

Asymmetrically Modified Silica Particles: A Simple Particulate Surfactant for Stabilization of Oil Droplets in Water

Yoshiko K. Takahara,[†] Shigeru Ikeda,^{*,†,‡} Satoru Ishino,[†] Koji Tachi,[†] Keita Ikeue,[‡] Takao Sakata,[†] Toshiaki Hasegawa,[†] Hirotarō Mori,[†] Michio Matsumura,[†] and Bunsho Ohtani[§]

Contribution from the Research Center for Solar Energy Chemistry, Osaka University, 1-3 Machikaneyama, Toyonaka 560-8531, Japan, PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi 332-0012, Japan, Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, 7-1, Mihogaoka, Ibaraki 567-0047, Japan, and Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan

Received October 22, 2004; E-mail: sikeda@chem.es.osaka-u.ac.jp

Abstract: Spherical silica particles that are able to assemble at a phase boundary of a dual-phase mixture of water and an immiscible organic solvent were prepared by a partial modification of their surface hydroxyl groups with an alkylsilylation agent. Scanning electron microscopic observation of these particles in which their remaining surface hydroxyl groups 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. We found that these particles could form a micellar structure in water in the presence of an organic solution of a toluene/polystyrene mixture. The micellar structure was evidenced by formation of golf-ball-like polystyrene particles with dimples imprinting morphologies of the hydrophobic part of modified silica particles.

Introduction

Spherical colloid particles have recently received much attention because of the wide ranges of their applications for material synthesis. These particles, for example, represent the simplest form of building blocks that can be readily self-assembled into three-dimensionally ordered structures, i.e., colloidal crystals.¹ Such a system has various potential applications, such as templates for the fabrication of nano- and microporous materials² and use in photonic crystal devices.³ Coating of colloidal particles with layers of materials such as polymers, metal oxides, and metal nanoparticles, resulting in the formation of core-shell composites,⁴ has been another subject of intense investigations. These materials are interesting

because they have characteristics unique to composite particles⁵ and because they can be used as precursors of hollow spheres.⁶

Such functional particulate materials have been prepared by modification of the surfaces of spherical particles by in situ or post-reaction with appropriate agents, which are suited to desired applications. For example, the surface hydrophobicity of spherical silica particles was controlled by a post-modification of surface hydroxyl groups with an alkylsilane agent;⁷ the hydrophobic-hydrophilic balance is tunable by changing the amount of the agent used as a modifier.⁸ Particles modified by conventional methods had surfaces with homogeneous or symmetrical structure. If we could modify half of the surface of each silica particle with a hydrophobic agent and leave the

[†] Osaka University.

[‡] PRESTO, Japan Science and Technology Agency.

[§] Hokkaido University.

- (1) (a) Sunkara, H. B.; Jethmalani, J. M.; Ford, W. T. *Chem. Mater.* **1994**, *6*, 362–364. (b) Weissman, J. M.; Sunkara, H. B.; Tse, A. S.; Asher, S. A. *Science* **1996**, *274*, 959–963.
- (2) (a) Zakhidov, A. A.; Baughman, R. H.; Iqbal, Z.; Cui, C.; Khayrullin, I.; Dantas, S. O.; Marti, J.; Ralchenko, V. G. *Science* **1998**, *282*, 897–901. (b) Johnson, S. A.; Ollivier, P. J.; Mallouk, T. E. *Science* **1999**, *283*, 963–965. (c) Jiang, P.; Cizeron, J.; Bertone, J. F.; Colvin, V. L. *J. Am. Chem. Soc.* **1999**, *121*, 7957–7958. (d) Jiang, P.; Hwang, K. S.; Mittleman, D. M.; Bertone, J. F.; Colvin, V. L. *J. Am. Chem. Soc.* **1999**, *121*, 11630–11637. (e) Velev, O. D.; Kaler, E. W. *Adv. Mater.* **2000**, *12*, 531–534. (f) Sen, T.; Tiddy, G. J. T.; Casci, J. L.; Anderson, M. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 4649–4653.
- (3) (a) Holtz, J. M.; Asher, S. A. *Nature* **1997**, *389*, 829–832. (b) Vlasov, Y. A.; Yao, N.; Norris, D. J. *Adv. Mater.* **1999**, *11*, 165–169. (c) Blanco, A.; Chomski, E.; Grabtchak, M. I.; John, S.; Leonard, S. W.; Lopez, C.; Meseguer, F.; Miguez, H.; Mondia, J. P.; Ozin, G. A.; Toader, O.; van Driel, H. M. *Nature* **2000**, *405*, 437–440. (d) Zhang, H.; Cooper, A. I. *Chem. Mater.* **2002**, *14*, 4017–4020.

