

A New Route to Zinc-Blende CdSe Nanocrystals: Mechanism and Synthesis

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Received: May 12, 2005

We report the possible mechanism of forming of CdSe nanocrystals in the high boiling point solvents with long alkane chains and a novel Non-TOP-Based route to zinc-blende CdSe nanocrystals. A new mechanism shows that there exists a redox reaction in the long alkane chain solvents: Se is reduced to H₂Se gas; at the same time, the long alkane chains are oxidated to alkene chains; then, the Cd complex reacts with H₂Se to form CdSe nanocrystals. Possible chemical reaction equations involved in the process of forming the CdSe nanocrystals have been discussed. The alkene chain and H₂Se were detected respectively by a series of experiments to support the new mechanism. Under the guidance of this mechanism, we have developed a much cheaper and greener Non-TOP-Based route for the synthesis of a size series of high-quality zinc-blende (cubic) CdSe nanocrystals. Low-cost, green, and environmentally friendlier reagents are used, without use of expensive solvents such as trioctylphosphine (TOP) or tributylphosphine (TBP). The new route enables us to achieve high-quality CdSe nanocrystals with sharp ultraviolet and visible (UV–vis) absorption peaks, controllable size (2.0–5.0 nm), bright photoluminescence (PL), narrow PL full width of half-maximum (fwhm) (29–48 nm), and high PL quantum yield (up to 60%) without any size sorting.

Introduction

Colloidal CdSe nanocrystals (NCs) have attracted broad attention in recent years for use in a variety of applications including biological fluorescent labels,^{1,2} light emitting diodes,³ lasers,⁴ and solar cells.⁵ To attain these ends, it is of primary importance to develop low-cost, green, fast, and mass-production routes for synthesis of CdSe NCs with the desired quality.

Many works on the synthesis of CdSe NCs have been reported, including routes such as the single molecule precursor route,^{6–8} the solvothermal route,^{9,10} the sonochemical route,¹¹ the microwave irradiation route,¹² the organometallic precursor route,^{13,14} and the nonorganometallic precursor route.^{15–19} The organometallic precursor route was developed by Murray et al. in 1993, which involved the reaction of cadmium organometallic precursor Cd(CH₃)₂ with a Se precursor,¹⁴ but it is generally acknowledged that the reactant Cd(CH₃)₂ is an expensive, pyrophoric, and hazardous material. In 2000, Peng et al. developed a relatively much simpler and greener nonorganometallic precursor route using inexpensive and little toxic CdO instead of Cd(CH₃)₂ to produce CdSe NCs.^{15,16} Recently, using noncoordinating solvents such as octadecene (ODE) instead of coordinating solvents such as trioctylphosphine oxide (TOPO) has been extensively studied.^{18,19} In general, Peng's route and its alternatives involve the injection of a trioctylphosphine selenide (TOPSe)/TOP solution to a Cd solution. Thus the reaction media involve at least three components, namely, the solvents TOPO (or ODE), the Cd solution, and the TOP-Se (or

TBP-Se) solution. Here, we name them as the TOP-Based route. Hundreds and hundreds of papers have already been published based on this route.

However, little knowledge has been obtained for the mechanism of the formation of the CdSe NCs by the TOP-Based route. In particular, to the best of our knowledge, no chemical reaction equations on TOP-Based route have been discussed in the literature. Furthermore, in fact, the costs of large-scale synthesis of NCs are still very high for using expensive solvents such as TOP (or TBP). In addition, TOP (or TBP) is hazardous, unstable, and not an environmentally friendly solvent. Hence it is critical for both fundamental research and industry application for us to develop a cheaper and greener Non-TOP-Based route for large-scale synthesis of high-quality CdSe NCs.

