

## Direct Observation of Amphiphilic Silica Particles Assembled at an Oil–Water Interface

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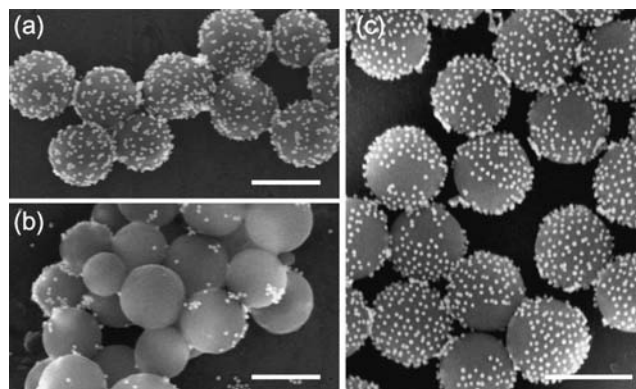
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The location of amphiphilic silica particles, on which have both hydrophobic and hydrophilic surfaces, at a *n*-decane–water interface was investigated. By scanning electron microscopy observation of the particles fixed at the interface with a curable poly(dimethylsiloxane), we found that each hemisphere of an amphiphilic particle is immersed in the oil or aqueous phase.

Modulation of the surface wettability of colloid particles with various liquids is an important issue for both applications in several industrial materials and fundamental studies to clarify behaviors of the particles at liquid interfaces.<sup>1</sup> Recently, we have developed a simple method for preparing particles having both hydrophobic and hydrophilic surfaces on each particle by a partial modification of the external surfaces of hydrophilic particles with a long-chain alkylsilane agent.<sup>2,3</sup> One of the attractive features is that these particles are spontaneously assembled at a liquid–liquid phase boundary between aqueous and water-immiscible organic compounds and act as efficient catalysts for chemical reactions between agents presented in the aqueous and the oil phases.<sup>2</sup> Moreover, we have found that these particles form a micellar assembly to solubilize hydrophobic polymers and/or particles as surfactant molecules.<sup>3</sup>

In our previous study, we also examined the asymmetric surface structures of particles in which their hydrophilic surfaces had been modified with colloidal gold particles by scanning electron microscopy (SEM).<sup>3a</sup> However, critical information of the location of these particles at liquid–liquid interfaces is still unknown. In the present study, we therefore focused on the behavior of amphiphilic particles at liquid–liquid dual-phase systems by a direct observation technique using SEM.

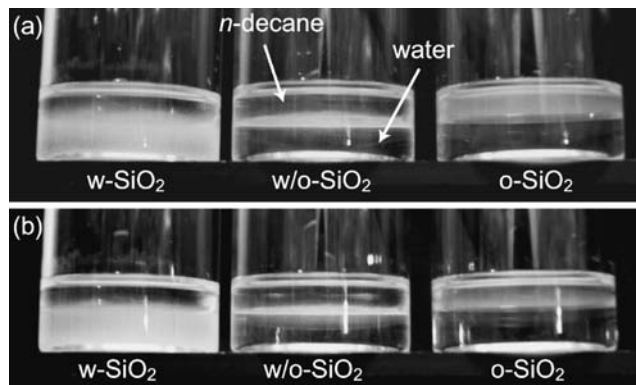
Spherical monodispersed silica particles (SiO<sub>2</sub>) of 250 nm in diameter were prepared by Stöber's method.<sup>4</sup> Amphiphilic SiO<sub>2</sub> (w/o-SiO<sub>2</sub>) particles and hydrophobic SiO<sub>2</sub> particles on which their surfaces were fully covered with alkylsilane (o-SiO<sub>2</sub>) were prepared by a previously reported procedure.<sup>3</sup> To verify the amphiphilic surface structure of w/o-SiO<sub>2</sub> particles, their hydrophilic surfaces were selectively modified with colloidal gold particles.<sup>3,5</sup> Figure 1 shows typical SEM images of thus-obtained particles. Images of SiO<sub>2</sub> and o-SiO<sub>2</sub> particles that had been treated by the same procedure as that used for modification of gold particles on w/o-SiO<sub>2</sub> particles are also shown for comparison. The surfaces of SiO<sub>2</sub> particles were fully covered with gold particles because of the presence of hydroxyl groups covering the entire surface of each SiO<sub>2</sub> particle (Figure 1a). On the other hand, owing to the full coverage of alkylsilyl groups over the surface of an o-SiO<sub>2</sub> particle, almost no gold particles were observed on o-SiO<sub>2</sub> particles (Figure 1b). These results suggest that gold particles are grafted only to the hydroxyl-terminated surface remaining on a w/o-SiO<sub>2</sub> particle. As expected, only a part of the surface of most w/o-SiO<sub>2</sub> particles was covered with



**Figure 1.** SEM images of (a) SiO<sub>2</sub>, (b) o-SiO<sub>2</sub>, and (c) w/o-SiO<sub>2</sub> treated with gold colloids. Scale bars correspond to 300 nm.

gold particles (Figure 1c), indicating that each w/o-SiO<sub>2</sub> particle used in the present study has both hydrophilic and hydrophobic surfaces.

