CdS Nanocrystal/Chelate Polymer Hybrid Systems: Controls of Optical and Morphological Properties by Monochromatic Photoirradiation

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ABSTRACT: Photo-controlled synthesis of CdS nanocrystal/polymer hybrids was demonstrated on the basis of in situ reaction between Cd^{2+} and S^{2-} in chelate polymer microparticles under monochromatic photoirradiation. The hybrids were characterized by absorption microspectroscopy, optical microscopy and transmission electron microscopy. In the presence of oxygen, photoirradiation on the reaction mixture resulted in photodissolution of CdS and this also rendered photoflocculation of the crystals in the polymer. This demonstrated that the morphologies of the nanocrystal in the polymer host with a layer-by-layer dispersion structure can be controlled by an appropriate choice of the irradiation conditions. In the presence of an electrolyte (i.e., NaCl) during the hybrid formation, flocculation of CdS was suppressed. The spectrum responsible for photodissolved CdS exhibited a prominent peak at around 468 nm. The results were reasonably explained by competition between formation and photodissolution of the CdS nanocrystals.

KEY WORDS CdS / Nanocrystal/Polymer Hybrid / Quantum Size Effect / Photoflocculation / Morphology / Photodissolution / Electrolyte

Size effects in mesoscopic systems of semiconductors (semiconductor nanocrystals) represented by CdS or CdSe, which are the intermediates between molecular and bulk systems, have been of great interest, and studied extensively for their spectroscopic, photochemical and photophysical properties in recent years.¹⁻⁴ The size dependence of the optical properties such as a large binding energy, a giant oscillator strength, large optical nonlinearity, and a short radiative time of semiconductor nanocrystals is a consequence of an exciton or electron-hole pair confinement in nanometer dimension.^{1, 5-6} In order to study these characteristic properties of nanocrystals, solution-phase methods have made possible preparation of well-defined nanocrystals, and studies on chemical/physical properties of nanocrystals have advanced by such new synthetic approaches.^{4, 6-8} For further development of basic science and applications in the relevant field, however, regulations of nanocrystal size, distributions, and surface defects are still important and worth studying in detail.

For size control of CdS nanocrystals, for instance, a photoetching method has been developed in aqueous solutions.⁷⁻¹⁰ This is based on the photochemical properties of II-VI semiconductors which are photoanodically dissolved in the presence of oxygen.⁹ When CdS is irradiated with a light energy exceeding the bandgap, electron-hole pairs are generated. When the electrons are scavenged, the holes in the valence band dissolve the semiconductor by the reaction with O_2 .⁷ The net reaction of photodissolution of CdS in the presence of O_2 can be thus described as,

and the quantum yield of the reaction has been reported to be ~ 0.04 in an aerated colloidal aqueous solution.⁹ Under photoillumination with a certain light energy, CdS nanocrystals whose bandgap energies are lower than the incident light energy are photochemically etched as described above, while those with the bandgap energies higher than the light energy are not excited and, thus, photoetching of CdS does not proceed.

This method is very useful for nanocrystal size tuning of CdS by an appropriate choice of the irradiation wavelength. However, the photoetching method accompanies a remarkable decrease in absorbance or number of CdS nanocrystals in a sample solution.^{7,10} Clearly, such phenomena are not preferable for various applications of semiconductor nanocrystals.

On the other hand, developments of functional materials and/or devices such as nonlinear optical materials,¹¹ photoconductive materials¹² and assembled nanostructures¹³ have also attracted current attention on the basis of hybridization of nanocrystals with another solid matrix. Among various matrices as a host medium, organic polymers are expected to provide both good mechanical and optical properties for nanocrystals, and also expected to stabilize the nanocrystals. In practice, a few studies on semiconductor nanocrystal/polymer hybrids have been reported: CdS or PbS nanocrystals in Nafion (perfluoroethylenesulfonic acid polymer),^{14,15} polyvinylcarbazole,¹² or acrylonitrile-styrene copolymer.¹⁶ For constructing nanocrystal/polymer hybrids, similar preparation methods to those in a solution phase are considered to be applicable. Furthermore, interesting dispersion morphologies and/or size distributions of nanocrystals different from those in solution are expected in the hybrids. However, such a study has been rarely explored.

