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Surface modification of CdS quantum dots with fluorinated thiophenol

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CdS nanocrystallites prepared by capping with pentafluorothiophenol, 2,3,5,6-tetrafluorothiophenol or 4-fluorothiophenol are characterized as quantum dots by TEM, FTIR, NMR, UV–VIS and fluorescence spectroscopy. The crystalline size tends to increase with an increase in the number of fluorine atoms in the capping molecules while maintaining high solubility in organic solvents, with solubility in alcohols depending on the number of fluorine atoms in the capping molecules. Pentafluorophenyl-capped CdS nanocrystallites have the highest solubilities in alcohols, and exhibit quantum dot photocatalysis in methanol, leading to the efficient two-electron transfer photoreduction under visible-light irradiation.

Semiconductor nanocrystallites have attracted much attention in terms of their photochemical and photophysical properties based on the size-dependent confinement of the charge carriers.¹⁻⁵ The properties of semiconductor nanocrystallites are determined not only by the particle size but also by the surface conditions of the nanocrystallites because of their large surface-to-volume ratios. Consequently, it is important to control both size and surface conditions of semiconductor nanocrystallites for studies and applications.

Recently, synthetic procedures have been developed to stabilize and isolate size-controlled nanocrystallites by surface modification with organic molecules.⁶⁻¹⁹ The surfacemodified nanocrystallites are interesting materials in view of isolable zero-dimensional quantum materials, i.e., quantum boxes or dots. Several reports on their physical and optical properties have appeared recently. For example, there are some reports in which surface modification with organic molecules leads to enhancement in the emission efficiency of semiconductor nanocrystallites.^{8,17-27} The fluorescence behaviour of the surface-modified nanocrystallites is becoming well understood by using time-resolved fluorescence spectroscopy.^{8,20-27} A few reports also discuss photocatalysis of the surface-modified semiconductor nanocrystallites. 12b, 16, 28, 29 Such surface modification also affects the solubility of the semiconductor nanocrystallites.^{7,10-14,17} Herron et al.¹¹ reported that phenyl-capped CdS nanocrystallites prepared by reacting Cd^{2+} and S^{2-} in the presence of thiophenol can redissolve in DMF, acetonitrile, or THF but not in methanol. In contrast, as reported in a preliminary paper,³⁰ pentafluorophenyl-capped CdS nanocrystallites prepared in a similar manner were found to have a high solubility in methanol or ethanol.

Although the physical and chemical properties of various surface-modified semiconductor nanocrystallites have been reported, no report on systematic effects of capping molecules on the properties of nanocrystallites has been published. In the present study, we prepared and characterized quantized CdS nanocrystallites capped with fluorinated thiophenols, *i.e.*, pentafluorothiophenol (ϕ_{5F}), 2,3,5,6-tetrafluorothiophenol (ϕ_{4F}), or 4-fluorothiophenol (ϕ_{1F}), as well as with thiophenol (ϕ). The crystalline size, optical properties, solubility and photocatalysis of the surface-modified CdS nanocrystallites (capped-CdSs) were compared in order to investigate effects of the surface molecules on chemical and physical properties of

the semiconductor nanocrystallites.

Experimental

Materials

Cadmium acetate dihydrate [Guaranteed Reagent (GR) grade, nacalai tesque] and sodium sulfide enneahydrate (GR grade, Wako Pure Chemical Industries) were used as received. Thiophenol (nacalai tesque), 4-fluorothiophenol (Aldrich), 2,3, 5,6-tetrafluorothiophenol (Aldrich) and pentafluorothiophenol (Aldrich) were purified by vacuum distillation immediately prior to use. Methanol (GR grade, Wako Pure Chemical Industries), acetonitrile (GR grade, Wako Pure Chemical Industries), and triethylamine (TEA) (GR grade, Wako Pure Chemical Industries) were purified by fractional distillation immediately prior to use. N,N-Dimethylformamide (DMF) (spectral grade, Dojin Chemical Laboratories) was used without further purification. Aromatic ketones were obtained from the following sources: benzophenone (GR grade) from nacalai tesque, 4-chlorobenzophenone (GR grade) and 4,4'dichlorobenzophenone (GR grade) from Wako Pure Chemical Industries, and 4-methoxybenzophenone (GR grade) and 4,4'dimethoxybenzophenone (GR grade) from Aldrich. 4-Cyanobenzophenone was prepared by coupling 4-cyanobenzovl chloride and benzene by Friedel-Crafts reaction.