- (4) (a) Hofman-Caris, C. H. M. *New J. Chem.* **1994**, *18*, 1087–1096. (b) Huang, C. L.; Matijevic, E. *J. Mater. Res.* **1995**, *10*, 1327–1334. (c) Fleming, M. S.; Mandal, T. K.; Walt, D. R. *Chem. Mater.* **2001**, *13*, 2210–2216. (d) Graf, C.; Vossen, D. L. J.; Imhof, A.; van Blaaderen, A. *Langmuir* **2003**, *19*, 6693–6700.
- (5) (a) Westcott, S. L.; Oldenburg, S. T.; Lee, T. R.; Halas, N. J. *Langmuir* **1998**, *14*, 5396–5401. (b) Caruso, F. *Adv. Mater.* **2001**, *13*, 11–22. (c) Graf, C.; van Blaaderen, A. *Langmuir* **2002**, *18*, 524–534. (d) Matsuno, R.; Yamamoto, K.; Otsuka, H.; Takahara, A. *Chem. Mater.* **2003**, *15*, 3–5. (e) Hiramatsu, H.; Osterloh, F. E. *Langmuir* **2003**, *19*, 7003–7011.
- (6) (a) Caruso, R. A.; Sush, A.; Caruso, F. *Chem. Mater.* **2001**, *13*, 400–409. (b) Imhof, A. *Langmuir* **2001**, *17*, 3579–3585. (c) Tissot, I.; Reymond, J. P.; Lefebvre, F.; Bourgeat-Lami, E. *Chem. Mater.* **2002**, *14*, 1325–1331. (d) Kim, S.-W.; Kim, M.; Lee, W. Y.; Hyeon, T. *J. Am. Chem. Soc.* **2002**, *124*, 7642–7643. (e) Jang, J.; Li, X. L.; Oh, J. H. *Chem. Commun.* **2004**, 794–795.
- (7) (a) Fadeev, A. Y.; Eroshenko, V. A. *J. Colloid Interface Sci.* **1997**, *187*, 275–282. (b) Brandriss, S.; Margel, S. *Langmuir* **1993**, *9*, 1232–1240. (c) Stenger, D. A.; Georger, J. H.; Dulcey, C. S.; Hickman, J. J.; Rudolph, A. S.; Nielsen, T. B.; Mccort, S. M.; Calvert, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 8435–8442. (d) Ogawa, H.; Sawamura, K.; Chihara, T. *Catal. Lett.* **1992**, *16*, 39–42.
- (8) Stevens, M. J. *Langmuir* **1999**, *15*, 2773–2778.

rest unmodified, we would obtain amphiphilic silica, or an asymmetrical structure. The anisotropic surface structure would be useful for many applications.

There have been a few methods reported for site-selective modification of the surfaces of spherical particles to obtain materials having intrinsic asymmetry.⁹ These methods are generally based on arrangement of the target particles at a gas–liquid, liquid–liquid, or liquid–solid interface followed by attachment of desired agents from one phase. However, since scaling up the batch size to yield a large quantity of products is difficult by using these methods, applications of these methods have been limited.

Recently, we have developed a facile method for preparing a large quantity of catalyst particles, each having both hydrophobic and hydrophilic surfaces, by partial modification of the external surfaces with a long-chain alkylsilane agent.¹⁰ One of the most notable features of the particles is that particles thus-obtained spontaneously assemble at a liquid–liquid phase boundary between aqueous and water-immiscible organic liquids. This property provides these particles efficient catalytic activities for chemical reactions occurring between agents separately included in aqueous and oil phases.

To prove the asymmetric structure of these catalyst particles, we labeled the hydrophilic surface with a fluorescent dye molecule and observed fluorescence from part of each particle under a fluorescent microscope.^{10c} However, because of the insufficient resolution of fluorescence microscopy and because of the wide range of particle sizes of catalyst particles used, the asymmetric surface structure could not be accurately demonstrated.

In the present study, therefore, we tried to demonstrate the usefulness of the method for making an asymmetric structure using monodispersed spherical silica particles with a submicrometer size. To identify different surface properties on a particle, we attached gold particles to the hydrophilic surface and monitored the gold particles with a scanning electron microscope. Moreover, we used these amphiphilic silica particles as a surfactant to solubilize organic materials in water. Evidence for a micellar structure was formation of golf-ball-like polymer particles with dimples imprinting spherical morphologies of the surfactant particles.

