Semiconductors

DOI: 10.1002/anie.200502279

Synthesis of CdSe and CdTe Nanocrystals without Precursor Injection**

Yongan Andrew Yang, Huimeng Wu,
*Kathryn R. Williams, and Y. Charles Cao**

With the growing interest in applications based on nanoscale materials[1] comes a need for an industrial-scale synthesis of colloidal semiconductor nanocrystals with uniform size and shape and well-confined surface passivation. To date, the most successful and widely used nanocrystal synthesis relies on rapid precursor injection.[2,3] However, it is difficult to scale up such a synthesis for making nanocrystals in large quantities (e.g., tens to hundreds of kilograms).[4] Therefore, there is a need to develop nanocrystal synthesis without precursor injection.

Although many publications have described the synthesis of semiconductor nanocrystals without precursor injection,[5] only a few of them have led to nanocrystals with very good monodispersity.[5a–c] However, these nanocrystals exhibit optical properties inferior to those of nanocrystals produced by the injection method. They normally do not show as many multiple exciton absorption peaks, which are critical for nanocrystal applications in advanced optical and electronic devices. Recently, we reported a non-injection-based synthesis of CdS nanocrystals.[4] The sample quality (i.e., size distribution and optical properties) is as good as that of the best CdS nanocrystals synthesized by using precursor injection. Nucleation initiators are important to the CdS synthesis, but unfortunately, such nucleation initiators are not readily available for making nanocrystals with other compositions. Herein, we report how to design a noninjection synthesis for making high-quality CdSe and CdTe nanocrystals without nucleation initiators.

The formation of high-quality nanocrystals is often favored at high temperatures (e.g., >200 °C). This factor creates a major challenge for making monodispersed nanocrystals through a noninjection synthesis because such a synthesis involves a period of increasing temperature over a broad range (e.g., from room temperature to over 200 °C). If the reactivity of a precursor is too high, this broad change of temperature often leads to concurrent nucleation and growth of nanocrystals in the synthesis, which results in products with poor monodispersity. However, if the precursors are too stable, a very small number of nuclei may form, which leads to uncontrollable particle growth. (Note that suitable nucleation initiators could lead to a synthesis of monodisperse nanocrystals in this case.) Therefore, when suitable nucleation initiators are not available, only precursors with suitable reactivity can result in monodisperse nanocrystals. In general, the ideal precursors should exhibit no (or very low) reactivity below the desired temperature for growth of the chosen nanocrystals, but they should also exhibit high reactivity when the temperature reaches the desired point.

To test this hypothesis, we first designed a noninjection synthesis for making CdSe nanocrystals. We chose 240 °C as the growth temperature, which was in accordance with the lesson learned from the injection-based synthesis of CdSe nanocrystals.[2,3] At this growth temperature, pure cadmium myristate is a suitable cadmium precursor because it has a decomposition point at about 226 °C.[6] Selenium powder can be an effective selenium precursor for two reasons: 1) it has a melting point at 221 °C;[6] 2) it is insoluble in octadecene (ODE) at room temperature and becomes slightly soluble at temperatures over 190 °C. As selenium has low solubility in ODE, it is unreactive with cadmium myristate up to 200 °C. In a typical synthesis (see Experimental Section for detailed conditions), small particles (i.e., nuclei) suddenly appeared at 210 °C (Figures 1a and b). As the nanocrystals grew, the number of particles quickly increased to a maximum, and then during further growth it continued to decrease. Significantly, about 72 % of the particles formed in the initial stage disappeared after two hours of growth, while the size distribution of the nanocrystals continued to become more narrow throughout the synthesis (Figure 1c–e). Such size