Herein, we show a new viewpoint on the formation of the CdSe NCs in the high boiling point solvents with long alkane chains and the possible chemical reaction equations involved have been put forward. Understanding this mechanism, we have developed a much cheaper and greener Non-TOP-Based route for the synthesis of a size series of high-quality zinc-blende CdSe NCs by injection of Cd oleic acid (Cd-OA) solution into a Se solution without use of TOP (or TBP). The advantages of the present protocol are the following: (1) our synthesis route is much greener than the TOP-Based route because the as-used solvents oleic acid and paraffin liquid are both natural products with no toxicity; (2) we describe a much lower cost synthesis route for the synthesis of CdSe NCs, which is of great value for both laboratory research and industrial applications; (3) the obtained NCs are all zinc-blende (cubic) phase, while in the TOP-Based route the synthesized CdSe NCs are in the common wurtzite (hexagonal) phase, which casts new light on the investigation of the property difference between the zinc-blende (cubic) and wurtzite (hexagonal) phase of the CdSe NCs; and (4) to the best of our knowledge, this is the first modification

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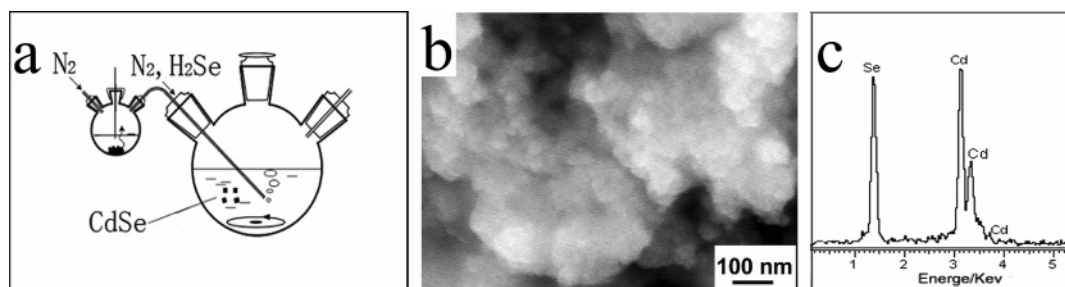
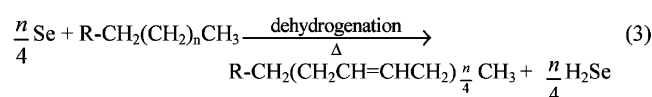
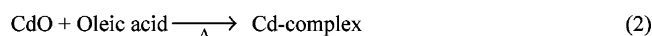
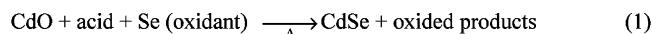


Figure 1. (a) Sketch map for the formation of H_2Se and alkene; (b) SEM image of the precipitations; (c) corresponding EDX pattern of the precipitations.

SCHEME 1: Possible Chemical Reactions Involved in the Formation of CdSe NCs^a



^a Equation 1 is the general reaction equation of the formation of the CdSe NCs in the long alkane chain solvents; eq 3 is a process involving dissolution of Se powder in paraffin liquid and a dehydrogenation reaction to generate H_2Se and alkene in situ.

to the Se source without TOP (or TBP) which, since the original procedure published by Murray et al.,¹³ always consisted of a complex between Se and TOP.

Mechanism

Although the synthesis of CdSe NCs has been intensively investigated in the past decade, little knowledge has been obtained on the synthesis of CdSe NCs by the TOP-Based route. Furthermore, no chemical reaction equations have been put forward in the literature. We put forward here a new viewpoint on the formation of the CdSe NCs in the high boiling point solvents with long alkane chains. In the process of the formation of the CdSe NCs, there exists a redox reaction: Se acts as the oxidant and CdSe as the reduction product, while the carbon atom in the long alkane chains acts as the reducing agent and the long alkane chains should be the oxidation product. In experiments, under heating, the Se is reduced to H_2Se gas, while the long alkane chain is oxidized to the long alkene chain. At the same time, CdO reacts with the acid (such as oleic acid (OA), hexylphosphonic acid (HPA), and tetradecylphosphonic acid (TDPA)) to form the Cd complex. Finally, the Cd complex reacts with H_2Se to form CdSe NCs.

Scheme 1 shows the possible chemical reactions involved in the formation of CdSe NCs taking our Non-TOP-Base route as an example. Equation 1 summarizes the general redox reaction for the formation of the CdSe NCs. Equation 2 demonstrates that the CdO reacts with the oleic acid to generate Cd-OA solution, which is similar to the former report.¹⁶ Equation 3 is a process involving Se powder dissolved in paraffin liquid and a dehydrogenation reaction to generate H_2Se gas in situ. Three reasons may play important roles in the formation of stable homogeneous Se solution: (1) the melting point of as-used Se powder is 217 °C, thus liquid-state Se could be formed at a temperature of near or above 217 °C in the paraffin liquid; (2) the liquid state of Se can be well dispersed in the paraffin liquid or other solvents with long alkane chains; and (3) H_2Se can be

