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Control of Photoluminescence Properties of CdSe Nanocrystals in Growth

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Abstract: The photoluminescence (PL) quantum yield (QY) of CdSe nanocrystals during their growth under a given set of initial conditions increases monotonically to a certain maximum value and then decreases gradually. Such a maximum is denoted as a PL "bright point", which does not always overlap with the minimum point of the PL peak width for the same reaction. The experimental results suggest that the existence of the PL bright point is a general phenomenon during the growth of semiconductor nanocrystals and likely is a signature of an optimal surface structure/reconstruction of the nanocrystals grown under a given set of initial conditions. The position of the bright point, the highest PL QY, the types of the bright points (sharp or flat), the sharpness of the PL peak, etc., were all strongly dependent on the initial Cd:Se ratio of the precursors in the solution. A large excess of the selenium precursor, with 5−10 times more selenium precursor than the amount of the cadmium precursor, was found necessary to achieve a high PL QY value and a narrow emission profile. The existence of the PL bright point and the sensitive temporal variation of the PL QY during the growth of semiconductor nanocrystals can explain the unpredictable nature and poor reproducibility of the PL properties of the as-prepared semiconductor nanocrystals observed previously. Furthermore, the knowledge gained in this study enabled us to reproducibly synthesize highly luminescent CdSe nanocrystals through a relatively simple and safe synthetic scheme. In a traditionally weak emission window for CdSe nanocrystals, the orange-red optical window, the PL QY of the as-prepared CdSe nanocrystals reached as high as 85% at room temperature, and the full width at half-maximum of the corresponding PL peak was as narrow as 23 nm, about 65−80 meV depending on the emitting position. The PL properties of the as-prepared CdSe nanocrystals are stable upon aging for at least several months. These as-prepared nanocrystals represent a series of best emitters that are highly efficient, highly pure in emission color, stable, and continuously tunable by simply varying the size of the nanocrystals.

Introduction

Colloidal semiconductor nanocrystals have generated great fundamental and technical interest in recent years.[1−3] The size-dependent emission is probably the most attractive property of semiconductor nanocrystals. For example, by one simple synthetic scheme, it is possible to synthesize differently sized CdSe nanocrystals that emit from blue to red with very pure color. These nanocrystal-based emitters can be used for many purposes, such as light-emitting diodes,[4,5] lasers,[6,7] biomedical tags,[8−10] etc. For this reason, the control of the photoluminescence (PL) properties of semiconductor nanocrystals has been a major goal for developing synthetic chemistry for colloidal semiconductor nanocrystals. To our knowledge, this issue still remains mostly unsolved at present.

The emission properties of semiconductor nanocrystals can be characterized by four fundamental parameters, which are the brightness, the emission color, the color purity, and the stability of the emission. Due to quantum size effects,[3] the band gap of CdSe nanocrystals increases as their size decreases, and thus the emission color of the band-edge PL of the nanocrystals shifts continuously from red (centered at 650 nm) to blue (centered at 450 nm) as the size of the nanocrystals decreases. Since the emission color of semiconductor nanocrystals is strongly dependent on size[3] and shape,[11] the color purity of the emission becomes dependent on the size and shape distribution of a nanocrystal sample. Therefore, the control of the emission color and color purity is likely a matter of the control of the size/shape and size/shape distribution of the semiconductor nano-

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crystals, regarding which the recent studies have provided a reasonable knowledge basis.[11−15] The other two parameters, however, cannot yet be correlated with certain structural parameters or some adjustable growth conditions of a given synthetic scheme. As a result, the PL brightness, measured by PL quantum yield (QY), and the stability of the emission of the as-prepared semiconductor nanocrystals are not easy to predict and generally vary from synthesis to synthesis.

CdSe nanocrystals with close to monodisperse size distribution and high crystallinity became available in the early 1990s by use of dimethylcadmium as the cadmium precursor.[15,16] This organometallic approach has been well developed during the past 10 years in terms of the control over the size,[14] shape,[11−13] and size/shape distribution of the resulting CdSe nanocrystals. The recently introduced alternative routes with safe and inexpensive cadmium precursors and ligands[17−19]promoted the synthesis of CdSe nanocrystals to an easily adoptable level. In principle, with knowledge regarding the control over the size/shape and size/shape distribution of the CdSe nanocrystals, the emission color and the purity of the color can be controlled to a certain extent. At present, the purity of the emission color of a CdSe nanocrystal sample is still significantly worse than that of the single particle emission. The typical full width at half-maximum (fwhm) of the PL peak of the CdSe nanocrystal ensemble at room temperature, around 27−40 nm,[4,20] is noticeably broader than that observed by single dot spectroscopy (typically <20 nm),[1] indicating inhomogeneous emission properties of the nanocrystals.

