Synthesis of Magnetic Composite Particles of γ-Fe_2O_3@SiO_2 and the Control of the Structural Color of the Colloidal Crystal by Magnetic Fields

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(Received May 18, 2004; CL-040567)

Nearly monodisperse silica spheres with a diameter of ca. 140 nm containing magnetic cores of γ-Fe_2O_3 were synthesized following a similar method by Stöber[1] and Philipse.[2] Rendering a structural color was successfully achieved by thorough deionization of the aqueous suspension of the spheres. The magnetic tunability of the structural color of the colloidal crystal was demonstrated. The optical property was characterized by UV–vis reflection spectra.

Recently, colloidal crystals attract much attention of researchers aiming the realization of three-dimensional photonic crystals.[3,4] Bragg diffraction by the periodic structure of dielectric materials is the basis of photonic properties.[5] Dilute charged colloidal crystals are interesting since the crystal structure is sustained by the electrically repulsive interaction and is affected by ionic atmosphere of the solvent.[6,7] They are useful to the study of photonic crystals owing to the flexible structure. Colloidal crystals composed of magnetic particles are particularly promising in this respect for its in situ tunability using external magnetic fields. Wagner et al. reported synthesis of magnetic composite particles ($CoFe_2O_4$@SiO_2) and the control of the structural color of the suspension by magnetic fields.[8] Philipse et al. reported the synthesis of magnetic particle of γ-Fe_2O_3@SiO_2.[2] However, they did not present the formation of the colloidal crystal, possibly because of relatively poor uniformity of the particles. The aim of this work is the improvement for the synthesis of γ-Fe_2O_3@SiO_2 particles and the realization of the colloidal crystallization. Moreover, spectroscopic characterization of the crystal is presented.

All reagents were purchased from Wako Pure Chemical Industries, LTD. Fine γ-Fe_2O_3 particles were prepared by coprecipitation.[9] 2.08 g of $FeCl_2$ and 5.22 g of $FeCl_3$ were dissolved in 380-mL ultrapure water, and 20 mL of 25% NH_3 was added to the solution with acute agitation for one hour. After ultrafine γ-Fe_2O_3 particles were flocculated, the supernatant liquid was removed by decantation. 40 mL of 2 M HNO_3 was added to the sediment with stirring for 5 min. 60 mL of 0.35 M $Fe(NO_3)_3$ was slowly added to the solution boiling for 1 h. After standing for a while, the supernatant was again removed by decantation. The dark reddish-brown sedimentation was washed with 2 M HNO_3, and precipitated using a permanent magnet. The dark reddish-brown precipitate was dissolved in 1 L of distilled water. The point of zero charge of γ-Fe_2O_3 particles was lowered by adding a 0.01 M citric acid solution until precipitation was visible.[9] The precipitate was separated by filtration, and dissolved in 40 mL of 20% tetraethylammoniumhydroxide (TEAH).

Controlling the number density of the core particles is very important to synthesize monodisperse composite particles.[10] The target number is 4.5×10^{10} particles/mL. In order to synthesize composite particles (Fe_2O_3@SiO_2), 0.5 mL of the TEAH solution is mixed with ultrapure water and added to 720-mL of 2-propanol and 240-mL of ethanol. Tetraethylorthosilicate and 25% NH_3 were added with sonication. After 1 h of agitation, yellow ocher particles were synthesized. To remove stray ions from the suspension, the particles were separated using a centrifuge and diluted in ultrapure water. The last procedure was repeated several times to complete deionization.

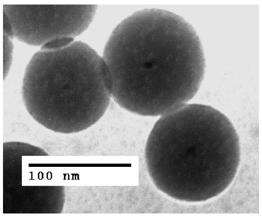

Figure 1. Transmission electron micrograph of colloidal core-shell particles. Ferromagnetic core can be seen as a dark spot at the center of particles.

Figure 1 shows a transmission electron micrograph of the particles synthesized. A magnetic core was found at the center of each particle, which is visible as a dark spot in a gray sphere in Figure 1. The average diameter of particles is 144 nm, which is estimated using a particle analyzer (UPA-150; Microtrac, Inc). The standard deviation of diameter was 43 nm, which was relatively large possibly owing to the partial aggregation of particles.

Colloidal crystals are known to have a face-centered-cubic (fcc) crystal structure typically.[11] The (111) facet is parallel with the wall of the container. The distance between the nearest (111) faces of the colloidal crystal was determined from reflection spectra. The reflection spectra were measured with a UV–vis. spectrometer (UV-570, JASCO Corp.) equipped with a rotatable stage and an integrating sphere. A rectangular quartz cell filled with the colloidal crystal was placed on the rotatable stage. The incident and reflective angles were set to be identical. Figure 2a shows reflection spectra with altering incident angles. The peak of the reflection spectra shifted to shorter wavelengths with increasing incident angles. The reason for rather large peak width is not clear. However, the shapes of the peak for different incident angles are quite similar, which may mean the (111) faces near the cell wall were well defined. In Figure 2b, the wavelength of the reflection peak is plotted against the incident angle. The distance between (111) faces (α) was obtained as 240 nm using the relation of $\alpha = (\lambda/2)[1 - (\sin\theta/n)^2]^{1/2}$ (λ: the peak wavelength of reflection spectra, θ: incident angle, n: the volume average of the refractive index of the suspension).[12] The volume average of the refractive index (n) was decided from the relation to be 1.37. This value is reasonable since it is close to the refractive index of pure water (1.33).

