The Effect of Dispersion Media on Photoluminescence of Colloidal CdSe Nanocrystals Synthesized from TOP

Kui Yu,*,† Badruz Zaman,† Shanti Singh,† Dashan Wang,‡ and John A. Ripmeester†

Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada, and Institute for Chemical Process and Environmental Technology, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

Received September 8, 2004. Revised Manuscript Received January 18, 2005

The media used for dispersion have a significant effect on the photoluminescent (PL) efficiency of colloidal CdSe nanocrystals, in addition to synthetic parameters. The investigated dispersion media were water-insoluble hexanes (Hex), toluene (Tol), chloroform ($CHCl_3$), and water-miscible tetrahydrofuran (THF); in addition, a water−THF mixture (25%, weight), a tri-*n*-octylphosphine (TOP)−Hex mixture (25%, weight), and a TOP−THF mixture (25%, weight) were also explored as dispersion media. Solvent-dependent equilibriums affect the number of surface-adsorbed molecules available for surface passivation and the removal of surface ligands, with both concentration and additives (such as TOP) and time playing a role, so that PL intensities can either be enhanced or diminished depending on the detailed conditions. Moreover, an enhancement is not possible at low concentrations of nanocrystals after days of storage, as dissociation of the surface ligands plays a major role and leads to the formation of the other fluorescent species causing baseline uprising. The colloidal CdSe nanocrystals used were synthesized in a reaction medium consisting of tri-*n*-octylphosphine (TOP), with cadium oxide (CdO) as the Cd precursor and TOPSe as the Se source.

Introduction

CdSe nanocrystals, with an exciton Bohr radius (α) of 5.6 nm, constitute a model system suitable for studying size-dependent properties in the strong-confinement regime;[1] in addition, they have emerged as one of the most promising materials among the II−VI and III−V semiconductor materials suitable for applications on the basis of size-dependent emissions.[2] Thus, in modern materials chemistry, the development of synthetic routes to produce high-quality colloidal CdSe semiconductor nanocrystals has become a significant activity because of their fundamental and technical importance.[3−7] However, little effort has been expended toward their photoluminescent efficiency affected by their dispersing media.

In this study, we address the issues of photoluminescent (PL) properties of colloidal CdSe nanocrystals affected by dispersion media, conferring the dissociation of the surface ligands in dispersion and surface passivation and the formation of small species. The CdSe nanocrystals were synthesized via a nonorganometallic approach recently developed in our laboratories.[8] This nonorganometallic approach involves a reaction medium consisting of TOP, without other chemicals such as tri-*n*-octylphosphine oxide (TOPO), acids, or amines added; also, the synthesis can be performed in air without an inert atmosphere protection. Our synthetic approach is as simple as adding a Se-source (TOPSe) solution in TOP to a solution of CdO in TOP at a high nucleation temperature (300 °C), followed by a growth period at a lower temperature (250 °C). Such a ready approach has proved itself to be highly reproducible and good for high-quality and large-scale production, because of a slow growth in size during a long growth period (such as 2−10 min);[8] photoluminescent (PL) quantum yield (QY) reached about 30% in the best case in Hex and about half of that in THF.

Experimental Section

Using CdO as the Cd source is much safer and easier for the syntheses of CdSe nanocrystals than using $Cd(CH_3)_2$).[5−7] Our ready

---

* To whom correspondence should be addressed. Tel: 613-993-9273; fax: 613-998-7833; e-mail: kui.yu@nrc.ca.

† Steacie Institute for Molecular Sciences.

‡ Institute for Chemical Process and Environmental Technology.

(1) (a) Bawendi, M. G.; Carroll, P. J.; Wilson, W. L.; Brus, L. E. *J. Chem. Phys.* **1992**, *96*, 946. (b) Nirmal, M.; Norris, D. J.; Kuno, M.; Bawendi, M. G.; Efros, A. L.; Rosen, M. *Phys. Rev. Lett.* **1995**, *75*, 3728. (c) Kuno, M.; Lee, J. K.; Dabbousi, B. O.; Mikulec, F. V.; Bawendi, M. G. *J. Chem. Phys.* **1997**, *106*, 9869.

(2) (a) Klarreich, E. *Nature* **2001**, *413*, 450. (b) Seydel, C. *Science* **2003**, *300*, 80. (c) A. Miyawaki, A.; Sawano, A.; Kogure, T. *Imaging Cell Biol.* **2003**, *S1*.

(3) (a) Weller, H. *Adv. Mater.* **1993**, *5*, 88. (b) Nirmal, M.; Brus, L. *Acc. Chem. Res.* **1999** *32*, 407. (c) Hu, J.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999** *32*, 435. (d) Lannoo, M.; Delerue, C.; Allan, G.; Niquet, Y.-M. *Philos. Trans. R. Soc. London* **2003**, *361*, 259−273.

(4) (a) Brennan, J. G.; Siegrist, T.; Carol, P. J.; Stuczynski, S. M.; Brus, L. E.; Steigerwald, M. *J. Am. Chem. Soc.* **1989**, *111*, 4141. (b) Trindade, T.; O'Brien, P. *Chem. Mater.* **2001**, *13*, 3843.

(5) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706−8715.

(6) Peng, X.; Wicham, J.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1998**, *120*, 5343.

(7) (a) Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2001**, *123*, 183−184. (b) Qu, L. Peng, X. *J. Am. Chem. Soc.* **2002**, *124*, 2049.

(8) (a) Yu, K.; Singh, S.; Patrito, N.; Chu, V. *Langmuir* **2004**, *20*, 11161. (b) Yu, K.; Zaman, B.; Romanova, S.; Wang, D.; Ripmeeste, J. A. *Small* **2005**, *3*, 332. (c) Yu, K.; Zaman, B.; Singh, S.; Wang, D.; Ripmeeste, J. A. *J. NanoSci. NanoTec.* **2005**, *4*, 659. (d) Yu, K.; Zaman, B.; Ripmeeste, J. A. *J. NanoSci. NanoTec.* **2005**, *4*, 669. (e) Yu, K. unpublished results. Our ^{31}P NMR MAS HPDEC identified five resonances for our CdSe/TOP nanoparticles using several different spin rates. None correspond to TOP (−32 ppm) or TOPO (47 ppm). We suspect there are several different linkages to Cd and Se. At present, it is difficult to assign these peaks to identify the nature and composition of the ligands. We have different opinions on that reported by Becerra, L. R.; Murray, C. B.; Griffin, R. G.; Bawendi, M. G. *J. Chem. Phys.* **1994**, *100*, 3297.

10.1021/cm048457l CCC: $30.25

approach involves the preparation of two solutions: a TOPSe/TOP solution and a CdO/TOP solution. In a typical synthesis carried out in air, the TOPSe/TOP solution consisted of ca. 3.82 mg Se (0.05 mmol, 300 mesh, Alpha Products) and ca. 0.483 g TOP (Aldrich, 90%), while the CdO/TOP solution consisted of ca. 12.83 mg CdO (0.10 mmol) and ca. 2.065 g TOP. The CdO/TOP solution was prepared as the calculated amounts of CdO (air-stable reddish-brown powder, Aldrich, 99.99%) and TOP were first loaded in a 50-mL three-necked flask; this flask was open to air and ambient pressure via a small gas inlet and was equipped with a stopper and thermometer, without lubricating grease applied. Afterward, the suspension was heated; a clear colorless solution was observed to reflux on the sides of the flask at ca. 280 °C within 60−120 min. This Cd-precursor solution was further heated to 320 °C and then cooled to 300 °C for the swift injection of the TOPSe/TOP solution. Thus, the total Se concentration was ca. 18 mmol/kg, with a 2Cd-to-1Se molar ratio in the present study. The present study does not address the issue of the nature and composition of the surface ligands. Regarding the 10% impurity in TOP, Aldrich commented that the majority of the impurities should be octylphosphine oxide, then some isomers of TOP, and only few dioctylphosphines. We added 4% and 10% amine into TOP to synthesize CdSe. Surprisingly, no significant difference was observed with/without amine addition. See Supporting Information for the absorption and emission spectra of CdSe synthesized with/without added amine.