The control over the PL QY and emission stability of the CdSe nanocrystals synthesized through either the traditional organometallic approach or the alternative routes is still rather poor. The best PL QY reported for the as-prepared nanocrystals at room temperature are around 20% in the wavelength range between 520 and 600 nm and about a few percent or lower in the wavelength window above 600 nm and below 520 nm.[4,19,20] The stability and the reproducibility of the PL QY are both not predictable.[19] With some inorganic and organic surface passivation after the synthesis, the PL QY of CdSe nanocrystals is boosted to as high as over 50% in the 520−600 nm window,[20−23] but the efficiency for the orange-red color window is still low. Especially for red (around 650 nm), the PL QY of the nanocrystals in solution was nearly zero, like the as-prepared CdSe nanocrystals.[4,20]

The difficulty in controlling and tuning the PL properties of CdSe and other semiconductor nanocrystals is caused by a lack of referrable knowledge related to this issue. This motivated us to complete a systematic study on the relationship between the optical properties of the as-prepared CdSe nanocrystals and a variety of growth conditions. Due to the failure of orange-red emitting materials in general, efforts were mainly concentrated on the wavelength region between 600 nm (orange) and 650 nm (red).

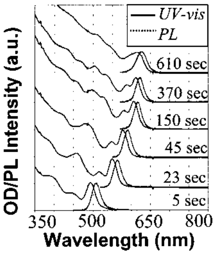

Figure 1. Temporal evolution of UV−vis and PL spectra of a growth reaction of CdSe nanocrystals. See the typical synthesis for details.

Experimental Section

Chemicals. Trioctylphosphine oxide (TOPO), tributylphosphine (TBP), hexadecylamine, octadecylamine, stearic acid, CdO, and Se powder were purchased from Aldrich. Methanol, toluene, dodecylamine, chloroform, and acetone were purchased from VWR.

Synthesis and Characterization of CdSe Nanocrystals. Most details of the synthetic and characterizing methods were similar to the ones reported previously.[12,18,19] A typical synthesis is as follows. CdO, 0.0127 g (0.1 mmol), and 0.1140 g (0.4 mmol) of stearic acid were loaded into a 25 mL three-neck flask and heated to 150 °C under Ar flow. After CdO was completely dissolved, the mixture was allowed to cool to room temperature. TOPO and hexadecylamine, 1.94 g of each, were added to the flask, and the mixture was heated to 320 °C under Ar flow to form an optically clear solution. At this temperature, the Se solution containing 0.079 g (1 mmol) of Se dissolved in 0.238 g (1.18 mmol) of TBP and 1.681 g of dioctylamine was swiftly injected into the reaction flask. After the injection, the temperature was set at 290 °C for the growth of the nanocrystals. At various time intervals, aliquots with a needle-tip amount of the reaction mixture were removed and diluted by chloroform. Insoluble white solid, if it existed, was separated by centrifugation and decantation prior to any further measurements. The UV−vis and PL spectra of the aliquots were recorded promptly (see Figure 1). A Jeol 100 CX transmission electron microscope was used for measuring the size and size distribution of the resulting nanocrystals by depositing them on carbon-coated copper grids. The powder X-ray diffraction (XRD) patterns were employed to check the crystallinity of the final products after extensive purification to remove excess ligands and reaction precursors (see below).

The reaction mixture of a reaction was mixed with about 15 mL of chloroform after the reaction mixture was allowed to cool to 30−50 °C and was not completely solidified. The nanocrystal solution was separated from the insoluble white or reddish solid floating on the top of the chloroform solution by centrifugation and decantation. The nanocrystals were precipitated by adding methanol or acetone into the chloroform solution and isolated by centrifugation and decantation. The resulting wet precipitate was stored for future use.

For the XRD and X-ray photoelectron spectroscopy measurements, the wet precipitate was dissolved in chloroform and then precipitated from the chloroform solution by adding methanol or acetone. The precipitate was isolated by centrifugation and decantation. This cycle of the dissolution, precipitation, centrifugation, and decantation was repeated at least three times prior to the measurements.