Apparatus

High-resolution transmission electron microscopy (TEM) images and electron diffraction patterns were obtained on a Hitachi H-9000, operating at 300 kV. UV–VIS absorption spectra were measured on a Hitachi U-3300 spectrophotometer. Emission spectra were measured at room temperature on a Hitachi Model 850 fluorescence spectrophotometer. FTIR spectra were obtained on a Perkin-Elmer 2000 FTIR spectrophotometer using the KBr method. ¹H NMR data were obtained on a Bruker AM-600 spectrometer (600 MHz), and ¹⁹F NMR data on a JEOL JNM-GSX-400 spectrometer (400 MHz).

Preparation of surface-modified CdS nanocrystallites (capped-CdSs)

As reported in the previous paper,³⁰ pentafluorophenylcapped CdS nanocrystallites (ϕ_{5F} -CdS) were prepared under

argon atmosphere as follows; to a methanol-acetonitrile solution (4:1 v/v) (100 ml) of Cd(MeCO₂)₂ (0.1 M) were added an aqueous methanol solution (1:1 v/v) (67 ml) of Na₂S (0.1 M) and an acetonitrile solution (33 ml) of C_6F_5SH (0.2 m). The resulting cloudy yellowish orange solution was evaporated to dryness in vacuo, and the crude orange powder was washed with distilled water, dried and extracted by methanol. The extract was filtered and evaporated to dryness in vacuo, yielding ϕ_{5F} -CdS as a yellowish orange powder. Phenyl-, 4fluorophenyl- or 2,3,5,6-tetrafluorophenyl-capped CdS nanocrystallites (ϕ -, ϕ_{1F} - or ϕ_{4F} -CdS) were similarly prepared by using thiophenol, 4-fluorothiophenol or 2,3,5,6-tetrafluorothiophenol as capping reagents, respectively. Acetonitrile was used instead of methanol for extraction in the preparation of ϕ - and ϕ_{1F} -CdS. Yields: ϕ_{5F} -CdS, 1.26 g; ϕ_{4F} -CdS, 1.09 g; ϕ_{1F} -CdS, 1.50 g; ϕ -CdS, 0.45 g (Found: ϕ_{5F} -CdS; C, 24.88; H, 0.3; F, 31.08; S, 13.58; Cd, 27.7%. ϕ_{4F} -CdS; C, 29.36; H, 0.75; F, 30.34; S, 14.90; Cd, 23.2%. ϕ_{1F} -CdS; C, 23.87; H, 1.62; F, 5.76; S, 15.94; Cd, 43.5%. φ-CdS; C, 24.09; H, 1.39; S, 17.93; Cd, 51.1%).

Surface characterization

Capped-CdSs were analysed by FTIR and NMR spectroscopy. FTIR spectra of capped-CdSs showed the absorption peaks due to each thiophenolate: ϕ_{5F} -CdS; 1630, 1510, 1480, 1090, 1010, 980, 860, 810 cm⁻¹: ϕ_{4F} -CdS; 3000, 1575, 1485, 1435, 1230, 1170, 1125, 1045, 1015, 915, 890, 840 cm⁻¹: ϕ_{1F} -CdS; 3070, 1590, 1490, 1420, 1230, 1160, 1080, 1010, 820 cm⁻¹: ϕ -CdS; 3050, 1570, 1470, 1430, 1410, 1075, 1015, 730 cm⁻¹. In contrast, no peak was observed around 2500 cm⁻¹ due to S—H stretching vibrations of thiols, indicating the absence of physically adsorbed thiol molecules on the surface of capped-CdSs. In other words, the FTIR analysis indicates that S—H bonds of the thiols have been cleaved and the resulting thiolate should be bound to the CdS nanocrystallite surface.