The optical properties of the growing nanocrystals were monitored for a couple of hours: after the swift injection of the TOPSe/TOP solution, aliquots of the reaction solution were removed at different intervals (30 s to 1 h) and kept in vials; afterward, 10 μL of each sample was dispersed into 2 mL of solvents, which were nonpolar Hexanes (Hex) and polar tetrahydrofuran (THF).

Additionally, several other solvents including $CHCl_3$ and toluene (Tol), and mixtures such as a 25% (wt) water−THF mixture, a 25% TOP−THF mixture, and a 25% TOP−Hex mixture, were also used to explore the environments of dispersion affecting the PL efficiency and the baseline uprising: 10 μL of each sample was dispersed into 2 mL of solvent.

The UV and PL properties of the dispersions were studied at room temperature, with UV spectra acquired on a Perkin-Elmer Lambda 45 UV−vis spectrometer and PL spectra on a Fluoromax-3 spectrometer (Jobin Yvon Horiba, Instruments SA) under the same setting with a 450 W Xe lamp as the excitation source and an excitation wavelength of 350 nanometer (nm) and spectra-recording beginning at 400 nm.

Powder X-ray diffraction (XRD) was obtained from CdSe precipitate after repeated solvent/nonsolvent (THF/MeOH (anhydrous)) precipitations. The XRD samples were prepared by the evaporation of MeOH from CdSe/MeOH dispersions loaded on low background glass plates. Diffraction patterns were thus recorded at room temperature on a Scintag XDS2000 diffractometer, using graphite monochromatized Cu Kα radiation ($\lambda = 1.79$ Å) in the $\theta-\theta$ mode. Samples were usually scanned over a range of $2° < 2\theta < 60°$ at an increment of 0.5°/min, giving a total acquisition time of ca. 2 h.

The prepared nanocrystals were directly imaged by transmission electron microscopy (TEM). The TEM samples were prepared by several rounds of precipitation of the CdSe nanocrystals from THF/MeOH solutions; afterward, the CdSe precipitate was suspended in acetone followed by sonication. Subsequently, one drop of the dilute CdSe/acetone suspension was placed onto a carbon-coated holey TEM copper grid and was dried in air. Finally, the dried grid was loaded into a double tilt sample holder. The sample TEM grid was thus examined on a Philips CM20 STEM operated at 200 kV and equipped with a Gatan UltraScan 1000 CCD camera.

Results and Discussion

It is known that colloidal CdSe semiconductor nanocrystals grow in size during reaction, and reaction media play an essential role in controlling the growth kinetics and afterward the optical performance. Accordingly, the optical performance of CdSe nanocrystals from one identical synthetic batch but with different growth periods can be different because of diverse surface quality.[5−7] Hence, the present study on CdSe photoluminescent (PL) properties affected by dispersing environments is followed by sample identity, including the information on XRD, TEM, and sample synthetic history, with the growth kinetics monitored as the temporal evolution of the optical properties of the growing nanocrystals. Aiming at good surface quality for high PL efficiency, we also address parameters such as PL solvent sensitivity, PL stability after days of storage in either dispersed or solid states, as well as nonresonant Stokes shift[1] for the nanocrystals with different growth time.

1. Dispersion Media Effects on PL Efficiency. It is a general phenomenon that the CdSe nanocrystals prepared via our nonorganometallic approach exhibit insensitive absorption but sensitive emission when dispersed in different environments;[8] examples are shown in part 2 that UV spectra of our CdSe nanocrystals are not sensitive to their dispersion media. Thus, the change in PL intensity here indicates the change in PL efficiency also. It is known that the colloidal CdSe nanocrystals with different growth periods exhibit different PL efficiency because of different surface quality.[5−7] Thus, the nanocrystals, with different growth time but from one identical synthetic batch described in our Experimental Section, are used to test the dispersion media affecting the PL intensity.

1.1. Solvent Effects. With Hex (black), toluene (Tol, green), chloroform ($CHCl_3$, purple), THF (red), and a 25% (weight) water−THF mixture (blue) as the media of choice, the emission spectra of the 0.5-min (top), 4-min (middle), and 20-min (bottom) CdSe nanocrystals are shown in Figure 1, using the same intensity scale. The emission PL spectra recorded right after dispersion are presented in the left part of Figure 1, while those recorded from the same dispersions but after 6 days are presented in the right part of Figure 1; the dispersions were kept in the dark at ca. 5 °C to minimize photooxidation and solvent evaporation; during storage, there was a little solvent evaporation detected; before measurements, such loss was compensated by the addition of an equivalent amount of solvent, together with a warming up of dispersions to room temperature. In the present study, all dispersions were stored under the same conditions and afterward measured in the same way.

In general, the nanocrystals exhibit smaller PL intensity in THF than in $CHCl_3$, Tol, and Hex; meanwhile, the nanocrystals exhibit some decrease in PL intensity on going from Hex and Tol to $CHCl_3$ as well as a decrease on going from pure THF to the THF−water mixture. An example is shown with the 4-min nanocrystals (Figure 1 middle left). Regarding Hex and Tol, they show evidence of slightly different effects on PL intensity of nanocrystals with different growth time: the 0.5-min and 4-min nanocrystals (Figure 1 top and middle) exhibit a trivial decrease in PL intensity on