PL QY Measurements. The PL spectra of a given sample of the CdSe nanocrystals and an organic dye, whose PL spectrum overlaps significantly with that of the nanocrystal sample, were measured under the same setting of a Hitachi 2500 spectrophotometer. The scanning

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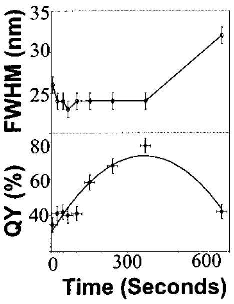

Figure 2. Temporal evolution of PL QY (bottom panel) and PL fwhm (top panel) of the reaction shown in Figure 1. The solid lines are trend lines added to guide the eyes.

step of the spectrophotometer was set as 1 nm and marked as the error bars in the related figures. The optical density (OD) at the excitation wavelength of the dye and the nanocrystal sample was set to a similar value. The OD at either the first exciton absorption peak of the nanocrystals or the main absorption peak of the dye was below 0.1 in order to avoid any significant reabsorption. The PL QY of the nanocrystal sample was finally obtained by comparing the integrated PL intensities of the nanocrystals and the corresponding dye. The measurement error of the PL QY was estimated to be about 5% and reported in the related figures as the error bars.

The PL QY values of the following dyes were provided by the vendor (Exciton).

name	coumarin 540	R6G	R3B	R640	LD690
absorption (nm)	458	528	550	570	616
PL QY (%)	62	95	50	100	63

Results

Reaction System. The recently discovered alternative ligands and precursors for the synthesis of CdSe nanocrystals at elevated temperatures[18,19] provided us a decent database to design a synthetic system that generates CdSe nanocrystals with acceptable emission properties. Among all the ligands reported, primary amines have shown the most promising results for achieving high PL efficiency for a variety of semiconductor nanocrystals.[20,21,24−26] The presence of stearic acid was proven to be helpful for the formation of large-sized CdSe nanocrystals,[19] which emit in the orange-red window. In addition, cadmium stearate in amines can bear significantly high temperatures, which is required for the formation of semiconductor nanocrystals with high structural quality. TOPO was found to be a good cosolvent to depress the solidification rate during sampling and further increase the reaction temperature.[19]

The experimental results revealed that this chosen system indeed generated large CdSe nanocrystals emitting well in red. A synthesis with a large excess of the selenium precursor, the initial Cd:Se ratio of the precursors in the solution equal to 1:10, provided a striking boost of the PL QY of the as-prepared CdSe nanocrystals, which reached up to 80% (Figures 1 and 2) and was independent of the excitation wavelength (see the photoluminescence excitation spectra in the Supporting Information). The PL and UV−vis absorption spectra of several samples shown in Figure 1 are extremely sharp, with about 23−24 nm of their fwhm of the PL spectra and up to 6−7 features of the absorption spectra.

PL Bright Point. The temporal evolution of the PL QY and the fwhm of the PL peak of the as-synthesized nanocrystals of the reaction shown in Figure 1 is plotted in Figure 2. The PL QY of the as-prepared nanocrystals increased monotonically to a maximum and then gradually fell down (Figure 2, bottom). For convenience, the position with the maximum PL QY will be called "PL bright point" or, simply, the bright point. The fwhm of the PL spectrum in wavelength possessed a minimum (Figure 2, top). The bright point and the minimum point of the PL fwhm did not overlap for the reaction shown in Figure 2. As described below, the relative position of the bright point and the minimum point of the PL fwhm varied significantly when the initial Cd:Se ratio of the precursors in a reaction was changed (Figures 3 and 4).

We observed that the existence of a PL bright point is a general phenomenon for different types of semiconductor nanocrystals with different shapes or grown in different solvent systems. The current system is the best one for studying this phenomenon because of the high PL QY and the small fwhm of the PL spectra of the resulting nanocrystals.

PL QY fwhm vs the Initial Cd:Se Ratio of the Precursors. The PL QY of CdSe nanocrystals does not seem very sensitive to the imperfection of the crystallinity of the nanocrystals caused by the stacking faults, because the PL QY of wurtzite CdSe nanocrystals with almost no stacking faults and those with some zinc blende stacking faults in each nanocrystal did not show much difference.[15,19,20] In contrast, the PL QY is very sensitive to the surface environment of the nanocrystals. For instance, certain types of organic ligands or inorganic passivation[19−23] on the surface of nanocrystals have improved the PL QY of semiconductor nanocrystals dramatically.