¹⁹F NMR spectra of capped-CdSs showed signals as follows: ϕ_{5F} -CdS in [²H₄]methanol; δ 26.6 (s, 2F), -6.7 (s, ϕ_{4F} -CdS 3F) vs. hexafluorobenzene (C_6F_6) : in [²H₄]methanol; δ 29.8 (m, 2F), 20.9 (t, 2F) vs. C₆F₆: ϕ_{1F} -CdS in $(CD_3)_2SO$; δ 48.9 (m, 1F) vs. C_6F_6 . ¹H NMR spectra of capped-CdSs: ϕ_{4F} -CdS in [²H₄]methanol; δ 6.71 (t, 1H) vs. SiMe₄: ϕ_{1F} -CdS in (CD₃)₂SO; δ 7.56 (q, 2H), 7.25 (t, 2H) vs. SiMe₄: ϕ -CdS in (CD₃)₂SO; δ 7.53 (d, 2H), 7.39 (t, 2H), 7.32 (t, 1H) vs. SiMe₄. These NMR signals of the capped-CdSs were different from those of Cd-thiolate complexes: Cd(SPh)₂ in $[^{2}H_{4}]$ methanol; ^{19}F , δ 26.5 (d, 2F), -5.8 (t, 1F), -6.2 (t, 2F) vs. C₆F₆: Cd(SC₆HF₄)₂ in [$^{2}H_{4}$]methanol; ^{19}F , δ 29.3 (m, 2F), 21.5 (m, 2F) vs. C₆F₆; ^{1}H , δ 6.80 (m, 1H) vs. SiMe₄: Cd(SC₆H₄F)₂ in (CD₃)₂SO; ^{19}F , δ 40.1 (s, 1F) vs. C₆F₆; ^{1}H , δ 7.22 (q, 2H), 6.73 (t, 2H) vs. $SiMe_4$: $Cd(SPh)_2$ in $(CD_3)_2SO$; ¹H, δ 7.27 (d, 2H), 6.87 (t, 3H) vs. SiMe₄, and from those of thiol molecules: C_6F_5SH in $[^{2}H_4]$ methanol; ^{19}F , δ 22.6 (d, 2F), -0.1 ppm (t, 1F), -3.2 (t, 2F) vs. C_6F_6 : C_6HF_4SH in $[{}^{2}H_{4}]$ methanol; ${}^{19}F$, δ 25.1 (m, 2F), 24.0 (m, 2F) vs. C₆F₆; ¹H, δ 7.20 (t, 1H) vs. SiMe₄: C₆H₄FSH in (CD₃)₂SO; ¹⁹F, δ 44.4 (m, 1F) vs. C_6F_6 ; ¹H δ 7.33 (q, 2H), 7.11 (t, 2H) vs. SiMe₄: PhSH in (CD₃)₂SO; ¹H, δ 7.29 (d, 2H), 7.24 (t, 2H), 7.12 (t, 1H) vs. SiMe₄. These differences in the NMR signals indicate the magnetic anisotropy of the phenyl rings on the surface of CdS nanocrystallites caused by successful capping of thiolate groups on the CdS nanocrystallites.

Determination of the solubility of capped-CdSs

Saturated solutions of capped-CdSs in various solvents were prepared. The solubilities of the capped-CdSs were determined by measuring the absorption of these clear solutions at 400 nm after appropriate dilution.

General procedure for photoreaction with capped-CdSs as photocatalysts

Photoreduction of various aromatic ketones was generally carried out as follows; a reaction mixture of DMF or methanol solution (2 ml) containing ϕ -CdS (1 mg) or ϕ_{5F} -CdS (2 mg) as a photocatalyst, TEA (1 M) as a sacrificial electron donor and a benzophenone derivative (2 mM) as a substrate was fixed into a Pyrex tube (8 mm diameter). The resulting argon-flashed DMF or methanol solution was sealed with a rubber stopper, and then irradiated at $\lambda > 400$ nm with a 300 W halogen-tungsten lamp through a saturated sodium nitrite filter in a water bath.

Analysis of ketones, alcohols and pinacols (see Scheme 1) was carried out by liquid chromatography using a Cosmosil-ODS column (150 mm \times 4.6 mm) and a UV detector (at 230 nm) (TOSOH UV-8000). As an eluent, a mixture of methanol and buffered aqueous solution (KH₂PO₄–NaOH; pH = 7) (6:4 v/v) was employed at an eluent rate of 0.5 ml min⁻¹. Diethylamine and acetaldehyde were analysed by gas chromatography on a Shimadzu GC-7A using an ASC-L column (3 m \times 3 mm) at 180 °C.

