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Photochemically Tunable Colloidal Crystals

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Monodispersed particles of diameter 50–500 nm can self-assemble to form colloidal crystals in solution or in the dried state.[1,2] Colloidal crystals in solution exhibit many of the phases of condensed matter. As the lattice constants of colloidal crystals are of similar order to the wavelength of visible light, phase transitions may be expected to greatly affect light propagation in these materials. Thermal effects,[3] rheological forces,[4] and the application of an external electric field[5,6] have been applied in order to control the phase of the colloidal suspensions. However, a major technological challenge still exists to tune the interparticle interaction via photoirradiation and thus control the phase transition. According to Derjaguin–Landau–Verwey–Overbeek (DLVO) theory or Ise–Sogami theory,[7–11] particles in colloidal suspensions are stabilized by electrostatic interactions, which are a function of the charge density on the particles and the ion density in solution. In this paper, photochemical control of the arrangement of particles was achieved by changing the free ion concentration and the particle charge in the colloid crystals. The method we describe is interesting not only from the viewpoint of photonic band gap crystals[12–18] but also for the general study of condensed matter since it provides a new method for the study of cooperative phenomena, such as ordering, phase transitions, and the stability of the resulting phases.

The photoresponsive colloidal suspensions were fabricated by dispersing silica particles into ethanol solutions containing 5 mM malachite green carbinol base (MG). Particles with diameters of 101 nm (Nissan Chemical Co. Japan) and 550 nm (Catalyst & Chemicals Ind. Co. Japan) were used for the spectral measurements and the microscopic observations, respectively. Spectral measurements were carried out for samples with volume densities


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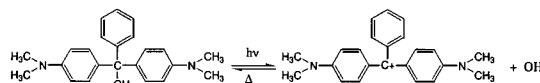
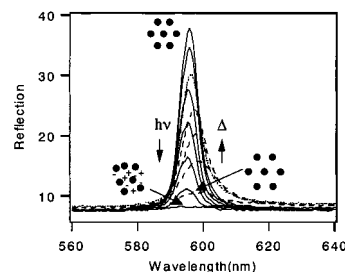**Figure 1.** Photoionization of malachite green carbinol base.

Figure 2. Changes in the reflection spectra of sample A during photoinduced melting and recrystallization. The solid lines show the spectra after light illumination for 0, 16, 24, 28, 32, 40, and 60 s. The dashed lines show the spectra after the illumination has been stopped for 1 h, subsequently measured every 10 min. The dotted line is the spectrum after the illumination has been stopped for 18 h.

of 4% (sample A) and 8.5% (sample B). Particles in ethanol solution containing MG can be crystallized in the dark after 1 week. The crystallization process is unaffected by the presence of MG,[19] since MG is a neutral molecule in ethanol solution in the dark (Figure 1).[20] Kossel line measurements show that all the samples crystallize into a face-centered cubic (FCC) structure. The (111) planes of colloidal crystals with the FCC structure are known to order parallel to the cell surface. Light diffraction satisfies the Bragg diffraction law.[1] Figures 2 and 3a show the 0° reflection spectra for samples A and B, respectively. Light of around 596 and 450 nm was rejected by samples A and B as a result of diffraction. From these spectra, the interparticle distances were calculated to be 270 and 203 nm, respectively.

Order–disorder phase transitions were induced by ultraviolet (UV) light irradiation (wavelength = 300 nm, light intensity = 2 mW). The neutral MG molecules were ionized into two charged fragments, MG^+ and OH^- (Figure 1) by irradiation, which was confirmed by the increase in the absorption of MG^+ at 622 nm. After illumination, the interparticle interactions are reduced, since free ions generated by irradiation screen the electrostatic forces between particles. When the number of generated ions exceeds a critical value, a melting of the colloidal crystals can be induced.[21] The progress of the order–disorder phase transition could be directly observed microscopically (Figure 4). The microscopic observation was carried out for the sample with a volume density of 8% (sample C). The observations show that the photoinduced melting originates from point defects, vacancies, and grain-boundaries. Furthermore, a superheating phenomenon was observed in defect-free regions. The change in the light propagation behavior is shown in Figures 2 and 3a. The intensity of the light diffracted from the (111) planes decrease as the melting of the ordered structure proceeds. After the phase transition, no significant light intensity is diffracted from the melted colloidal suspension. The results indicate that the transmission and diffraction of light at a given wavelength can be controlled by irradiation.

A phase transition from the disordered state to an ordered metastable one, with a different periodicity, was observed after the melting of crystals. Figures 2 and 3a show that after stopping the irradiation, new diffraction peaks appeared at 598 and 460

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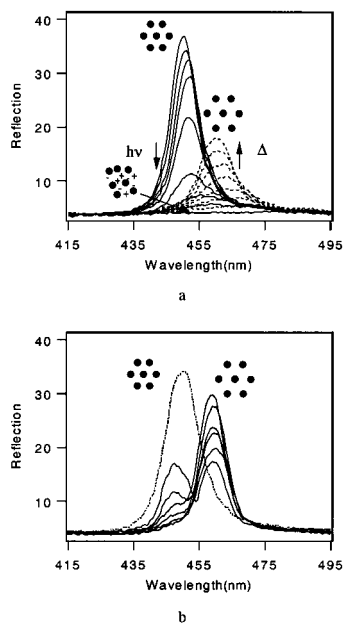(21) Lowen, H. *Phys. Rep.* **1994**, *237*, 249–324.