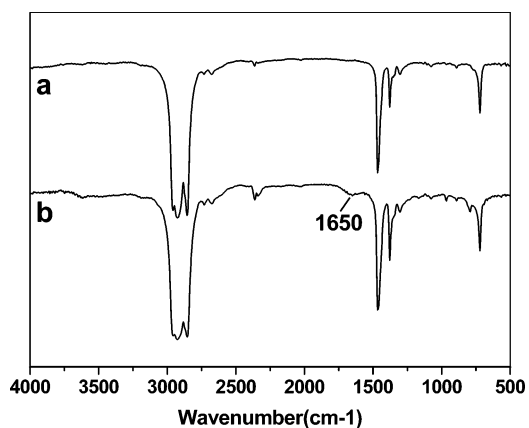


Figure 2. FTIR spectra of *n*-hexadecane mixed with Se powder before heating (a) and after heating (b). The absorption band at 1650 cm^{-1} is the characteristic of C=C stretching.

decomposed to Se reversibly at the present temperatures. However, it is worth noting that if the temperature rose to above 300 °C, a great deal of H_2Se gas would be released immediately, thus the moderate temperature is favorable for the formation of Se solutions. Equation 4 describes that Cd-OA reacts with the H_2Se gas to form CdSe NCs.

To prove this mechanism, we carried out several experiments to identify the H_2Se and alkene as seen from Figure 1a. In the small three-necked flask, Se powder was mixed with the paraffin liquid. In the right large three-necked flask, CdNO_3 solution was deaerated by N_2 bubbling. When the Se mixture was carefully heated to 300 °C, a great amount of colorless gas was generated and then conducted to the large three-necked flask, passed through the solution together with a slow nitrogen flow. Dark-red precipitations appeared immediately in the large three-necked flask. The obtained precipitations were filtrated, washed with distilled water, and dried in the air at 50 °C. The Scanning Electron Microscopy (SEM) image in Figure 1b shows the morphology of the as-precipitated particles. The Energy-dispersive X-ray (EDX) spectrum in Figure 1c shows the compositions of only Cd and Se. The atomic ratio of Cd and Se was 0.535:0.465 calculated from the EDX results. The results indicate that the dark-red precipitations are CdSe. Experiments replacing the paraffin liquid with other long alky chain solvents such as olefin, octadecene (ODE), and *n*-hexadecane with Se powder were also carried out. H_2Se was also generated at similar conditions. To obtain further evidence, we also identified the formation of alkene by Fourier transform infrared (FTIR) spectroscopy. In a typical experiment, analytical grade *n*-hexadecane was mixed with Se powder and heated at 300 °C under N_2 protection. Figure 2 displays the FTIR spectra of the mixture before heating and after heating. After heating, an absorption band at 1650 cm^{-1} has clearly appeared, which is the characteristic of C=C stretching. This feature suggests the

formation of alkene after heating. The absorption band at 2350 cm^{-1} comes from the CO_2 gas in the air. All the other features in the FTIR spectra come from the long alkane chain. Thus, both the H_2Se and alkene were identified to support our mechanism. Our procedure was inspired by the simple solvothermal route, which described that aromatization of tetralin to naphthalene by Se could generate H_2Se in situ.¹¹ Significantly, it is worth noting that heating selenium with paraffin wax would generate H_2Se gas, and this reaction was discovered as early as 1909.²² Unfortunately, it has been long ignored.

Experimental Section

Chemicals. CdO (99.5%), Se powder (99.9%), oleic acid (OA) (analytical grade), paraffin liquid (chemical grade, with boiling point higher than $300\text{ }^\circ\text{C}$), *n*-hexadecane (analytical grade), *n*-hexane (analytical grade), and methanol (analytical grade) were obtained from Beijing Chemical Reagent Ltd., China, and used as obtained. Rhodamine B (with a photoluminescence quantum yield of 90% in methanol) was obtained from Alfa Aesar.