Results and Discussion

Characterization of capped-CdSs

A direct observation of capped-CdSs by TEM indicates that most particles were roughly spherical and not aggregated, showing clearly resolved lattice fringes (Fig. 1). Electron diffraction patterns of the capped-CdSs confirmed that they had cubic crystalline structure. The size distributions determined from TEM images show that all the capped-CdSs consisted of nanoparticles with narrow size distributions (Fig. 2). The mean diameters were determined to be 3.5 nm for ϕ_{5F} -CdS, 3.1 nm for ϕ_{4F} -CdS, 2.8 nm for ϕ_{1F} -CdS and 2.5 nm for ϕ -CdS, respectively. Note that the size of capped-CdSs decreased upon decreasing the number of fluorine atoms in the capping molecules ($C_6F_5SH > C_6F_4HSH > C_6FH_4SH >$ PhSH). Herron et al. proposed that the size of phenyl-capped CdS nanocrystallites should be determined by the relative rate of the propagation (cluster growth) to termination (surface capping) reaction.¹¹ Taking this into account, the order in the size of capped-CdSs could be explained as due to the order in the rate of the termination reaction. The increase in the rate of the termination reaction should be due to the higher nucleophilicity of the thiolate $(C_6F_5S^- < C_6HF_4S^- < C_6H_4FS^- <$ PhS⁻), leading to the smaller size of the capped-CdSs. These results imply that the size of CdS nanocrystallites can be con-



Fig. 1 TEM image of ϕ_{5F} -CdS at a magnification of 1 730 000



Fig. 2 Size distributions of capped-CdSs determined from TEM images: (a) ϕ_{sF} -CdS, (b) ϕ_{4F} -CdS, (c) ϕ_{1F} -CdS, and (d) ϕ -CdS

trolled by the choice of the capping molecules, *i.e.*, nucleophilicity of the thiolate, without changing the concentration of the capping molecule.

The absorption and emission spectra of capped-CdSs were measured in DMF (Fig. 3), since all the capped-CdSs could be redissolved in DMF. ϕ_{5F} -CdS in DMF was characterized by the steep absorption onset at 480 nm. The absorption onset (shoulder) at a shorter wavelength than the bandgap in bulk CdS (520 nm) is attributed to the size quantization effect. Note that the shoulder of the absorption of capped-CdSs [ϕ_{5F} -CdS, 430 nm (2.88 eV); ϕ_{4F} -CdS, 410 nm (3.02 eV); ϕ_{1F} -CdS, 370 nm (3.35 eV); ϕ -CdS, 350 nm (3.54 eV)] shifted to shorter wavelength upon decreasing the number of fluorine atoms in the capping molecules (C₆F₅SH > C₆F₄HSH > C₆FH₄SH > PhSH). These shifts reflect the change of the bandgap in



Fig. 3 Absorption and emission spectra of capped-CdSs in DMF: (a) ϕ_{5F} -CdS, (b) ϕ_{4F} -CdS, (c) ϕ_{1F} -CdS, and (d) ϕ -CdS. The absorption spectra were normalized at 400 nm. The excitation wavelength was 400 nm.

capped-CdSs. The relation between the size and the bandgap of capped-CdSs, as determined by TEM and absorption measurements, agrees well with the theoretical estimation using the tight-binding approximation.³¹

 ϕ_{SF} -CdS had a broad emission spectrum with λ_{max} at 640 nm, $\phi_{4\rm F}$ -CdS at 600 nm, $\phi_{1\rm F}$ -CdS at 590 nm and ϕ -CdS at 580 nm, respectively, when excited with 400 nm light. These broad emissions can be attributed to radiative recombinations of e^--h^+ pairs at deep trap sites, e.g., sulfur anion vacancies on the surface.³² The blue-shift of the emission peak wavelength should reflect the greater band gap upon decreasing the number of fluorine atoms in the capping molecules. Additionally, we already found that non-capped CdS nanocrystallites (CdS-0) which were freshly prepared by mixing methanol solutions of $Cd(ClO_4)_2$ and Na_2S showed little emission despite the same morphology (2-5 nm diameter, cubic).³³ The difference in the emission properties shows that the surface modification with thiophenol groups should lead to the suppression of non-radiative recombination, resulting in enhancement of the emission intensity.34

