

Single-Precursor, One-Pot Versatile Synthesis under near Ambient Conditions of Tunable, Single and Dual Band Fluorescing Metal Sulfide Nanoparticles

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Synthesis of tunable fluorescing semiconductor chalcogenide nanoparticles, their study, and applications are at the forefront of current research.¹ In recent years effective synthetic routes for the production of cadmium chalcogenide particles (CdS, CdTe, and CdSe) have been developed.^{2–4} The stronger fluorescing particles involve TOPO/TOP (trioctylphosphineoxide/trioctyl phosphine) methods,^{2,3} which however, utilize highly toxic, flammable, air-sensitive, and explosive precursors, and require relatively high temperatures (~250–350 °C). Very recently it was shown that less hazardous precursors could be used in a single-pot manner to produce CdS particles,^{5–8} although the method still employs the TOPO/TOP system at high temperature and in an inert environment.

We describe here a generic method for producing high-quality metal sulfide nanoparticles of a controllable and narrow size distribution in the nanometric range, with quantum-confinement wavelength-tunable optical absorption and (narrow band) excitonic emission (with and without significant deep-trap broad emission peaks). Furthermore, it is a one-pot method using a single, convenient precursor (applicable to a variety of metal ions and capping agents) and is carried out under mild conditions (50–150 °C), usually exposed to the ambient.⁹ Additionally, this procedure allows easy control of the relative intensities of the excitonic short-wave versus surface-state long-wave emission. The general wisdom has been that to obtain crystalline particles with sharp resonances their synthesis requires high temperatures and rigorously air-free conditions. However, we have produced such high-quality particles at relatively low temperatures, even under normal atmospheric benchtop conditions.

As precursor we use metal salts of alkylxanthates (usually long-chain alkyl xanthates), $R-CH_2-CH_2-O-CS_2^-$. Transition metal ions readily form air-stable insoluble xanthate salts. Previously we used hexadecyl xanthates, HDX, to produce and cap metal nanoparticles.¹⁰ Recently Nair et al.⁵ used ethyl xanthate for the production of CdS particles in the TOP/TOPO method.

Here we discuss the production of CdS nanoparticles. Heating the metal xanthate in an appropriate solvent readily yields the metal sulfide at a relatively low temperature, which depends on the specific solvent used. In the presence of a strong electron-donating solvent, (e.g., hexadecylamine (HDA)) the metal sulfide particles form at a temperature as low as 70 °C. The reaction is carried out by heating the precursor in a simple test tube without any air-sensitive technique.⁹ Control of the size is obtained by adjusting the reaction temperature (70–120 °C, for HDA), or the concentration of the metal xanthate. The synthesis follows classical colloid La Mer behavior:¹¹ higher temperatures and higher precursor concentrations favor faster particle nucleation, resulting in more numerous and smaller particles.

Figure 1 shows a transmission electron microscopy (TEM) micrograph of CdS particles produced at 70 °C from HDA and the histograms of the size distribution for particles grown at 70 and 90 °C

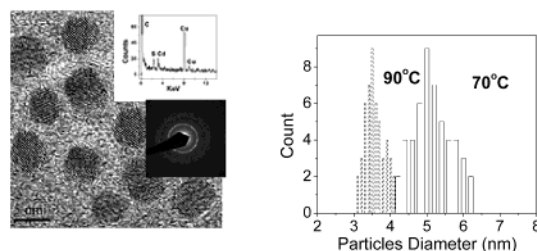


Figure 1. TEM of CdS nanoparticles produced in HDA at 70 °C. (Top insert) EDS spectrum; (bottom insert) diffraction pattern. Size distribution histograms of particles grown at 70 and 90 °C (both annealed at 120 °C).

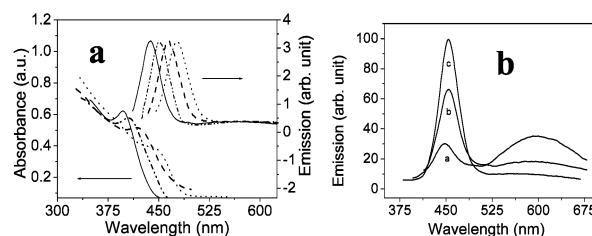


Figure 2. (a) Absorption and emission (370 nm excitation) spectra of CdS particles synthesized at different temperatures. The rightmost curves correspond to 70 °C with increasing 10 °C increments between the curves, going to the left. (b) Tuning of excitonic versus surface photoluminescence of CdS particles by annealing at 120 °C. Annealing time (a) 0 min, (b) 45 min, and (c) 75 min.

°C. Nearly monodisperse particles are observed with average diameters of $5.2(\pm 0.6)$ and $3.5(\pm 0.4)$ nm, respectively.

The number of nucleation centers which form initially (and the ensuing number of particles) is inversely proportional to the final average particle volume. That number depends on the activation energy for the nucleation via an Arrhenius exponential term. On the basis of these considerations and the results of Figure 1 we estimate the activation energy for the nucleation of CdS particles from cadmium xanthate in HDA to be 55kJ/mol.

From electron diffraction in the TEM, the plane distances are found to be 0.335, 0.208, and 0.176 nm, which match the (110), (220), and (311) planes of CdS.