Synthesis. A typical synthetic procedure of the CdSe NCs is briefly described below. First, 20 mmol of CdO, 9.6 mL of oleic acid, and 40 mL of paraffin liquid were loaded in a three-neck flask. At about $150\text{ }^\circ\text{C}$, a reddish CdO powder was dissolved gradually and generated a light yellowish homogeneous solution (solution A). Then 1 mmol of Se powder in 50 mL of paraffin liquid was carefully heated to $220\text{ }^\circ\text{C}$ with rapid stirring (solution B) in another three-necked flask. The solution turned orange, and then wine red. Then about 5 mL of solution A (containing about 2 mmol of Cd precursor) was swiftly injected into solution B during rapid stirring. After the injection, the temperature dropped to $210\text{ }^\circ\text{C}$ immediately, then rose to $220\text{ }^\circ\text{C}$ in 0.5 min. The final temperature was maintained at $220\text{ }^\circ\text{C}$ for the growth of CdSe NCs. The synthesis can be carried out under nitrogen or open to air. Aliquots were taken at different time intervals, and UV-vis and PL spectra were recorded for each aliquot. Finally the reaction mixture was cooled to room temperature and methanol was added to precipitate CdSe NCs. The precipitated CdSe NCs were separated by centrifugation, further washed with methanol several times, and dried in the air at $50\text{ }^\circ\text{C}$ for characterization.

Characterization. Fourier transform infrared (FTIR) spectra were recorded with a Bio-Rad FTIR spectrometer FTS 165. Ultraviolet and visible absorption (UV-vis) spectra were recorded with a JASCO 570 spectrophotometer at room temperature. The aliquots were diluted with *n*-hexane directly for characterization without any size sorting. Photoluminescence (PL) spectra were measured with a PTI-C-700 fluorescence spectrometer. The photoluminescence quantum yield (PL QY) was obtained following the same procedure used previously²¹ by comparison with a standard (Rhodamine B in methanol) and using data derived from the luminescence and the absorption spectra as the following: $\Phi = \Phi'(I/I')(A'/A)(n/n')^2$. In this equation, I (sample) and I' (standard) are the integrated emission peak areas, upon 400 nm excitation; A (sample) and A' (standard) are the absorption at 400 nm; n (sample) and n' (standard) are the refractive indices of the solvents; and Φ and Φ' are the PL QY for the sample and the standard, respectively.

A JEOL JEM-200CX microscope operating at 160 kV in the bright-field mode was used for Transmission Electron Microscopy (TEM). High-resolution TEM (HRTEM) was performed on a JEOL JEM-2010 electron microscope operating at 200 kV. Samples for TEM and HRTEM were prepared by putting a drop of *n*-hexane diluted solution of CdSe NCs onto an amorphous

carbon substrate supported on a copper grid and then allowing the solvent to evaporate at room temperature. Energy-dispersive X-ray spectroscopic (EDX) measurement was performed on powder samples deposited on aluminum substrates and using a Hitachi S-4300 Scanning Electron Field Emission Microscope operating at 15 kV. X-ray powder diffraction (XRD) employed a Japan Regaku D/max γ A X-ray diffractometer equipped with graphite monochromatized Cu $K\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$) irradiated with a scanning rate of 0.02 deg/s . The crystallite sizes of the as-synthesized CdSe NCs were estimated by the Debye-Scherrer formula ($L = 0.9\lambda/B \cos\theta$), where L is the coherence length, B is the full width at half-maximum (fwhm) of the peak, λ is the wavelength of the X-ray radiation, and θ is the angle of diffraction. Purified powder CdSe NCs were crushed into fine powder for the XRD analysis.

Results and Discussion

Low-cost and green reagents were used for the synthesis of CdSe NCs. In the present study, the green precursor CdO powder and Se powder were chosen as the Cd source and Se source, respectively. Paraffin liquid was selected as the solvent whose molecular formula can be expressed as $\text{CH}_3(\text{CH}_2)_n\text{CH}_3$, ($n = 16-22$). It is a colorless liquid at room temperature and boiled at above $300\text{ }^\circ\text{C}$. As a solvent, it is cheaper, environmentally friendlier, and more stable in the atmosphere than the reported solvents such as TOPO or ODE. The role of the acid in the synthesis of the CdSe NCs is to dissolve CdO powder and form homogeneous Cd solution and act as the capping ligand in the formation of the NCs. Herein a natural product oleic acid was used as the acid, which is much cheaper and environmentally friendlier than hexylphosphonic acid (HPA) or tetradecylphosphonic acid (TDPA).¹⁵ In the previous TOP-Based route, it was acknowledged that the role of the TOP or TBP solvents was to dissolve Se powder to form homogeneous Se solution. In the present study, it is found that homogeneous Se solution was formed by simply heating Se powder with paraffin liquid during rapid stirring. Significantly, it is found that the new synthesis route can be carried out under nitrogen or open to air. We believe that the present process is due to the fact that the oleic acid and paraffin liquid are very stable in the atmosphere, while TOP and TBP are unstable in the atmosphere, thus the process must be performed under nitrogen or in the glovebox.

