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Preparation of Quantized-CdS Doped Poly(Methyl Methacrylate) Films. Optical and Morphological Properties

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Optically transparent poly(methyl methacrylate) films incorporated with CdS quantum crystallites are prepared by using pyridine-soluble phenyl-capped CdS microcrystallites(av. 2 –8 nm). The morphology of the CdS in the films is characterized by UV-vis spectroscopy and TEM, and the film doped with av. 8-nm CdS is found to have large third-order nonlinearity by degenerate four-wave mixing technique.

Since the large third-order nonlinearity was disclosed in glasses doped with very small CdS_xSe_{1-x} particles,1) semiconductor microcrystallites whose diameter is less than 10 nm have currently been of much interest in view of photochemical and photophysical effects of quantum confinement as three dimensional quantum materials.2) Recently, synthetic procedures have been developed to prepare under the control of size and uniformity of quantized semiconductors.3,4) On the other hand, we have recently revealed that ZnS and CdS dispersions freshly prepared in solution consist of quantized particles and their loose aggregates and then show effective activities of photo-induced charge separation, leading to almost quantitative photoredox reactions.5,6) With these in view, pioneering properties of quantized semiconductors has been focused as a new class of optical material.7) In particular, quantized semiconductor particles which may show high solubility in organic solvent have become interesting and promising for preparation of optically novel organic polymers. In this paper, we report the preparation of poly(methyl methacrylate) (PMMA) film incorporated with phenyl-capped CdS quantum crystallites, and disclose the morphology and the third-order optical nonlinearity of the phenyl-capped quantized CdS in the film.

The phenyl-capped CdS particles (Φ-CdS) were prepared according to the modified method of AT&T Bell Laboratories, i.e. during the reaction of Cd^{2+} with $S(TMS)_2$ (TMS=trimethylsilyl) in Aerosol OT (AOT)/H_2O/heptane reversed micelle solution, the surface of the resulting CdS microcrystallites was *in site* stabilized with PhS(TMS) under adjustment of the $S(TMS)_2$-to-PhS(TMS) ratio (Table 1).3) Φ-CdS-A was precipitated by the addition of PhS(TMS), but Φ-CdS-B and Φ-CdS-C were precipitated only when a few

Table 1. Preparation and Properties of Phenyl-capped CdS and Their Doped PMMA Films

Expt. conditions [a)]	Φ-CdS-A	Φ-CdS-B	Φ-CdS-C
Cd^{2+} [b)]	0.5 cm^3(0.5 mmol)	0.5 cm^3(0.5 mmol)	0.5 cm^3(0.5 mmol)
$S(TMS)_2$ [c)]	0.1 cm^3(0.1 mmol)	0.25 cm^3(0.25 mmol)	0.4 cm^3(0.4 mmol)
PhS(TMS) [d)]	1.14 cm^3(0.80 mmol)	0.71 cm^3(0.50 mmol)	0.29 cm^3(0.20 mmol)
Particle size [e)]	2.4 nm	6.2 nm	7.9 nm
Expt. conditions and results	Φ-CdS-A PMMA film	Φ-CdS-B PMMA film	Φ-CdS-C PMMA film
PMMA [f)]/pyridine [g)]	250 mg/20 cm^3	250 mg/20 cm^3	250 mg/20 cm^3
Φ-CdS/pyridine	5.5 mg/2 cm^3	5.2 mg/2 cm^3	4.2 mg/2 cm^3
Thickness [h)]	53 μ	60 μ	78 μ
$\chi^{(3)}$	$<10^{-14}$ esu	6.2×10^{-12} esu	1.6×10^{-11} esu

a) In AOT/H_2O/heptane reversed micelle solution (15 g/2 cm^3/500 cm^3). b) As perchlorate solution (1 M). c) As heptane solution (1 M). d) As heptane solution (0.7 M). e) Determined by the dynamic light scattering technique with Dynamic Light Scattering Spectrophotometer DLS-700 (Otsuka Electronics). f) The gift from Mitsubishi Rayon CO., Ltd.; d=1.19, n_D=1.49. Purified by reprecipitation from the toluene solution using methanol before use. g) The pyridine solution was centrifuged (4 000 RPM 5 times) to eliminate very small suspended impurities of all kinds and the supernatant solution was used for the film preparation. h) Determined by a thickness gauge.

drops (5 drops) of pyridine were added in the reversed micellar reaction mixture. The precipitated CdS's were collected by a ultracentrifuge, washed with petroleum ether using an ultrasonic washer, collected by the ultracentrifuge and dried in vacuo at 40 °C.