On the basis of the above facts, it is reasonable to rationalize that the control of the surface, probably a reconstructed surface, of semiconductor nanocrystals themselves may be very important for controlling and improving their PL properties. It is well-known that a specific surface structure/reconstruction of compound semiconductor thin films epitaxially grown by molecular beam epitaxy (MBE) often requires a very high and defined concentration (beam equivalent pressure, BEP) ratio between the two components. For example, the epitaxial growth of the 2 × 4 surface reconstruction of GaAs requires the BEP ratio between As_4 and Ga to be controlled around 15,[27] which means a very high atomic ratio between arsenic and gallium. The necessity of such a highly biased precursor ratio has been considered as a result of the distinguishable chemical reactivities of the two precursors. In comparison, the atomic ratio of the cadmium and selenium precursors has traditionally been set close to 1 for the synthesis of colloidal CdSe nanocrystals, although the chemical reactivities of the two precursors are significantly different.

The experimental results unambiguously revealed that the initial Cd:Se ratio of the precursors is a determining factor for the emission properties of the as-synthesized nanocrystals. The results illustrated in Figure 3 are from four representative reactions among one series of experiments, because the initial Cd:Se ratio was varied between 2:1 and 1:10, and the concentration product of the initial cadmium and selenium precursors was set as a constant for all of the reactions. It was difficult to

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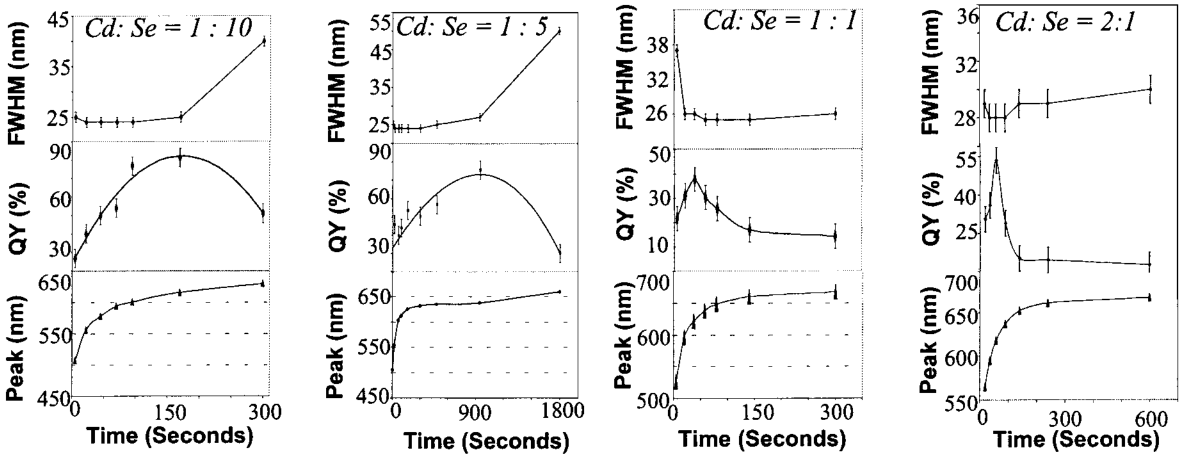

Figure 3. Temporal evolution of fwhm, PL QY, and PL peak position of four different reactions with different initial Cd:Se ratio of the precursors as shown in the plot. For all four reactions, the initial concentration product of the two precursors was fixed as 1411 (mmol/kg)^2. The other conditions were the same as those of the typical synthesis. Trend lines (solid lines) are added for each plot to guide the eyes.

execute a growth reaction with a large excess of Cd, for which only very small amounts of nuclei were formed in a relatively long period of time and these nuclei grew very fast to insoluble large sizes.

Figure 3 shows that each individual reaction possessed a minimum PL fwhm as the reaction proceeded. The minimum of the PL fwhm gradually increased while the initial Cd:Se ratio of the precursors increased from 1:10 to 2:1. The average size at the minimum point of the PL fwhm increased as the initial Cd:Se precursor ratio increased.

