

Synthesis of High Quality Zinc Blende CdSe Nanocrystals

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Highly homogeneous and luminescent CdSe colloidal nanocrystals in the less common zinc blende crystal structure have been obtained at high temperature in a noncoordinating organic solvent. The key parameter appears to be the addition of a phosphonic acid to the trioctylphosphine–selenium complex before its injection into the hot cadmium mixture, while the role of temperature is less relevant. Compared to standard (wurtzite) colloidal CdSe preparations, we find that the growth rate is considerably reduced, and the energy gap between the first two absorption bands becomes larger.

Introduction

Synthesis of semiconductor (SC) nanocrystals (NCs) by means of pyrolysis in hot surfactant mixtures has evolved over the last 10 years to produce a variety of high quality materials in colloidal solutions ranging from II–VI NCs, for example, CdS, CdSe, CdTe, HgTe,^{1–6} ZnS, ZnSe, and ZnTe,^{7–9} to III–V, for example, InAs and InP,^{6,10} and IV–VI, for example, PbS and PbSe, NCs.^{11–13} The great advantage of colloidal methods is their ability to produce large quantities of NCs with control of both size and shape.^{14–18} The key parameter of this chemical synthesis is to separate the nucleation step from the growth of the nanocrystal. This is achieved by injection of room temperature organometallic precursors into a hot surfactant solution. The separation of the nucleation from the growth is essential to produce high quality NCs with a narrow distribution of sizes. Moreover, the crystalline structure of the seed particles during nucleation determines the final shape of the NCs, provided no structural phase transitions occur during growth.

CdSe is one of the most popular NCs produced by chemical methods. Bulk CdSe exists in two crystalline lattice structures: wurtzite (W, hexagonal) and zinc blende (ZB, cubic). These structures only differ in the stacking sequence of the CdSe hexagonally packed layers. The W structure has an ABABAB stacking sequence along the [0001] direction, while the ZB structure has an ABCABC stacking sequence along the [111] direction. The energy difference between these two forms is small. ZB is the stable room temperature phase, but it transforms reversibly to the W structure above a critical temperature of 95±5 °C.¹⁹

The traditional synthesis of high quality spherical CdSe NCs is usually carried out at temperatures >300 °C, and it always yields dots with a W lattice structure, sometimes with a few ZB stacking faults.¹ Although the seed particles have a ZB

structure at the beginning of the growth, a structural phase transition to the W structure occurs as the particles grow in size.^{1,18,20} In aqueous solution at low temperature, Rogach et al. obtained ZB CdSe NCs of sizes depending on the capping agents: 1.4–2.2 nm using thioalcohols, 2.0–3.2 nm with thioacids.²¹ Using a similar method, Vossmeier et al. obtained CdS in both the W and ZB structures depending on the stabilizer, thioglycerol or polyphosphates, respectively.²² Qu et al.²³ in a study on CdSe synthesis in trioctylphosphine oxide (TOPO) in the presence of amines mentioned preference for the ZB structure if Se was injected below 230 °C but did not show spectra. Using a noncoordinating solvent and a phosphonic acid (PA), Yu et al.²⁴ synthesized ZB CdTe NCs of controlled size. They attributed their results to the effect of the ligands on monomers, in their case the cadmium atoms. Indeed, they injected cadmium–PA complexes as the Cd precursors, which are less reactive than other soluble precursors, such as fatty acid salts for which they obtained W CdTe NCs.

Here, we present a new method for the synthesis of high quality size-controlled CdSe dots having the ZB lattice structure. Contrary to the synthesis reported by Rogach et al., we prepared our sample at high temperature in an organic medium. As with Yu et al.'s CdTe synthesis, it is based on the use of alkyl PA, but here, we add it to the Se solution. To the best of our knowledge, this is the first modification to the Se source which, since the original recipe published by Murray et al.,¹ always consisted of a complex between Se and a trialkylphosphine. We also find that the injection temperature is not a crucial parameter in the synthesis.