Experimental Section

Materials. Reagent-grade tetraethyl orthosilicate (TEOS) was obtained from Aldrich, and *n*-octadecyltrimethoxysilane (ODMS) and *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPTMS) were obtained from Gelest. The highest available grade of toluene, triethylamine, ethanol, hydrogen tetrachloroaurate (III) tetrahydrate (HAuCl₄), trisodium citrate dihydrate (Na–CA), a 28 wt % solution of ammonia, and polystyrene (PS) beads (*M_w* = 200 000) were purchased from WAKO. Fifty weight-percent of aqueous hydrofluoric acid (HF) solution was supplied from Morita Chemical Co. All reagents were

used as received. Laboratory-grade water with a measured resistivity of 18.2 MΩ·cm was prepared by using a Milli-Q pure water system (YAMATO, Millipore).

Silica Particles. Four kinds of spherical monodispersed silica particles with diameters of 250, 300, 400, and 660 nm were used in this study. The sample with a size of 300 nm in diameter was supplied by Nippon Shokubai (SEAHOSTER KEP30), and others were prepared by the Stöber method as follows.¹¹ To an Erlenmeyer flask of 500 cm³ capacity was added 250 cm³ of mixed solution composed of water, ethanol, and ammonia. The molar composition of the mixed solution was altered, depending on the desired size of silica particles. The compositions were water/ethanol/ammonia = 3.75/3.1/0.0625, 3.75/3.07/0.125, and 3.75/2.4/1.55 for the syntheses of silica particles of 250, 400, and 660, nm in diameter, respectively. To each of these aqueous solutions, 70 mmol of TEOS was added. The mixture was shaken at a rotation rate of 100 rpm using an ASONE SRR-2 reciprocal shaker for 2 h at room temperature, and white products were formed. They were collected by centrifugation (15 000–20 000 rpm, 15 min) and washed by repeating redispersion in pure ethanol at least five times. The final precipitates were dried at 383 K under vacuum. These bare samples are called w-SIO.

Surface Modification of w-SIO with an Alkylsilylation Agent.¹⁰ To 50 cm³ of toluene containing 2.5 mmol of ODMS was added a mixture of 2.5 g of w-SIO thoroughly mixed with 0.3 cm³ of water, and the suspension was stirred for 2 min at room temperature. After the addition of triethylamine (2.5 mmol), the suspension was further stirred for 10 min at room temperature. Then the solid was collected by centrifugation (3000 rpm, 10 min), washed twice with ethanol (50 cm³), and dried at 383 K for 3 h under vacuum. The thus-obtained silica particles partially covered with alkylsilyl groups on their external surfaces were called w/o-SIO. As a reference, modified silica particles whose external surfaces were thoroughly covered with alkylsilane were also prepared without mixing water in the first step of the above-described procedure for preparation of w/o-SIO; they are called o-SIO.

Preparation of Aqueous Colloidal Dispersion of Gold Particles. An aqueous suspension of citrate-stabilized colloidal gold particles (20–50 nm) was prepared by the method reported by Frens.¹² To 50 cm³ of aqueous HAuCl₄ solution (0.01 wt %) heated to boiling was added 0.6 cm³ of aqueous solution containing 0.23 mmol of Na–CA. During boiling for 5 min, the initially blue-colored solution turned red, indicating the formation of monodispersed gold particles. After cooling the solution at room temperature, 0.03 mmol Na–CA was dissolved, and the solution was stored at room temperature for later use.

Loading of Gold Particles on the Hydrophilic Surfaces of Bare and Modified SiO₂. Attachment of colloidal gold particles to silica particles was performed using a procedure similar to that reported in the literature.¹³ To 50 cm³ of toluene containing 21 mmol of AEAPTMS was added 0.5 g of w-SIO, w/o-SIO, or o-SIO. After stirring the suspension for 16 h at room temperature, the solid was collected by centrifugation (3000 rpm, 5 min), washed five times with 50 cm³ of ethanol, and dried at 383 K for 2.5 h under vacuum. As-obtained aminoalkylated silica particles (0.5 mg) were then dispersed in 1 cm³ of water, and the suspension was added dropwise to 10 cm³ of the above prepared citrate-stabilized colloidal gold solution. After stirring overnight at room temperature, the silica particles were centrifugally separated from the solution containing unreacted gold particles.