The temporal evolution of the size and size distribution of CdSe NCs was studied by UV-vis absorption spectra. Figure 3 revealed that the size of the CdSe NCs could be close to monodisperse, represented by the sharp absorption peaks if the growth stops in the "focusing of size distribution" regime.¹⁵ After the injection of the Cd solution, the reaction was almost instantaneous and the solution quickly developed to a deep orange-red color. Figure 3a revealed that at the growth temperature of $220\text{ }^\circ\text{C}$, the small CdSe NCs with an absorption peak at 468 nm would be formed in 0.2 min and then developed to bigger NCs with an absorption peak at 510 nm in 0.5 min, then the absorbance peak of the NCs reached 512 nm in 90 min. Thus as the aging process from 0.5 min to 90 min, the size of the NCs remained almost unchanged. Similar results were obtained when the concentration of the precursors was doubled as shown in Figure 3b. In Figure 3c, when the reaction temperature rose to $240\text{ }^\circ\text{C}$, the size of the CdSe NCs remained unchanged from 0.2 to 45 min, indicating that the nucleation and growth process was less than 0.2 min. Generally, it is reasonable to summarize that the experiments could be terminated after about 1 min growth in the present study. These

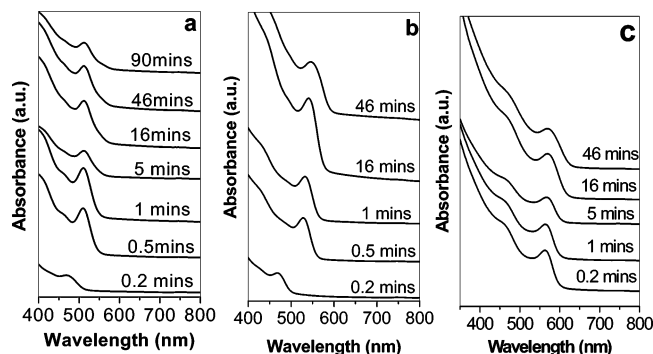


Figure 3. Temporal evolution of the UV–vis absorption spectra of the as-prepared CdSe NCs: (a) growth at 220 °C, the monomer concentration is 1 mmol of Se powder in 50 mL of paraffin liquid; (b) growth at 220 °C, 2 mmol of Se powder in 50 mL of paraffin liquid; and (c) growth at 240 °C, 1 mmol of Se powder in 50 mL of paraffin liquid. The Cd:Se precursor ratio (2:1) was the same in the above three experiments.

nucleation and growth processes were easy to control to obtain the CdSe NCs with the desired size, which would be a benefit for the laboratory synthesis and industrial production. It is believed that the capping ligand oleic acid not only determined the rate of growth but also played a major role in determining the number and size of the nuclei formed during injection. This aspect of growth kinetics has been well studied by Bullen and Mulvaney recently in a system of injection TOPSe to Cd solution with oleic acid as the acid and the capping ligand in octadecene (ODE).¹⁹ By systematically changing the concentration and the temperature, it was possible to finely tune the size of the CdSe NCs. As shown in Figure 3, the absorption peak was at 510, 532, and 563 nm for Figure 3, panels a, b, and c, respectively, after 1 min of growth. This indicates that the bigger CdSe NCs will form at high temperatures and at higher concentration.

