sub> particles were mixed, added to 10 cm<sup>3</sup> of water, and sonicated for 2 h in an ice bath. After standing the mixture overnight at room temperature, white precipitates thus-obtained in the bottom part of the aqueous phase were collected and dried at 333 K. As a reference, a composite of PS (core)-w/o-SiO<sub>2</sub> (shell) was also prepared without addition of o-SiO<sub>2</sub> in the above-described procedure.<sup>7</sup>

Fig. 1a–1c show typical SEM images of thus-obtained composites. As has been reported previously, without addition of o-SiO<sub>2</sub> during the above-described procedure, w/o-SiO<sub>2</sub> forms a spherical assembly (Fig. 1a) with sizes of 2–3 μm in diameter under the present conditions.<sup>7</sup> As can be seen in Fig. 1b and c, the tightly packed micellar assemblies of SiO<sub>2</sub> particles were also observed when o-SiO<sub>2</sub> particles were mixed with w/o-SiO<sub>2</sub> particles. It was impossible to determine whether the w/o-SiO<sub>2</sub> particles or o-SiO<sub>2</sub> particles formed the assembly when w/o-SiO<sub>2</sub> and o-SiO<sub>2</sub> particles with the same sizes (250 nm) were employed (Fig. 1b). However, the composite obtained from w/o-SiO<sub>2</sub> (400 nm) and o-SiO<sub>2</sub>

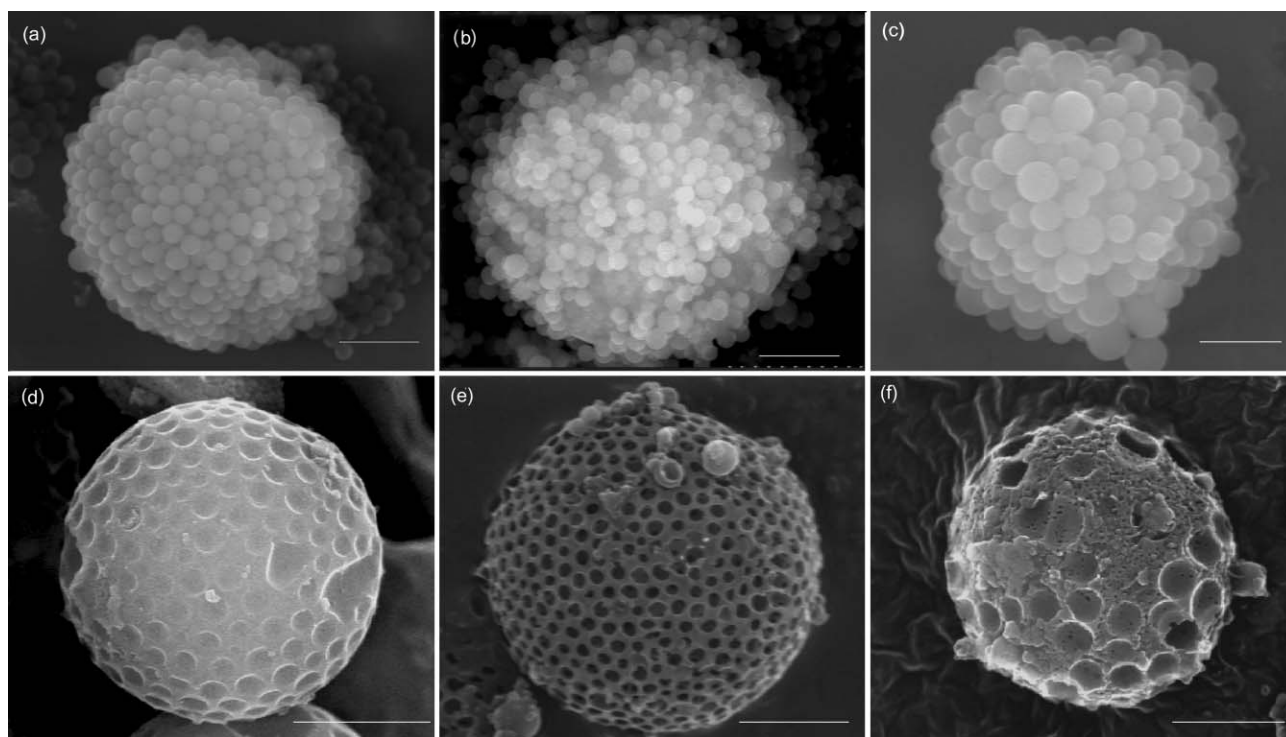
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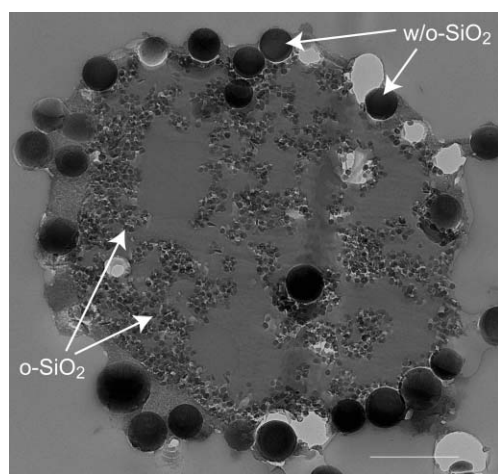