Preparation of a Micelle-Like Assembly and Production of Spherical Polystyrene. To 3 cm³ of toluene containing 0.5 g of PS beads was added 0.2 g of w/o-SIO, and the mixture was sonicated for a few minutes in an ice bath to give a stable dispersion of w/o-SIO without sedimentation. Composites of w/o-SIO (shell) and PS/toluene (core) were made in water by adding 10 cm³ of water followed by

- (9) (a) Takei, H.; Shimizu, N. *Langmuir* **1997**, *13*, 1865–1868. (b) Fujimoto, K.; Nakahama, K.; Shidara, M.; Kawaguchi, H. *Langmuir* **1999**, *15*, 4630–4635. (c) Petit, L.; Manaud, J.-P.; Mingotaud, C.; Ravaine, S.; Duguet, E. *Mater. Lett.* **2001**, *51*, 478–484.
- (10) (a) Nur, H.; Ikeda, S.; Ohtani, B. *Chem. Commun.* **2000**, 2235–2236. (b) Nur, H.; Ikeda, S.; Ohtani, B. *J. Catal.* **2001**, *204*, 402–408. (c) Ikeda, S.; Nur, H.; Sawadaishi, T.; Ijio, K.; Shimomura, M.; Ohtani, B. *Langmuir* **2001**, *17*, 7976–7979. (d) Ikeda, S.; Nur, H.; Wu, P.; Tatsumi, T.; Ohtani, B. *Stud. Surf. Sci. Catal.* **2003**, *145*, 251–254. (e) Ikeda, S.; Kowata, Y.; Ikeue, K.; Matsumura, M.; Ohtani, B. *Appl. Catal., A* **2004**, *265*, 69–74. (f) Ikeue, K.; Ikeda, S.; Watanabe, A.; Ohtani, B. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2523–2528.

- (11) Stöber, W.; Fink, A. *J. Colloid Interface Sci.* **1968**, *26*, 62–69.
- (12) Frens, G. *Nature Phys. Sci.* **1973**, *241*, 20–22.
- (13) (a) Sadtler, B.; Wei, A. *Chem. Commun.* **2002**, 1604–1605. (b) Sato, T.; Brown, D.; Johnson, B. F. G. *Chem. Commun.* **1997**, 1007–1008.

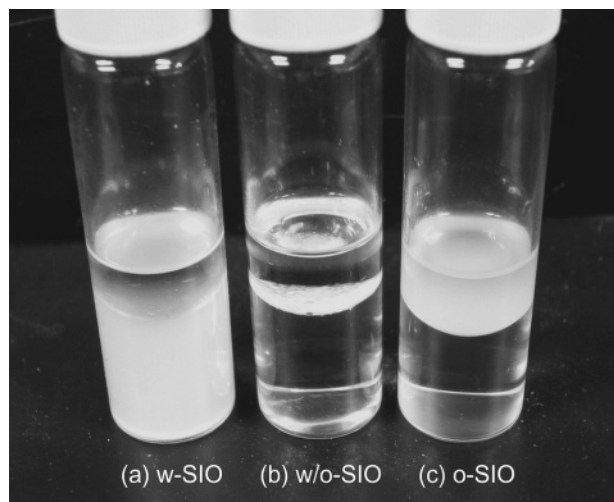


Figure 1. Locations of bare and alkylsilylated silica particles added to a water–toluene dual-phase system: (a) w-SiO, (b) w/o-SiO, (c) o-SiO. The photographs were taken for samples prepared from silica particles with a diameter of 400 nm.

sonication for 1 h in an ice bath. After precipitation of the composites by standing the suspension overnight at room temperature, the organic phase was removed and the aqueous phase was slowly evaporated at 333 K to dryness. Then, as-obtained powders were treated with 50% HF solution to dissolve silica particles (HF solution is very hazardous and corrosive and should be handled according to the MSDS guidelines), and the remaining white powder was collected and dried at 333 K.

Characterization. The morphology of the particles was examined using a Hitachi S-5000 FEG scanning electron microscope (SEM) at a voltage of 20 kV. All samples were attached on a grid by a double-sided tape made of electricity-conductive carbon.

