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Preparation of Surface-modified CdS Microcrystallites. Enhancement of Solubility in Alcohols by Capping with Pentafluorothiophenol

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Pentafluorophenyl-capped CdS microcrystallites (av. 3-6 nm in diameter) are prepared and characterized by TEM and ^{19}F NMR spectroscopy. Although the similarly prepared phenyl-capped CdS microcrystallites is insoluble in alcohols, the capping with perfluorinated phenyl groups induces high solubility in methanol and ethanol.

Semiconductor microcrystallites have attracted much attention from the viewpoints of photochemical and photophysical effects of quantum confinement.[1] Recently, such three dimensional quantum materials were stably isolated under the control of size and uniformity by capping of the surface with thiophenol group.[2,3] Another important point of the surface modification is to give high solubility in organic solvent to such inorganic microcrystallites, which makes it possible to obtain their organic colloidal solutions[2] or transparent organic polymers doped with such microcrystallites.[4] Herron et al. recently reported phenyl-capped CdS microcrystallites synthesized by reacting Cd^{2+} and S^{2-} in the presence of thiophenol has excellent solubility in DMF, acetonitrile, or THF but not in methanol. In this paper, we report one-pot synthesis of pentafluorophenyl-capped CdS microcrystallites, and their outstandingly enhanced solubility in alcohols.

Pentafluorophenyl-capped CdS particles (ϕ_F-CdS) were prepared under an argon atmosphere as follows; to a methanol-acetonitrile (AN) solution (4:1) (100 mL) of 0.1 M (M = mol dm^{-3}) $Cd(CH_3COO)_2$ were added an aqueous methanol solution (1:1) (67 mL) of 0.1 M Na_2S, and then an AN solution (33 mL) of 0.2 M pentafluorothiophenol. The order of the addition is based on our findings that the initial CdS microcrystallites formed from Cd^{2+} and S^{2-} are rather stable and keep the narrow size distribution in solution, and then minimizing the formation of $Cd(C_6F_5S)_2$.[5] 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_F-CdS powder. The phenyl-capped CdS microcrystallites (ϕ-CdS) were similarly prepared by using AN instead of methanol for extraction and characterized according to the reported method.[2]

The ϕ_F-CdS were analyzed by ^{19}F NMR in CD_3OD; -135.6 (s, 2F), -168.9 (s, 3F) ppm *vs.* CF_2Cl_2.[6] The ^{19}F NMR spectrum is quite different from those of $Cd(C_6F_5S)_2$ [-135.7 (d, 2F), -168.0 (t, 1F), -168.4 (t, 2F)] and C_6F_5SH [-139.6 (d, 2F), -162.3 (s, 1F), -165.4 (s, 2F)]. The difference between these signals may be explained as due to magnetic anisotropy of the pentafluorophenyl rings on ϕ_F-CdS, supporting the successful

modification with C_6F_5SH.

TEM observation (Fig. 1) reveals that ϕ_F-CdS consist of microcrystallites with a narrow size distribution ranging from 3 to 6 nm, showing clearly resolved lattice fringe of the cubic structure of CdS. Further, ϕ_F-CdS were found to be redissolved in organic solvent such as methanol, DMF, DMSO, and pyridine. ϕ_F-CdS dissolved in DMF has an absorption spectrum with onset at 480 nm, and the emission at λmax around 600 nm when excited at 400-nm light. The spectral characteristics are comparable with those of freshly prepared CdS microcrystallites and ϕ-CdS, implying no notable effect of the capping on spectral properties of CdS microcrystallites.

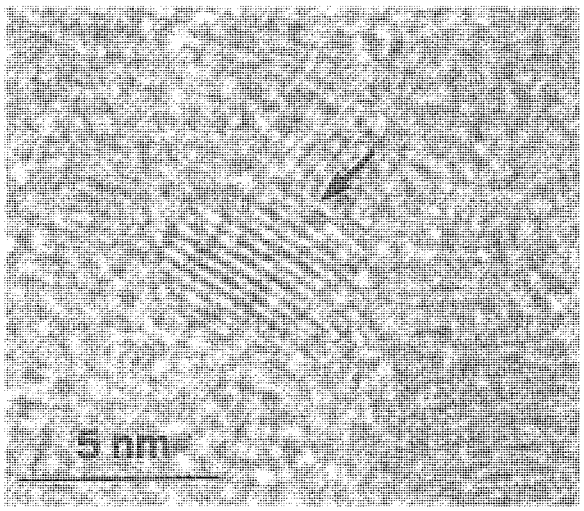

Fig. 1. Transmission electron micrograph of ϕ_F-CdS; Magnificaion 5900000 ×.

As an incredible effect of the capping with pentafluorophenyl groups, ϕ_F-CdS becomes very soluble in alcohols. As shown in Table 1, the solubility of ϕ-CdS and ϕ_F-CdS in several organic solvents was determined from the absorbance of the saturated colloidal solution of each CdS microcrystallites. ϕ_F-CdS has now been found to have very high solubility in methanol and ethanol, giving highly viscous solutions when dissolved to saturation, while ϕ-CdS is hardly soluble. Further investigation on surface modified semiconductor microcrystallites are currently in progress.

Table 1. Solubility of ϕ_F-CdS and ϕ-CdS in Various Organic Solvents

Solvent	Solubility / g dm^{-3}	
	ϕ_F-CdS	ϕ-CdS
Methanol	> 400	0
Ethanol	> 400	0
2-Propanol	27	0
DMF	> 400	> 400
DMSO	> 400	> 400
Pyridine	36	100

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