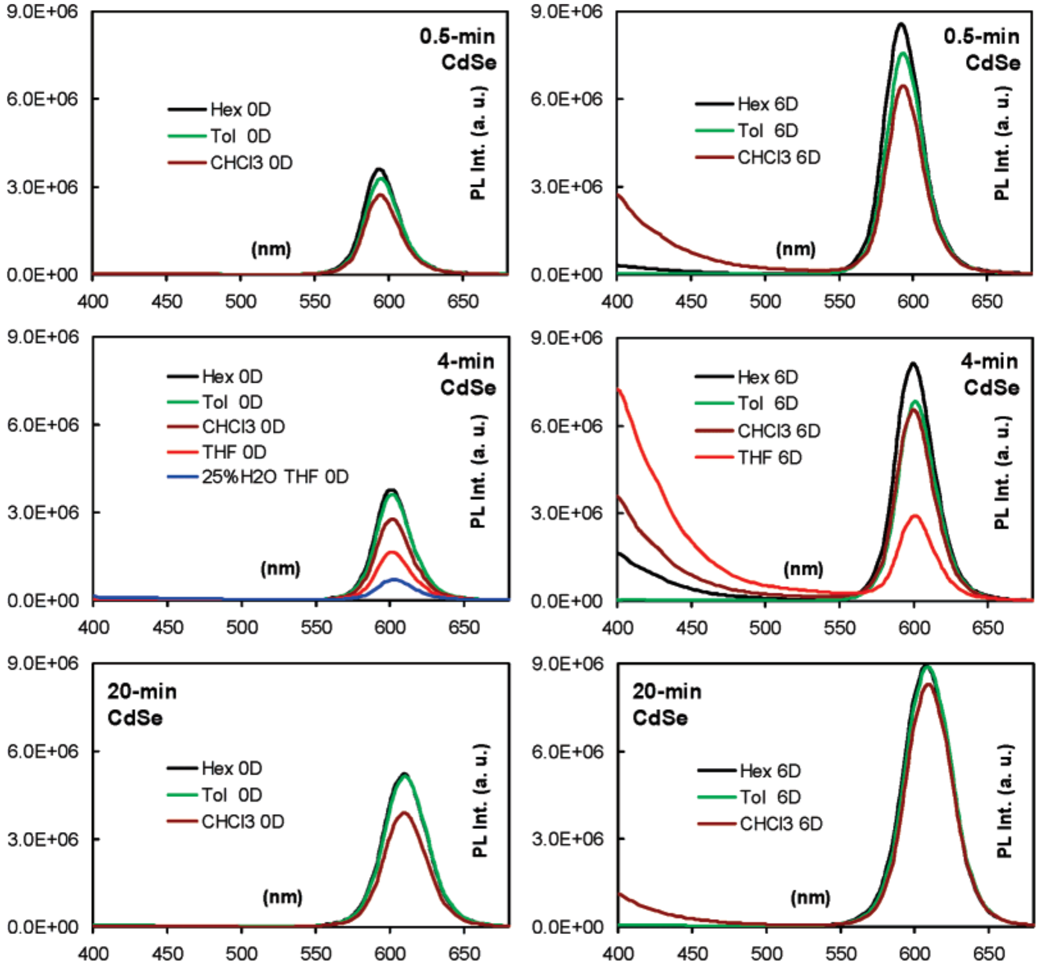

Figure 1. PL spectra (left) acquired for the 0.5-min (top), 4-min (middle), and 20-min (bottom) nanocrystals dispersed in various solvents represented by different colors, with black, Hex; green, Tol, purple, $CHCl_3$; red, THF; and blue, 25% water−THF mixture. Corresponding PL spectra (right) were acquired after 6 days of storage in the dark at 5 °C. The nanocrystals are from the synthetic batch shown in Figure 8 (but after 1 day in the dark at 5 °C stored as a solid).

going from Hex to Tol (Figure 1 left); such a difference is enhanced after 6 days of storage (Figure 1 right). However, the 20-min nanocrystals (Figure 1 bottom left) exhibit an identical PL intensity in Hex and in Tol as well as after 6 days of storage (Figure 1 bottom right).

After 6 days of storage, the nanocrystal dispersions ordinarily showed substantial enhancement in PL intensity as well as slight blueshifts (less than 2 nm), except the THF−water mixture, in which precipitation took place. At the same time, a rise in the baseline at less than ca. 500 nm after 6 days is evident, especially for the nanocrystals in $CHCl_3$ and THF.

Therefore, it seems reasonable to conclude that there is a different degree of surface defects exposed in the various dispersing media because of the removal of surface ligands: because the nanocrystals exhibit an increase in PL efficiency on going from the water−THF mixture to THF, $CHCl_3$, and Tol and Hex, accordingly, the removal of surface ligands minimizes. In the mixture, the removal is so substantial that the remaining ligands are not enough to provide colloidal stability and precipitation takes place slowly. In THF and $CHCl_3$ (after days of dispersion), the removal is so much that a baseline uprising takes place (as detected below ca. 500 nm), which indicates the possible appearance of other fluorescent species, which, we argue, arise from dissociation of the surface ligands of the colloidal CdSe nanocrystals. Similar to the removal of surface ligands, another process takes place simultaneously: the adsorption of small molecules onto the nanocrystal surface, causing an increase in PL intensity in the dispersions;[9] such an increase is observed after storage. Hence, the PL efficiency of the colloidal CdSe nanocrystals is affected by dispersing environments as well as dispersion storage periods, in addition to synthetic history.

1.2. Additive TOP Effects. Now, nonpolar water-insoluble Hex and polar water-miscible THF are chosen as dispersion environments to examine PL intensity affected by the presence of TOP (25 wt %) in the two environments. The 1-min, 10-min, and 120-min nanocrystals prepared from the synthetic batch with the reaction medium consisting of TOP, as described in our Experimental Section, are used to test such additive TOP effects. The emission spectra recorded for the nanocrystals dispersed in Hex (black) and the TOP−Hex mixture (red) are presented in Figure 2, while those recorded from the THF (black) and TOP−THF mixture (red) dispersions are presented in Figure 3. The left parts in Figures 2 and 3 are from as-dispersed dispersions and the right parts are from the corresponding 6-day dispersions. The same intensity scale is used for any two emission spectra from the same dispersion but recorded before (left) and after 6 days of storage (right) in Figures 2 and 3.

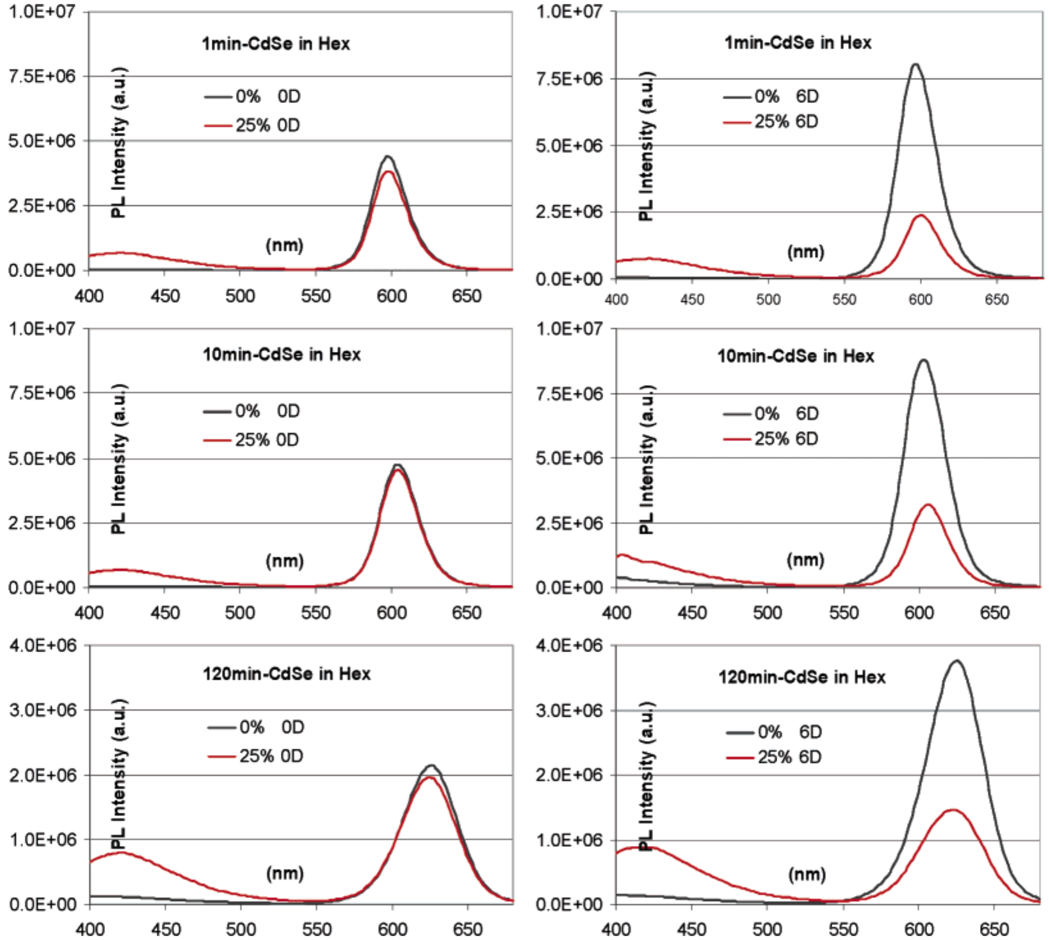

Figure 2. PL spectra (left) acquired for 1-min (top), 10-min (middle), and 120-min (bottom) nanocrystals dispersed in Hex (black) and 25% TOP−Hex mixture (red). Corresponding PL spectra (right) were acquired after 6 days of storage in the dark at 5 °C. The nanocrystals are from the synthetic batch shown in Figure 8 (but after 2 days in the dark at 5 °C stored as a solid).