Results and Discussion

Surface Structures of SiO₂ Particles Covered with Alkylsilyl Groups. Figure 1 shows photographs of w-SiO, w/o-SiO, and o-SiO particles suspended in a dual-phase mixture of water and toluene: all of the particles were 400 nm in diameter. Due to the presence of surface hydroxyl groups on their surfaces, w-SiO particles dispersed only in water. On the other hand, the o-SiO sample, whose surface was made fully hydrophobic by treatment with ODMS,¹⁴ dispersed well in toluene.

The aim of our study was to make amphiphilic silica particles and to reveal and utilize their unique properties. Figure 1b is the picture of the w/o-SiO sample that was endowed with amphiphilicity. In contrast to w-SiO and o-SiO particles, the w/o-SiO particles stayed at the interface between water and toluene, suggesting that the surfaces of the w/o-SiO particles are amphiphilic. The w/o-SiO sample was prepared as follows. A small amount of water (0.3 cm³) was added to dried w-SiO powder just before the reaction with ODMS. The added water induced tight adhesion between the particles, leading to their aggregation. Since the amount of water is limited, the outer surface of the aggregates is probably not covered with water. Hence, the hydrophobic agent ODMS reacts only with the hydroxyl groups exposed to the outer surface of the aggregates, and the inside remains unchanged. This leads to an asymmetric structure for each particle, which has both hydroxyl and

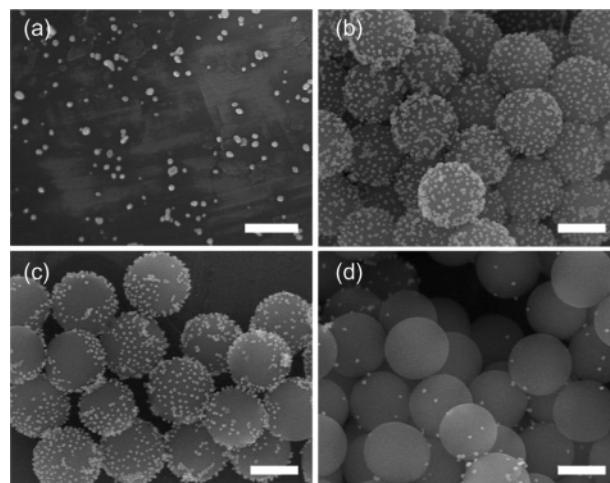


Figure 2. SEM images of (a) citrate-stabilized gold particles and those attached to AEAPTMS-treated (b) w-SiO, (c) w/o-SiO, and (d) o-SiO particles. Representative images for samples made of silica particles of 400 nm in diameter are shown. Scale bars correspond to 300 nm.

alkylsilyl faces. Spontaneous assembling of particles at the water–toluene boundary as seen in Figure 1b was observed for the w/o-SiO samples made of silica particles with different sizes (250, 300, and 660 nm in diameter). The assembling was also observed when benzene, hexane, or other water-immiscible liquids were used instead of toluene.

To confirm the presence of hydrophilic and hydrophobic parts on a w/o-SiO particle by using SEM, we tried to differentiate these parts by loading gold nanoparticles as observable markers only on the hydrophilic parts. After w/o-SiO powder had been treated with AEAPTMS, which aminoalkylates the surface hydroxyl groups, colloidal gold particles with diameters ranging from 20 to 50 nm (Figure 2a) were attached through electrostatic interaction between amino groups (positive) and the surfaces of gold particles (negative).^{5a} The same treatment was applied to the w-SiO and o-SiO particles. Due to the existence of hydroxyl groups over the entire surface of a w-SiO particle and on one part (hydrophilic face) of the w/o-SiO particle surface, the gold particles were expected to cover the whole surface of w-SiO and a part of the w/o-SiO surface. It was also expected that o-SiO would not be covered with gold particles. Panels b–d in Figure 2 show typical SEM images for w-SiO, w/o-SiO, and o-SiO particles after the treatment. As expected, gold particles were homogeneously attached to the entire surface of a w-SiO particle, i.e., the surface of a w-SiO particle was fully covered with gold particles (Figure 2b). On the other hand, the surfaces of the o-SiO particles were hardly covered with gold particles (Figure 2d). For the w/o-SiO particle, Figure 2c clearly shows that only a part of each particle was covered with gold particles, indicating an asymmetric surface structure with hydrophilic and hydrophobic parts. It should be noted that the area covered with gold particles is larger than the uncovered area, as seen in Figure 2c. This suggests that when treated with ODMS, a larger part of each particle faced the water phase, leaving that area hydrophilic. It should also be noted that the w/o-SiO samples made of silica particles with different diameters (250, 300, and 660 nm) showed nearly the same asymmetric structure after loading gold particles under SEM observation (see Supporting Information). Thus, in the present preparation conditions, it is likely that less than half of the surface of a w/o-SiO particle is hydrophobic and that hydroxyl

(14) (a) Sagiv, J. *J. Am. Chem. Soc.* **1980**, *102*, 92–98. (b) Silberzan, P.; Léger, L.; Ausserré, D.; Benattar, J. *J. Langmuir* **1991**, *7*, 1647–1651.