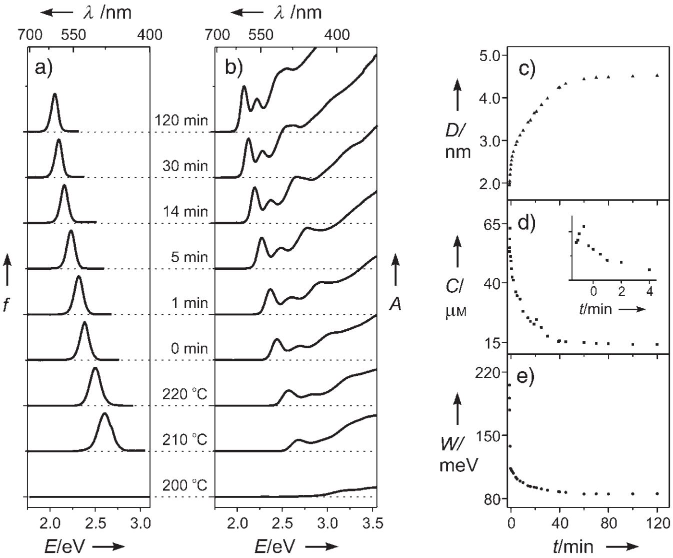

Figure 1. Temporal evolution of a) the fluorescence (*f*) spectrum, b) the absorption spectrum, c) the diameter (*D*) of the nanocrystals, d) (and inset) the concentration (*C*) of the nanocrystals, and e) full width at half-maximum (FWHM) of the fluorescence spectrum during the CdSe synthesis. The size and concentration of the nanocrystals were obtained according to a reported procedure.[2b, 3b]

---

[*] Dr. Y. A. Yang, H. Wu, Dr. K. R. Williams, Prof. Y. C. Cao
Department of Chemistry
University of Florida
Gainesville, FL 32611 (USA)
Fax: (+1) 352-392-0588
E-mail: cao@chem.ufl.edu

[**] Y.C.C. acknowledges the University of Florida and the ACS Petroleum Research Fund for financial support. We thank Charles R. Martin and Willard W. Harrison for helpful discussions, and Kerry Siebein for technical assistance.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

focusing is not likely to arise from diffusion-limited growth because this growth does not lead to a decreasing number of nanocrystals.[2b] Additional investigation is required to understand the detailed mechanism involved in this phenomenon.

The addition of oleic acid during the synthesis is important to control the quality of the nanocrystals. Without oleic acid, the nanocrystals show absorption spectra with a tail of higher intensity at the low-energy end after their diameter reaches around 3.0 nm and with further growth, they show broad absorption spectra (Figure 2, dotted lines). Such spectral changes are normally attributed to broadening of the particle size distribution due to Ostwald ripening. However, in this synthesis we found that the phenomenon was caused by particle aggregation as it could be reversed by adding a small amount of oleic acid into the growth solution (Figure 2, solid lines). After this addition, nanocrystal growth turned out to be extremely stable. The size distribution of the nanocrystals further narrowed with particle growth (Figure 1), and the narrow size distribution was maintained for at least 16 h at the reaction temperature.

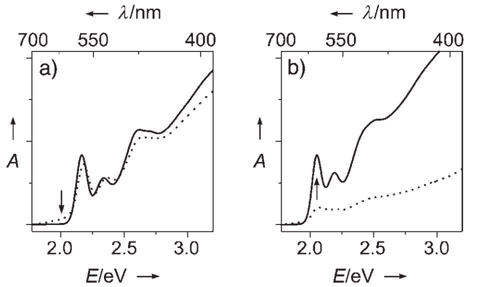

Figure 2. Absorption spectra of CdSe nanocrystals with (solid lines) and without (dotted lines) oleic acid a) after 16 min of growth and b) after 60 min of growth.

Without size sorting, typical CdSe nanocrystals from this synthesis show sizes with a standard deviation (σ) of less than 5 % (see Figure 3 d) and a quantum yield of photoluminescence (PL) of about 30 to 40 %. Interestingly, these nanocrystals have a zinc-blende (ZB) structure but not a wurtzite (W) structure. Although these two crystal phases produce similar X-ray powder diffraction (XRD) results with nanocrystals, the XRD pattern of 4.0-nm particles shows unambiguous evidence that the particles have a ZB structure (Figure 3 a): a) the valley between the the (220) and (311) peaks is deep; b) the (400) peak is at 61.0°; c) the (620) peak is at 106.2°. In the case of wurtzite crystals, there are no peaks in these positions.[2a,4,6] This structural assignment is consistent with the high-resolution transmission electron microscopy (HRTEM) observation (JEOL-JEM 2010 operated at 200 kV): a square cross-fringe pattern represents an ordered distance of 0.22 nm, which corresponds to the lattice spacing of the (220) faces in ZB CdSe (Figure 3 a, inset). Such a cross-fringe pattern does not exist in a wurtzite structure. Note that ZB CdSe nanocrystals have been made recently by an injection-based synthesis.[7] However, this synthesis only led to high-quality nanocrystals in very small sizes, and these small nanocrystals show nearly identical XRD patterns to those of small wurtzite nanocrystals made by Bawendi and coworkers.[2a] In contrast, the noninjection method presented in this paper can also result in larger CdSe nanocrystals, which allow us to unambiguously identify ZB nanocrystals.