As shown in the left part in Figure 2, the nanocrystals with 1-min (top), 10-min (middle), and 120-min (bottom) growth time exhibit similar or slight decreases in PL intensity on going from Hex to the TOP−Hex mixture (25% TOP by weight). After 6 days as shown in the right part of Figure 2, an enhanced PL intensity is detected for the Hex dispersions but a decrease is seen for the 25% TOP−Hex dispersions. On the other hand, as shown in Figure 3, the nanocrystals exhibit similar PL intensities in THF and in the 25% TOP−THF mixture; after 6 days, enhanced PL intensity is detected for both THF and the mixture medium, except for the 1-min nanocrystals in the TOP−THF mixture that exhibit a decrease but with a significant rise in the baseline below ca. 500 nm.

On the basis of the above experiment observation, it seems reasonable to suggest that a certain amount of surface ligands leave the nanocrystals, and, at the same time, a certain number of small molecules are required for surface passivation. The net result can be either an enhanced or a diminished PL intensity depending on the nature and the composition of the dispersion medium (and, of course, the nanocrystals themselves). For example, during storage in $CHCl_3$, surface passivation by small molecules is more important than the leaving of surface ligands, and an enhancement in PL intensity is seen after days of storage. However, matters are reversed in the 25% TOP−Hex mixture. The variable effect of TOP in Hex on the PL efficiency of the colloidal CdSe nanocrystals sheds new light on the use of TOP during size-selective precipitation.[10]

1.3. Dilution Effects on the Baseline Uprising. To test our arguments on the formation of other fluorescence species thus causing the baseline uprising (below ca. 500 nm) and on the dissociation of surface ligands, dilution experiments were carried out on the 4-min nanocrystals dispersed in Hex and THF. At the same concentration, the two starting dispersions in Hex and in THF, so-called Dispersion 1, have the same number of nanocrystals; sequential dilution is performed by adding Hex or THF into the Hex or THF dispersions, respectively, and the resulting dispersions are so-called Dispersions 2−6, with a continuous decrease in concentration.

The emission spectra of Dispersions 1−6 in Hex (top) and in THF (down) are shown in Figure 4 with black, blue, red, pink, purple, and green, respectively, while the degree of dilution for Dispersions 1−6 is summarized in Figure 5 as indicated by relative concentration. The spectra shown in the left and right parts of Figure 4 are recorded before and after 6 days of storage, respectively. The intensity scale of the emission spectra for the Hex dispersions (top) is twice larger than that for the THF dispersions (bottom), because

---

(9) Myung, N.; Bae, Y.; Bard, A. J. *Nano Lett.* **2003**, *107*, 489.
(10) Talapin, D. V.; Rogach, A. L.; Shevchenko, E. V.; Kornowski, A.; Haase, M.; Weller, H. *J. Am. Chem. Soc.* **2002**, *124*, 5782.

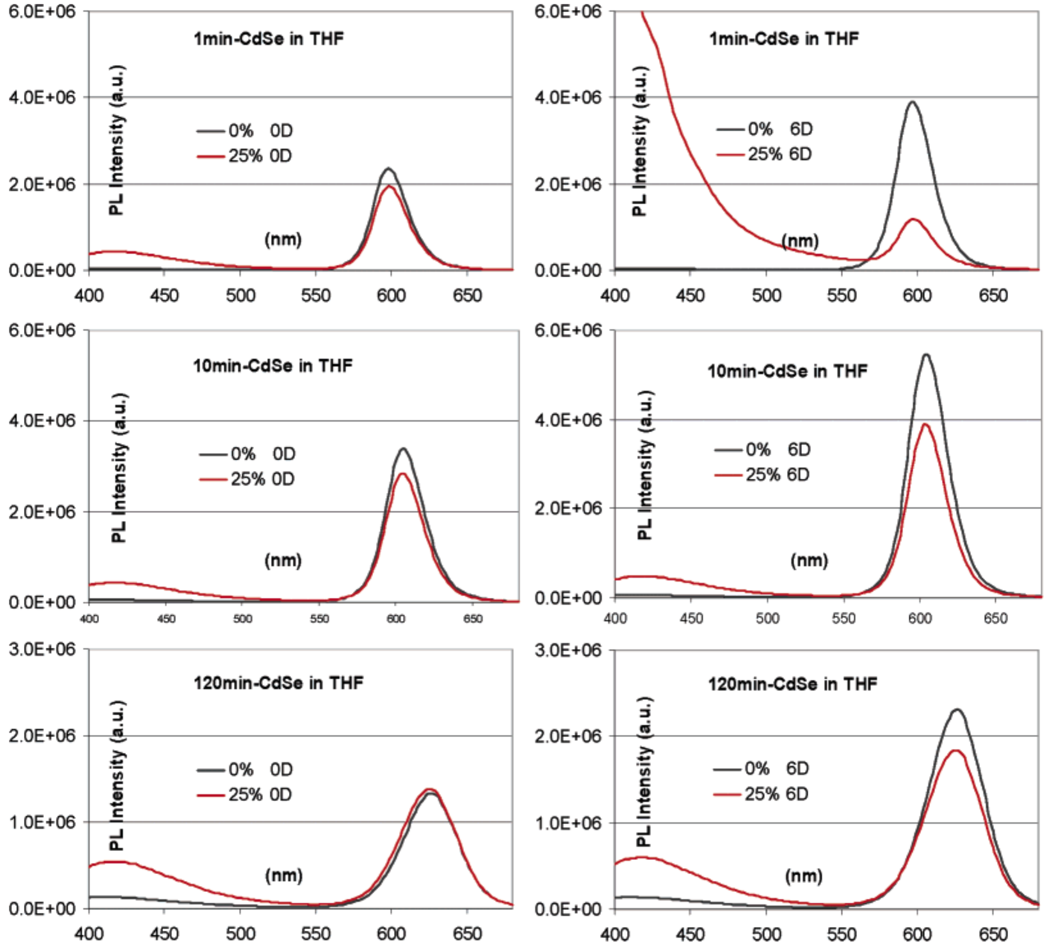

Figure 3. PL spectra (left) acquired for 1-min (top), 10-min (middle), and 120-min (bottom) nanocrystals dispersed in THF (black) and 25% TOP−THF mixture (red). Corresponding PL spectra (right) were acquired after 6 days of storage in the dark at 5 °C. The nanocrystals are from the synthetic batch shown in Figure 8 (but after 2 days in the dark at 5 °C stored as a solid).

of a considerable decrease in PL intensity on going from Hex to THF. Meanwhile, the same intensity scale is used for the spectra of the dispersions before (left) and after (right) storage, to directly demonstrate the change of PL properties after storage.

Figure 4 shows a decrease in PL intensity during dilution; at the same time, Dispersions 1−6 with a decrease in concentration (as shown in Figure 5) exhibit different change in PL intensity after days of storage. After 6 days, the PL intensity of Dispersions 1−5 in Hex increases, but that of Dispersion 6 decreases. Meanwhile, the PL intensity of Dispersions 1−4 in THF increases, and that of Dispersions 5 and 6 decreases so much that the original emission peaks become flat. Dispersions 1 and 2 in Hex and in THF after 6 days are not shown in the right part of Figure 4 (because of their high PL intensity). THF Dispersions 3−6 exhibit a much more significant rise in baseline below ca. 540 nm than the corresponding ones in Hex. Interestingly, the PL intensity of the band gap emission around 600 nm continuously decreases from THF Dispersion 3, to 4, to 5, and to 6, while the PL intensity for the emission range less than ca. 540 nm continuously decreases from Dispersion 5, to 6, to 4, and to 3. These two decrease sequences are easy to understand, demonstrating that both the number of surface ligands removed and the number of the fluorescent species formed (which PL below ca. 540 nm) increase from Dispersion 3, to 4, to 6, and to 5; Dispersion 6 has a smaller number of surface ligands than Dispersion 5 because of less nanocrystals.

Accordingly, the change in emission intensity of Hex Dispersions 1−6 and THF Dispersions 1−6 after 6 days of storage, consisting of the enhancement and decrease of the band gap emission as well as the baseline rise, designates the arguments that in one identical dispersion medium, one identical CdSe ensemble in more dilute dispersion can exhibit more baseline uprising because of more surface ligand removal and more fluorescent species formed. Also, at the same dispersion concentration, one identical CdSe ensemble can exhibit more baseline uprising in THF than in Hex, because of more surface ligand removal and more fluorescent species formed.