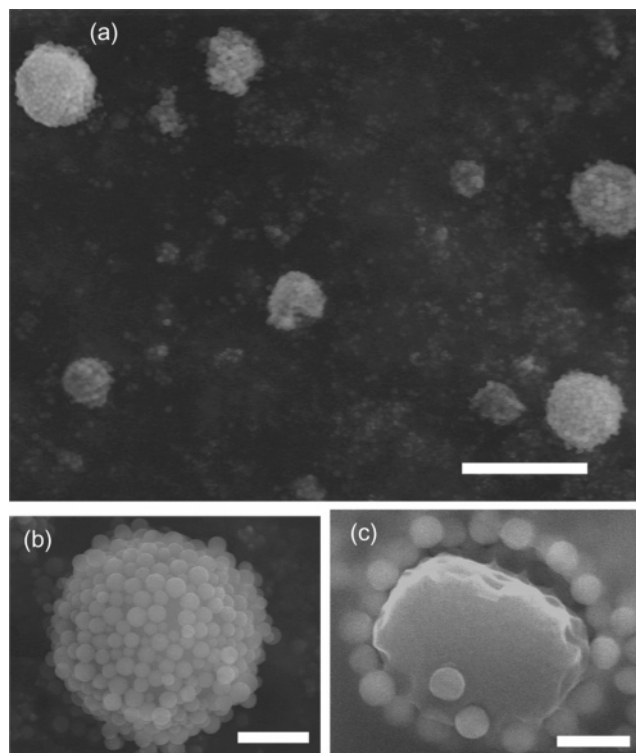


Figure 3. SEM images of w/o-SIO precipitates obtained from the dual-phase mixture of water and toluene containing PS. Typical images with relatively (a) low or (b) high magnification and those of (c) a cross section are shown. Silica particles of 250 nm in diameter were used as bare samples. Scale bars correspond to (a) 5.0 μm , (b) 1.0 μm , (c) 500 nm.

groups are exposed on more than half of the surface, retaining hydrophilicity (see below).

Micelle Formation of Amphiphilic w/o-SIO Particles. The asymmetric surface structure of w/o-SIO particles with both hydrophilic and hydrophobic parts must be responsible to their assembling at the water–toluene interface. Since this function is analogous to that of molecular surfactants, we expected that these modified particles have similar functions: w/o-SIO forms micelles that solubilize water-immiscible organic compounds in water. To confirm this possibility, we tried to fabricate oil-in-water-type assemblies using w/o-SIO as a solid surfactant in the aqueous phase. For direct visualization of the assembly by SEM observation, the assembled structure was solidified with an encapsulated hydrophobic polymer to extract the particles from the aqueous phase as follows. A suspension of w/o-SIO particles in toluene containing polystyrene (PS) was prepared and was mixed with water. By sonication of the mixture, the dual-phase mixture became a white suspension. After standing overnight, the liquid separated into two phases, and precipitates appeared at the bottom. We collected the precipitates by removing the toluene phase, and w/o-SIO particles were still suspended at the phase boundary. Then the remaining aqueous phase was evaporated to dryness. Panels a and b of Figure 3 show representative SEM images of the thus-obtained precipitate prepared from w/o-SIO particles with an average diameter of 250 nm. On the surfaces of precipitate particles with diameters of 2–3 μm , tightly packed spherical assemblies of w/o-SIO particles were observed. A cross section of the w/o-SIO assembly¹⁵ (Figure 3c) clearly shows that w/o-SIO particles of 250 nm in diameter surround a micrometer-sized lump. As discussed below, since the lump was found to be composed of

