Semiconductor Photocatalysis:[1] Size Control of Surface-Capped CdS Nanocrystallites and the Quantum Size Effect in Their Photocatalysis

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Size-controlled CdS nanocrystallites were prepared by using thiophenol or hexanethiol as a capping reagent by controlling the ratio of Cd^{2+} to bis(trimethylsilyl) sulfide ($S(TMS)_2$) as a source of the sulfide ion in reversed micelles. Their solubility and photocatalysis were examined. A series of size-controlled phenyl-capped CdS nanocrystallites catalyze the photoreduction of aromatic ketones in the presence of triethylamine as an electron donor under visible-light irradiation. The photocatalytic activity is affected by the particle size, i.e., the reducing power of the photogenerated electron on CdS nanocrystallites toward the ketones increases with decreasing the particle size. The enhancement of photocatalytic activity observed by reducing the particle size should be ascribed to not only a negative shift of the conduction band edge, but also suppression of the formation of surface defects.

A quantum size effect is induced for semiconductor particles by reducing their size to less than 10 nm.[2,3] This effect has been observed as a blue shift of the absorption edge and the effective emission spectra due to the confinement of electrons and holes in quantum dots.[4] It has been predicted that photogenerated electrons in quantum-size semiconductor particles are long-lived and possess a high reducing power.[5] Therefore, reducing the size of semiconductor particles should result in an enhancement of the photocatalytic activity of semiconductors for redox reactions induced by photogenerated electrons and holes.

There have only been a few reports concerning an enhancement of the photocatalysis of semiconductors induced by a reduction of the particles sizes in this context.[6—12] All of these studies showed just a qualitative increase in the photocatalytic activity of nano-scale particles when compared with micro-scale particles. In order to obtain direct evidence of a nano-scale size effect on a gradual variation of the photocatalysis, we attempted to prepare size-controlled nano-structured CdS by using a reversed micelle method.[13,14] This paper concerns the preparation and characterization of CdS nanocrystallites surface-capped with a phenyl or hexyl group, and with their photocatalysis. An enhancement of the photocatalytic activity has been vividly observed by decreasing the particle size.

Experimental

Reagents. Bis(2-ethylhexyl) sulfosuccinate (Aerosol-OT; abbreviated as AOT, purchased from Aldrich Chemical Company, Inc., 99% purity) was purified as described below; it was dissolved in petroleum ether, and the solution was filtered to remove particles. The filtrate was evaporated to dryness. $Cd(ClO_4)_2{\cdot}6H_2O$ (Mitsuwa Chemicals, 99%), $Cd(CH_3COO)_2{\cdot}2H_2O$ (Nacalai Tesque Inc., Special Grade), and $Na_2S{\cdot}9H_2O$ (Wako Pure Chemical Industries, Ltd., Special Grade) were used without further purification. Bis(trimethylsilyl) sulfide ($S(TMS)_2$) was synthesized via a literature method.[15—17] Phenylthiotrimethylsilane (PhS(TMS)) was purchased from Aldrich Chemical Company, Inc. Thiophenol (First Grade) was purchased from Nacalai Tesque Inc. Hexyltrimethylsilane (RS(TMS)) was synthesized as described below. A solution of methyllithium (1.4 M, 100 ml, 1 M=1 mol dm^{-3}) in diethyl ether was added to diethyl ether containing hexanethiol (10 g). After the evolution of methane ceased, chlorotrimethylsilane (15.1 g) was dropped into the solution. After being stirred for 12 h, the product was separated by evaporation and purified by distillation in vacuo. Methanol and acetonitrile were purified by conventional distillation. Pyridine (special grade) and distilled water (HLPC grade) were used as purchased from Wako Pure Chemical Industries, Ltd.