Solubility of capped-CdSs in organic solvents

Capped-CdSs can redissolve in various organic solvents. Table 1 shows the solubility of capped-CdSs in several organic solvents. Note that all the capped-CdSs redissolve in DMF ($\varepsilon = 36.71 \text{ M}$)³⁵ cm⁻¹ and Me₂SO ($\varepsilon = 46.68$)³⁵ which have high relative permittivities, while capped-CdSs were insoluble in solvents of low relative permittivities such as hexane ($\varepsilon = 1.89$),³⁵ cm⁻¹ diethyl ether ($\varepsilon = 1.89$),³⁵ or chloroform ($\varepsilon = 4.81$).³⁵ These results show that polar solvents are required to redissolve capped-CdSs.³⁶

The dependence of the solubility of capped-CdSs on the capping molecules was remarkable in the case of intermediate polar solvents. ϕ_{5F} -CdS could not be redissolved in acetonitrile or THF while ϕ -CdS was soluble in these solvents. ϕ_{5F} -CdS had very low solubility in acetone, while ϕ -CdS had high solubility in this solvent. Note that the solubility of capped-CdSs in acetonitrile, acetone, THF and pyridine increased with decreasing the number of fluorine atoms in the capping molecules $(\phi_{5F}\text{-}CdS < \phi_{4F}\text{-}CdS < \phi_{1F}\text{-}CdS < \phi_{-}CdS)$. On the other hand, it is of note that ϕ_{5F} -CdS had high solubility in alcohols, such as methanol, ethanol and propan-2-ol, in which ϕ -CdS was not soluble. None of the capped-CdSs redissolved in water. The solubility of capped-CdSs in alcohols increased upon increasing the number of fluorine atoms in the capping molecules $(\phi_{5F}\text{-}CdS > \phi_{4F}\text{-}CdS > \phi_{1F}\text{-}CdS > \phi_{-}CdS)$ corresponding also to an increase in the crystalline size of the capped-CdSs. Thus, the solubility largely depends on the capping molecules and not on the crystalline size. This observation should be rationalized as being due to specific intermolecular interactions between the solvent and the capping molecules. It appears that the C-F bond is capable of significant interactions with proton donors. This fact leads to an assumption that hydrogen bonding between electronegative fluorine atoms and the hydroxy group of alcohols assumes an

 Table 1
 Solubility of surface-modified
 CdS nanocrystallites in various solvents

	solubility/g dm ⁻³				
solvent	ϕ_{5F} -CdS	ϕ_{4F} -CdS	ϕ_{1F} -CdS	φ-CdS	
methanol	>400	120	82	0	
ethanol	>400	100	61	0	
propan-2-ol	27	18	4.8	0	
acetonitrile	0	2.3	26	47	
acetone	0.03	0.13	25	320	
THF	0	2.5	3.8	150	
DMF	>400	>400	>400	>400	
Me ₂ SO	>400	> 400	>400	>400	
pyridine	36	48	90	100	

Table 2	CdS-catalysed	photoreduction	of aromatic	ketones v	with	TEA in	۱DMF
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substrate ArCOAr'					yield ^d (%)	
Ar	Ar'	$-E_{1/2}^{\operatorname{red} b}/\operatorname{V} vs.$ SCE	catalyst	conv. ^c (%)	alcohol	pinacol
p-CNC ₆ H ₄	Ph	1.42	ϕ_{5F} -CdS ϕ -CdS	100 100	85 78	trace 0
p-ClC ₆ H ₄	p-ClC ₆ H ₄	1.67	ϕ_{sF} -CdS ϕ -CdS	98 98	29 50	69 25
p-ClC ₆ H ₄	Ph	1.75	ϕ -CdS ϕ_{sF} -CdS ϕ -CdS	100 74 99	25 16 14	30 53 37
Ph	Ph	1.83	ϕ -CdS ^e ϕ_{5F} -CdS ϕ -CdS	100 54 100	16 24 10	50 23 50
p-MeOC ₆ H ₄	Ph	1.90	φ-CdS ^e φ _{5F} -CdS φ-CdS	100 3 100	0 0 11	80 0 40
$p-MeOC_6H_4$	<i>p</i> -MeOC ₆ H ₄	2.02	ϕ_{sF} -CdS ϕ -CdS	0 60	0 10	0 34

^{*a*} Irradiation in DMF at $\lambda > 400$ nm for 6 h. ^{*b*} Reported polarographic half-wave reduction potentials in acetonitrile. See ref. 33. ^{*c*} Conversion of the substrate. ^{*d*} Yields are based on substrate converted. ^{*e*} Phenyl-capped CdS nanocrystallites (4 nm, cubic) prepared in reversed micelles. See ref. 12*b*.