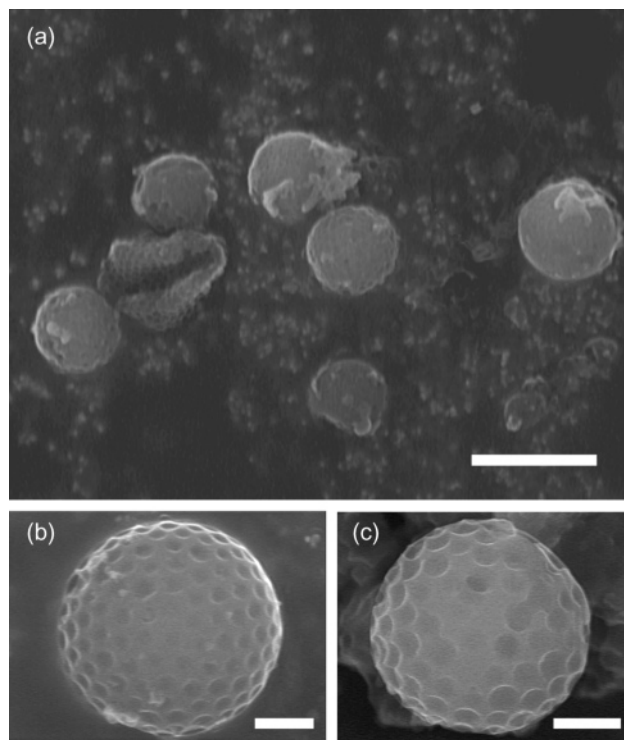


Figure 4. SEM images of PS particles isolated from the w/o-SIO assemblies shown in Figure 3. Scale bars correspond to (a) 3.0 μm , (b, c) 500 nm.

PS, this image indicates that the observed spherical assemblies of w/o-SIO particles have a PS (core)–w/o-SIO (shell) structure.

Although precipitates were obtained when w-SIO particles were used in the above-described procedure instead of w/o-SIO particles, the resulting precipitates were simple aggregates of original w-SIO particles. When o-SIO particles were used for comparison, no stable dispersion and/or precipitates in the aqueous phase were observed: both organic and aqueous phases hardly changed from the initial dual-phase system. On the other hand, when w/o-SIO particles with different diameters (300, 400, and 660 nm) were used, spherical assemblies of the particles similar to those shown in Figure 3 were observed. These results indicate that only w/o-SIO particles can form core–shell-type spherical assemblies.

For further investigation of the structure of particle assemblies, SiO₂ components were removed by dissolving them with aqueous HF solution. Figure 4 shows a typical SEM image of the remaining residue derived from an assembly composed of w/o-SIO particles (250 nm in diameter). Spherical particles of ca. 2–3 μm in diameter with semispherical dimples on their surfaces were obtained. Since they completely vanished upon heating at 773 K for 1 h, these particles should be made solely of PS. Compared to w/o-SIO assemblies shown in Figure 3, the diameters of the PS particles seem to be relatively small or almost comparable. Moreover, the precipitates of w-SIO particles gave negligible amounts of irregular-shaped PS lumps after treatment with aqueous HF solution. From these results and facts, it is reasonable to assume that the spherical, dimpled PS particles are attributed to the cores of the PS (core)–w/o-SIO (shell) composite. This assumption is strongly supported by the

(15) The sample for this observation was prepared by cutting epoxy-resin-stabilized w/o-SIO particle assemblies with a microtome into ca. 2 μm of thickness.

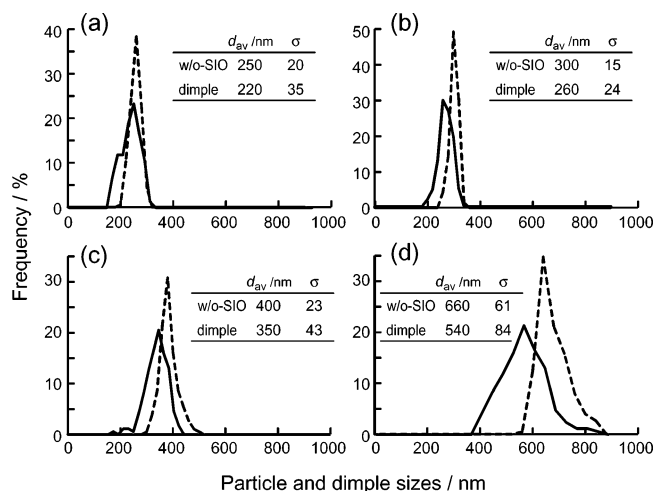


Figure 5. Size distributions of w/o-SiO₂ particles (dotted lines) and semispherical dimples on as-obtained PS particles (solid lines) determined by SEM observations. (a, b, c, d) Plots of size distributions of w/o-SiO₂ particles of 250, 300, 400, and 660 nm in diameter, respectively, and semispherical dimples on PS particles derived from them. Insets of these plots indicate average diameters (d_{av}) and standard deviations (σ) of w/o-SiO₂ particles and dimples on PS spheres.

cross-sectional image of the core–shell composite shown in Figure 3c. Although the core shown in the image is not spherical (probably due to distortion of the structure that occurred when the composite was cut with a microtome) several spherical dimples with sizes comparable to the diameter of the w/o-SiO₂ particle were also observed on the surface of the core lump.