Preparation of CdS Nanocrystallites in AOT Reversed Micelles. Phenyl-capped CdS particles (ϕ-CdS) were prepared according to a modified method reported by Steigerwald et al.,[13] i.e., during the reaction of Cd^{2+} with $S(TMS)_2$ (TMS=trimethylsilyl) in an AOT/H_2O/heptane reversed-micelle solution; the surface of the resulting CdS microcrystallites was in situ stabilized with PhS(TMS) under adjustment of the $S(TMS)_2$-to-PhS(TMS) ratio.[14]

The reversed-micelle solution was prepared by adding AOT (15 g) and water (2 ml) to heptane (500 ml). The mixture was magnetically stirred until it became homogeneous. To this solution were added a $Cd(ClO_4)_2$ aqueous solution (1 M, 0.5 ml) and a heptane solution of $S(TMS)_2$ (1 M), resulting in the formation of CdS in the reversed micelles. Subsequently, a heptane solution of PhS(TMS) (1 M) was added to the solution in order to obtain the ϕ-CdS. Finally, the introduction of pyridine destroyed the reversed micelles and enabled the separation of ϕ-CdS by centrifuging. The resulting yellow powder of ϕ-CdS was thoroughly washed with petroleum ether, and dried in vacuo.

CdS nanocrystallites capped with a hexyl group were prepared in the same manner as described above using RS(TMS) as the capping reagent (denoted as R-CdS, hereafter).

Analytical Measurements. Analytical measurements were carried out to characterize ϕ-CdS and R-CdS with the following instruments: Hitachi spectrophotometers (220-A and U-3300) for absorption spectra, a Hitachi fluorescence photometer (850) for the emission spectra, a JASCO infrared absorption spectrometer (260-10) for the IR spectra and a JNM-PMX-100 or JNM-GSX-400 for the NMR spectra.

Dynamic light scattering (Otsuka Denshi DLS 700) and TEM (Hitachi Model H-9000) were employed in order to obtain information about the diameters and crystal structures.

Determination of the Solubility. Saturated solutions of capped CdS nanocrystallites in various solvents were prepared. The solubilities of the nanocrystallites were determined by measuring the absorption of these solutions at 320 nm after appropriate dilution.

Photoreduction of Methyl Viologen. A methyl viologen (MV^{2+}) aqueous solution (4 mmol) was introduced into a DMSO solution (4 ml) of ϕ-CdS in a quartz-made UV cell (10 mm×10 mm) under an Ar atmosphere, and then irradiated with monochromatic light (λ=400 nm). The concentration of the reduced species ($MV^{+\cdot}$) was determined by measuring the absorption intensity of this species at 606 nm.

Photoreduction of Aromatic Ketones. A substrate (2 mM) and triethylamine (0.5 M) as an electron donor were introduced into and *N*,*N*-dimethylformamide (DMF) solution (4 ml) of size-controlled ϕ-CdS in a reaction vessel (a pyrex tube with 8 mm-diameter). The resulting solution was bubbled with argon. The reaction vessel was sealed with a rubber cap and then irradiated through a filter containing a $NaNO_2$ aq solution with a tungsten–halogen lamp under water-cooling (λ>400 nm). The substrates and products were analyzed quantitatively by HPLC.

Results and Discussion

Characterization of Phenyl-Capped CdS. IR and NMR spectra were measured in order to characterize phenyl-capped CdS (ϕ-CdS). The presence of a capping reagent on the surface of ϕ-CdS was supported by the IR absorption peaks assigned to ring stretching of the benzene ring (1500 and 1583 cm^{-1}) and C–S stretching (700 cm^{-1}), by the ^1H NMR peaks assigned to the protons of phenyl group, and by the ^{13}C NMR peaks (ϕ-CdS; 127.0 ppm, 127.3, 129.2, 135.7, free PhSH; 125.4 ppm, 128.9, 129.2, 130.7) assigned to carbons of phenyl group. In the ^1H NMR spectrum measured in a DMSO-d_6 solution, the peaks assigned to protons in the phenyl group split into three groups, which shifted down field more than those of $Cd(SPh)_2$ and the thiophenol molecule (PhSH): ϕ-CdS: 7.32 ppm (t, 1H), 7.39 (t, 2H), 7.54 (d, 2H); $Cd(SPh)_2$: 6.85 (t, 1H), 6.93 (t, 2H), 7.30 (d, 2H); PhSH: 7.12 (t, 1H), 7.24 (t, 2H), 7.29 (d, 2H). The down-field shift supports the successful modification with PhS(TMS), and may be explained as being due to the magnetic anisotropy of the phenyl rings on ϕ-CdS.