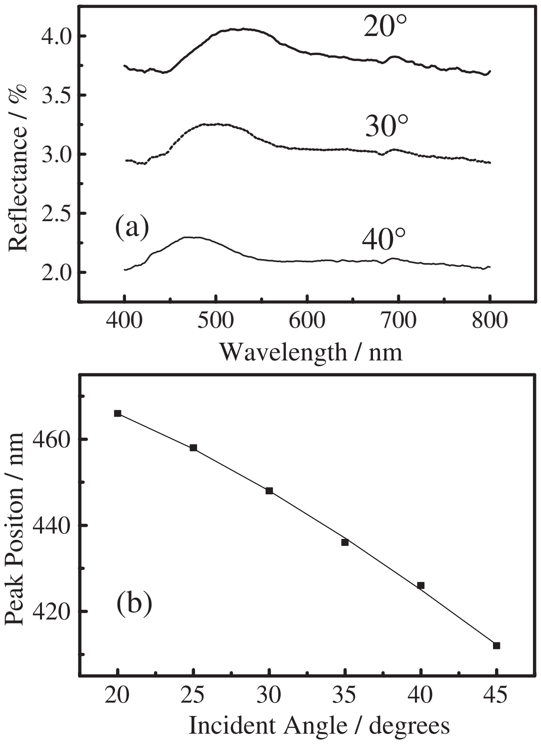

Figure 2. (a) Reflection spectra of the colloidal crystal of composite magnetic particles with incident and reflected angle angles of 20°, 30°, and 40°. The baseline of each spectrum is vertically shifted for clarity. (b) Incident angle dependence of the peak wavelength of Bragg diffraction.

In Figure 3, pictures showing the change of the structural color by magnetic fields are presented. In Figure 3a, the colloidal crystal with a structural color (violet) is seen at the middle of the container. The apparent sedimentation of the crystal phase and the disordered phase above it may indicate the critical concentration for the crystallization. In order to perturb the interaction between particles, a permanent magnet (SmCo, 0.3 T) was attached at the top of the container. The structural color changed gradually from violet to green as shown in Figure 3b and became stationary after about 8 h. This change of the structural color means the expansion of the lattice. Since magnetic particles are attracted toward the magnet at the top and this cancels the gravity acting on the particles. Therefore, the particle density decreases and lattice spacing increases. After removing the magnet, the color was reverted to violet within half an hour. Figure 3c shows reflection spectra with and without magnetic fields. The peak wavelength was 504 nm (without magnetic field) and 520 nm (with magnetic field). A rather irregular deformation of the shape of the peak was observed upon magnetization. This is possibly due to imperfect colloidal crystallization, since the probe beam was rather wide (100 µm × 10 mm), which incidented both of the ordered and disordered phases. The rate of the change of the structural color is rather slow. It is reported that the phase transition of the colloidal crystal is quite slow.[13] Further characterization of reflection spectra is under progress.

In summary, we have succeeded in rendering the structural color of the γ-Fe_2O_3@SiO_2 magnetic colloid. The crystal constant was obtained from UV–vis reflective spectra. Magnetic tuning of the structural color was demonstrated.

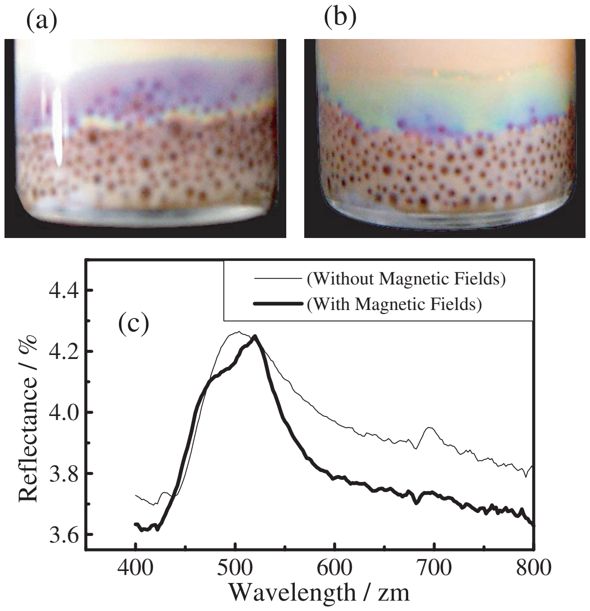

Figure 3. Color photographs of a composite magnetic colloidal crystal. Red spheres are ion-exchange resin beads. Structural color is seen in the middle of photographs and it changes from violet (a) to green (b) when magnetic fields are applied. (c) Difference of reflection spectra without and with magnetic fields. The peak of the reflection spectra is 508 nm in absence of magnetic fields and shifted to 520 nm in presence of magnetic fields.

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Published on the web (Advance View) July 31, 2004; DOI 10.1246/cl.2004.1106