The phenyl-capped CdS microcrystallites were analyzed by high resolution ^1H NMR (400 MHz). The phenyl protons split into three groups, which shift downfield more than those of $Cd(SPh)_2$; Φ-CdS-B in DMSO: 7.32 (t, 1H), 7.39 (t, 2H), 7.54 (d, 2H); $Cd(SPh)_2$ in DMSO: 6.85 (t, 1H), 6.93 (t, 2H), 7.30 (d, 2H). The downfield shift is consistent with the successful modification with PhS(TMS) and may be explained as due to the magnetic anisotropy of phenyl rings on Φ-CdS. The ^1H NMR analysis also indicated that pyridine molecules should not be removed from Φ-CdS-B and C by the above-mentioned work-up. The case was also true for AOT molecules.

Φ-CdS's thus obtained were found to have excellent solubility in pyridine and gave transparent pyridine solutions. The size distribution of Φ-CdS's dissolved in pyridine was determined by dynamic light scattering technique as shown in Fig. 1. The size distribution is not broad for each Φ-CdS, supporting the successful control of the size by adjusting the $S(TMS)_2$-to-PhS(TMS) ratio in the reversed micelle system.[4)]

For the preparation of PMMA films doped with each Φ-CdS, the PMMA-pyridine solution was mixed with each Φ-CdS-pyridine solution, and quartz plates were coated with the resulting solutions. After the coated plates were dried in vacuo for 2 h at 70 °C, transparent Φ-CdS doped PMMA films (which contain ca. 2% Φ-CdS) were obtained on

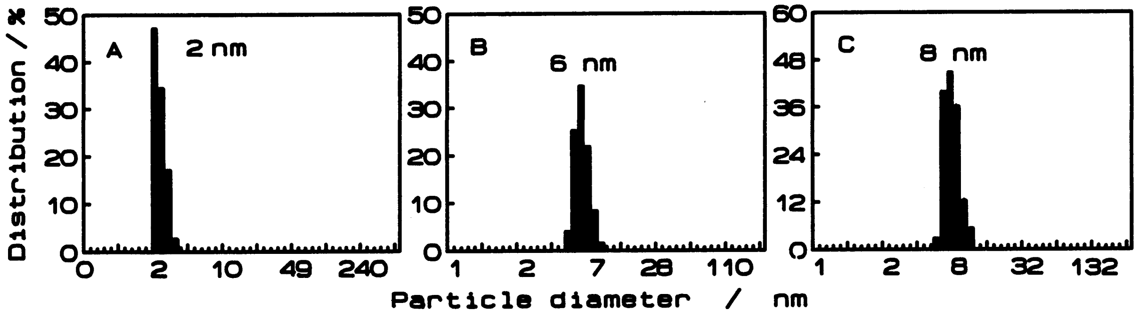

Fig. 1. Size distribution of Φ-CdS in pyridine.

quartz plates (Table 1).

A series of UV-vis spectra are almost identical (Fig. 2a-c) for the corresponding CdS microcrystallites formed in the reversed micelle solution, Φ-CdS's, and those in the PMMA film, implying that the size was maintained during the modification with PhS(TMS) and the incorporation in the PMMA films.

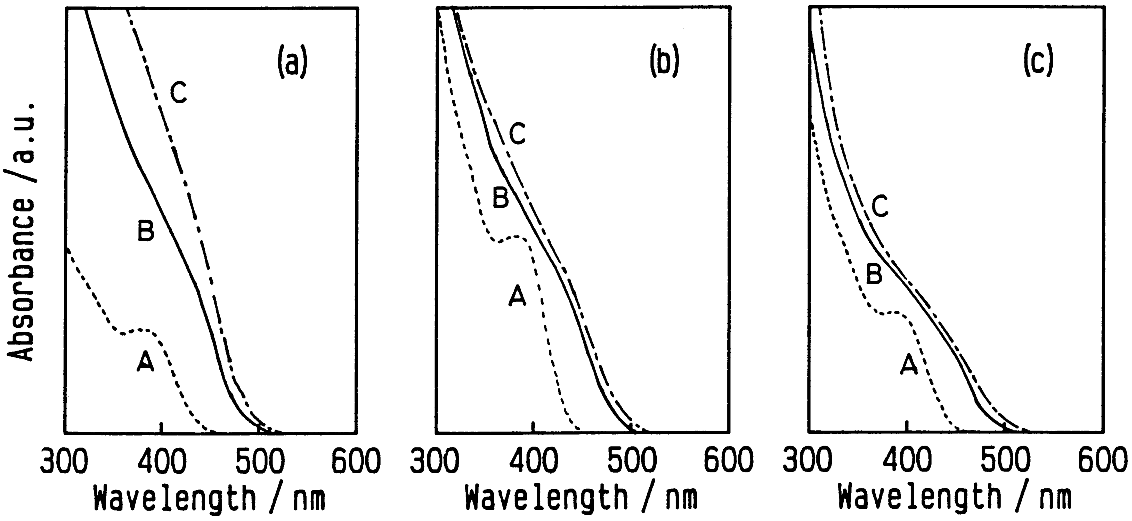

Fig. 2. Absorption spectra of quantized CdS measured at room temperature; (a) formed in reversed micelle, (b) Φ-CdS in pyridine, (c) Φ-CdS in PMMA.