Experimental Section

Materials. Cadmium oxide (CdO, Fluka, 99%), selenium powder (Riedel, 99%), oleic acid (Aldrich, 90%), trioctylphosphine (TOP, Fluka, 90%), 1-octadecene (ODE, Fluka, 95%), octadecylamine (ODA, Aldrich, 97%), hexadecylamine (HDA, Aldrich, 97%), and tetradecylphosphonic acid (TDPA, Alfa, 97%) were the materials used in this study.

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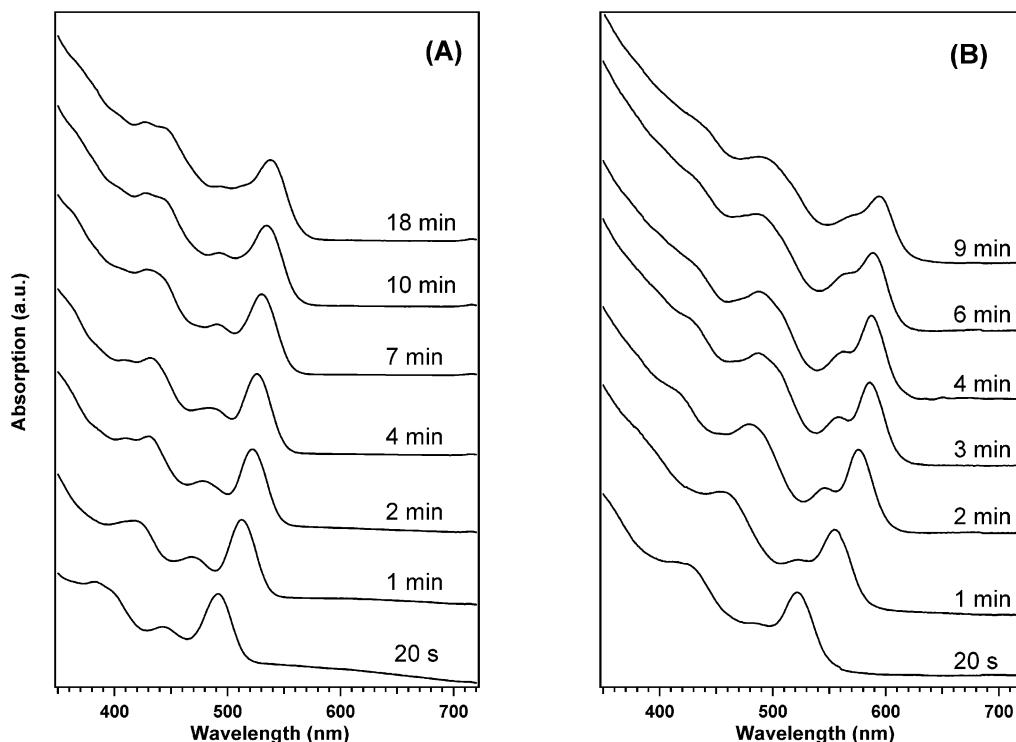


Figure 1. Temporal evolution of the growth of CdSe NCs prepared in oleic acid, in the presence of alkyl PA (A) and according to the recipe of Talapin et al.⁵ (B).

Methods. A mixture of 0.25 g of CdO, 2 g of oleic acid, and 6 mL of ODE was loaded into a three-neck flask and heated under nitrogen until the reddish CdO powder completely dissolved and the solution became clear and colorless. In another flask, the Se solution was prepared by dissolving 0.2 g of Se powder in 3 mL of TOP. Then, 3 g of ODA and 2 g of TDPA were added to the Se solution. This was heated until the solution became clear. The Se solution was injected quickly into the reaction flask at 240 °C. The temperature dropped to 190 °C and then raised again to 210 °C and remained at this value throughout the course of growth. For comparison, CdSe NCs were prepared (a) by the same synthesis adding TDPA to the Cd solution, instead of the Se solution, and (b) by the method of Talapin et al.,^{5,6} using HDA and TOPO as capping agents. Both syntheses yielded similar results, that is, wurtzite dots.