As shown in Figure 4, the estimated size range of CdSe NCs was approximately between 2.0 and 5.0 nm by fitting the Peng's data²³ with a simple effective mass approximation (EMA) model proposed by Brus.²⁴ The corresponding PL peak position for the CdSe NCs with reasonable emission brightness is between 486 and 618 nm (Figure 4). Without any size sorting, all UV–vis and PL spectra of the as-prepared CdSe NCs shown in Figure 4 are comparable to the best optical spectra of CdSe NCs, which were obtained through alternative approaches with solvents such as TOP.^{15–19} A typical PL fwhm peak of those as-prepared samples is in the range between 29 and 48 nm. NCs in this size range with the optical properties shown in Figure 4 can be reproducibly synthesized. The PL QY was obtained by using a conventional route, integrating the PL band of CdSe in *n*-hexane and comparing the intensity to that of Rhodamine B in methanol.²¹ The PL quantum yield was found to be about 60% for 2.8 nm CdSe NCs measured at room temperature. The PL QY of the small (2.0 nm) NCs and the big NCs (5.0 nm) are about 33% and 11%, respectively. It is believed that the high PL QY of the CdSe NCs can be attributed to the well oleic acid capped surfaces and good monodispersity of the CdSe NCs.

Figure 5, parts a and b, shows the typical TEM and HRTEM images of the as-synthesized oleic acid capped CdSe NCs with the excitonic absorption peak of the NCs at 562 nm. The TEM and the HRTEM confirmed that the size distribution of the as-synthesized CdSe NCs was nearly monodisperse with the average size of 4.0 nm, which is consistent with the fitting from the excitonic absorption peak of the NCs at 562 nm. The existence of lattice planes on the HRTEM confirmed the good

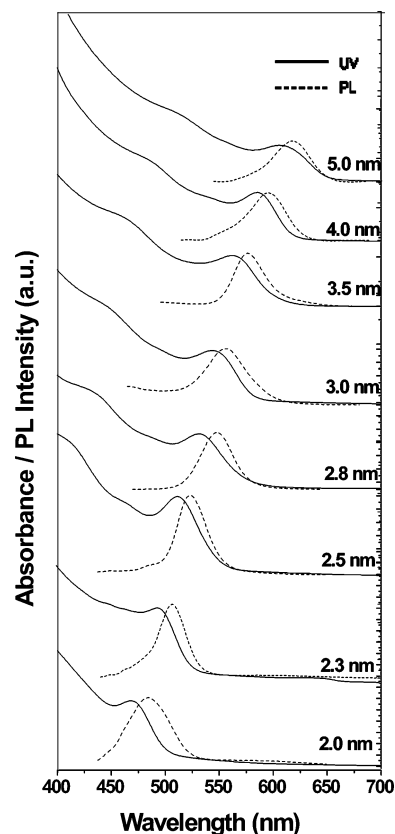


Figure 4. UV–vis absorption and PL spectra of the as-prepared CdSe NCs. From bottom to the top, the positions of PL peaks in nm (and PL quantum yield (PL QY)) are as follows: 486 (33%), 510 (47%), 525 (55%), 548 (60%), 556 (53%), 579 (30%), 596 (21%), and 618 (11%).

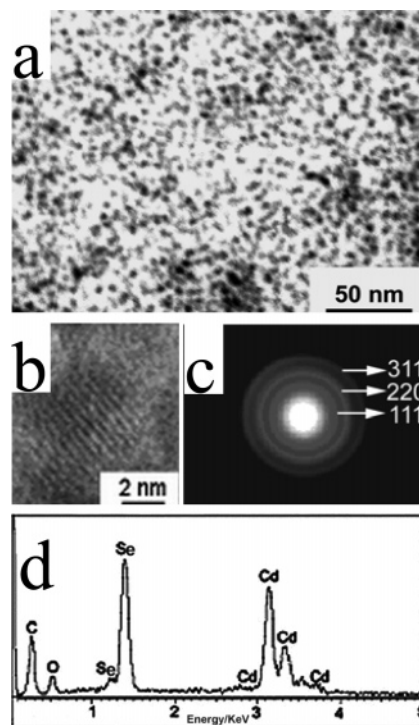


Figure 5. (a) TEM image, (b) HRTEM image, (c) SAED pattern, and (d) EDX pattern of the as-prepared oleic acid capped CdSe NCs with the excitonic absorption peak at 562 nm.

crystallinity of the CdSe NCs. The selected area electron diffraction (SAED) pattern of about 40 CdSe NCs in Figure 5c

