Incorporation of Dyes into Silica–Surfactant Mesostructured Nanoparticles as a Nanoscale Host Material for Organic Molecules

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Various kinds of organic dye molecules were successfully incorporated into silica–surfactant nanoparticles with a hexagonally ordered mesostructure. The dye-incorporated composite particles, which had a diameter of ca. 30 nm, exhibited specific fluorescent properties and pH sensitivity derived from the organic molecules.

Mesoscopically ordered silicate materials have been produced by the organization of surfactant molecules and silica-precursor species since the synthesis of the M41S family.[1] Recently, mesostructured silica has attracted much attention as a host for sensing molecules, organic dyes, catalysts, drugs, and many other guest molecules with a wide variety of functionalities.[2,3] Various kinds of dye molecules have already been incorporated into mesostructured silica.[4–8] The micellar phase of the mesostructures facilitated a homogeneous distribution of guest molecules due to its permeability.[9,10] Nanoscale particles of mesostructured silica prepared using various techniques[11–19] would be useful in the fields of sensing, optical applications, and drug delivery because of a remarkable potential because of their remarkable potential, easy-to-handle form, highly accessible mesopores, and high optical transparency. Although organic dye molecules were covalently linked to the silica framework of mesoporous nanoparticles,[8] versatile methods are still required for the preparation of dye-incorporated nanoparticles with ordered mesostructures. In this letter, we describe the fabrication of nanoparticles of silica–surfactant mesostructures incorporated with various kinds of dye molecules using a binary surfactant system.

As a typical synthesis procedure,[19] tetraethoxysilane (TEOS) was added to a hydrochloric acid solution (pH 2) in which cetyltrimethylammonium chloride (CTA^+Cl^-), a triblock copolymer (Pluronic F127; $EO_{106}PO_{60}EO_{106}$), and dye molecules (thymol blue, pyrene, methylene blue, rhodamine B, eosin Y, and pyranine) were previously dissolved. After the precursor solution was stirred at room temperature for 12 h, aqueous ammonia (NH_4OH, 28 mass %) was introduced into the solution. A typical ratio of the chemical composition of the resultant suspensions was $1.0TEOS:0.2CTA^+Cl^-:0.01F127:0.0002dye:3.3NH_4OH:124H_2O$. The disperse medium was evaporated for the analysis of powdery samples. The structural analysis was carried out by using a field emission transmission electron microscope (FETEM, FEI Tecnai F20) operated at 200 kV and a field emission scanning electron microscope (FESEM, Hitachi S-4700) operated at 5.0 kV. FETEM analysis included a scanning transmission mode using a high-angle annular dark-field detector (STEM-HAADF) and an energy-filtered imaging mode (Gatan Imaging Filter model 607).

Photographs of suspensions containing dye-incorporated silica–surfactant composite nanoparticles and their photoluminescence (PL) are shown in Figure 1. All the samples retained the color and luminescent properties of incorporated dyes. The suspensions were transparent, and no precipitation occurred for several months.

The FETEM observation (Figures 2a and 2b) revealed that nanoparticles with a diameter as small as ca. 30 nm had periodic 2D hexagonal mesostructures. According to the electron energy-loss spectrum (Figure S1, Supporting Information), a filtered image for the mapping of sulfur was used to investigate the inclusion behavior of the dye molecules. The unfiltered and filtered images (Figures 2c and 2d) indicate that sulfate substituents in the pyranine molecules were detected on the silica nanoparticles.

Powdery samples of the functionalized particles were easily obtained by evaporating the disperse medium of the suspension (Figure 3a). Transparent thin films consisting of nanoparticles were produced by spin-coating of the suspension (Figures 3b and 3e). After washing with water, the powdery samples retained a high percentage of the introduced dye. We observed intense luminescence from the dye incorporated in the powders and thin films (Figures 3c and 3d). Thymol blue- and pyranine-incorporated powders showed an easy response to the pH when immersed in an acid or alkaline aqueous solution (Figure 4).

Mesostructured silica nanoparticles were produced using the binary surfactant system.[19] The structural control is ascribed to the balance between the ordered assembly of anionic silicates and a cationic surfactant (CTA^+) through electrostatic interaction and the inhibition of grain growth with a nonionic surfactant (F127) through hydrogen bonds.[20] Thus, the mesostructured nanoparticles were composed of an ordered array of CTA^+ micelles and were covered with F127. Dye molecules could be incorporated into nanoparticles in different ways depending upon the characteristics of the molecules. Hydrophobic dyes (e.g., pyrene and thymol blue) were first solubilized by surfactant micelles into aqueous solutions. The PL spectrum of pyrene incorporated into the silica–surfactant mesostructure was similar to that in a CTA^+Cl^- aqueous solution rather than in an F127 solution (Figure S2, Supporting Information). Hence, pyrene was incorporated in the micellar phase of CTA^+ in the mesostructures, not in the F127 layer covering the nanoparticles. Moreover, the contribution of excimer emission of around 475 nm in the PL spectrum of the mesostructure was smaller than that of the CTA^+Cl^- solution. Thus, the dye molecules are suggested to be contained in rod-like assembly of the surfactant in the mesostructure, whereas spherical micelles behaved as a host of the dye in the solution.