Figure 5 summarizes the dilution experiments (the left part of Figure 4): taking the concentration of Hex and THF Dispersion 1 as 1, the concentrations of Dispersions 2−6 are thus calculated on the basis of our dilution experiments. With the PL intensity (integration area) of Hex Dispersion 1 as 1, the relative PL intensities of Hex Dispersions 1−6 (solid square symbols) and THF Dispersions 1−6 (open square symbols) are calculated and plotted in Figure 5 against their relative concentration, with corresponding labels 1−6: the *X* axis represents relative concentration and the left *Y* axis represents relative PL intensity. Furthermore, for Dispersions 1−6, the decrease in the PL intensity on going from Hex to THF is simply quantified as the decrease

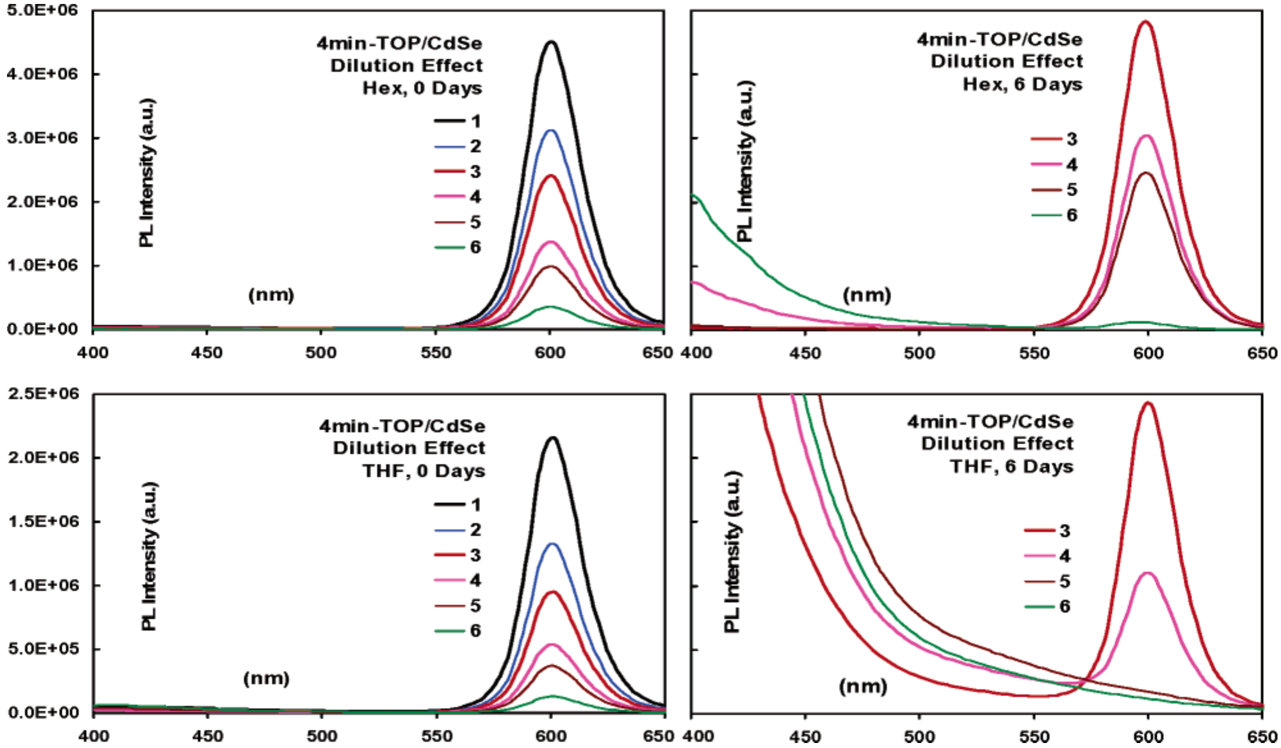

Figure 4. PL spectra (left) of the sequential dilution experiments (top Hex and bottom THF), with black, Dispersion 1; blue, 2; red, 3; pink, 4; purple, 5; and green, 6. Corresponding PL spectra (right) of Dispersions 3−6 were acquired after 6 days of storage in the dark at 5 °C. The nanocrystals are from the synthetic batch shown in Figure 8 (but after 3 days in the dark at 5 °C stored as a solid).

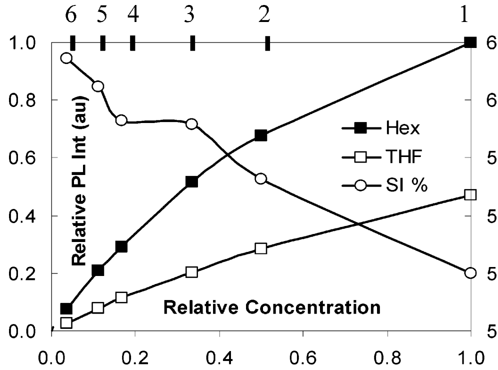

Figure 5. Illustration of the decrease of the PL intensity (left *y* axis, squares) (relative to the Dispersion 1 in Hex with its concentration as 1 and PL intensity as 1), as well as the increase of the sensitivity index (right *y* axis, circles) during the sequential dilution experiments by Hex (solid square) and THF (open square). The dispersions are indicated correspondingly by numbers 1−6. The SI is calculated by SI = $\Delta I/I_{\text{Hex}} = (I_{\text{Hex}} - I_{\text{THF}})/I_{\text{Hex}}$, where I_{Hex} and I_{THF} are the PL intensity (integrated area) in Hex and in THF, respectively.

percentage by

$$\text{SI} = \Delta I/I_{\text{Hex}} = (I_{\text{Hex}} - I_{\text{THF}})/I_{\text{Hex}} \tag{1}$$

where I_{Hex} and I_{THF} are the PL intensity (integration area) in Hex and in THF, respectively. The calculated values of the SI parameter (circle symbols) versus the relative concentrations during the dilution are also plotted in Figure 5 with the right *Y* axis the SI parameter.

The SI parameter can also be defined by the decrease percentage of the PL efficiency on going from Hex to THF, but with the corresponding value calculated by eq 1 also, because of the similarity of the absorption spectra of the Hex and THF dispersions. Consequently, the values of the SI parameter indicate the sensitivity of the PL efficiency on going from Hex to THF: a larger value indicates a larger decrease and is thus more sensitive on going from Hex to THF. As shown in Figure 5, such sensitivity is a function of dispersion concentration: the values of the SI parameter increase along with dilution, indicating that the colloidal CdSe nanocrystals become more and more sensitive to environments on going from nonpolar Hex to polar THF when the concentration decreases. Therefore, for one identical CdSe ensemble, its optical performance including storage stability is highly related to the dispersion environment as well as dispersion concentration; in addition, the environmental sensitivity of the optical performance is also related to the dispersion concentration. Accordingly, it is important to identify detailed CdSe dispersion parameters, including the nature and composition of the dispersion medium and the CdSe concentration, together with synthetic history, when exploring the optical performance of colloidal CdSe nanocrystals for various applications such as environmental sensing.

2. Sample Identity. 2.1 XRD and TEM. The CdSe nanocrystals prepared in air from the reaction medium of TOP as described in the Experimental Section show equivalent wurtzite crystal structure and similar transmission electron microscopy (TEM) features as those prepared using the published approaches.[3−7] Powder X-ray diffraction data (a) of a 10-min nanocrystal ensemble from the synthesis described in the Experimental Section is shown in Figure 6, together with that recorded from the bulk wurtzite CdSe (b). Figure 6 demonstrates that the CdSe nanocrystal ensemble exhibits a wurtzite crystal structure with the lattice spacing similar to that of the bulk wurtzite materials. This 10-min ensemble was directly imaged by TEM: a bright field TEM

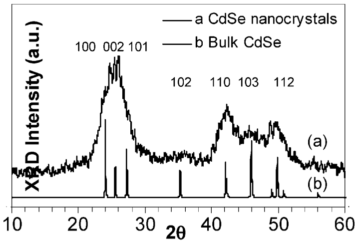

Figure 6. X-ray diffraction (XRD) patterns of a 10-min CdSe ensemble (a) synthesized from the batch described in the Experimental Section and of the bulk wurtzite CdSe (b).