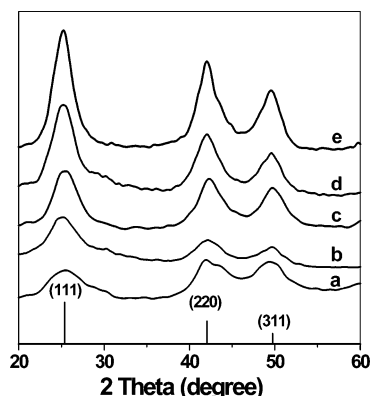


Figure 6. The XRD patterns of the as-prepared CdSe NCs. The vertical bars are corresponding to JCPDS file No. 19-0191.

can also be indexed to the cubic phase of CdSe. The EDX measurements on the same sample indicated the presence of Cd, Se, O, and C, which confirmed that the sample was OA-capped CdSe NCs. Given the binding of anionic oleic acid as the capping ligand on the surface of NCs, it is assumed the surfaces of the NCs are cadmium rich. The atomic ratio of Cd and Se is 0.546:0.454 calculated from the EDX results, which is consistent with this assumption.

Interestingly, the CdSe NCs synthesized by the new route have a different crystal structure from those made by organometallic precursor methods or nonorganometallic precursor methods (zinc blende vs wurtzite, respectively). The powder XRD patterns of the five different CdSe NCs samples are shown in Figure 6. All five samples have characteristic features matching the bulk cubic CdSe pattern. These diffraction features appearing at about 25.3°, 47.8°, and 56.3° correspond to the (111), (220), and (311) planes of the zinc-blende phase of CdSe (Joint Committee on Powder Diffraction Standards file No. 19-0191). Although the zinc-blende and the wurtzite phases could produce similar X-ray powder diffraction (XRD) results in NCs, the XRD pattern herein shows unambiguous evidence that the particles are of a zinc-blende structure: (1) the (102) diffraction is clearly not shown at 35.1°; (2) the valley between the (220) and (311) diffraction is deep, but in the case of wurtzite crystals, a peak should appear at 45.8° for (103) diffraction; and (3) this structural assignment is consistent with the SAED patterns. The main reason is the relative lower growth temperature compared to the previous study, which may play an important role in the form of the zinc-blende phase, not the wurtzite phase. In thermodynamics, it is notable that zinc blende is the most stable form at lower temperature, while wurtzite is more stable in high temperature. In the present study the zinc-blende phase is preferred for growth at the moderate temperature (200–240 °C), while the wurtzite phase is preferred for growth at higher temperatures (about 300 °C) in the previous study.^{15–18} As expected, the XRD peaks of the CdSe NCs were considerably broadened compared to those of the bulk CdSe due to the finite size of these NCs. As shown in Figure 6, the broadness of the diffraction peaks of the CdSe NCs is increased gradually with a decrease of NCs sizes. From the bottom to the top, the mean crystals sizes are 1.9 (for a), 2.5 (for b), 3.1 (for c), 3.6 (for d), and 4.8 nm (for e), respectively, calculated from (111) reflection by the Scherrer formula. The calculated values are in agreement with what were obtained from the size fitting from excitonic absorption peaks.

Conclusions

In summary, we demonstrated a new viewpoint on the mechanism in the formation of the CdSe NCs in high boiling point solvents with long alkane chains. The chemical reaction equations involved in the formation of the CdSe NCs have been put forward. Based on the understanding of the mechanism, we have developed a low-cost and green Non-TOP-Based route for synthesizing a size series of high-quality zinc-blende (cubic) CdSe NCs. Choosing paraffin liquid and oleic acid as the reaction medium without expensive, toxic, and not environmentally friendly TOP (or TBP) significantly simplified the reaction for green and low-cost synthesis of the CdSe NCs. Heating Se powder with paraffin liquid leads to a dehydrogenation reaction to generate H₂Se gas, which plays a crucial role in the formation of the CdSe NCs. The UV–vis absorption study revealed a fast growth process in the formation of high-quality CdSe NCs. The phases of the as-synthesized CdSe NCs were zinc blende (cubic), not wurtzite (hexagonal). By the suitable choice of source and synthetic parameters, it is reasonable to expect that the present study could be extended to other green and low-cost routes for large-scale synthesis of high-quality NCs.

Acknowledgment. The current investigations were financially supported by the Hi-Tech Research and Development Program of China (863) (2002AA302108) and the National Natural Science Foundation of China (60372009, 20301015).

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