Besides, these spectroscopic analyses showed the presence of residual AOT and pyridine on ϕ-CdS. The IR absorption peaks assigned to $-SO_3Na$ (1000, 1100—1300 cm^{-1}) and –C=O (1740 cm^{-1}) and the ^1H NMR peaks at the high magnetic field assigned to protons bound to sp^3 carbons indicated the presence of AOT in ϕ-CdS.[17] The ^1H NMR spectrum also showed the presence of residual pyridine; 6.97, 7.59, 8.57 ppm. These spectroscopic data show that the surface of ϕ-CdS was covered not only with the capping reagent, but also with small amounts of residual AOT and pyridine. These residual organic compounds could affect the surface properties of ϕ-CdS.

A direct observation of ϕ-CdS by transmission electron microscopy (TEM) revealed that most particles ranged from 2 to 5 nm in diameter (see Fig. 1). They clearly showed a resolved lattice fringe with a spacing of 3.36×10^{-1} nm, which supports the cubic structure of CdS.

The above characterization with the spectroscopies and the TEM analysis indicates that CdS nanocrystallites with a narrow-diameter distribution are preparable and that their surface is chemically modified by thiophenol, as reported by Steigerwald et al.[13]

Size-Control of Surface-Modified CdS Nanocrystallites. Steigerwald et al. have reported that the crystal growth of CdS nanocrystallites could be controlled by using a reversed micelles as a constraint reaction field.[13] In order to obtain size-controlled ϕ-CdS, the authors reinvestigated this study on crystal growth. The same quantities of $Cd(ClO_4)_2$ and $S(TMS)_2$ as those used in the preparation of CdS were added to the solution successively after the preparation of CdS nanocrystallites in reversed micelles. PhS(TMS) was added to terminate the crystal growth at the final stage of the preparation. Steigerwald et al. measured only the absorption spectra for an evaluation of the particle diameters of CdS, and presumed the growth of the particle size based on the red-shift in the absorption. We observed a stepwise growth of the crystal size by measuring the particle size of ϕ-CdS redissolved in pyridine with the dynamic light scattering (DLS). The mean di-

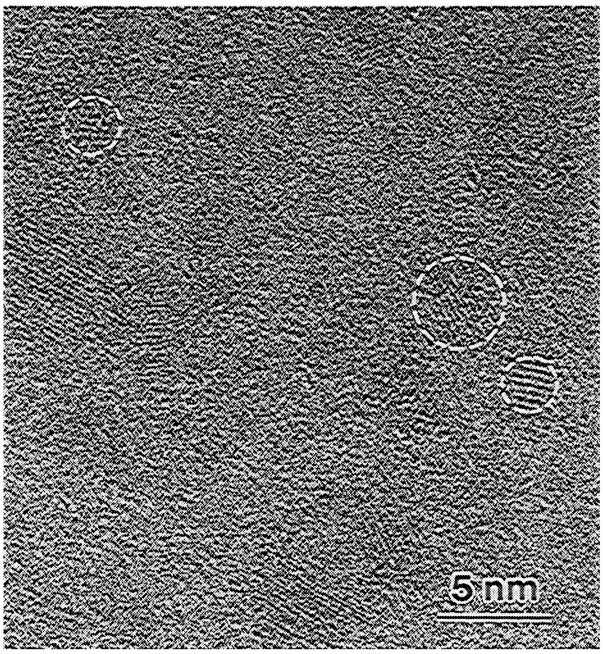


Fig. 1. Transmission electron micrograph of ϕ-CdS prepared by the reversed micelle method. The preparation conditions are described in the experimental section. The quantity of $S(TMS)_2$ added was 0.25 mol.

ameter of ϕ-CdS was 4 nm, just as prepared, and increased to 10 nm by the repeated addition of reagents. It was further increased to 13 nm by a one-more-time addition of reagents. The observation of the particle size indicates that the surface of CdS nanocrystallites is reactive in reverse micelles and that crystal growth is not accompanied by a broadening of the size distribution.