The temporal evolution of the PL QY can be classified into two types. The two reactions with a great excess of the selenium precursor, the initial Cd:Se ratios equal to 1:10 and 1:5, demonstrated a pattern similar to that of the reaction shown in Figure 2, with a relatively flat PL bright point, a positive wavelength difference between the bright point and the minimum point of the PL fwhm ($\Delta\lambda$), and a relatively high PL QY at the bright point. The other two reactions, with the initial Cd:Se precursor ratios equal to 2:1 and 1:1, differed from the reactions with a great excess of the selenium precursor in several aspects. One, the PL QY values at the bright point were lower. Two, the bright points were sharp maxima instead of flat ones. Three, the bright point overlapped with the minimum point of the PL fwhm for the reaction with 2:1 initial Cd:Se ratio, and it appeared at the short-wavelength side of the minimum point of the PL fwhm for the reaction started with a Cd:Se ratio of 1:1.

The influence of the initial Cd:Se precursor ratio on the PL properties of the CdSe nanocrystals shown in Figure 3 can be further exhibited by Figure 4. The top panel in Figure 4 summarizes the relationship between the PL QY at the bright point vs the initial Cd:Se ratio of the precursors in the solution. This demonstrates that a significant excess of one of the precursors promoted the formation of CdSe nanocrystals with a high PL QY. The middle panel illustrates the trend of $\Delta\lambda$ vs the initial Cd:Se ratio of the precursors: $\Delta\lambda = \lambda_b - \lambda_m$, where λ_b and λ_m are the wavelength values at the bright point and the minimum point of the PL fwhm, respectively. The reaction time needed to reach the PL bright point for each reaction is also plotted in Figure 4 (bottom panel), which indicates that a high PL QY is not simply associated with the reaction time.

Within the reaction conditions tested, all of the trends shown in Figure 4 were repeatedly observed. All experiments shown in Figures 3 and 4 were performed under the same conditions, with the initial concentration product of the two precursors as a constant. Similar results were also obtained by fixing the concentration of either the cadmium or selenium precursor equal to 0.0167 mol/kg and varying the concentration of the other precursor.

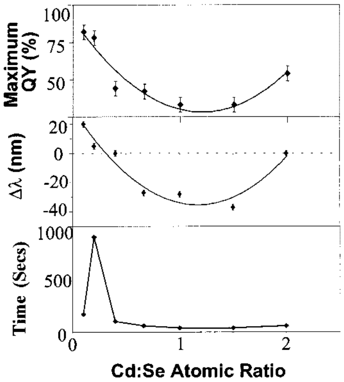

Figure 4. Maximum PL QY (top panel), $\Delta\lambda$ (middle panel), and reaction time needed to reach the PL bright point (bottom panel) vs the initial Cd:Se ratio of the precursors. $\Delta\lambda = \lambda_b - \lambda_m$, where λ_b and λ_m are the wavelengths at the bright point and the minimum point of the PL fwhm, respectively. For all reactions, the initial concentration product of the two precursors was fixed as 1411 (mmol/kg)^2.

PL QY vs PL Peak Position. Though efforts were mainly focused on the growth of CdSe nanocrystals emitting in the orange-red window, preliminary results implied that the method and the concept can be extended to the synthesis of CdSe nanocrystals emitting other visible colors by varying the total concentration of the initial precursors, types of the precursors, the solvent system, the reaction temperatures, and the growth time. The achieved PL QY of the as-synthesized CdSe nanocrystals vs their emission peak position is plotted in Figure 5, top panel. For each data point, the corresponding *y*- and *x*-axis values respectively represent the PL QY and the emission peak position of the given sample. The PL spectra of several CdSe nanocrystal samples with different emission colors are demonstrated in Figure 5, bottom panel. In comparison to the as-prepared CdSe nanocrystals reported previously, the CdSe nanocrystals shown in Figure 5 possess significantly greater PL QY and narrower emission peak width.

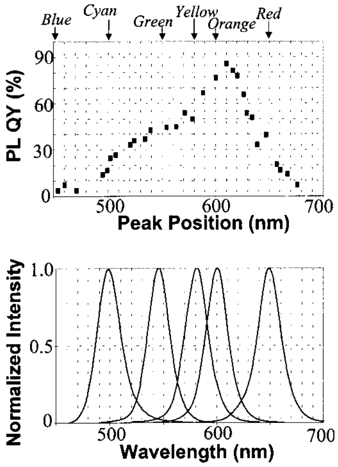

Figure 5. PL QY of different-sized CdSe nanocrystals vs their emission peak positions (top panel), and the PL spectra of several CdSe nanocrystal samples at different emission positions (bottom panel). See text for details.

