Preparation of nanosized CdS particles using decomposition of P_2S_5 in a non-aqueous solvent

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Nanosized CdS particles of $\leq$6 nm average diameter are prepared at ambient conditions by use of controlled hydrolysis of P_2S_5 in absolute ethanol initiated by addition of an alcoholic $Cd(NO_3)_2 \cdot 4H_2O$ solution, resulting in an excitonic absorption peak of the particles at 350 nm corresponding to a LUMO–HOMO gap energy of 3.1 eV.

Quantum size effects exhibited by nanosized particles of metals and semiconductors[1] are essentially dependent upon particle diameter.[2] It is hence highly important for practical applications to synthesize such particles at desirable sizes with narrow size distribution in a substantial amount in an easy-to-handle form. Liquid-phase synthesis of very fine particles at low temperature appears to be advantageous not only for precise size control but also for versatility in processing, *e.g.* fabrication of solid devices by sol–gel techniques. There have been a great number of studies on the preparation of nanosized particles of group II–VI semiconductors. Nanoparticles of metal sulfides such as CdS and ZnS have widely been prepared by direct contact of gaseous H_2S to metal cations in solutions or on solid surfaces.[3] Liquid-phase preparation of the sulfide particles has also been conducted, generally by mixing aqueous solutions of the corresponding metal salt and Na_2S.[4,5] Although size-selective precipitation has been reported to achieve virtually monodisperse nanosized particles,[6,7] inevitable inhomogeneity at an early stage of mixing might broaden the size distribution of the initial products even by such liquid-mixing techniques. Here, we report a new preparative technique of nanosized CdS particles under mild and controllable conditions by utilizing homogeneous release of S^{2-} from controlled decomposition of P_2S_5 in non-aqueous solvents.

It is known that P_2S_5 readily decomposes in the presence of water, generating phosphoric acid and S^{2-}.[8] If hydrolysis of dissolved P_2S_5 occurs at an appropriate rate in a non-aqueous solvent, it would cause a sufficiently low and uniformly increasing concentration of S^{2-} in the solution, without abrupt formation of gaseous H_2S which might disturb the liquid phase and may cause uneven nucleation at an early stage. In the presence of metal cations such as Cd and Zn in the solution, the slowly increasing S^{2-} concentration would be able to establish significant supersaturation of metal sulfide which will lead to a sufficiently small and uniform particle size.

Ethanol appeared to be the best solvent in terms of solubility of P_2S_5 and $Cd(NO_3)_2$ which we used as the Cd^{2+} source. In a preliminary experiment, a mixture of ethanol solutions of P_2S_5 and $Cd(NO_3)_2$ formed a yellow precipitate. An EDX spectrum of the precipitate was identical to that of commercially purchased CdS (> 99.999%), confirming the chemical composition of the precipitate as Cd/S = 1. UV–VIS diffuse-reflectance spectroscopy also confirmed that the absorption edge of the precipitate observed at 515 nm corresponds well to the bandgap energy of 2.45 eV for bulk CdS. However, even in the presence of protective polymers such as poly(*N*-vinyl-2-pyrrolidone) (PVP), the preparation of nanosized CdS particles with solvents containing substantial amounts of water failed, with precipitation being observed, implying that rapid decomposition of P_2S_5 may cause uneven concentrations of S^{2-} in the liquid phase. Finally, drying of solvents was revealed to be crucial to obtain well dispersed fine particles of CdS. Ethanol dried with 4 Å molecular sieves was filtered with a membrane filter of 0.2 μm pore size, and was immediately used as the solvent for starting solutions of $Cd(NO_3)_2$, P_2S_5 and PVP. Typically, 2 cm^3 of a 1 mmol dm^{-3} $Cd(NO_3)_2$ solution was added to 20 cm^3 of a 2 g dm^{-3} PVP solution, then 2 cm^3 of a freshly prepared 0.2 mmol dm^{-3} P_2S_5 solution was added. These conditions correspond to the stoichiometry $[Cd^{2+}]/[S^{2-}] = 1$. All procedures were carried out under ambient temperature and air.

The mixed solution of $Cd(NO_3)_2$ and P_2S_5 in the presence of PVP using ethanol without drying looked transparent and was pale yellow. As shown in Fig 1(*a*), a new distinct absorption appeared at 415 nm in the UV–VIS spectrum of the solution after mixing, at a wavelength corresponding well to the excitonic absorption of CdS ultrafine particles previously reported.[5] This solution was, however, somewhat unstable, tending to precipitate during storage. By contrast, the mixed solutions using absolute ethanol are almost colourless and completely transparent and stable for a long period of time (> 6 months). There was no evidence for precipitation on centrifuging the colourless transparent solution. As seen in Fig. 1(*b*), the solution shows an absorption spectrum characteristic of nanosized CdS particles, and the excitonic peak as well as the fundamental absorption edge are shifted significantly towards shorter wavelengths with a peak at 350 nm and the absorption threshold at 420 nm. A TEM/EDX study revealed that the colourless transparent solution was actually a stable dispersion of exceedingly small particles, and confirmed the chemical composition of the particles as Cd/S ≈ 1 using commercial CdS