On the other hand, Petit et al. pointed out a tendency that the particle size depends on the ratio of the quantities of cadmium cation and sulfide anion ($[Cd^{2+}]/[S^{2-}]$).[19] We also investigated the change in the particle size of CdS nanocrystallites with a gradual increase in the $[Cd^{2+}]/[S^{2-}]$ ratio by adding $S(TMS)_2$ using the reversed-micelle method. It has been revealed in the present work that the quantity of $S(TMS)_2$ added into the emulsion is a decisive factor in determining the size of the CdS nanocrystallites. Figures 2 and 3 show the change in the size distributions of ϕ-CdS and R-CdS prepared by adding $S(TMS)_2$ at various quantities, respectively. When the quantity of $S(TMS)_2$ was increased stepwise close to that of $Cd(ClO_4)_2$, the diameter was gradually increased from 2 to 10 nm without any broadening of the size distribution. The correlation between the quantity of $S(TMS)_2$ and the mean diameters is shown in Fig. 4, demonstrating the increase in the particle size with an increase in the amount of $S(TMS)_2$. Such size control could also be achieved by using hexanethiol instead of thiophenol (Figs. 3 and 4).

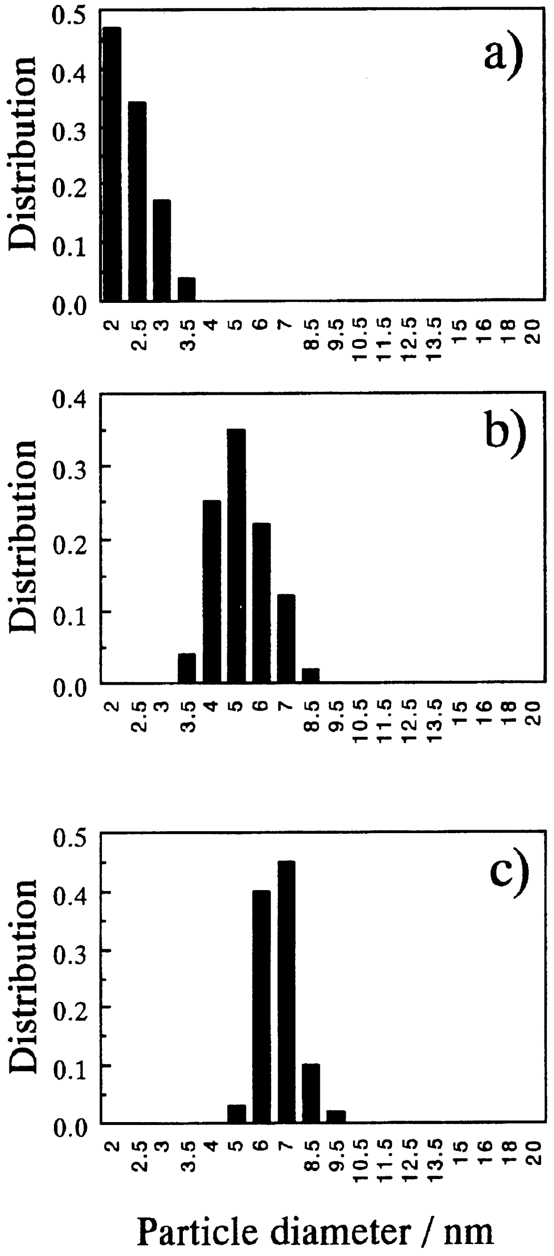


Fig. 2. Size distribution of ϕ-CdS prepared with various quantities of $S(TMS)_2$. a) 0.1 mmol; b) 0.25 mmol; c) 0.4 mmol.

Figures 5 and 6 show the absorption spectra of ϕ-CdS and R-CdS prepared using various quantities of $S(TMS)_2$. The absorption onsets of ϕ-CdS and R-CdS were shifted to longer wavelength along with an increase in the quantity of added $S(TMS)_2$, which can be explained as being due to the growth of the particle size. The onset shift from 433 to 483 nm for ϕ-CdS prepared with a quantity of $S(TMS)_2$ at 0.1 to 0.4 mmol corresponded to the change in the particle size from 2 to 7 nm, determined by DLS. A similar shift of the onset was also observed along with a decrease in the particle size for R-CdS. The shoulders observed for the spectra of ϕ-CdS and R-CdS prepared using 0.1 mmol of