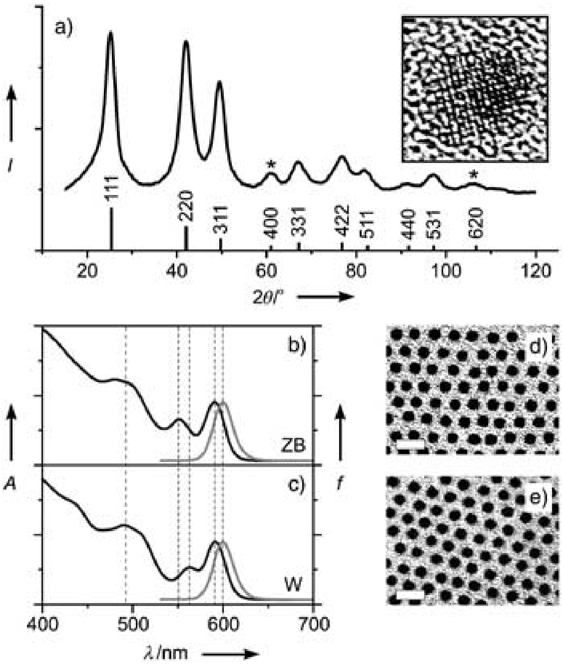

Figure 3. a) XRD pattern of 4.0-nm-diameter ZB CdSe nanocrystals. The standard diffraction peak positions and relative intensities of bulk ZB CdSe are indicated. The inset shows an HRTEM image (5 nm × 5 nm) of the nanocrystal sample. b) Absorption (black) and emission (gray) spectra of the ZB CdSe sample. c) Absorption (black) and emission (gray) spectra of a wurtzite (W) CdSe nanocrystal sample made by chalcogen precursor injection according to a reported procedure.[3a] d, e) TEM images of ZB (d) and W (e) CdSe nanocrystals. Scale bar: 10 nm.

Indeed, zinc-blende and wurtzite CdSe nanocrystals can be easily distinguished by their optical properties (Figure 3 b–e). For both cases, nanocrystals with an identical position of the absorption peak for the first exciton transition band are nearly identical in size. The Stokes shifts of the emission peaks are nearly identical and PL quantum yields of band-gap emissions are similar. However, the fine structures in their absorption spectra are different. The gap between the first ($1S_{3/2}1S_e$) and second ($2S_{3/2}1S_e$) exciton transition peaks for ZB particles is clearly wider than that for W particles. The peak positions for the exciton transitions with higher energies also vary for these two types of CdSe nanocrystals. These differences in the absorption spectra originate from the different electronic band structures at the center of the Brillouin zone for these two types of crystal phases.[8]

To further demonstrate the power of noninjection synthesis, we synthesized nonspherical CdSe nanocrystals. In the case of a ZB structure, nonspherical particles are normally cubes, tetrahedral pyramids, or triangular prisms, and these particles have a higher surface energy than spherical particles.[9] Therefore, making nonspherical particles requires growth conditions with a high chemical potential, which we thought could be achieved by increasing the per-particle concentration of the precursors.[6] To create such conditions, we chose a method to decrease the number of initial nuclei while leaving the precursor concentration unchanged. Because more reactive precursors can lead to fewer nuclei,[4] we used tributylphosphine selenide (TBPSe) in place of selenium powder for making CdSe nanocrystals. Indeed, the number of nuclei at the initial stage in this synthesis decreased by 75 % as compared with the synthesis with selenium powder; after 30 min, tetrahedral particles with edge length of 5.0 nm and σ of 7 % were formed. The high uniformity of these nanocrystals allows the formation of ordered, triangular close-packed nanocrystal assemblies on TEM grids (Figure 4).