We have been interested in fabrication of semiconductor nanocrystal/organic polymer hybrids as a possible approach to fine controls of both crystal size and their morphologies in polymeric media. Previously, we reported in situ syntheses of CdS nanocrystals in chelate polymer microparticles through the reaction of Cd^{2+} -incorporated resin beads with an aqueous Na_2S solution, and demonstrated that the size and morphological properties of the nanocrystals could be controlled by the host polymer particle size, the concentration of Na_2S , and addition of a foreign electrolyte.^{1 7-19} Unique dispersion textures of CdS nanocrystals were also observed in the hybrids; the nanocrystals were distributed homogeneously in the surface region of the polymer particles, while they were flocculated inside the polymer with a layer-by-layer distribution.

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In this study, we explored in situ synthesis of CdS/polymer hybrids under photoillumination: photoetching. We expect that the present method prevents a decrease in the number of nanocrystals by photodissolution, and that the crystal size and dispersion textures of CdS can be controlled by photoirradiation. As an interesting result of the study, furthermore, we found photoinduced flocculation of CdS nanocrystals in the polymer host for the first time. Thus, dispersion characteristics of CdS in the polymer has been shown to be controlled by photoirradiation. In this article, we report general features and the mechanisms of the photo-controlled syntheses of CdS in a chelate polymer resin.

EXPERIMENTAL

Chemicals

A chelate polymer resin (Chelex 100; 200-400 mesh, Analytical Grade, Bio-Rad Laboratories), constituted of a styrene-divinylbenzene copolymer having iminodiacetate ligands, was used as a host matrix for preparation of CdS nanocrystals. The resin was washed before use in a manner as reported previously.¹⁷ Cadmium acetate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$; GR grade, Kanto Chemical), sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$; GR grade, Wako Pure Chemicals), and sodium chloride (NaCl ; GR grade, Kanto Chemical) were used as received.

Syntheses of CdS/polymer Hybrids under Laser Irradiation

The polymer resin particles (0.075 g, dried weight) were soaked in an aqueous $\text{Cd}(\text{CH}_3\text{COO})_2$ solution (8.4×10^{-3} M, 3.5 mL) for 10 min under sonication, and stored for 48 h at room temperature. The Cd^{2+} -incorporated polymer particles were then washed with distilled water several times.

CdS nanocrystals/polymer hybrids (samples **a**) were prepared as follows. The Cd^{2+} -incorporated polymer beads were dispersed in 7.0 mL of distilled water for 10 min under stirring. Monochromatic light at 458 or 488 nm from an Ar^+ laser (Coherent, Innova 70) expanded through a concave lens to ~ 50 mm in diameter was then irradiated to the sample solution in a glass cell, and simultaneously, a freshly-prepared aqueous Na_2S solution (1.1×10^{-3} M, 70 mL) was added to the solution under aerated condition. Laser power was set 0.1 W throughout the study. The polymer particles turned pale yellow slowly, showing in situ formation of CdS in the chelate polymer. After stirring for 2 h under photoirradiation, the solution was filtered to collect the prepared hybrids. The hybrid particles were washed thoroughly with water and ethanol, and then dried under vacuum: sample **a**⁴⁵⁸ or **a**⁴⁸⁸ is abbreviated as that prepared under 458 or 488 nm irradiation, respectively. The CdS/polymer sample was also prepared under the dark by analogous procedures with those described above (sample **a**^{dark}).

Samples **b** were obtained by the procedures analogous to those employed for samples **a**. However, the Cd^{2+} -polymer particles were pretreated with 7.0 mL of an aqueous NaCl solution (0.5 M) for 10 min before addition of the Na_2S solution and laser irradiation (458 and 488 nm). After 2 h stirring under photoirradiation, the sample solution was filtered to collect the hybrids. After working-up procedures analogous to those for sample **a**, the particles were dried in vacuo: sample **b**⁴⁵⁸ or **b**⁴⁸⁸ is abbreviated as that prepared under 458 or 488 nm irradiation, respectively. Sample **b**^{dark} was also prepared under the dark.