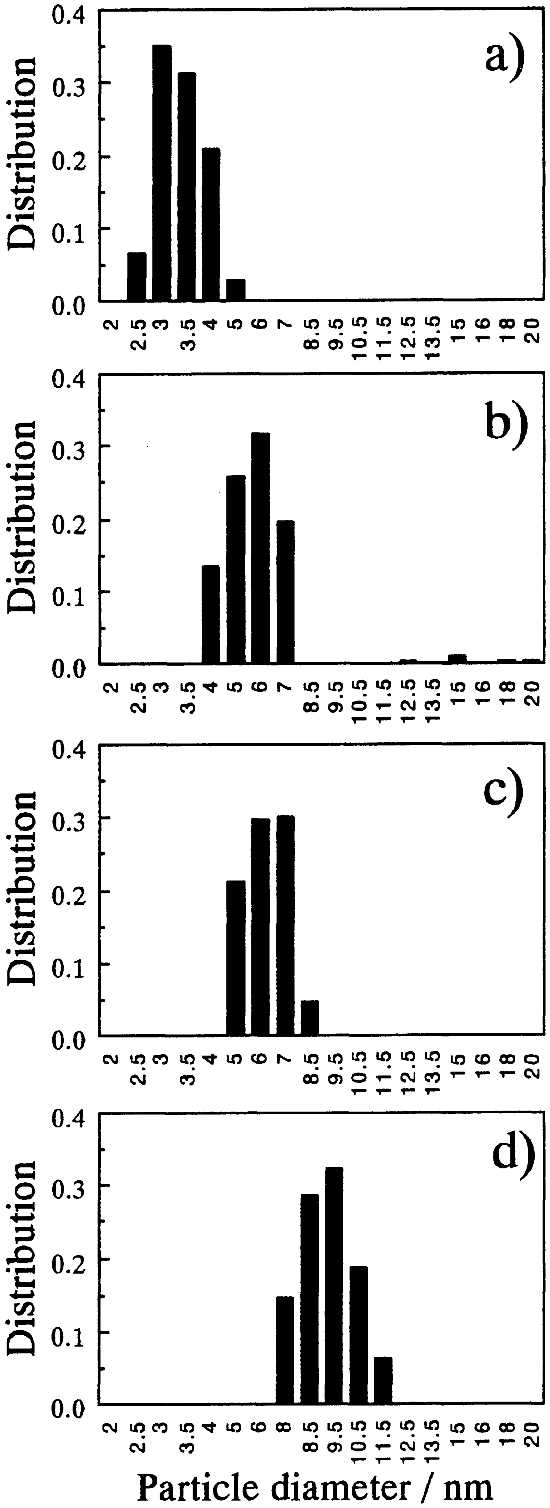


Fig. 3. Size distribution of R-CdS prepared with various quantities of $S(TMS)_2$. a) 0.1 mmol; b) 0.25 mmol; c) 0.33 mmol; d) 0.45 mmol.

$S(TMS)_2$ are probably due to exciton absorption induced for the small-size particles. The wavelength and shift of the absorption onset, depending on the particle size observed in the present experiments, are well coincident with those determined by electron microscopy, fluorescence quenching with methyl viologen, and X-ray diffraction by Weller et al.[20] This clearly proves the occurrence of a quantum size effect in ϕ-CdS and R-CdS prepared in the present work.[21]

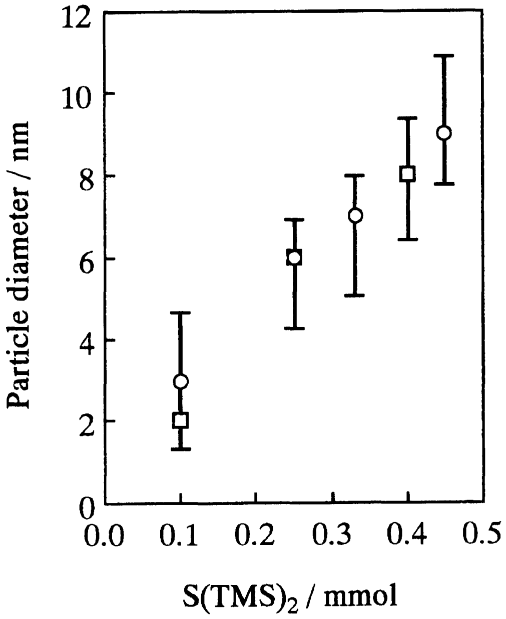


Fig. 4. Dependence of the particle diameter on the quantity of $S(TMS)_2$. The marks (○) and (□) indicate the mean diameter of ϕ-CdS and R-CdS, respectively. The bar along the vertical axis shows the distribution width of the particle diameter.