Stability of the Optical Properties. The PL properties of the as-prepared CdSe nanocrystals, including the PL QY, the peak position, and the PL fwhm, did not show any detectable change upon aging in air for several months, if no precipitation occurred. Occasionally, the nanocrystals precipitated out of the solution, indicating loss of surface ligands. If this occurred, the precipitated aggregates normally could not be redispersed in solution even with additional primary amines. However, by adding methanol or acetone into the chloroform solution of the CdSe nanocrystals, the precipitation of the nanocrystals from their concentrated solutions could be performed without damaging the optical properties of the nanocrystals. Such a precipitation process, however, decreased the PL QY and the nanocrystals became insoluble gradually if it was repeated several times. It is likely that repeated precipitation and dissolution may have removed some of the primary amine ligands from the surface of the nanocrystals. It was reported previously that amines are not strong ligands to CdSe nanocrystals and are quite labile on the surface of the nanocrystals.[21] To solve this stability issue associated with losing ligands, flexible dendron ligands with an amine group at their focal point are worth testing.[28,29]

Shape, Crystal Structure, and Composition. The nanocrystals synthesized by the current approach were of a dot shape confirmed by transmission electron microscopy (TEM) (Figure 6, top left panel). The size distribution determined by TEM was typically around 5−10%. The crystal structure of the resulting nanocrystals was quite sensitive to the reaction temperature and the chain length of the amines. For the reactions that occurred below 230 °C and in a solvent containing dodecylamine (DDA), the XRD patterns of the resulting CdSe nanocrystals were very much like that of zinc blende CdSe. At high temperatures (above 270 °C), octyldecylamine (ODA) helped in the formation of the nanocrystals, which exhibited diffraction patterns similar to those of almost perfect wurtzite CdSe nanocrystals.[19] At temperatures between 250 and 320 °C and in a solvent containing hexyldecylamine (HDA), synthesis always produced CdSe nanocrystals with the wurtzite structure with 1−2 stacking faults perpendicular to the (001) axis (a typical pattern in Figure 6, bottom panel),[15] regardless of the initial Cd:Se ratio of the precursors in the solution. The results presented in this paper except those mentioned are all related to the reactions carried out at 270−320 °C in a solvent containing HDA.

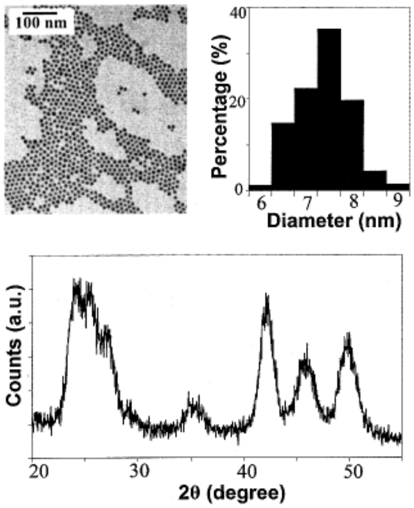

Figure 6. TEM image of a sample of CdSe nanocrystals (top left panel), the corresponding size distribution histograms (top right panel), and the X-ray diffraction pattern (bottom panel) of the same sample. The crystalline domain calculated from the Debye−Sherrer equation is very close to the average size obtained from the statistics of the TEM image.

The Cd:Se atomic ratio of the resulting CdSe nanocrystals was determined to be close to 1:1 within experimental error by X-ray photoelectron spectroscopy despite the large difference in the initial Cd:Se ratio of the precursors added into the reaction solutions. This indicates that the composition of the CdSe nanocrystals synthesized under different conditions mentioned above was not seriously distorted, which is similar to the results observed in the MBE structures.