Apparatus

Absorption spectra of single CdS/polymer particles were measured with a microspectroscopy system consisting of an optical microscope (Nikon; Optiphot 2) and a polychromator-multichannel photodetector (Hamamatsu Photonics; PMA-11) set as reported previously.¹⁷⁻¹⁹ Polymer particles were dispersed in water, and single polymer particles with the diameter of 100–110 μm were selected in a solution sample for the measurements.

The photographs of single CdS/polymer particles under the optical microscope were obtained using a video printer (Mitsubishi; CP710), whose images were measured with a CCD video camera (Sony; Model DXC-930) equipped to the microscope. Transmission electron microscopy (TEM) was conducted by using a JEOL JEM 100CX electron microscope. An ultrathin section of the sample was prepared by cutting CdS/polymer hybrids embedded in an epoxy resin.

RESULTS AND DISCUSSION

Photoirradiation Effects on CdS/Polymer Hybrids Formation

Figure 1 shows absorption spectra of CdS nanocrystals for samples **a** without and with photoirradiation at the reaction times (*t*) of 30 min and 2 h. At *t* = 30 min, all the samples (**a**⁴⁵⁸, **a**⁴⁸⁸, and **a**^{dark}) gave analogous results. With increasing *t*, the absorbance of CdS increased while the spectral band shape was almost independent of the reaction conditions, indicating relatively slow nanocrystal formation with a similar size distribution. At *t* = 2 h, however, a difference in the absorbance was observed with the sequence of **a**^{dark} > **a**⁴⁸⁸ > **a**⁴⁵⁸ as seen in Figure 1. The absorption spectrum of the CdS/polymer sample prepared by photoirradiation under the N_2 -gas purged condition was quite similar to that of sample **a**^{dark}. The results indicate that photoanodic dissolution of CdS also takes place simultaneously with the formation of CdS nanocrystals in the polymer. Thus, the nanocrystal formation/growth of CdS in the chelate polymer is suppressed by photoirradiation, and suppression of the CdS formation is more pronounced by a shorter wavelength light irradiation with the same intensity.

Since a decrease in the absorbance of CdS was observed under photoirradiation, changes in the morphologies of CdS nanocrystal dispersion are also expected. Previous studies

Figure 1. Absorption spectra of CdS nanocrystals for samples **a** without and with photoirradiation at the reaction times (*t*) of 2 h (a–c) and 30 min (d).

demonstrated that CdS nanocrystals with a zincblend structure were distributed only in the surface regions of the chelate polymer with a layer-by-layer structure, and a ring shade in the polymer particle was observed under an optical microscope owing to slight light scattering by the flocculated nanocrystals.^{17,18} We also revealed that the distance (L) from the polymer surface to the periphery of the ring corresponded to the thickness of the dispersion layer of the produced CdS. Thus, the effects of photoirradiation on L were examined for samples **a**. Figure 2 shows an L dependence of the absorbance at 450 nm for each sample. Since the spectral band shape was quite similar between the samples, the absorbance at 450 nm is proportional to the amount of CdS dispersed in the L layer. The shorter was the irradiation wavelength, the smaller was L . The results indicate that dispersion of the CdS nanocrystals in the polymer can be controlled by monochromatic photoirradiation and its photon energy. This is a characteristic feature for in situ preparation of the nanocrystal/polymer hybrids, since the CdS formation proceeds from the surface toward the inside of the polymer particle. If the density of CdS nanocrystals in the polymer is the same with each other, the absorbance should increase linearly with increasing L ($2L$ corresponds to the optical path length) as shown by the dotted line in Figure 2. However, the absorbance obtained under photoirradiation is larger than that expected from the unirradiated sample with a given L , indicating that the density of the nanocrystals in the polymer varies by photoirradiation, and irradiation at a shorter wavelength renders the nanocrystal density to be larger in the polymer.