When suspensions of SiO<sub>2</sub>, w/o-SiO<sub>2</sub>, and o-SiO<sub>2</sub> particles in isopropyl alcohol were gently placed onto the interface of a dual-phase mixture of *n*-decane and water by a pipette, significant differences in their behavior were observed. Figure 2 shows photographs of thus-obtained suspensions just after addition of these particles and those after standing for 30 min. The original SiO<sub>2</sub> particles were not located at the interface as expected from their surface hydrophilicity: they are instantly dispersed in the aqueous phase. On the other hand, o-SiO<sub>2</sub> particles tended to disperse in the oil phase because of their hydrophobic surface properties, while they gradually settled at the interface under the influence of gravity. Compared to these samples, it is clear that w/o-SiO<sub>2</sub> particles feasibly spread at the interface just after



**Figure 2.** Photographs of SiO<sub>2</sub>, w/o-SiO<sub>2</sub>, and o-SiO<sub>2</sub> particles (a) just after addition to the *n*-decane–water dual-phase system and (b) those after standing them for 30 min.

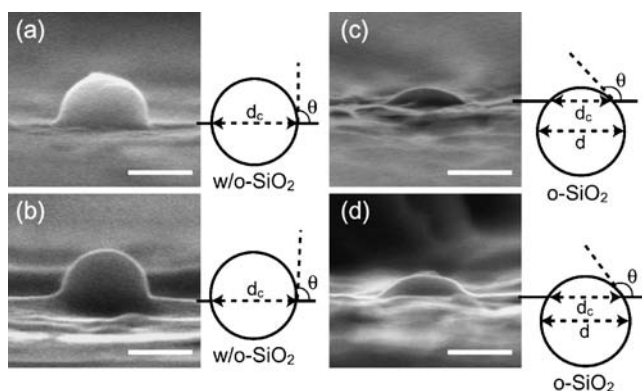
addition of the particles and retained their location. As discussed previously,<sup>3a</sup> the characteristic behavior of w/o-SiO<sub>2</sub> particles is attributed to the presence of both hydrophilic and hydrophobic surfaces on each particle; the hydrophilic and hydrophobic parts face to the aqueous and oil phases, respectively. Thus, even though hydrophobic o-SiO<sub>2</sub> particles were located at the boundary after standing for a while as shown in Figure 2b, the mesoscopic locations of w/o-SiO<sub>2</sub> particles should be different from those of o-SiO<sub>2</sub> particles.

On the basis of the above postulations, we determined the location of each w/o-SiO<sub>2</sub> particle using an SEM. For this purpose, samples were prepared by the gel trapping technique (GTT) which has been developed by Paunov.<sup>6</sup> The GTT is based on the fixing of particles spread on the interfaces by gelation of the aqueous phase with a nonadsorbing polysaccharide followed by lifting of the fixed particles with a curable poly(dimethylsiloxane) (PDMS). From the fact that the gelling agent in the aqueous phase does not change the interfacial tension of either the air–water or the oil–water interface, the location of the particles would not be influenced by the presence of the agent.<sup>6a</sup> A schematic procedure of the GTT is shown in the graphical abstract and details are given in supporting information.

Figure 3 shows representative SEM images of w/o-SiO<sub>2</sub> and o-SiO<sub>2</sub> particles embedded on the PDMS surface with the GTT at the *n*-decane–water interface. The visible part of the particle is originally immersed in the aqueous phase, and the part embedded in the PDMS is in contact with the oil phase. Thus, as a quantitative measure, the particle contact angles  $\theta$  at the *n*-decane–water interface were also determined from the SEM images using the following equation:

$$\sin \theta = d_c/d, \quad (1)$$

where  $d_c$  and  $d$  represent the particle contact line diameter and the true diameter of the particles, respectively.<sup>6</sup> The average contact angles of w/o-SiO<sub>2</sub> and o-SiO<sub>2</sub> particles by measuring more than 20 particles were ca. 90° and ca. 120°, respectively. The SEM images and contact angles of the particles indicate a difference in the locations of w/o-SiO<sub>2</sub> and o-SiO<sub>2</sub> particles assembled at the interfaces: the hemispheres of w/o-SiO<sub>2</sub> particles



**Figure 3.** SEM images of w/o-SiO<sub>2</sub> (a, b) and o-SiO<sub>2</sub> (c, d) particles with an average diameter of 250 nm embedded on the surface of PDMS. Scale bars correspond to 200 nm. Illustrations are fittings of the particle contact lines and profiles of the particles to measure the particle contact line diameters ( $d_c$ ) and the true diameters ( $d$ ) of the particles for determinations of contact angles ( $\theta$ ) (see Eq 1).

were exposed from the PDMS phase, while most parts of o-SiO<sub>2</sub> particles were embedded in the PDMS phase, i.e., each hemisphere of a w/o-SiO<sub>2</sub> particle was in contact with the aqueous or the oil phase, while an o-SiO<sub>2</sub> particle just floated on the aqueous phase in the dual-phase system. These results are consistent with the macroscopic behavior of these particles shown in Figure 2. Another notable point is that the results for w/o-SiO<sub>2</sub> particle seem to be different from the area of the hydrophobic regions of the surface of a w/o-SiO<sub>2</sub> particle as shown in Figure 1c, suggesting that the interfacial location is not determined only by the hydrophobic surface areas of a w/o-SiO<sub>2</sub> particle. One possible explanation is that the affinity of the alkylsilyl groups on the surface of a w/o-SiO<sub>2</sub> particle to the oil (*n*-decane) phase is higher than that of the hydroxyl groups to the aqueous phase, leading to a slight shift in the location to the oil phase. Further investigations of the effect of the composition the dual-phase mixture on the location of w/o-SiO<sub>2</sub> particles are now underway.

We have demonstrated a direct observation of the location of amphiphilic silica particles in a liquid–liquid dual-phase system. Although several authors have reported the interfacial location of spherical particles with surfaces having homogeneously controlled hydrophobicity,<sup>1,6</sup> there had been no report about the behavior of the amphiphilic particle. Thus, this finding should be useful information of the particle to be utilized for further applications.

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