Influence of the Nature of the Amines. Primary amines were found as an essential ingredient in the current system for growing nanocrystals with a high PL efficiency. Among all three primary amines tested, DDA was the worst, probably because the reaction temperatures of the related synthesis were limited below 230 °C. The ODA-related reactions yielded nanocrystals with a nearly perfect wurtzite structure and a moderately high PL QY at the bright points (50−60% with a large excess of the Se precursor). HDA was found to be the best primary amine in terms of generating the nanocrystals with a high PL QY. As a secondary amine, the presence of dioctylamine (DOA) barely affected the emission properties of the resulting CdSe nanocrystals, no matter whether it was originally in the hot cadmium solution or in the cold selenium solution. However, since it is much less toxic than tributylphosphine (TBP), most experiments were performed with DOA as the solvent of the selenium precursor (Se-TBP), instead of pure TBP.

Discussion

The existence of the PL bright point, before its origin is even explored, can explain why the PL properties of as-prepared semiconductor nanocrystals used to be unpredictable and unreproducible. Traditionally, the initial Cd:Se ratio of the precursors was set close to unity, which may result in a sharp bright point as shown in Figure 3. A time difference of tens of seconds could vary the PL QY several times, although the size and size distribution seemed to be unchanged. The synthesis of semiconductor nanocrystals has generally been either not

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monitored or just simply monitored by the absorption measurements, which at most provided only size and size distribution information on nanocrystals in the solution. The results described here indicate that if one cares about the PL properties of as-prepared semiconductor nanocrystals, the PL bright point should be identified for the adopted synthetic scheme prior to practical synthesis and the PL QY should be monitored closely during the growth.

The origin of the PL bright point during the growth of the nanocrystals cannot yet be definitely determined with the experimental results observed. In general, a low PL QY is considered as a result of the surface states located in the band gap of the nanocrystals, which act as trapping states for the photogenerated charges. These surface trapping states are originated from the dangling bonds of some of the surface atoms.[30] The ligands on the surface of nanocrystals may remove some or all of the surface trapping states and increase the PL QY of the nanocrystals. Theoretical treatments indicate that the efficiency of the electronic passivation provided by the surface ligands depend strongly on the surface structure and the nature of the surface states of the nanocrystals themselves.[30] If the surface ligands could provide a good electronic passivation for the surface states of the nanocrystals, a high PL QY should be expected. By comparing the PL QY of the nanocrystals coated by different amine ligands, one could conclude that the ligands' passivation should have played a vital role in the high PL QY of the resulting CdSe nanocrystals. However, it is hard for surface passivation alone to explain the existence of the PL bright point, the temporal evolution pattern of the PL properties, and the relationship between the PL QY at the bright point and the Cd:Se ratio of the initial precursors in solution. For example, the reactions illustrated in Figures 3 and 4 were all performed with a nearly identical concentration of HDA, about 2 g of HDA in the hot cadmium solution before the injection. It is difficult to imagine that, in a matter of tens of seconds, the surface passivation of the nanocrystals in the solution varied so much and forced the PL QY to increase several times to reach a maximum, and then to decrease to a fraction of the maximum value.

As mentioned above, the surface trapping states are believed to be from the dangling bonds of some of the surface atoms of the nanocrystals.[30] Consequently, the nature and density of the surface trapping states should strongly depend on the surface structure of the nanocrystals. Furthermore, the atomic configuration of the surface of a nanocrystal should significantly affect the efficiency of the electronic passivation provided by the surface ligands. The latter effect can be visualized by simply considering the steric effect of the surface configuration of the nanocrystals on the packing of the surface ligands. For these two reasons, the surface structure of the CdSe nanocrystals themselves should play an important role in determining the PL properties of the nanocrystals. This thought leads to a natural assumption that the PL bright point is a signature of an optimal surface structure/reconstruction of the CdSe nanocrystals grown under certain conditions, which minimizes the surface states located in the band gap of the resulting nanocrystals. It is difficult to experimentally examine the surface structure of colloidal nanocrystals at present,[31] and theoretical considerations may be a good choice in order to clarify this issue.[30] We also noticed that surface reconstruction was recently proposed to explain the variations of the PL properties of CdSe nanocrystals under different environments.[32]