The monodispersity of the particles is manifested in the spectrum (Figure 2a) by the presence of a clear absorption peak rather than an absorbance shoulder or threshold.^{2,12} Theoretically calculating the size of the particles¹³ (using an effective mass ratio of 0.2) gives 3.1 and 5.3 nm for the sizes of the two preparations of Figure 1, which are in agreement with the TEM results. The quantum confinement shifts the narrow emission band (~30–35 nm fwhm) from ~440 nm to 480 nm. The quantum efficiency of these unshelled particles at 412 nm excitation is $2.0 \pm 0.2\%$ (calculated from a comparison to perylene).

Figure 2b shows the emission spectrum from CdS particles that have been gradually annealed at ~120 °C. Initially the particles

exhibit a strong broad emission around 600 nm (associated with deep-surface traps),¹⁴ while the excitonic ~ 450 nm fluorescence is weak. As annealing proceeds, the long wavelength emission loses intensity, while the shorter wavelength peak steadily grows. The assignment of the ~ 600 nm broad band to surface states is confirmed also by the fact that a simple wash of the particles with methanol, as well as adding HDA to suspended particles, decreases the integrated intensity of this emission (and increases that of the sharp excitonic emission). Thus, we can control the spectroscopic behavior of the particles, not only by tuning the wavelength of the excitonic emission but also by adjusting the excitonic/surface emission intensity ratio.

Replacing HDA with TOPO^{2,3,14,15} in the synthesis of CdS particles using Cd HDX, requires higher temperatures (> 120 °C) and longer times than in HDA. The particles (~ 5 nm, by TEM) in dichloromethane show an absorption shoulder at 450 nm and a narrow band emission at 480 nm ($\lambda_{\text{exc}} = 370$ nm). However, using TOP or TBP (tributyl phosphine) as solvents (excluding TOPO altogether) results in the formation of CdS particles from Cd-xanthates even at room temperature upon standing overnight, in sheer contrast to the "TOP/TOPO" route using Cd(CH₃)₂ which proceeds at 250–350 °C. These findings indicate the crucial role of Lewis bases in lowering the reaction temperature (involving, most probably, a β -elimination mechanism as in the Chugaev reaction).¹⁶ Also in differential scanning calorimetry (DSC), solid Cd HDX exhibits a major endothermic transition at 131 °C, with two minor ones at 91 and 108 °C, in HDA a broad transition is observed already at ~ 70 °C, while in TOPO no transition appears up to 200 °C.

An interesting transition is observed with the change of the initially yellow solution into orange-red and finally red, when the reaction temperature is increased above 150 °C. The corresponding fluorescence spectra lose the sharp excitonic peak; low-intensity and broad twin peaks are observed between 450 and 650 nm instead. TEM indicates that the initially spherical particles develop facets and appear in polygonal shapes. At low HDA/Cd ratio we observe after heating at 150 °C ~ 5 nm wide and 20–50 nm long crystalline CdS rods. The suspension grows brown-red and the excitonic emission at 500 nm becomes less intense.

We use the same simple one-precursor approach to produce core/shell structures. Heating (at 70 °C) zinc HDX in the presence of CdS particles we synthesized core-shell CdS/ZnS particles. Annealing was carried out at 150 °C. The shelling is evidenced from (1) the slight blue shift of the exciton emission peak from 450 to 436 nm, (2) the ~ 7 -fold increase of the quantum yield of the excitonic fluorescence of the CdS particles (from ~ 2 to $13.9 \pm 0.3\%$), (3) the thermal stability of the shelled particles compared to the bare ones (the shelled particles do not undergo the shape transition at 150 °C discussed above), and (4) the further decrease of the broad defect-originated long-wavelength fluorescence.

We extended our method to the production of Zn, Cu, Mn, Hg, and Pb sulfides using their respective alkylxanthate salts, and the general behavior is similar to that of cadmium. In addition, a large variety of capping agents (e.g., thiols, amines, phosphines, etc.) can be used for stabilizing these particles.

In conclusion, we reported here a simple and versatile method for the controlled production of high-quality tunable metal sulfide nanoparticles using a generic precursor in a single-pot, low-temperature process. The method is general, applies to a large variety of (transition) metal sulfides and different capping agents, and enables convenient, one-pot production of core-shell structures.

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Supporting Information Available: Plot of DSC of Cd-HDX (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>

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- (9) Typically 0.5 g of HDA is loaded in a dry test tube, heated to 120 °C, and cooled to 50 °C; 0.05 g of cadmium hexadecylxanthate is then added. The mixture is stirred until a homogeneous solution is obtained and then heated to the desired reaction temperature 70–100 °C. The reaction is monitored by fluorescence. The reaction mixture is held at this temperature for 20–30 min, and then the temperature is increased to 120 °C for 90 min (often with a few, ~ 2 min, interludes at 140 °C) to complete the reaction and for annealing. Subsequently, the temperature is slowly decreased to 70 °C, and methanol is added for flocculation. The deposit is washed several times with absolute methanol, dried at room temperature, and stored in the dark. Solvents such as chloroform, dichloromethane, toluene, tetrahydrofuran, etc. can be used for redispersion.
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