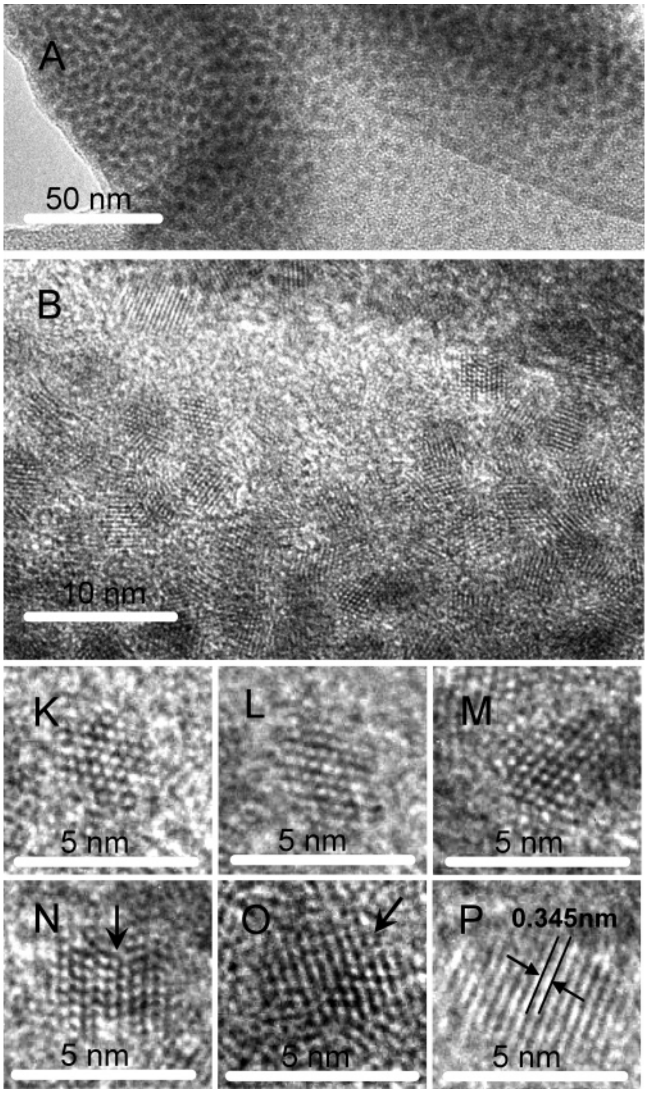

Figure 7. A bright field TEM image (A) and a high-resolution TEM image (B) of the CdSe nanocrystals whose XRD pattern is shown in Figure 6a. Examples of two-dimensional and one-dimensional lattice images are presented by particles K−O and particle P, respectively. Particles K−M exhibit no defects, while particles N−O do.

image and a high-resolution TEM image are presented in the A and B parts in Figure 7. The nanocrystals are spherical in shape and ca. 4.0 nm in diameter with deviation less than 5%. Examples of the nanocrystals exhibiting two-dimensional lattice structure (particles K−O) and one-dimensional lattice structure (particle P) are also presented: crystal defects are not observed in particles K−M, while in particles N−O they are indicated by arrows. The *d* spacing of particle P was measured to be 0.345 nm.[12] Therefore, it is fair to conclude that our CdSe nanocrystals are high-quality regarding crystallinity, spherical shape, and distribution, as well as uniform in size.

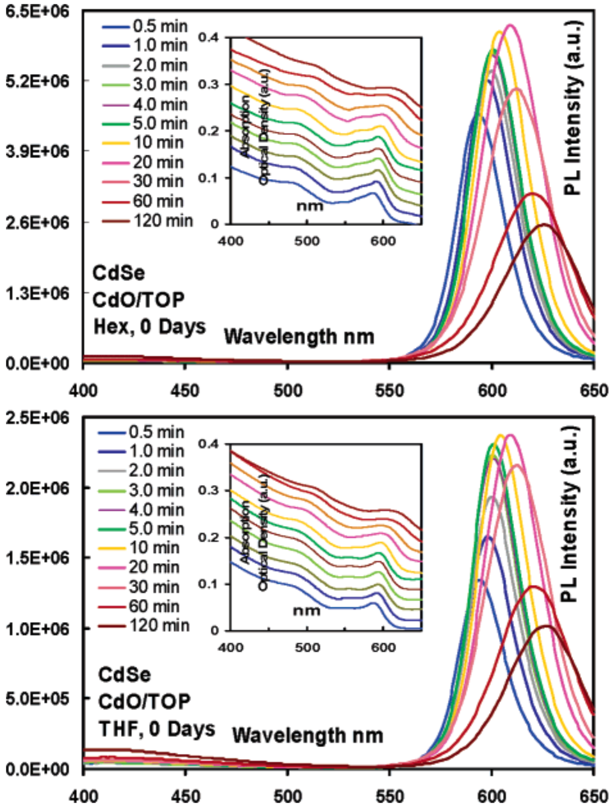

Figure 8. Temporal evolution of the emission of the growing CdSe nanocrystals (as-prepared) in Hex (top) and in THF (bottom), together with the corresponding UV−vis absorption spectra (offset, insert). The growth periods are indicated.

2.2. Growth Kinetics and PL Storage Stability. The nanocrystals investigated above were synthesized with a nonorganometallic approach different from those reported.[3−7] Since different approaches possess different growth kinetics, which is important for surface quality, a slow growth in size is preferred.[10,11] To have a complete picture of the dispersion media affecting the PL properties, it is necessary to provide the synthetic kinetics of the CdSe nanocrystals investigated above. Usually, the growth kinetics can be easily monitored by the temporal evolution of the optical properties of the growing nanocrystals. The temporal evolution of the band gap positions of the absorption and emission is indicative of the growth kinetics in size, and the temporal evolution of the PL full width at half-maximum (fwhm) in wavelength units, to some extent, indicates the development of the size distribution of the growing nanocrystals.[7b]

The emission spectra of the as-prepared CdSe nanocrystals (from the reaction described in the Experimental Section and with different growth periods) dispersed in Hex (top) and in THF (bottom) are presented in Figure 8, together with the offset absorption spectra inserted correspondingly, since PL is a spontaneous emission process with photon absorption

---

(11) (a) Jackson, K. A. *J. Cryst. Growth* **1999**, *198/199*, 1. (b) Scneidman, V. A.; Jackson, K. A.; Beatty, K. M. *J. Cryst. Growth* **2000**, *212*, 546.

(12) Tamargo, M. C. *Optoelectronic Properties of Semiconductors and Superlattices in II−VI Semiconductor Materials and Their Applications*; Sheridan Books: Ann Arbor, MI, 2002; p 118; reports Wurizte CdSe a = 0.430 nm and c = 0.7013 nm.