A certain type of surface structure or surface reconstruction of compound semiconductor thin films grown by the MBE technique can only be accomplished by providing the system with a biased but stable ratio of the two precursors.[27] The most favorable surface reconstruction in a solution reaction with a defined number of monomeric units is likely only stable for a short period of time due to the rapid variation of both the monomer concentrations and the Cd:Se ratio of the precursors in the solution. Around the focusing point of the size distribution,[14] the monomers on the surface of nanocrystals should be at equilibrium with the monomers in the solution, which provides a relatively suitable environment to reach an optimal surface structure/reconstruction. This is probably why the bright point and the focusing point are somewhat close to each other although they do not overlap (see discussions below). When a growth reaction is far away from the focusing point, the monomers have a great tendency either to add onto the surface of the nanocrystals at the beginning stage of the reaction or to permanently leave the surface of the nanocrystals in the defocusing region.[14] The overdriving of the monomers in either mode will interrupt the process for the system to reach an optimal surface structure/reconstruction. The farther away from the focusing window, the more the reaction is overdriven, and hence, the worse the surface structure/reconstruction should be.

If one precursor was initially in large excess, the concentration of that monomer in the solution should be considered as a constant after the growth reaction proceeds for a short period of time. This would provide a desirable condition for the construction of the most favorable surface structure/reconstruction for the nanocrystals in the solution. Consequently, the PL QY might reach a higher level. This is probably why the PL QY at the bright point increased as the initial Cd:Se ratio of the precursors departed from 1:1. Furthermore, it is also consistent with the appearance of a flat bright point at highly biased Cd:Se ratios and a relatively sharp one when the ratio approached 1.

Presumably, the optimal surface structure/reconstruction argument is also consistent with the good stability of the optical properties of the CdSe nanocrystals because a more stable surface should be more inert to possible chemical and structural changes.

It is interesting to compare the focusing point of size distribution reported previously[14] and the PL bright point observed in this work. The PL fwhm is related to the size distribution of the nanocrystal dot as mentioned above. Consequently, the temporal evolution of the PL fwhm is associated with that of the size distribution of the nanocrystals. Since the PL QY and the intrinsic fwhm of the nanocrystals in a solution may vary from one size to another, there is no trivial way to faithfully extract the exact size distribution from the PL spectrum of a given sample. However, it is possible to approximately express the size distribution of an ensemble of nanocrystals by

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(30) For example, Fu, H.; Zunger, A. *Phys. Rev. B: Condens. Matter* **1997**, *56*, 1496−1508.

(31) Hamad, K. S.; Roth, R.; Rockenberger, J.; van Buuren, T.; Alivisatos, A. P. *Phys. Rev. Lett.* **1999**, *83*, 3474−3477.

(32) Hess, B. C.; Okhrimenko, I. G.; Davis, R. C.; Stevens, B. C.; Schulzke, Q. A.; Wright, K. C.; Bass, C. D.; Evans, C. D.; Summers, S. L. *Phys. Rev. Lett.* **2001**, *86*, 3132−3135.

using the PL fwhm of the sample. The correlation of the size and the emission peak wavelength reported by Peng et al.[14] can be numerically fitted into an exponential function (see Supporting Information). If we take the same assumptions suggested by Peng et al., a δ function emission for each single size and the same emission efficiency for different sizes in a sample, simple mathematic treatments indicates that the relative size standard deviation of a given sample is determined by the PL fwhm expressed as a wavelength and is independent of the emission peak position or the average size of the nanocrystals (see Supporting Information). Therefore, the PL fwhm evolution pattern in wavelength can be approximately interpreted as the temporal evolution of the size distribution of the nanocrystals. This implies that the PL bright point and the focusing point of size distribution for the same reaction does not always overlap though they may appear close to each other (Figures 2−4).

Summary

During the growth process, the PL QY of the as-prepared semiconductor nanocrystals increased monotonically in the early stage and then gradually decreased after it reached a maximum at a certain point, the PL bright point. This critical point is different from the other type of critical point, the focusing point of size distribution reported previously.[14] The position of the bright point, the PL QY, the fwhm of the PL spectra, and several other parameters of the growth process of the CdSe nanocrystals were all strongly dependent on the initial Cd:Se ratio of the precursors in the solution. The CdSe nanocrystals synthesized by this alternative method represents a series of excellent emitters in the orange-red color window in terms of their PL QY, the fwhm of the PL spectra, and the stability of the emission. Finally, the existence of the bright point was suggested as a signature of the optimal surface structure/reconstruction of the nanocrystals at a given set of initial growth conditions.

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Supporting Information Available: Photoluminescence excitation spectra and correlation of the size and emission peak wavelengths of nanocrystals. This information is available free of charge via the Internet at http://pubs.acs.org.

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