In order to obtain clear information about the dispersion characteristics of CdS, TEM (transmission electron microscopy) measurements were performed. Figures 3 and 4 show TEM images of the cross section of CdS/polymer hybrids for samples **a**^{dark} and **a**⁴⁵⁸, respectively.

The parts a, b, and c in Figures 3 and 4 show the images of the regions at around the polymer surface, ~ 10 , and ~ 15 μm inside from the polymer surface, respectively. No crystals were observed in the center region of the polymer. A layer-by-layer distribution structure of CdS was observed for both samples. No flocculation of CdS nanocrystals (diameter: 3–4 nm) was observed in the polymer surface region, while the nanocrystals (diameter: 4–7 nm) flocculate to produce larger particles inside the polymer. The size of the flocculated CdS crystals increases on going from the polymer surface to inner

Figure 2. L (thickness of the dispersion layer) dependence of the absorbance at 450 nm for samples **a**.

Figure 3. TEM images of the CdS/polymer hybrid for sample **a**^{dark}. (a), (b), and (c) are the images of a region next to the surface, ~ 10 μm inner from the surface, and ~ 15 μm inside from the surface, respectively.

Figure 4. TEM images of the CdS/polymer hybrid for sample **a**⁴⁵⁸. (a), (b), and (c) show images at around the surface region, ~ 10 μm inner from the surface, and ~ 15 μm inside from the surface, respectively.

regions as recognized by the fact that the morphology changes from the surface (Figures 3a or 4a) to the inside (Figures 3b or 4b). A remarkable difference was observed in the parts c in Figures 3 and 4. For sample **a**^{dark}, the flocculated structure seen at ~ 10 μm inside from the polymer surface was similar to that at ~ 15 μm , while flocculation proceeded drastically on going from ~ 10 μm to ~ 15 μm for sample **a**⁴⁵⁸. The results indicate that photo-induced flocculation occurs during the formation of the CdS/polymer hybrids. The directional photoflocculation is characteristic to the CdS/polymer hybrid. Since the size of the nanocrystals does not change (4–7 nm) inside the polymer, it is reasonable that the shape of the absorption spectrum is independent of the reaction conditions as demonstrated in Figure 1. It is noteworthy that the CdS crystal formation is terminated at ~ 15 μm inside from the polymer surface for sample **a**⁴⁵⁸, which is in good accordance with the length (L) from the surface to the ring structure in the polymer (Figure 2).

Mechanism of Morphological Changes of CdS Nanocrystals in the Chelate Polymer

It has been demonstrated for the first time that the dispersion properties of CdS in the host polymer and their flocculated state can be controlled by photoirradiation during the CdS nanocrystal/polymer hybrid formation processes. For further fine controls of the properties of the CdS/polymer hybrids, the

factors determining the dispersion characteristics of CdS and its mechanisms are worth elucidating.

According to the quantum size effect, the transition energy or bandgap energy of a nanocrystal should correspond uniquely to its crystal size.¹ When CdS nanocrystals grow to a size corresponding to the irradiation light wavelength, they absorb incident light to produce electron-hole pairs. Some of them are deactivated by recombination, leading to successive growth to larger CdS crystals. On the other hand, the excited CdS survived from electron-hole recombination would react with oxygen, and the nanocrystals in the chelate polymer are photodissolved completely.^{19,20} As a result, Cd²⁺ ions are generated in the polymer during photoillumination. When Na₂S diffuses from the polymer surface into the inner region, CdS nanocrystals are produced again through the reaction between Cd²⁺ and HS⁻.²¹ The formation-photodissolution cycle(s) of CdS would proceed in the polymer and this leads to an apparent decrease in the rate of Na₂S diffusion. Since the number of CdS nucleus decreases, CdS should flocculate: photoflocculation. The apparent decrease in the Na₂S diffusion rate in the polymer upon photoirradiation makes the CdS nanocrystal dispersion layer (*L*) shorter, and it also accelerates the crystal flocculation as mentioned above. When the hybrid is prepared by shorter wavelength monochromatic light irradiation, excitation of CdS takes place more efficiently owing to a large absorption index of CdS at the shorter wavelength. Therefore, photodissolution of CdS will exceed to deactivation by electron-hole pair recombination. This should accompany consumption of a large amount of S²⁻ in the polymer, leading to a small value of *L*. The proposed mechanism is summarized in Scheme 1, and this is what is observed in the present experiments (Figure 2). Regulation of the morphologies of CdS nanocrystal dispersion by monochromatic light irradiation is highly characteristic to the CdS/polymer hybrids.