appreciable role in the solubility. However, considering that the hydrogen bonding is generally weaker than that involving C—O and C—N groups,³⁷ it appears that not only the hydrogen bonding but also a specific interaction between the electron-deficient perfluorophenyl ring and electron-rich oxygen atom of the alcohols may also contribute to the enhancement in the solubility.[†] We conclude that the solubility of capped-CdSs in organic solvents can be controlled by the choice of the capping molecules. In particular, capping with fluorinated phenyl groups induces solubility of capped-CdSs in alcohols.

Photocatalysis of capped-CdSs

We reported that phenyl-capped CdS nanocrystallites prepared by the reversed micelle method show a visible-light induced photocatalytic activity for reduction of aromatic ketones in DMF, giving alcohols and pinacols in the presence of TEA as an electron donor.^{12b} ϕ_{SF} -CdS prepared in the present work also showed comparable photocatalytic activities in DMF under the same conditions (Table 2), giving alcohols and pinacols as well as ϕ -CdS (Scheme 1).[‡]

Photocatalytic activity of capped-CdSs was also examined in methanol. We found that ϕ_{SF} -CdS shows characteristic



† In order to estimate the specific interaction, semi-empirical molecular orbital calculations were carried out with the MOPAC program (ver. 6.0) using PM3³⁸ parameters, and we evaluated the stabilization energy in the interaction between methanol and the capping reagent. The methanol molecule was located above the ring of the thiol molecule (C₆F₅SH) in the direction in which its dipole momentum was perpendicular to the phenyl ring plane and allowed to approach to the centre of the phenyl ring through the oxygen atom of the methanol. The heat of formation showed a minimum at a distance of 3.6 Å between the oxygen atom and the phenyl ring plane of C₆F₅SH [$\Delta E = -0.92$ kcal mol⁻¹ (1 cal = 4.184 J)]. The stabilization energy may imply that the oxygen atom of methanol strongly interacts with the electron-deficient perfluorophenyl ring.

[‡] Note that ϕ_{SF} -CdS could not photocatalyse reduction of 4,4'dimethoxybenzophenone which has a reduction potential of -2.02 V vs. SCE, while ϕ -CdS catalysed photoreduction of the benzophenone derivative. The difference in the photocatalysis between ϕ_{SF} -CdS and ϕ -CdS arises from the difference in the crystallite size, *i.e.*, the bandgap energy, as described above. photocatalysis in methanol for the reduction of aromatic ketones. Fig. 4 shows time-conversion plots for the photoreduction of benzophenone catalysed by $\phi_{\rm 5F}$ -CdS in methanol with TEA as a sacrificial electron donor under visible-light ($\lambda > 400$ nm) irradiation.§ After a 30 min induction period, benzophenone was effectively photoreduced to benzhydrol which was a two-electron transfer reduction product. In this system, formation of H₂ and benzpinacol, which are oneelectron transfer reduction products, was not observed.

Table 3 summarizes the results in methanol for the photoreduction of various aromatic ketones catalysed by capped-CdSs as well as by *in situ* prepared CdS nanocrystallites (CdS-0) and commercially available micrometre-sized bulk CdS powder (CdS-Ald). TEA was employed as a sacrificial electron donor and irradiation with visible light ($\lambda > 400$ nm) was performed for 6 h. As reported in the previous paper,³³ both CdS-0 and CdS-Ald catalysed photoreduction of the aromatic ketones whose reduction potential was more positive than - 1.55 V vs. SCE. Interestingly, ϕ_{sF} -CdS showed effec-



Fig. 4 Time-conversion plots for photoreduction of benzophenone catalysed by ϕ_{sF} -CdS in methanol: benzophenone (\bigcirc); benzhydrol \bullet

As oxidation products, diethylamine and acetaldehyde were detected during photocatalysis, and were formed by hydrolysis of the initial oxidation product, [Et₂N = CHMe]^{+.33,39}

