**Preparation of "Golf Ball"-Like Polystyrene Microspheres *via* A Novel Micelle-Type Assembly Composed of Solid Spherical Particles**

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Surfactants, molecules having both hydrophobic and hydrophilic regions and/or groups, are widely used in forms of micelles, self-assemblies in a solvent, for synthesis of molecular sieves and nanoparticles, and for reaction media for organic synthesis and catalysis. Here, we have found that a novel category of surfactants, which were based on spherical solid particles, have realized their micelle-type assemblies in water, and have demonstrated to use as templates to synthesize spherical polymers with "golf-ball" like dimpled surfaces.

For the fabrication of particles with amphiphilicity analogous to that of surfactants, we have recently developed a method for modifying a part of the external surface of inorganic oxides with hydrophobic alkylsilane agents.[1-4] Here, we used spherical $SiO_2$ particles with average diameters ranging from ca. 0.3 to 10 μm and modified a part of their external surface with *n*-octadecyltrimethoxysilane using the reported procedures, and thus-obtained particles were labeled $SIO_{part}$.

Typical procedures for making $SIO_{part}$ assemblies and spherical polystyrene (PS) particles are shown in Fig. 1. A suspension of $SIO_{part}$ in toluene containing non-structural PS was prepared and was added to water. After sonication of the mixture for 1 h, the initially transparent aqueous phase became turbid, indicating the transfer of $SIO_{part}$ from the organic phase to the aqueous phase. To collect the particles in the aqueous phase, the mixture was left standing overnight until most of the particles had precipitated. Then, the aqueous and organic phases were removed by filtration and evaporation.

A representative SEM image of the thus-obtained precipitate prepared form the $SiO_2$ particles with average diameter of ca. 0.3 μm (Fig. 2a) indicates the formation of spherical assemblies of silica particles of ca. 2.8 μm in diameter (Fig. 2b). Fig. 2c shows a typical SEM image of the organic residue, PS, after dissolving $SiO_2$ components with aqueous hydrogen fluoride. Spherical particles of ca. 2.0 μm in diameter with spherical dimples on their surfaces were obtained. It should be noted that the diameters of PS particles are smaller than or comparable to those of assembles of $SIO_{part}$ (Fig. 3). From these results, it is reasonable to consider that the spherical dimpled PS particles originate from the $SIO_{part}$ assemblies.

Thus, we have obtained evidence of the formation of a particle assembly analogous to micelles of organic surfactants. The particles, furthermore, act as structure-directing agents for the syntheses of spherical materials having dimpled surface structures. The "solid spherical surfactant" might be broken new ground in colloidal chemistry and material science.

references

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3) S. Ikeda et al, *Langmuir* **17**, 7976 (2001)
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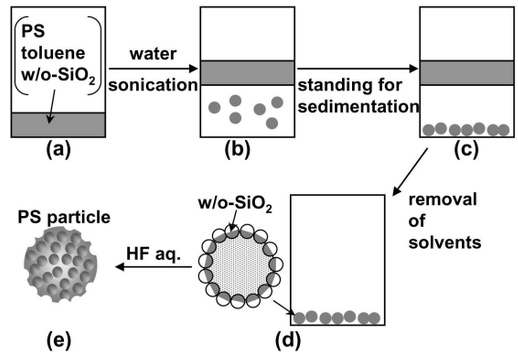


*Fig.1 A schematic outlines of the procedure for making $SIO_{part}$ assemblies and PS particles with dimpled surface morphology.*

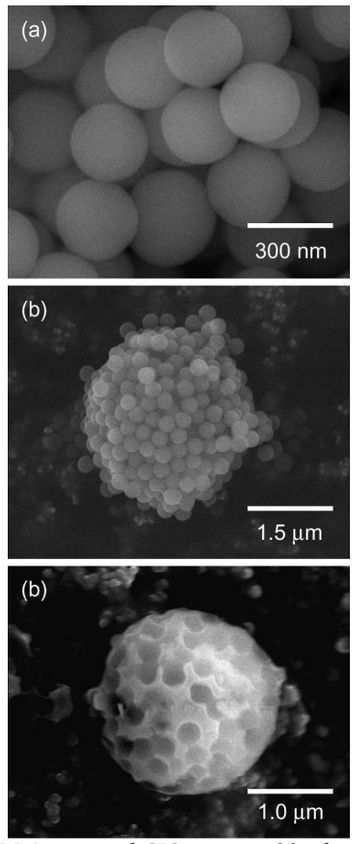


*Fig. 2 SEM images of $SIO_{part}$-assembly formation and spherical PS particle production. **a**, bare $SiO_2$. **b**, typical image of $SIO_{part}$ assembly. **c**, typical image of a PS particle produced by a treatment of the $SIO_{part}$ assembly with aqueous hydrogen fluoride.*

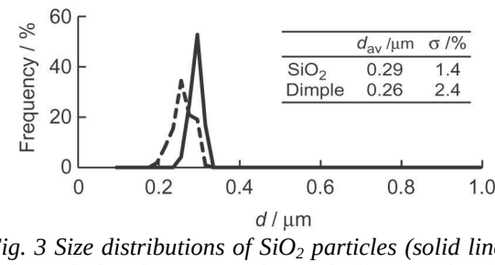


*Fig. 3 Size distributions of $SiO_2$ particles (solid line) and spherical dimples on as-obtained PS particles (dotted line) determined by SEM observations. Insets of these plots indicate average diameters ($d_{av}$) and standard deviations ($\sigma$) of $SiO_2$ and dimples on PS particles.*