Direct TEM observation of Φ-CdS-A reveals that many particles ranged from 1.5 to 4 nm, showing clearly resolved lattice fringe whose spacing was 3.36 A as shown in Fig. 3, which supports the cubic structure of CdS. Φ-CdS-A PMMA film was peeled off and embedded in an epoxy resin. Vertical sections of the film in the resin were sliced to desired thickness (80 nm) with an ultramicrotome and were fixed on copper grids and examined by high resolution microscopy. As shown in Figs. 3a and 3b, Φ-CdS-A particles are uniformly dispersed with the formation of secondary hollow particles whose diameter ranges from 5 to 15 nm and they consist of a few primary particles whose size ranges from 1.5 to 3.5 nm. These observations strongly suggest that Φ-CdS particles should have no tendency to aggregate to larger particles because of the surface modification, and that the surface stabilization with PhS(TMS) should work on very small CdS microcrystallites (ca. 3 nm).

To determine the macroscopic effective $\chi^{(3)}$ of the Φ-CdS doped PMMA films, we

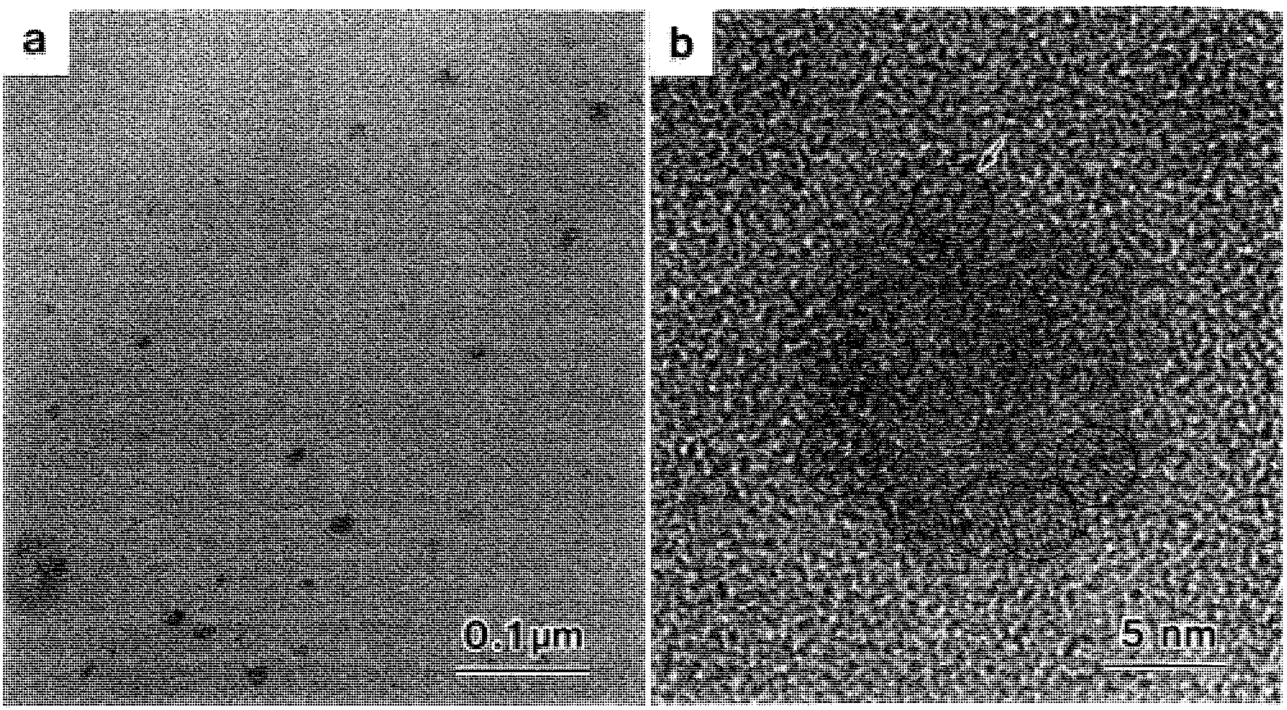

Fig. 3. Transmission electron micrographs of Φ-CdS-A in PMMA film obtained with a Hitachi Model H-9000 equipped with a tilting device (±10 degrees) and operated at 300 kV (Cs=0.9 mm): (a) bright-field image, (b) high resolution image of a secondary particle (ca. 15 nm). Encircled (3 nm) in (b) are some of the primary particles composing the secondary particle.

used a degenerate four-wave mixing technique. The detail of this technique will be reported elsewhere. As shown in Table 1, it has been found that the third-order nonlinearity increases with the increase in size of Φ-CdS and it is noteworthy that $\chi^{(3)}$ of Φ-CdS-C is quite comparable with that of CdS_xSe_{1-x} doped glass, HOYA Y-52, whose $\chi^{(3)}$ we determined to be 1.1×10^{-11} under the comparable conditions.

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