To monitor the reaction during the growth process, aliquots of the mixture were removed from the reaction flask at regular time intervals and dissolved in toluene. To isolate the CdSe NCs from the organic subproducts and from unreacted materials, the sample was cleaned twice. Each time, a mixture of methanol and acetone was added to the sample and then centrifuged. The CdSe NCs precipitated out and were redissolved in toluene (see refs 25 and 26 for the cleaning procedure).

The shape and size of the NCs were determined by transmission electron microscopy (TEM) with a Philips CM20 microscope, operating at an accelerating voltage of 200 kV. A drop from a very dilute sample solution was deposited on an amorphous carbon–copper grid and left to evaporate at room temperature. X-ray diffraction (XRD) measurements were carried out with a Philips X’Pert powder diffractometer operating with a Cu anode. The samples were prepared by precipitating with methanol from the washed toluene solution. The precipitate was exsiccated on disoriented silicon wafers.

For the absorption and luminescence measurements, the sample was dispersed in 10 mm fluorescence cuvettes, filled with toluene. Absorption spectra were recorded with a Perkin-

Elmer Lambda 35 spectrometer. Photoluminescence spectra were measured in a SPEX Fluorolog 2 system, using a Thermo-Oriel 150 W tungsten lamp as the excitation source. Quantum yields, estimated by comparison with the emission of rhodamine 6G, were in all cases found to be at least of the order of 25%.

Results and Discussion

Figure 1 compares the UV–vis absorption spectra for a series of samples with the alkyl PA (A) and by the traditional recipe,^{5,6} which yields W dots (B). Note the times at which the spectra are recorded, which highlight the difference in growth rates. For samples having the same band gap absorption wavelength, the growth occurs within the first minute with Talapin et al.’s method, whereas it takes about 20 min if we add the PA (either to Cd or to Se). Also, we typically reach the end of the growth phase (before the beginning of Ostwald ripening) within 3 min with Talapin et al.’s method, while over 5 min are needed in the case of the present recipe. However, if the PA is added to Se, the Ostwald ripening starts for smaller dots (i.e., when the sample absorption onset is at a much smaller wavelength). Adding the PA to the Cd rather than to the SE, we obtain an evolution of the spectra (not shown) identical to that of Figure 1B, but they point to a rodlike sample.

Several features are resolved in both sets of absorption spectra, which points to a high sample homogeneity. In addition, from the narrow emission bands (fwhm of 25–26 nm, Figure 2) we estimate size distributions of 6–7% for the newly prepared NCs (compare, e.g., with ref 23). The absorption spectra of Figure 1 exhibit some subtle differences, which show up better in Figure 2A, where two spectra having the same band gap energy are superimposed. It appears that the PA synthesis yields particles that have a larger energy splitting between the first and second absorption bands than the TOPO one.^{5,6} This applies to the whole range of sizes, as seen in Figure 2B, which compares the first-to-second absorption band splitting as a function of band gap absorption for the two methods. The case