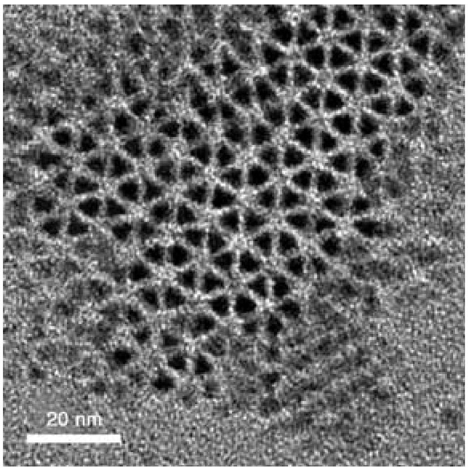

Figure 4. TEM image of tetrahedral CdSe nanocrystals.

Moreover, the principle for designing a noninjection synthesis can be applied to the synthesis of CdTe nanocrystals. The key point is to find suitable precursors. The reactivity of cadmium myristate with tellurium powder in ODE is too low, whereas with tributylphosphine telluride (TBPTe) it is too high. Neither case resulted in the formation of uniform nanocrystals. We then decreased the reactivity of the cadmium precursor by replacing cadmium myristate with cadmium octadecylphosphonate. The reaction between cadmium octadecylphosphonate and TBPTe just perfectly fits the need for growth of monodisperse CdTe nanocrystals. A typical synthesis led to CdTe nanocrystals with a size distribution of less than 5 %, which exhibit up to five exciton absorption bands (Figure 5). Such particle quality is at least comparable with that of the best particles made by the injection synthesis.[3b]

In summary, we reported the synthesis of high-quality CdSe and CdTe nanocrystals without precursor injection. This noninjection synthesis allows detailed control of nanocrystal size and shape. In addition, because it exhibits easily controllable nanocrystal-growth kinetics, such a synthesis is very important for a large-scale industrial preparation of CdSe and CdTe nanocrystals in which the rates of heating and cooling of reaction solutions are limited.

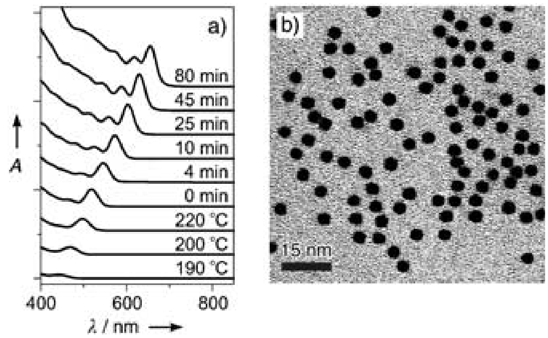

Figure 5. a) Temporal evolution of the absorption spectrum in CdTe nanocrystal synthesis. b) TEM image of CdTe nanocrystals with a first absorption peak at 625 nm.

Experimental Section

Cadmium myristate was prepared by an ex situ method: a solution of cadmium nitrate in methanol (0.05 M, 40 mL) was added to a solution of sodium myristate in methanol (0.025 M, 240 mL). The resulting white precipitate was washed twice with methanol and dried under vacuum overnight to remove all solvents. Note that the purity of cadmium myristate is important to the following CdSe nanocrystal syntheses.

Synthesis of spherical CdSe nanocrystals: selenium powder (0.05 mmol, 100 mesh from Aldrich) and cadmium myristate (0.1 mmol) were added into a three-neck flask with ODE (5.0 g). The mixture was degassed for 10 min under vacuum ($\approx 3\times10^{-2}$ Torr) at room temperature. Under a flow of Ar, the solution was stirred and heated to 240 °C at a rate of 25 K min^{-1}. Serial quantitative aliquots (50 μL) were taken for kinetic studies,[6] and the time was counted as zero when the temperature reached 240 °C. After the particle diameter had reached about 3.0 nm (i.e., the first absorption peak at 550 nm), a solution of oleic acid in ODE (0.05 M, 1.0 mL) was added dropwise into the reaction solution to stabilize the growth of the nanocrystals.