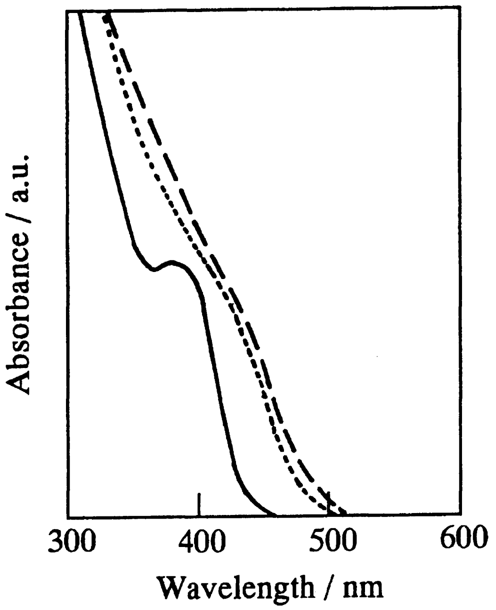


Fig. 5. Absorption spectra of ϕ-CdS prepared with various quantities of $S(TMS)_2$: —, 0.1 mmol; ---, 0.25 mmol; - -, 0.4 mmol.

It has become clearer in the present work that use of a reversed micelles as a constraint reaction field and control of the ratio of $[Cd^{2+}]/[S^{2-}]$ enables us to manipulate the particle size of CdS nanocrystallites.

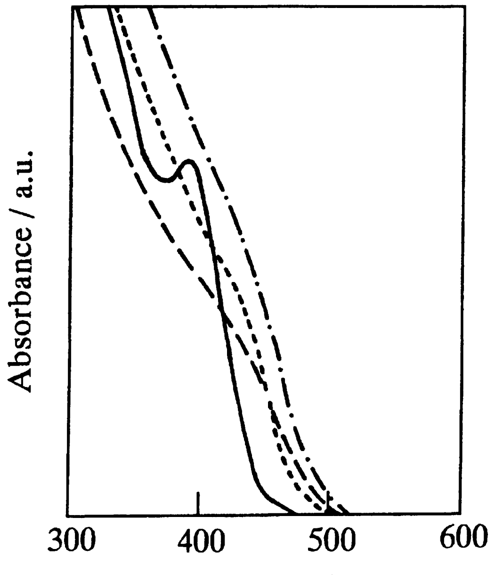


Fig. 6. Absorption spectra of R-CdS prepared with various quantities of $S(TMS)_2$: —, 0.1 mmol; - - -, 0.25 mmol; - -, 0.33 mmol; —•—, 0.45 mmol.

Table 1. Solubility of the Surface-Capped CdS Nanocrystallites in Various Solvents[a)]

Solvent	ϕ-CdS	R-CdS
CH_2Cl_2	12	48
Et_2O	0.16	0.61
MeCN	0	0
Me_2CO	0.038	0.031
THF	59	27
DMF	0.039	0
DMSO	13	0.044
MeOH	0	0

a) Solubilities are expressed in g dm^{-3}.

Solubility of Capped CdS. The solubilities of ϕ-CdS and R-CdS were examined quantitatively by measuring the absorption spectra of their saturated solutions in various solvents (Table 1). ϕ-CdS was very soluble into tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), and dichloromethane, as pointed out by Steigerwald et al.[13)] It was fairly soluble in *N*,*N*-dimethylformamide (DMF), diethyl ether, and acetone. R-CdS showed a higher solubility in dichloromethane, but a lower solubility in DMSO than did ϕ-CdS. The difference in solubility between ϕ-CdS and R-CdS implies that the surface capping with organic molecules should affect the solubility of CdS nanocrystallites in organic solvents.[22)]