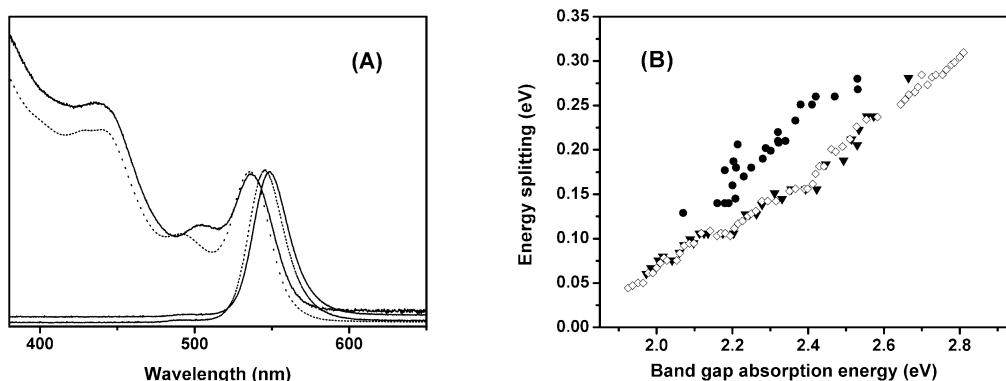


Figure 2. (A) Absorption and emission spectra of CdSe dots prepared by the traditional approach (solid lines)^{5,6} compared with a dot of the same band gap, prepared in the presence of alkyl PA (dashed lines). (B) First-to-second absorption band energy splitting as a function of the band gap absorption energy for CdSe NCs prepared with (solid circles) and without (solid triangles) the alkyl PA. The hollow diamonds represent the same plot from ref 27 for the case of W dots.

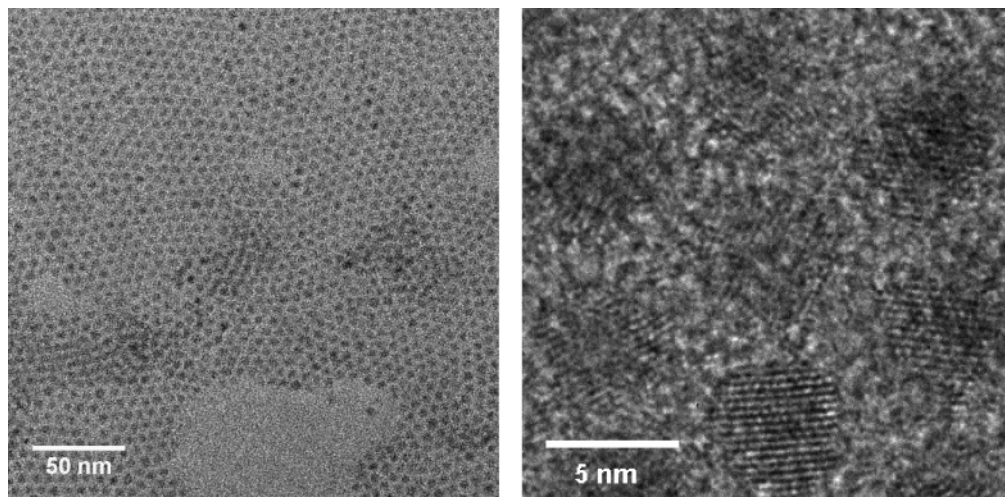


Figure 3. TEM (left) and high resolution TEM (right) images for CdSe nanocrystals (band gap absorption at 540 nm) prepared in the presence of alkyl PA.

without PA agrees very well with the same plot for W dots obtained by Norris et al.,²⁷ which is also shown in Figure 2B. In addition, some differences appear at higher energy (between 400 and 500 nm), which will be dealt with in a forthcoming publication. Last, the Stokes shifts are slightly different, as they differ by 12 meV (Figure 2A).

The origin of the differences in the electronic structure between the two preparations may arise from differences in shape, crystal structure, or surface structure. Therefore, we investigated the morphology and lattice structure of the NCs using TEM, high resolution TEM (HRTEM), and X-ray diffraction (XRD). Parts A and B of Figure 3 show, respectively, the TEM and HRTEM pictures of large CdSe nanocrystals (band gap absorption at ~ 540 nm) prepared with alkyl PA. The images clearly show that the nanocrystals are dotlike with a high uniformity in size and shape. Also (and as a consequence), they assemble in regular superlattices (Figure 3A). The HRTEM (Figure 3B) reveals the high crystallinity of the dots, as we can distinguish the different lattice planes. Furthermore, the dots appear quite spherical and no shape asymmetry is observed. Unfortunately, we do not identify the crystal phase, as this requires a well-defined orientation, to recognize the stacking sequence (see, e.g., refs 28 and 29). Figure 4 shows the XRD patterns obtained for dots prepared with (A) and without (B) PA, and Figure 5 shows a series of XRD spectra and their corresponding absorption spectra (inset) for dots prepared with the new recipe (with PA) but from different pots than in Figure