Since the absorption and PL spectra of anionic (eosin Y and pyranine) and cationic (methylene blue and rhodamine B) dye molecules in an aqueous solution were influenced by the addition of CTA^+Cl^-, the hydrophilic dyes interacted with CTA^+ micelles through electrostatic and/or hydrophobic interactions.

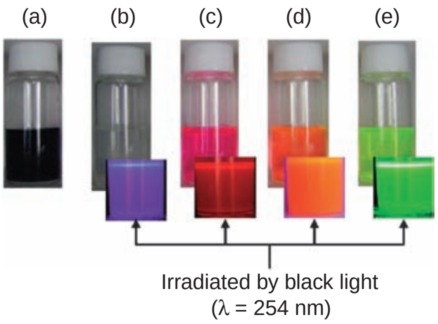

Figure 1. Photographs of colloidal suspension of silica–surfactant composite incorporating thymol blue (a), pyrene (b), rhodamine B (c), eosin Y (d), and pyranine (e).

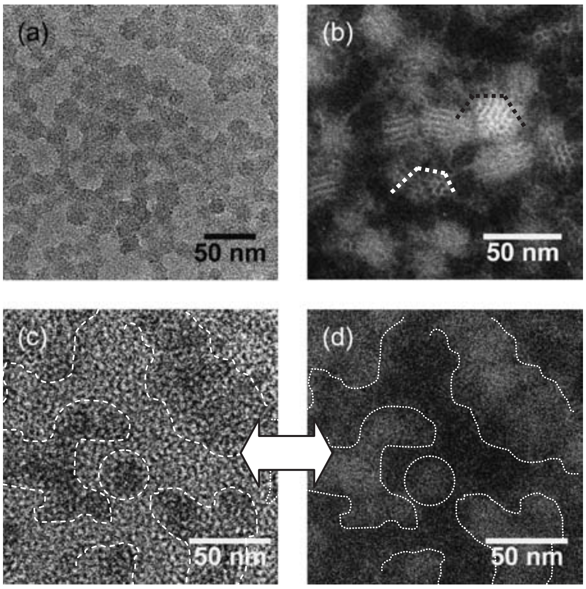

Figure 2. FETEM analysis of pyranine-incorporated mesostructures; (a) an FETEM image (bright field), (b) an HAADF-STEM image exhibiting ordered mesostructures, (c) a normal unfiltered image and (d) a filtered image for mapping of sulfate substituent in pyranine molecules. Doted lines in (b) indicate the hexagonal arrangement. Doted lines in (c) and (d) indicate the same areas of the images arrangement. Detailed imaging conditions were described in Supporting Information.

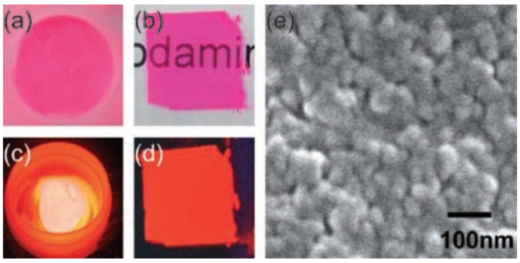

Figure 3. Photographs and an FESEM image of powder (a), (c) and a thin film (b), (d), (e) composed of the nanoparticles incorporating rhodamine B. Luminescence was observed under UV irradiation with a black light.

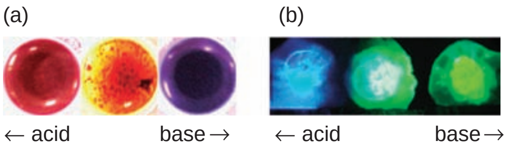

Figure 4. Photographs of the pH responses of thymol blue- (a) and pyranine-incorporated (b) powders. Luminescence of pyranine was observed under UV irradiation with a black light.

The PL spectra of the dye incorporated in the mesostructures were similar to those in the CTA$^+$ solutions. Thus, an ordered array of a silica–surfactant composite could be constructed by an assembly of anionic silicate and cationic CTA$^+$ micelles accompanied with the dye molecules. Consequently, it is possible that the hydrophilic dye molecules could be incorporated in the micelle phase and/or the silica/micelle interface in the mesostructures. However, further investigation is required to clarify the details of the status of hydrophilic dyes in the mesostructures.

In conclusion, we incorporated various organic dyes into silica–surfactant mesostructured nanoparticles with a simple procedure using a binary surfactant system. This work suggests that mesostructured silica nanoparticles could be applied as a new type of nanoscale host for functional organic molecules.

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