The solubility of the phenyl-capped CdS prepared with AOT reversed micelles according to Herron's report (denoted as ϕ-CdS(Herron)) was very different from that of ϕ-CdS prepared in reversed micelles.[22,23)] ϕ-CdS(Herron) was hardly soluble in dichloromethane and diethyl ether, but was much more soluble in THF, DMF, and DMSO than was ϕ-CdS. An NMR analysis revealed that ϕ-CdS showed signals due to an alkyl group in the region between 2 and 4 ppm and the aromatic proton signal due to pyridine, indicating the presence of residual AOT and pyridine on ϕ-CdS, as pointed out previously. These observations suggest that not only surface-capping with thiol derivatives, but also adsorbed molecules during a work-up should affect the solubility of CdS nanocrystallites in organic solvents.

Photoreactions. The photogenerated electron/hole pair of semiconductor particles may undergo redox reactions with adsorbed species by either a reduction of an electron acceptor, such as methyl viologen[24,25)] or aromatic ketones,[6,7)] or oxidation of electron donors, such as S^{2-} or triethylamine. Petit and Pileni compared the yield of photoreduced methyl viologen obtained in CdS–AOT reversed micelles at various Cd^{2+}/S^{2-} ratios, observing that the rate of photoreduced methyl viologen formation increased with decreasing Cd^{2+}/S^{2-} ratios, i.e., with increasing particle size.[19)] It was explained that, for small CdS particles, the electron escapes from the crystallites with a lower efficiency than that observed with large CdS particles. This fact is in conflict with the quantum size effect in photoinduced electron-transfer reactions. Thus, the photoreduction of methyl viologen was examined in a homogeneous ϕ-CdS/DMSO system by using isolated ϕ-CdS whose particle size was controlled by the repeated addition of $Cd(ClO_4)_2$ and $S(TMS)_2$, as described above. We have now found that the photoexcited state of ϕ-CdS can be quenched by methyl viologen in DMSO, accumulating the methyl viologen cation radical constantly (within 30 min) under irradiation of 400-nm monochromatic light, possibly through a concurrent oxidation of adsorbed S^{2-} on ϕ-CdS. The rates were determined to be 1.3×10^{-5}, 1.0×10^{-5}, and 0.7×10^{-5} mol h^{-1}, for ϕ-CdS (4 nm), ϕ-CdS (10 nm), and ϕ-CdS (13 nm); the numbers in the parentheses indicate the mean diameters, respectively. The smaller was the particle size of ϕ-CdS, the higher was the reduction rate. The enhancement of the photocatalytic reduction of methyl viologen by decreasing the size of CdS nano crystallites was also observed by Matsumoto et al.[25)] It could be ascribed to the photogeneration of a long-lived electron in the conduction band, rather than a shift of the conduction band edge, because the redox potential of methyl viologen (−0.45 V vs. NHE)[26)] is positioned far below the conduction band of even micro-scale CdS particles (−1.8 V vs. SCE).[27)] Surface states trapping the excited electron are assumed to be fewer for the small-size particles of ϕ-CdS, resulting in a photogeneration of the long-lived electron in the conduction band.[6,8)]

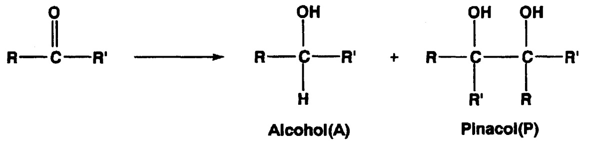
Further, aromatic ketones were found to be photoreduced with ϕ-CdS under irradiation ($\lambda>400$ nm) in the presence of triethylamine as a sacrificial electron donor (see Table 2). The products in this reaction were alcohol

Table 2. Photoreduction of Aromatic Ketones Catalyzed by ϕ-CdS of Various Particle Sizes in DMF