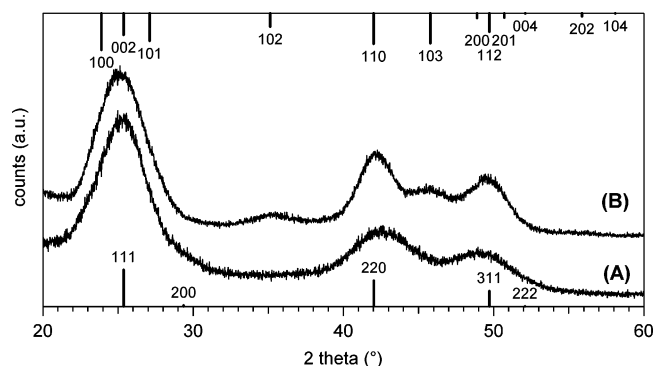


Figure 4. XRD pattern of CdSe NCs prepared with (A) and without (B) alkyl PA. The upper vertical bars represent the position of the diffraction peaks for the bulk wurtzite lattice structure, and their lengths are proportional to their intensity. The lower bars represent the same but for the zinc blende lattice structure. Trace A corresponds to a 2.5 nm ZB dot sample according to our TEM pictures and an absorption band gap at ~ 505 nm, while trace B corresponds to 4.2 nm W dots.

1A. Compared with the latter, they span a larger range of sizes, according to their band gap energy. Figure 4A shows a pattern typical of the ZB structure¹ with three distinct features: the first at $2\theta = 25^\circ$ is due to the (111) reflection, and the two broad features appearing at $2\theta = 42^\circ$ and 50° are due to the (220) and (311) reflections, respectively. The shoulder at $2\theta = 30^\circ$ is due to the (200) planes. This holds for the whole series of XRD patterns shown in Figure 5, and these results provide

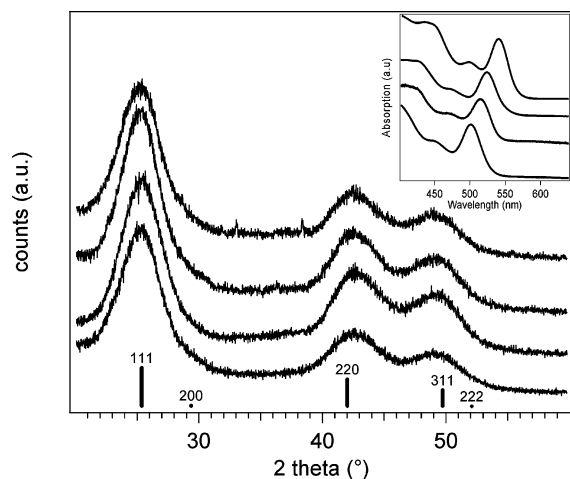


Figure 5. XRD pattern for a series of CdSe NCs prepared with alkyl PA, of different sizes corresponding (from top to bottom) to the absorption spectra shown in the inset. The vertical bars represent the position of the diffraction peaks for the bulk ZB lattice structure, and their lengths are proportional to their intensity.

strong evidence that the particles have a ZB structure. Moreover, the absence of the (102) reflection at $2\theta = 35^\circ$ and the (103) reflection at $2\theta = 46^\circ$, typical of the W lattice structure (see Figure 4B), further confirms the ZB structure. Last, Murray et al. obtained an apparent ZB XRD pattern for 2.0 nm NCs, and they could simulate the diffractogram with a W structure, after introducing a stacking fault, a prolate aspect ratio of 1.3, and a moderate surface disorder. Although the simulated spectrum contains features due to the ZB structure, it reveals deviations from our results (Figures 4A and 5), in that it shows the W(102) reflection, not present in our XRD data, which in turn exhibits the ZB(200) shoulder, missing in the simulation. Therefore, we unambiguously determine the dominant lattice structure to be ZB, even if stacking faults, isotropic lattice contraction, surface disorder, or a slightly asymmetric shape of the particle (prolate or oblate) may be present.