**Fig. 1** SEM images of spherical assemblies and PS particles prepared from (a, d) w/o-SiO<sub>2</sub> particles (250 nm), (b, e) w/o-SiO<sub>2</sub> particles (250 nm) with o-SiO<sub>2</sub> particles (250 nm), and (c, f) w/o-SiO<sub>2</sub> particles (400 nm) with o-SiO<sub>2</sub> particles (50 nm). Scale bars correspond to 1.0 μm.

(50 nm) particles (Fig. 1c) clearly shows the assembled structure composed of w/o-SiO<sub>2</sub> particles.

For further structural clarification of the composite, a cross-section of the composite obtained from w/o-SiO<sub>2</sub> (400 nm) and o-SiO<sub>2</sub> (50 nm) was observed by TEM. The sample for the observation was prepared by cutting an epoxy-resin-stabilized sample with a microtome into slices of *ca.* 200 nm of thickness.

A representative result is shown in Fig. 2. It is clear that w/o-SiO<sub>2</sub> particles of 400 nm in diameter surround a μm-sized lump, which was found to be composed of PS, and several o-SiO<sub>2</sub> particles of 50 nm in diameter. Hence, we confirmed that the



**Fig. 2** TEM image of a cross-section of the spherical assembly prepared from w/o-SiO<sub>2</sub> (400 nm) and o-SiO<sub>2</sub> particles (50 nm) (Fig. 1c). Scale bar corresponds to 1.0 μm.

assembly of amphiphilic w/o-SiO<sub>2</sub> particles encapsulate both hydrophobic components of PS and o-SiO<sub>2</sub> simultaneously to produce a core (PS and o-SiO<sub>2</sub>)-shell (w/o-SiO<sub>2</sub>) structure.

Fig. 1d–f show representative SEM images of PS particles obtained from the core-shell composites after dissolution of SiO<sub>2</sub> components with aqueous 50% HF solution. In our previous study,<sup>7</sup> we demonstrated that removal of w/o-SiO<sub>2</sub> particles from the PS (core)-w/o-SiO<sub>2</sub> (shell) composite with aqueous 50% HF solution resulted in the formation of microspheres having several semispherical dimples on their surfaces (*n*-PS, Fig. 1d). Since the core part of the composite was filled with PS, the resulting PS particles should be non-porous. On the other hand, the PS microspheres isolated from the PS and o-SiO<sub>2</sub> (core)-w/o-SiO<sub>2</sub> (shell) composites had porous structures, *i.e.*, in addition to the surface semispherical dimples, spherical pores were observed in the inner parts of the PS particles (Fig. 1e and 1f). Moreover, the size of those spherical pores varied depending on the particle size of o-SiO<sub>2</sub> used; much smaller pores were observed on the sample obtained using o-SiO<sub>2</sub> particles of 50 nm in diameter (*p*<sub>50</sub>-PS) than those on the sample obtained using o-SiO<sub>2</sub> particles of 250 nm in diameter (*p*<sub>250</sub>-PS). Hence, it is likely that the porous structures in the PS microspheres are the imprints of morphologies and sizes of o-SiO<sub>2</sub> particles used.

Table 1 shows BET surface areas and average particle sizes of *n*-PS, *p*<sub>250</sub>-PS, and *p*<sub>50</sub>-PS. The former were determined by N<sub>2</sub> absorption at 77 K and the latter were determined by measuring more than 100 samples on SEM images. The *n*-PS microspheres showed a BET surface area of 3 m<sup>2</sup> g<sup>-1</sup>. This value is slightly larger than the estimated surface area of PS microspheres without semispherical dimples (*ca.* 2 m<sup>2</sup> g<sup>-1</sup>), which was calculated from the density of PS (1.06 g cm<sup>-3</sup>) and the average particle size

**Table 1** Comparison of BET surface area and average particle size of *n*-PS, *p*<sub>250</sub>-PS and *p*<sub>50</sub>-PS

Sample	Sa <sub>BET</sub> <sup>a</sup> /m <sup>2</sup> g <sup>-1</sup>	P <sub>ave</sub> <sup>b</sup> /μm
<i>n</i> -PS	3.0	2.6
<i>p</i> <sub>250</sub> -PS	27.0	4.5
<i>p</i> <sub>50</sub> -PS	34.0	3.6

<sup>a</sup> BET surface area. <sup>b</sup> Average particle size.