Substrate	$-E_{1/2}^{\mathrm{red}}$ $^{a)}$	d (4nm)			d (10nm)			d (13nm)		
		Conv.$^{b)}$	A$^{c)}$	P$^{d)}$	Conv.$^{b)}$	A$^{c)}$	P$^{d)}$	Conv.$^{b)}$	A$^{c)}$	P$^{d)}$
p-ClPh–CO–p-ClPh	1.67	100	25	30	70	15	30	50	12	20
p-ClPh–CO–Ph	1.75	100	16	50	60	0	20	0	0	0
Ph–CO–Ph	1.83	100	0	80	0	0	0	0	0	0

a) Polarographic half-wave reduction potential vs. SCE measured in acetonitrile. b) Conversion in % of the substrate after irradiation of 4 h. c) Yield in % of alcohol based on the substrate converted. d) Yield in % of pinacol based on the substrate converted.

and pinacol (Eq. 1). Comparing the conversions of three ketones during 4 h-irradiation in the presence of three ϕ-CdS's of different particle sizes, the conversion showed the order ϕ-CdS (4 nm)>ϕ-CdS (10 nm)>ϕ-CdS (13 nm). Especially benzophenone was not photoreduced with ϕ-CdS (10 nm) and ϕ-CdS (13 nm), but was reduced only with ϕ-CdS (4 nm). The photoreduction of p-chlorobenzophenone did not occur on ϕ-CdS (13 nm). This clear-cut fact is attributed to a negative shift of the conduction band edge along with a decrease in the particle size. The lower edge of the conduction band of ϕ-CdS can be estimated by assuming that it corresponds to the reduction potentials of substrates reducible on each ϕ-CdS. They are estimated to be <-1.83 V vs. SCE for ϕ-CdS (4 nm), -1.83 V—-1.75 V vs. SCE for ϕ-CdS (10 nm), and -1.75 V—-1.67 V vs. SCE for ϕ-CdS (13 nm). Beside the shift of the lower edge of the conduction band, the long-lived electron should contribute to the enhancement of the photocatalytic reduction of ketones as well as in the photoreduction of methyl viologen. Diethylamine and acetaldehyde were formed in the photolysate. They are considered to be formed through the oxidation of triethylamine.



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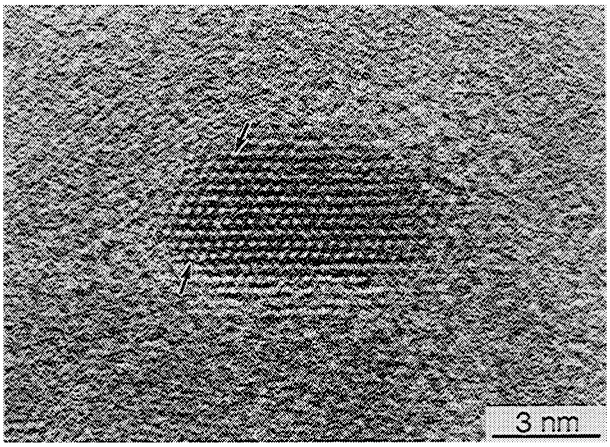

Fig. 7. Transmission electron microscopy of ϕ-CdS (13 nm).

A close examination of ϕ-CdS (13 nm) by TEM revealed that the lattice fringe is slightly and partly deformed (denoted by the arrows in the photograph of Fig. 7), indicating the presence of a strain of the lattice in the nanocrystallites, as shown in Fig. 7. In addition, though we could not judge the presence of the strain of the lattice in the smaller ϕ-CdS, due to their small images of TEM, the steep increase of the absorption onset in their absorption spectra suggests a smaller strain of the lattice in small ϕ-CdS. It could be derived from these facts that the nanocrystallites of ϕ-CdS (13 nm) have more stain in their lattice than does small ϕ-CdS, causing more defects in ϕ-CdS (13 nm), such as dislocations. Generally, the defects in semiconductor particles may work as trapping sites of photoformed electrons, leading to low efficiency in electron transfer to the substrates. Defects should be formed in the growth of the ϕ-CdS, contributing to the decreased efficiency in larger ϕ-CdS.

To the best of our knowledge, the present work produced the first experimental results demonstrating a gradual change in the reducing power of the excited electrons in semiconductor nano-scale particles with decreasing the particle size. The enhancement of the photocatalytic activity by reducing the particle size should be ascribed not only to a negative shift of the conduction band edge, but also to a suppression of the formation of the surface defects. In conclusion, the photoreactions induced by the active and effective electron/hole pair can be called semiconductor quantum box (dot) photocatalysis.

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