Scheme 1

Photoirradiation Effects on CdS/Polymer Hybrids Formation in the Presence of NaCl

It has been reported that the presence of an electrolyte (i.e., NaCl) during the synthetic procedures of the CdS/polymer hybrid leads to a faster apparent rate of Na₂S diffusion and it also prevents flocculation of CdS nanocrystals inside the polymer.¹⁸ This is another characteristics of the present system different from conventional solution phase synthesis of

CdS. Therefore, we studied photoirradiation effects on the CdS formation in the presence of NaCl analogous to those for samples a.

Figure 5 shows absorption spectra of the CdS nanocrystals for samples **b** without photoirradiation (sample **b**^{dark}) at *t* = 30 min and 2 h. The ring structure due to flocculation of the CdS nanocrystals was not observed in the polymer particles, indicating that flocculation of CdS was suppressed similar to the results reported previously.¹⁸ As a characteristic effect of NaCl, the initial rate of the CdS formation was fast compared

Figure 5. Absorption spectra of the CdS nanocrystals for sample **b**^{dark} at *t* = 30 min and 2 h. The inset shows the difference spectrum between that at *t* = 2 h and 30 min.

Figure 6. Absorption spectra of sample **b**⁴⁵⁸ at *t* = 30 min and 2 h. The inset shows the difference spectrum between that at *t* = 30 min and 2 h.

to that in the absence of NaCl. The faster rate of the CdS formation in the presence of NaCl is due to an increase in the rate of diffusion of HS^- in the polymer, as compared to that in the absence of NaCl. This has been interpreted by a change in the Donnan potential at the polymer particle/water interface.¹⁸ Since the addition of NaCl decreases the Donnan potential, the amount of HS^- diffused into the polymer increases as compared to that without NaCl. The inset in Figure 5 shows the difference spectrum between those at $t = 2$ h and 30 min. Since the band shape of the difference spectrum was almost the same with the absorption spectra observed at $t = 30$ min and 2 h, CdS nanocrystals with a similar size distribution were generated in the polymer during the reaction (90 min).

Upon laser irradiation at 458 nm, however, quite different optical properties of the CdS/polymer hybrids were observed. Figure 6 shows absorption spectra of sample **b**⁴⁵⁸ at $t = 30$ min and 2 h. According to the figure, the absorbance of CdS at $t = 30$ min was larger than that at 2 h. Since the absorbance change with t for the hybrid prepared under irradiation of an N_2 -gas purged sample was quite similar to that prepared under dark, it is concluded that Na^+ and Cl^- ions do not catalyze dissolution of CdS^{22,23} and the decrease in the absorbance is ascribed to photoanodic dissolution of CdS nanocrystals by oxygen. The result indicates that the rate of photodissolution exceeds to that of CdS formation. Moreover, the absorption spectrum at $t = 2$ h exhibited a more distinct excitonic shoulder compared to that at 30 min. Thus, the difference spectrum between at $t = 30$ min and 2 h was obtained as shown in the inset in Figure 6. A well-resolved peak was clearly observed at around 468 nm, which was longer than the irradiation wavelength (458 nm) by ~ 10 nm. The result indicates that larger-sized CdS nanocrystals compared to the size of CdS, which corresponds to the irradiation wavelength (~ 4 nm),¹ are selectively dissolved as expected from the quantum size effects. In the present system, however, since both dissolution and formation of CdS take place simultaneously in the polymer, the apparent shift (~ 10 nm) of the peak position of the difference spectrum compared to the irradiation wavelength is caused by the balance between dissolution and formation of the CdS nanocrystals.