Figure 3. Changes in the reflection spectra of sample B after irradiation. In (a) the solid lines show the changes during photoinduced melting. The spectra were measured every 30 s. The dashed lines show the recrystallization after the illumination has been stopped irradiation, with spectra measured every subsequent 10 min. In (b) we show the spectra associated with the structural phase transition after the irradiation has been stopped for 1.5 h. The solid lines are the spectra measured every hour, and the dotted line is the spectrum measured after 24 h.

Figure 4. Voronoi constructions of the nearest neighborhoods for one layer of particles during photoirradiation. The pictures are constructed using the microscopic images of the first layer particles. In the picture, every black point represents a particle in a crystalline state, and a white point represents a particle in a defect state. The lines show the boundary between neighboring particles. Part (a) shows the structure before irradiation. The particles form a hexagonal regular structure in the (111) plane. Part (b) shows the structure after irradiation for 40 s. No apparent structural change was observed, although the self-diffusion coefficient increased by a factor of 2 after 10 s. Part (c) shows the structure after irradiation for 50 s. The ordered structure has begun to melt in the vicinity of the defect. Part (d) shows the structure after irradiation for 70 s. The ordered structure has completely melted at this stage.

nm for samples A and B, respectively. The wavelength of these peaks is longer than those before irradiation by 2 and 10 nm, respectively. This means that after recrystallization, the interparticle distances increased by 0.8 and 4 nm, respectively. The metastable state of sample B was maintained for a time period greater than several hours. ζ-Potential measurements showed that the recrystallized particles have less surface charge than those before irradiation. This means that the change in interparticle distance is induced by the adsorption of MG$^+$ ions onto SiO$_2$ particles with a negative charge. UV−visible spectra show that the adsorbed MG$^+$ ions have a much longer lifetime than those of free ions in solution, allowing the formation of the new state. These results show that the wavelength of the diffracted light can be switched by irradiation. The mechanism for the expansion of the interparticle distance has yet to be fully clarified, but should involve the concentration of the photogenerated species and the amounts adsorbed on the particle surfaces. Two possibilities may be considered as follows. One is that there may be charge differences between the silica particles, due to differences in the amounts of adsorbed MG$^+$. The suspension would then be inhomogeneous and a separate quasi-equilibrium phase with lower crystalline density could form. Another possibility is that there may be a change in the balance between repulsive and long-range attractive forces induced by the changes in particle charge that occur during recrystallization. Ise−Sogami theory has predicted an expansion of interparticle distance by decreasing the particle charge.[22]

The spectral changes occurring during the recovery process are depicted in Figures 2 and 3. They show that the structure of the metastable state is restored to the original one via a thermal
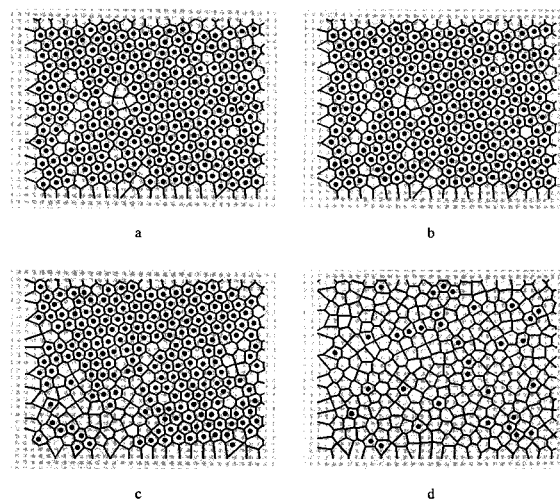
process. This means that the structural changes induced by photoirradiation are reversible. Furthermore, it was found that the recovery process depends on the volume density of the particles. For sample A, the 598-nm diffraction peak shifts toward the original position with time, accompanied by an increase in intensity. In contrast, for sample B, the 460-nm diffraction peak decreases with time and concomitantly the original peak at 450 nm appears. The continuous shrinkage of crystals observed in sample A can be considered to be a result of a continuous decrease in the surface charge of the particles. However, the discontinuous phase transition between different ordered phases, which was observed in sample B, is extraordinary from the viewpoint of a two-body interaction. This suggests that real colloidal systems are far more complicated than that predicted by the idealized theory. Although the origin of this phenomenon has not yet been clarified, the anomalous feature allows the diffracted waves to switch from a certain wavelength to another via a thermal process.

In conclusion, photoinduced phase transitions in colloidal crystals were realized by controlling the delicate balance of the interaction forces. It was found that light propagation could be modulated by these phase transitions. Our approach provides a new method to fabricate photoresponsive photonic crystals. Furthermore, this photoresponsive system provides an in situ method to study the interparticle interactions and the associated phase-transitional behavior.

Supporting Information Available: Schematic drawing of the experimental setup (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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