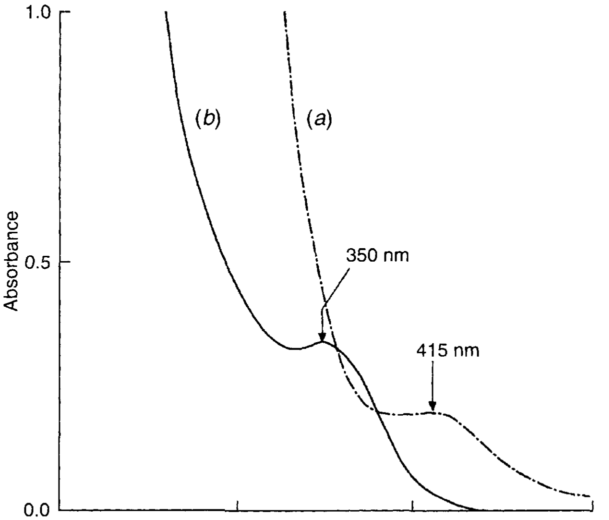

Fig. 1 UV–VIS absorption spectra of CdS nanoparticles prepared by decomposition of P_2S_5 in (*a*) ethanol without drying and (*b*) absolute ethanol, in the presence of PVP; $[Cd^{2+}] = [S^{2-}] = 1$ mmol dm^{-3}

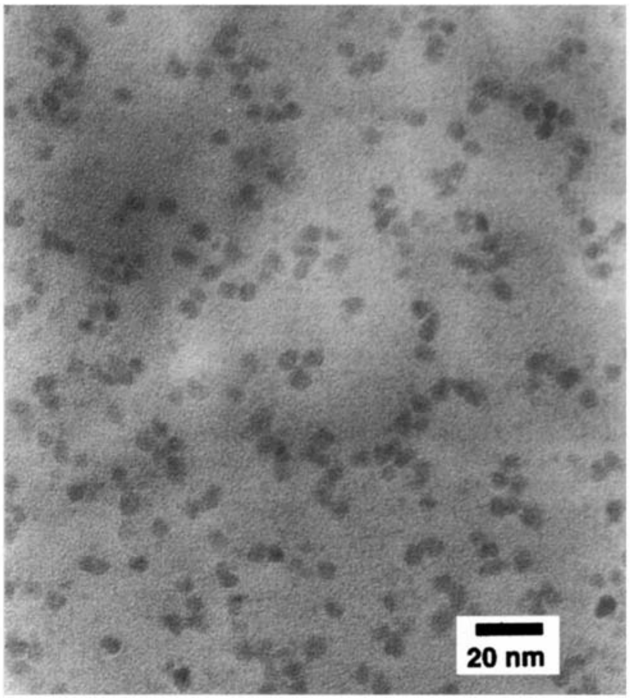

Fig. 2 Transmission electron micrograph of CdS nanoparticles prepared by decomposition of P_2S_5 in absolute ethanol in the presence of PVP; $[Cd^{2+}] = [S^{2-}] = 1$ mmol dm^{-3}

as a reference. Whereas the dispersion should also contain phosphorus derived from P_2S_5, the EDX peak intensity for P was almost negligible. Presumably, phosphorus remained in the liquid phase of the dispersion as phosphoric acid, and was carried away with the solvent during mounting of the particles on a sample grid when the TEM sample was prepared. These results confirm efficient separation of phosphorus from the reaction system to obtain nanosized sulfide particles avoiding incorporation of P. We thereby conclude that CdS nanoparticles are successfully prepared from P_2S_5 simply by mixing the starting solutions under ambient conditions. Complete hydrolysis of 1 mole of P_2S_5 requires 8 moles of water and forms 5 moles of S^{2-}. The amount of water of crystallization of cadmium nitrate should be sufficient on a basis of stoichiometry between Cd^{2+} and S^{2-}, since the nitrate salt contains 4 molecules of water per formula as $Cd(NO_3)_2 \cdot 4H_2O$. The drying procedure of the solvent is considered to be necessary to reduce the water content to a level sufficiently low to prevent abrupt decomposition of P_2S_5.

As seen in Fig. 2, the CdS particles prepared in absolute ethanol [with PVP of average molecular mass (M_{av}) of 360 000] have an average diameter (d_{av}) of 6.0 nm with a standard deviation (σ) of 1.2 nm as determined from TEM observations. With PVP of the lower M_{av}, σ becomes larger indicating broader size distributions, while d_{av} remained almost the same. The gap energy of the CdS particles was determined as 3.1 eV from the absorption edge (Fig. 1) by applying Tauc's equation for semiconductors with direct transitions.[9] This value is 0.6 eV larger than the bandgap energy of bulk CdS, indicating a significant blue shift of the LUMO–HOMO gap energy due to the quantum size effect in the particles. The blue shift observed here is noticeably larger than that calculated from d_{av}, even with the effective-mass approximation[10] which has been reported to overestimate the quantum size effect in nanosized CdS particles compared to the tight-binding approximation.[11,12] This implies that the sample would also contain much smaller particles undetected under our TEM observations. The versatility of the particle preparation in non-aqueous liquids was also shown by the fact that a TiO_2 gel embodying nanosized CdS particles was successfully obtained by adding the alcoholic dispersion of the particles to a solution of titanium tetraisopropoxide prior to hydrolysis and gelation. The simplicity of the present technique would be expected to offer a new widely accessible preparative method to obtain well controlled nanosized particles of metal sulfides.

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