Table 1. Redshift of Absorption and Emission Peak Positions (PP, in nm) of the Growing CdSe Nanocrystals Dispersed in Hex and in THF (Figure 8), Together with the Peak Positions of 0.5-min Nanocrystals, as well as Change of the PL fwhm (in nm), Together with the fwhm Values of 0.5-min Nanocrystals in Hex and in THF

GT (min)	Hex UV	Hex PL	THF UV	THF PL	Hex FWHM	THF FWHM
0.5	587	594	587	594	27	26
0.5−1	4	4	5	4	0	0
0.5−2	6	6	7	6	0	1
0.5−3	7	6	7	7	0	1
0.5−4	7	6	7	7	1	1
0.5−5	**7**	**6**	**7**	**7**	**1**	**1**
0.5−10	10	10	9	11	2	2
0.5−20	12	15	10	16	7	6
0.5−30	13	18	10	18	10	9
0.5−60	13	26	12	26	17	16
0.5−120	13	32	16	32	17	16

and emission. The curves of different colors in Figure 8 represent the growing nanocrystals sampled at various periods of growth; the same colors indicate identical growth periods; furthermore, the PL intensity scale for the Hex dispersions is larger than that for the THF dispersions, while the same optical density scale is used for the Hex and THF dispersions. The absorption spectra recorded in Hex and in THF (for one CdSe ensemble or even different CdSe ensembles) are very much similar; for example, the optical density (the height) of the first absorption peak, corresponding to the $1S_{3/2}-1S_e$ transition, is quite the same.[13,14] In addition to the general phenomenon that the CdSe nanocrystals prepared via our nonorganometallic approach exhibit insensitive absorption but sensitive emission when dispersed in different environments,[8] ensembles with different growth time exhibit significantly similar absorption but diverse emission.[8] Therefore, the temporal evolution of the PL intensity represents effectively the temporal evolution of the PL efficiency of the growing nanocrystals and, accordingly, the temporal evolution of the surface quality. Such representation is based on the fact that the nanocrystals grow a little in size during the entire growth periods (less than 17- and 33-nm redshifts of the band gap absorption and emission between 0.5 min to 120 min, respectively, as shown in Table 1). Thus, no normalization is carried out for the emission spectra.

The temporal evolution of the PL intensity detected in Hex and THF is similar: the PL intensity increases monotonically until 20 min of reaction time is reached and then decreases monotonically. Such enhancement takes longer growth periods than that reported with a 2Cd-to-Se nonorganometallic approach and with the reaction medium consisting of five components ((TOPO, TOP, one acid, and two amines) and with a much faster growth in size).[7b] On the basis of the temporal evolution of the PL efficiency indicated in Figure 8, it seems that the surface quality monotonically becomes better till 20-min growth time. Subsequently, it is necessary to study several nanocrystal ensembles with different growth periods rather than one ensemble, and it is necessary to provide the growth kinetics of the colloidal nanocrystals when investigating their PL properties, such as dispersing media affecting PL efficiency, as shown in Figures 1−3.

The temporal evolution of the UV and PL peak positions during synthesis is demonstrated in Figure 9A and that of the PL fwhm in Figure 9B (left *Y* axis). Furthermore, the redshifts of the absorption and emission peak positions of the growing nanocrystals as well as the increase of the PL fwhm are summarized and presented in Table 1. The redshift of the emission peak position is more sensitive than that of the absorption peak position for the nanocrystals at late stages of growth. On the basis of the absorption peak position in Hex, the average diameter is extracted from the relationship reported between the average size and the absorption peak position.[6] Accordingly, the temporal growth of the size (in nm) is presented in Figure 9B (right *Y* axis). Furthermore, nonresonant Stokes shift (NRSS), namely, the energy difference in meV between the absorption and emission, was calculated, and the temporal evolution of the NRSS (in meV) of the growing nanocrystals is shown in Figure 9C.

Figures 8 and 9 and Table 1 show that the band gap emission and absorption of the 0.5-min nanocrystals occur

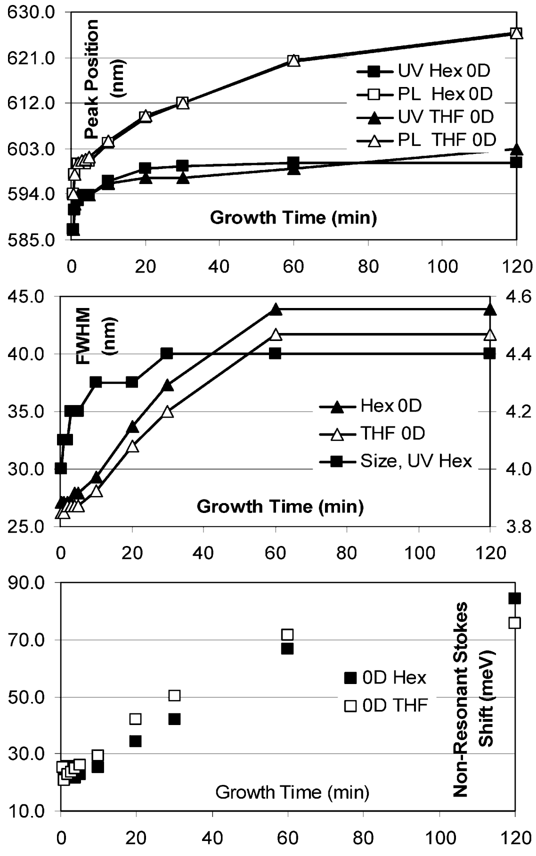

Figure 9. Temporal evolution of (top) the band-edge absorption and emission peak positions (PP, nm) of (middle) the PL fwhm (left *y* axis, triangles), the average diameter (right *y* axis, squares, on the basis of ref 6), and (bottom) the nonresonant Stokes shift (in meV).

---

[13] Ekimov, A. I.; Hache, E.; Schanne-Klein, M. G.; Ricard, D.; Flytzanis, C. *J. Opt. Soc. Am. B* **1993**, *10*, 100.

[14] Leatherdale, C. A.; Bawendi, M. G. *Phys. Rev. B* **2001**, *63*, 165315.

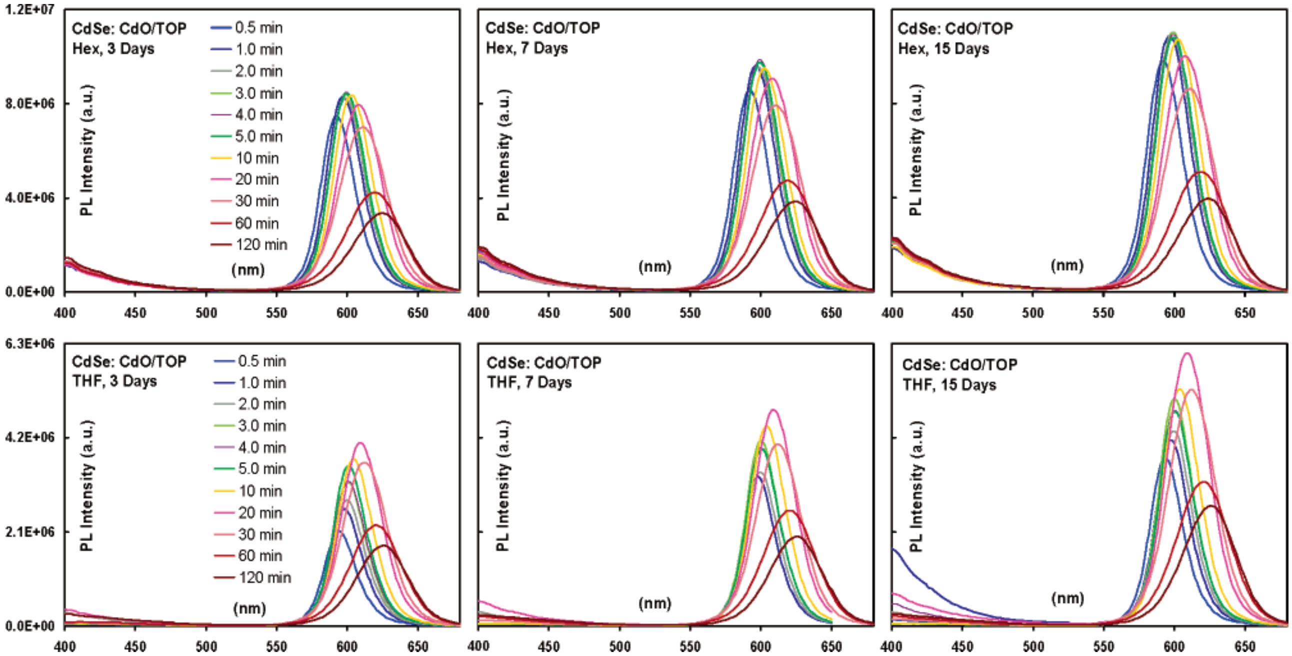

Figure 10. The change in PL properties, after 3 days (left), 7 days (middle), and 15 days (right), of the dispersions shown in Figure 8. During storage, these dispersions, namely, the as-synthesized nanocrystals in Hex (top) and in THF (bottom), were kept in the dark at 5 °C.