To clarify the origin of dimples on resulting PS particles, size distributions of dimples and the source SiO₂ particles were determined from SEM images by measuring more than 200 dimples and SiO₂ particles, and the results are shown in Figure 5. It is clear that sizes of dimples depend on sizes of SiO₂ particles used; the average diameter (d_{av}) of dimples was slightly smaller (ca. 80–90%) than that of w/o-SiO₂ particles in each sample and standard deviations (σ) of dimple sizes increased with that of w/o-SiO₂ particles. The hydrophobic regions of the surface of a w/o-SiO₂ particle seemed to be less than half of the whole external surface as mentioned above. This is probably the reason for the relatively small diameters of dimples on PS particles compared with the particle sizes of w/o-SiO₂ samples, because less than half of each w/o-SiO₂ particle in the assembly could soak in PS/toluene (organic) droplets, and the larger part remaining was exposed to the outer aqueous phase. All of the above-described results and considerations indicate that the dimples are imprinted patterns of the hydrophobic surface of w/o-SiO₂ particles assembled around PS particles, i.e., w/o-SiO₂ particles form spherical assemblies encapsulating water-immiscible organic compounds in aqueous media by facing their hydrophobic alkylsilylated side to the inner organic phase and their hydrophilic side to the outer aqueous phase.

It has been reported that spherical particles with surfaces having homogeneously controlled hydrophobicity could stabilize water-in-oil and/or oil-in-water emulsions by assembling at the water/oil interface.¹⁶ Compared with these findings, our results are new because the amphiphilic particles exhibit structural characteristics and behavior similar to those of molecular surfactants; spherical silica particles having both hydrophilic and hydrophobic surfaces form spherical assemblies encapsulating water-immiscible organic compounds in aqueous media. The results of theoretical analysis reported by Binks et al.¹⁷ suggest that the unique properties are due to the high levels of desorption energy of the amphiphilic particles existing at the water/oil interface compared with homogeneously modified particles. Indeed, no micelle-type assembly was obtained when o-SiO₂ with a relatively small amount of surface alkylsilyl groups was employed in the present conditions.

Conclusions

Spherical silica particles of submicrometer sizes having both hydrophilic and hydrophobic surfaces were prepared by a simple method for partial modification of the external surface with an alkylsilyl agent. The partial coverage of each spherical silica particle with alkylsilyl groups was proved by partial loading of gold nanoparticles, which have affinity only with the hydrophilic surface of these silica particles as-obtained. These asymmetrically modified particles showed amphiphilicity, being analogous to the molecular surfactants. Because of this property, they stabilize oil droplets in water, making a micellar structure. Since the surfactants are generally believed to be linear molecules having hydrophobic and hydrophilic moieties at both ends, the present material should be a novel type of surfactant, a “solid particular surfactant”. We believe, therefore, that the use of the asymmetric particles will open up a new category of heterogeneous systems for chemical reactions and material preparations.

Acknowledgment. We are grateful to Nippon Shokubai for the supply of silica particles.

Supporting Information Available: SEM images of 250, 300, and 660 nm w/o-SiO₂ particles modified with gold colloids, PS (core)-300, -400, and -660 nm w/o-SiO₂ (shell) assemblies, and spherical PS particles derived from PS (core)-300, -400, and -660 nm w/o-SiO₂ (shell) assemblies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA043581R

- (16) (a) Dinsmore, A. D.; Hsu, M. F.; Nikolaidis, M. G.; Marquez, M.; Bausch, A. R.; Weitz, D. A. *Science* **2002**, *298*, 1006–1009. (b) Binks, B. P.; Lumsdon, S. O. *Langmuir* **2000**, *16*, 2539–2547. (c) Aveyard, R.; Binks, B. P.; Clint, J. H. *Adv. Colloid Interface Sci.* **2003**, *100–102*, 503–546. (17) Binks, B. P.; Fletcher, P. D. I. *Langmuir* **2001**, *17*, 4708–4710.