Table 3	CdS-catalysed	photoreduction	of aromatic ketones	s with TEA in methanol ^a
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substrate ArCOAr'					yield ^d (%)	
Ar	Ar'	$-E_{1/2}^{redb}/V$ vs. SCE	catalyst	conv. ^c (%)	alcohol	pinacol
p-CNC ₆ H ₄	Ph	1.17	$\phi_{\rm 5F}$ -CdS	100	92	0
			ϕ -CdS	90	90	0
			CdS-0 ^e	100	95	0
			CdS-Ald ^e	100	90	0
p-ClC ₆ H ₄	$p-ClC_6H_4$	1.24	ϕ_{5F} -CdS	100	79	20
			ϕ -CdS	35	4	14
			CdS-0 ^e	98	90	4
			CdS-Ald ^e	98	4	94
$p-ClC_6H_4$	Ph	1.32	$\phi_{\rm SF}$ -CdS	96	100	0
			ϕ -CdS	23	0	7
			CdS-0 ^e	98	70	12
			CdS-Ald ^e	95	15	75
Ph	Ph	1.55	ϕ_{5F} -CdS	91	100	0
			ϕ -CdS	0	0	0
			CdS-0 ^e	100	88	11
			CdS-Ald ^e	100	28	65
$p-MeOC_6H_4$	Ph	1.56	ϕ 5F-CdS	20	100	0
			ϕ -CdS	0	0	0
			CdS-0 ^e	97	33	26
			CdS-Ald ^e	98	3	66

^{*a*} Irradiation in methanol at $\lambda > 400$ nm for 6 h. ^{*b*} Reported polarographic half-wave reduction potentials in methanol. ^{*c*} Conversion of the substrate. ^{*d*} Yields are based on substrate converted. ^{*e*} See ref. 33.

tive and selective photocatalysis, leading to the reduction of the ketones to the corresponding alcohols. However, ϕ -CdS could not catalyse photoreduction of benzophenone in methanol. When compared with the photocatalytic activities of various CdSs, it is found that $\phi_{\rm 5F}$ -CdS shows comparable photocatalytic activities to those of the in situ prepared CdS-0, rather than ϕ -CdS and CdS-Ald in methanol. ϕ_{5F} -CdS can redissolve in methanol to form a yellowish transparent solution, and shows similar reaction conditions to that of in situ prepared CdS-0 as a quantum dot photocatalyst. On the other hand, CdS-Ald and ϕ -CdS gave heterogeneous systems due to their insolubility in methanol. During the photocatalysis of $\phi_{\rm 5F}$ -CdS, we observed an induction period for the photoreduction (Fig. 4) and darkening of the photoreaction system.[†] The same phenomenon was observed in the photocatalysis of CdS-0 in methanol, which reflects the gradual formation of photogenerated lattice Cd^0 as active sites for successive and effective electron-transfer reduction.^{33,39} Thus, ϕ_{5F} -CdS in methanol should behave like CdS-0, leading to the formation of the active Cd⁰ on the surface, resulting in the effective and selective photocatalytic activities of ϕ_{5F} -CdS as quantum dots.

Conclusions

CdS nanocrystallites (ϕ_{5F} -CdS, ϕ_{4F} -CdS, and ϕ_{1F} -CdS) capped with pentafluorothiophenol, 2,3,5,6-tetrafluorothiophenol and 4-fluorothiophenol, respectively, show characteristic properties as surface-modified quantum dots with cubic structure as well as phenyl-capped CdS nanocrystallites (ϕ -CdS). The most significant effect by introducing fluorine atoms into the capping thiophenolate groups is a remarkable enhancement in solubility of the CdS nanocrystallites in alcohols. ϕ_{5F} -CdS acts as an efficient and selective quantum-dot photocatalyst in methanol, suggesting that the capping molecule affects the efficiency and selectivity of quantum dot photocatalysis in organic solvents.

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[†] We observed three important phenomena which explain the coloured photolysate as due to the formation of lattice Cd^0 : (*i*) Addition of methyl viologen to the dark coloured photolysate led to a change in colour of the photolysate to blue. (*ii*) The original yellow colour was restored when O_2 was introduced into the dark-coloured solution. (*iii*) The two-electron transfer reaction of benzophenone to benzhydrol (Ph₂CHOH) was suppressed with a concomitant increase in the one-electron transfer reaction giving benzpinacol [Ph₂C(OH)C(OH)Ph₂], when 2 mM of excess pentafluorothiophenol, which suppresses the formation of lattice Cd⁰, was added to the photocatalytic systems.

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