(2.6 μm). This is probably due to the existence of semispherical dimples on the surface of the *n*-PS microsphere. It is noteworthy that the *p*<sub>250</sub>-PS and *p*<sub>50</sub>-PS microspheres showed remarkably large surface areas in comparison with that of the *n*-PS microsphere even though they had relatively large particle sizes. These results give clear evidences for the porous structures of *p*<sub>250</sub>-PS and *p*<sub>50</sub>-PS microspheres. When we assumed a closely packed arrangement of o-SiO<sub>2</sub> particles in the hydrophobic core, the surface areas of the *p*<sub>250</sub>-PS and *p*<sub>50</sub>-PS microspheres were calculated to be 40 and 47 m<sup>2</sup> g<sup>-1</sup>, respectively. The relatively small surface areas of *p*<sub>250</sub>-PS and *p*<sub>50</sub>-PS microspheres shown in Table 1 were therefore attributed to the loose packing of o-SiO<sub>2</sub> particles in the core in the present conditions. This postulation is consistent with the cross-sectional SEM image shown in Fig. 2.

Thus, we have demonstrated that amphiphilic and hydrophobic particles act as templates for the syntheses of spherical porous materials having dimpled surface structures. The amphiphilic w/o-SiO<sub>2</sub> particles are assembled at the phase boundary of the PS/o-SiO<sub>2</sub>/toluene droplet in water, facing the hydrophobic surface to the oil droplet phase and the hydrophilic side to the outer water phase. In this situation, the droplets could be stabilized during the successive removal of the solvent (toluene) to retain the spherical structure. Then, removal of SiO<sub>2</sub> components from the composites provide PS particles having dimples and pores. Although we have only used a PS polymer as a starting material, we expect that the present method can be applied to spherical polymer syntheses by conventional polymerization techniques from monomer molecules to obtain higher yields of products. The polymers thus-obtained, moreover, should have potential applications in catalysts and adsorbents. Studies along these lines are now underway.

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## Notes and references

- (a) J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Shpepard, S. B. Mccullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834–10843; (b) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710–712; (c) S. Inagaki, A. Koiwai, N. Suzuki, Y. Fukushima and K. Kuroda, *Bull. Chem. Soc. Jpn.*, 1996, **5**, 1449–1457.
- (a) D. Y. Zhao, J. L. Feng, Q. S. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548–552; (b) S. Che, Z. Liu, T. Ohsuna, K. Sakamoto, O. Terasaki and T. Tatsumi, *Nature*, 2004, **429**, 281–284.
- (a) A. Imahof and D. J. Pine, *Nature*, 1997, **389**, 948–951; (b) J. L. Blin, A. Leonard, Z. Y. Yuan, L. Gigot, A. Vantomme, A. K. Cheetham and B. L. Su, *Angew. Chem. Int. Ed.*, 2003, **42**, 2872–2875.
- (a) T. Hyeon, S. S. Lee, J. Park, Y. Chung and H. Bin Na, *J. Am. Chem. Soc.*, 2001, **123**, 12798–12801; (b) N. R. Jana, L. Gearheart and C. J. Murphy, *Adv. Mater.*, 2001, **13**, 1389–1393; (c) L. M. Liz-Marzán and I. Lado-Touriño, *Langmuir*, 1996, **12**, 3585–3589.
- (a) J. Jang and H. Ha, *Langmuir*, 2002, **18**, 5613–5618; (b) L. M. Gan, C. H. Chew, K. C. Lee and S. C. Ng, *Polymer*, 1994, **35**, 2659–2664; (c) M. Antonietti and K. Landfester, *Prog. Polym. Sci.*, 2002, **27**, 689–757.
- (a) S. Jun, S. H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna and O. Terasaki, *J. Am. Chem. Soc.*, 2000, **122**, 10721–10713; (b) R. Ryoo, S. H. Joo, M. Kruk and M. Jaroniec, *Adv. Mater.*, 2001, **13**, 677–681; (c) C. Yu, J. Fan, B. Tian, D. Zhao and G. D. Stucky, *Adv. Mater.*, 2002, **14**, 1742–1745.
- Y. K. Takahara, S. Ikeda, K. Tachi, S. Ishino, K. Ikeue, M. Matsumura and B. Ohtani, *J. Am. Chem. Soc.*, 2005, **127**, 6271–6275.
- W. Stober, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, **26**, 62–69.
- (a) H. Nur, S. Ikeda and B. Ohtani, *Chem. Commun.*, 2000, 2235–2236; (b) H. Nur, S. Ikeda and B. Ohtani, *J. Catal.*, 2001, **204**, 402–408; (c) S. Ikeda, H. Nur, T. Sawadaishi, K. Ijiri, M. Shimomura and B. Ohtani, *Langmuir*, 2001, **17**, 7976–7979; (d) S. Ikeda, H. Nur, P. Wu, T. Tatsumi and B. Ohtani, *Stud. Surf. Sci. Catal.*, 2003, **145**, 251–254; (e) S. Ikeda, Y. Kowata, K. Ikeue, M. Matsumura and B. Ohtani, *Appl. Catal. A*, 2004, **265**, 69–74; (f) K. Ikeue, S. Ikeda, A. Watanabe and B. Ohtani, *Phys. Chem. Chem. Phys.*, 2004, **6**, 2523–2528.