The synthesis of tetrahedral CdSe nanocrystals followed a similar protocol as above, but TBPSe was used instead of selenium powder (cadmium myristate: 0.1 mmol, and TBPSe in ODE: 0.05 mmol of TBPSe in a mixture of tributylphosphine and ODE, 0.012 g and 0.5 g, respectively[2]).

In the synthesis of CdTe nanocrystals, cadmium octadecylphosphonate was made in situ: a mixture of CdO (0.1 mmol), octadecylphosphonic acid (0.22 mmol), and ODE (5.0 g) was heated to 300 °C to give a colorless solution. The solution was cooled to room temperature, and TBPTe (0.20 mmol in 0.19 g of tributylphosphine,[2a]) was added. The mixture was degassed, then stirred and heated to 240 °C (25 K min^{-1}) under a flow of Ar. Note that adding oleic acid is not needed during the CdTe synthesis.

Received: June 29, 2005

Keywords: crystal growth · fluorescence spectroscopy · nanotechnology · self-assembly · semiconductors

---

[1] a) A. P. Alivisatos, *Nat. Biotechnol.* **2004**, *22*, 47; b) H. Weller, *Philos. Trans. R. Soc. London Ser. A* **2003**, *361*, 229; c) M. Han, X. Gao, J. Z. Su, S. Nie, *Nat. Biotechnol.* **2001**, *19*, 631; d) M. Kazes, D. Y. Lewis, Y. Ebenstein, T. Mokari, U. Banin, *Adv. Mater.* **2002**, *14*, 317; e) L. Zhu, M. Zhu, J. K. Hurst, A. D. Q. Li, *J. Am. Chem. Soc.* **2005**, *127*, 8968.

[2] a) C. B. Murray, D. J. Norris, M. G. Bawendi, *J. Am. Chem. Soc.* **1993**, *115*, 8706; b) X. Peng, J. Wickham, A. P. Alivisatos, *J. Am. Chem. Soc.* **1998**, *120*, 5343.

[3] a) L. Qu, X. Peng, *J. Am. Chem. Soc.* **2002**, *124*, 2049; b) W. W. Yu, L. Qi, W. Guo, X. Peng, *Chem. Mater.* **2003**, *15*, 2854; c) R. Xie, U. Kolb, J. Li, T. Basché, A. Mews, *J. Am. Chem. Soc.* **2005**, *127*, 7480.

[4] Y. C. Cao, J. Wang, *J. Am. Chem. Soc.* **2004**, *126*, 14336.

[5] a) S. L. Cumberland, K. M. Hanif, A. Javier, G. A. Khitrov, G. F. Strouse, S. M. Woessner, C. Yun, *Chem. Mater.* **2002**, *14*, 1576; b) N. Pradhan, S. Efrima, *J. Am. Chem. Soc.* **2003**, *125*, 2050; c) D. V. Talapin, S. Haubold, A. L. Rogach, A. Kornowski, M. Haase, H. Weller, *J. Phys. Chem. B* **2001**, *105*, 2260; d) Y. Wang, N. J. Herron, *J. Phys. Chem.* **1991**, *95*, 525.

[6] See the Supporting Information.

[7] M. B. Mohamed, D. Tonti, A. Al-Salman, A. Chemseddine, M. Chergui, *J. Phys. Chem. B* **2005**, *109*, 10533.

[8] S. Ninomiya, S. Adachi, *J. Appl. Phys.* **1995**, *78*, 4681.

[9] a) R. Jin, Y. C. Cao, E. Hao, G. S. Métraux, G. C. Schatz, C. A. Mirkin, *Nature* **2003**, *425*, 487; b) F. Kim, S. Connor, H. Song, T. Kuykendall, P. Yang, *Angew. Chem.* **2004**, *116*, 3759; *Angew. Chem. Int. Ed.* **2004**, *43*, 3673.