We calculated the absorption spectrum of the photodissolved CdS component during the reaction (from $t = 30$ min to 2 h) by subtracting the spectrum of the hybrid prepared by irradiating sample **b**^{dark} (458 nm, 90 min) from that of sample **b**^{dark} itself. Figure 7a (i) shows the difference spectrum (photodissolution component) of the CdS nanocrystals in the polymer. A broad spectrum was observed without an excitonic-like peak, indicating that the size selective etching of the nanocrystals is not achieved by irradiating monochromatic laser light to the prepared hybrids. Since the spectrum in Fig. 7a (ii) corresponds to that at the balance between dissolution and formation of CdS (obtained in Figure 6, inset), the spectral difference between (i) and (ii) in Figure 7a, shown in Figure 7b, represents the spectrum of the formation component of CdS during the reaction. The spectrum shows that the absorption onset of the produced CdS nanocrystals is coincided with the incident wavelength, suggesting that CdS formation larger than ~ 4 nm (estimated by the quantum size effects) is suppressed by laser light irradiation. Therefore, a resolved peak observed apparently in the difference spectrum is explained reasonably by the balance between dissolution and formation of the CdS nanocrystals in the polymer.

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Figure 7. Upper: (i) Absorption difference spectrum that corresponds to the photodissolution component of the CdS nanocrystals in the polymer. (ii) Absorption difference spectrum that corresponds to the balance between dissolution and formation components of CdS (obtained in Figure 6, inset). Lower: Spectral difference between (i) and (ii).

It is noteworthy that photoirradiation at 488 nm during the CdS/polymer hybrids formation (sample **b**⁴⁸⁸) affords similar results with those for sample **b**^{dark}. Thus, competition between formation and dissolution of CdS would be of primary importance for size-selective nanocrystal dispersion of CdS in the polymer.

Characteristic Features of Photo-Controlled Syntheses of the CdS/Polymer Hybrids

It was demonstrated that the presence of NaCl in the reaction mixture promoted the initial rate of CdS formation and it also suppressed flocculation of CdS nanocrystals in the polymer. It was shown that this led to the morphological changes of the nanocrystals in the polymer host, although an addition of an electrolyte disturbs CdS nanocrystal formation in solution-phase synthesis.¹⁸ Monochromatic photoirradiation during the hybrid formation processes brought about a decrease in the rate of diffusion and the concentration of Na_2S in the polymer, due to consumption of the ion by the reaction with Cd^{2+} produced by photoanodic dissolution ($\text{CdS} + 2\text{O}_2 \rightarrow \text{Cd}^{2+} + \text{SO}_4^{2-}$). This rendered photoinduced morphological changes of CdS dispersion in the polymer matrix. The phenomena are owing to the directional formation of CdS from the polymer surface to the center of the particle. Thus, the layer-by-layer distribution of the nanocrystals (morphology) caused by flocculation of CdS in the polymer is controlled by monochromatic photoirradiation and/or the addition of an electrolyte as characteristic features of the CdS nanocrystal/polymer hybrids.

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20. Photo-redox decomposition of iminodiacetate groups by excited CdS nanocrystals should be also considered. Thus, IR spectrum measurements were explored for sample a^{dark} and the sample that photo-illuminated at 458 nm for 4 h. Although the illuminated sample showed photodissolution of CdS, the absorbance of the COO⁻ stretch band observed at ~1625 cm⁻¹ was almost unchanged for both samples. (The IR spectra were compared by normalizing the absorbance of the deformation band of the phenyl groups at 700cm⁻¹ for both samples.) The results indicate that photo-redox reaction by oxygen was the main origin for photodissolution of CdS.
21. Under the present condition, ionic species reacting with Cd²⁺ is HS⁻.
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23. It is known that Cl⁻ ions interact with the surface of CdS (*ref.* 22). However, this did not contribute to the present photoirradiation effects since the CdS/polymer sample prepared under N₂-gas purged conditions in the presence of NaCl did not result in photodissolution of CdS.