A last piece of evidence in favor of the ZB structure comes from the fact that, using the here prepared dots (with PA) as seeds, we have grown tetrapod-like CdSe nanoparticles.³⁰ Indeed, it is well established that such nanoparticles necessitate a ZB core on which arms with a wurtzite structure can grow, due to the fact that the [111] facets of the ZB dots are identical to the $\pm[0001]$ planes of the hexagonal lattice. This was demonstrated for the case of CdTe tetrapods³¹ and for tetrapods with a CdTe core and CdSe or CdS arms.³²

The above results show that it is possible to yield, in a controlled fashion, high quality CdSe NCs with the desired lattice structure. The most invoked factors, which determine the crystal structure of the NCs, are the injection temperature of the monomers, the growth temperature, and the nature of the ligands.^{24,33} To verify the role of the temperature, we injected the Se precursor solution (TOP–Se and TDPA) into the reaction mixture at temperatures of 210, 240, and 270 °C. In all cases, only ZB dots were obtained. In the absence of alkyl PA, only W dots were obtained. Therefore, the injection temperature is not a critical factor, while it appears that the alkyl PA is the important parameter.

In summary, our results show that adding the PA to TOP–Se (1) slows down the growth dramatically; (2) yields high quality dots of ZB structure, even when the dot size exceeds 3 nm; and (3) alters the pattern of optical transitions.

Point 1 can be explained, on one hand, by the possible formation of a less reactive Se precursor and, on the other hand,

by a stabilization of all facets. We checked whether the addition of the amine with the Cd or the Se makes a difference, but none was observed. On the other hand, its absence led to the formation of elongated shapes. Still, this does not exclude a surface stabilization. Such surface stabilization would freeze the crystal structure. In fact, the nucleation of CdSe produces clusters of ZB structure.²⁰ While, in general, a transition to the W structure occurs early in the growth, in our case this seems to be delayed, which allows us to obtain larger crystals with the ZB structure (point 2). Therefore, we suggest a more rigid ligand–crystal interface, as a cause behind our results. It slows down the growth, although it does not completely hinder it, and prevents the lattice plane from sliding, which is necessary for a structural phase transition. As shown by Alivisatos and co-workers, a phase transition implies shape change and thus a sudden and extended rearrangement of the whole surface configuration.³⁴ The tendency to adopt a W structure is indeed present also in our system, as we did observe some W features on diffractograms of samples grown for several hours. Interestingly, when using long polyphosphate chains as stabilizers, Vossmeier et al. obtained CdS nanocrystals with a ZB structure,²² which points to a surface stabilization.

Finally concerning point 3, we can rule out that the crystal shape is responsible, as the HRTEM pictures indicate. Surface effects on the electronic structure of dots are indeed more difficult to define and rule out. There are a number of instances^{21,35,36} of ZB clusters of Cd chalcogenides, which point to larger splittings between the lowest energy exciton transitions. Thus, while surface effects cannot be ruled out, it seems that the energy splitting between the first and second bands is determined by the lattice structure.

In conclusion, we have demonstrated the size-controlled growth of CdSe nanocrystals with a zinc blende lattice structure. Our results show that the crucial parameter in controlling the lattice structure is not the temperature but rather the type of ligand (alkylphosphonic acid), which also affects the growth rate. Our results also point to a different electronic structure of the zinc blende dots compared to the wurtzite ones.

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