at ca. 594 and 587 nm, respectively, in both Hex and THF, indicative of an orange emission color. In the early stages of growth (0.5−5 min), the peak positions redshift only ca. 7 nm; furthermore, there is little change in the peak positions during the 2−5 min growth periods, indicating a near-zero growth rate. These early-stage nanocrystals, with an average diameter of about 4.1 ± 0.1 nm (on the basis of ref 6, in good agreement with our TEM data shown above), exhibit nonresonant Stokes shift (NRSS) in the range of 20−25 emV, which is in the theoretical range, indicating good surface quality.[1c] The 0.5-min nanocrystals exhibit a PL fwhm of ca. 27 nm in Hex and 26 nm in THF; there is little increase during the early stages of growth; afterward, the PL fwhm increases evidently. Thus, it seems that defocusing in size took place after 10-min growth: size deviation of the 10-min ensemble shown in Figure 7A was less than 5%.

On going from Hex to THF, as shown in Figures 8 and 9 and Table 1, in addition to the decrease of the band gap PL efficiency of the growing nanocrystal ensemble, redshifts less than 1 nm of the PL peak position are detected, together with a difference in the PL fwhm of ca. 1 nm for the 0.5−10 min nanocrystals and ca. 2−3 nm for the later-stage nanocrystals. Such a difference of the PL peak position and PL fwhm on going from Hex to THF may also indicate high-quality surface: the low sensitivity indicates good surface quality[7b] and is likely to be attributed to a slow growth rate during the entire period of growth monitored (particularly 0.5−30 min). The size−growth rate of the CdSe nanocrystals from the present approach is very slow, as compared to that of the reported procedures.[7b]

It is easy to understand that storage stability is also a surface-quality indicator and is important for further modifications aiming at either fundamental research or at certain applications. Such stability is highly related to surface issues, including ligand equilibriums and small molecule adsorptions. Consequently, we present the examination on the PL change after days of storage for the CdSe nanocrystals shown in Figure 8. Figure 10 shows the PL spectra of the as-prepared nanocrystals dispersed in Hex (top) and in THF (bottom) for 3, 7, and 15 days (left, middle, and right, respectively). The emission spectra in Figure 10 use two intensity scales to illustrate the change in the PL intensity after storage: one for Hex dispersions and one for THF dispersions. An enhancement in the band-edge PL intensity in both Hex and THF during storage is noticeable; slight blueshifts of the PL peak position are detected, less than 1 nm in Hex and less than 0.5 nm in THF for 3-day storage. Moreover, a rise in the baseline less than 500 nm may indicate the formation of other fluorescent species; an enhancement of the baseline uprising is noticed with long storage.

In addition to dispersion, the CdSe samples were also kept as solids (in the dark at ca. 5 °C) for storage. Afterward, they were dispersed in Hex and THF, and their PL properties (thinner lines) were compared to the corresponding as-prepared dispersions without storage (thicker lines); examples are shown in Figure 11, with the PL spectra of the nanocrystals after 2-month storage as a solid (after synthesis) and afterward dispersed in Hex and THF; 10-min (black), 60-min (green), and 120-min (red) nanocrystals are investigated. The nanocrystals after 2-month storage as solids are still dispersible. Figure 11 suggests that the surface of the CdSe nanocrystals changes little after a few days of storage in solids; thus, the results presented in Figures 1−4, on the basis of the CdSe nanocrystals shown in Figure 6 but after 1−3 days of storage in solids, are meaningful.

Finally, it seems reasonable to conclude that the CdSe nanocrystals used in our study on dispersing media affecting PL efficiency, as shown in Figures 1−5, are high-quality, regarding crystallinity, size, shape, distribution, and surface quality. Such high quality is due to the synthetic approach with a slow growth in size: TOP is good to achieve a slow growth in size of CdSe nanocrystals. These nanocrystals are

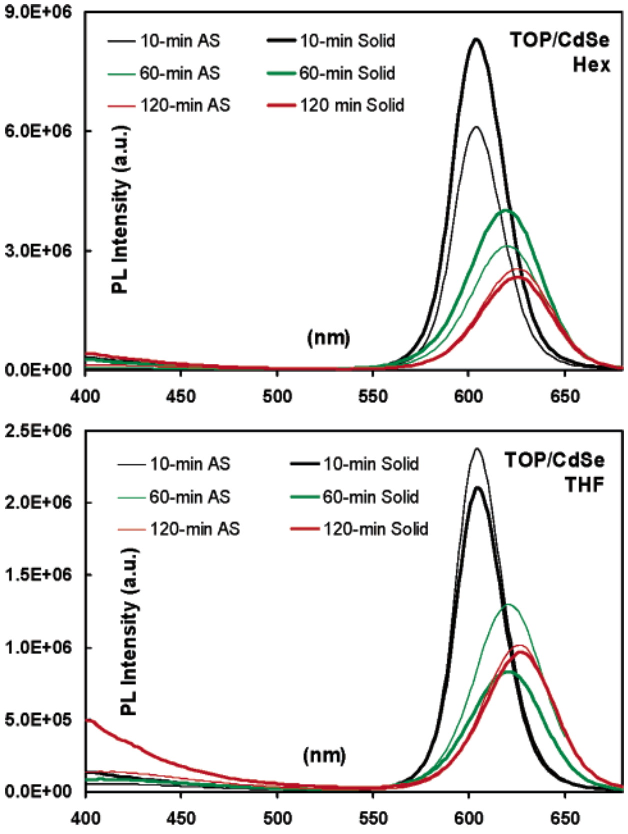

Figure 11. The change in PL properties of the as-synthesized nanocrystals (Figure 8) stored as a solid for 2 months after synthesis, as tested by the change in PL properties when the nanocrystals are dispersed in Hex (top) and in THF (bottom). The PL spectra with thinner lines are for the as-synthesized (AS) samples, and those with thicker lines are for the 2-month-old solid, redispersed samples. Black, green, and red lines are for 10-min, 60-min, and 120-min nanocrystals.

from the reaction with less than 5-nm redshift of band gap absorption, and emission occurred during 2−10 min growth periods; such a redshift can correspond to ca. 0.1-nm increase in size.[6] The high surface quality is indicated by low sensitivity of PL fwhm, peak position, and NRSS on going from Hex to THF, as well as by good storage stability of PL properties. The present CdSe nanocrystals should be a good system for studying fundamental problems such as the exciton gap-versus-size problem, in addition to PL efficiency affected by dispersing environments.

Conclusions

The present study addressed the nature and composition of dispersion media affecting photoluminescent (PL) efficiency of colloidal CdSe nanocrystals as well as the baseline uprising at lower wavelength (below ca. 500 nm) of emission spectra (with or without dispersion storage). The investigated dispersion media were water-insoluble hexanes (Hex), toluene (Tol), chloroform ($CHCl_3$), and water-miscible tetrahydrofuran (THF), together with three mixtures which were a water−THF mixture (25%, weight), a tri-*n*-octylphosphine (TOP)−Hex mixture (25%, weight), and a TOP−THF mixture (25%, weight). The difference in the PL efficiency and the baseline uprising are argued to be related to the removal of surface ligands and the formation of small species as well as small molecule passivation; such arguments are based on experimental observation: in addition to the different PL efficiency arising from the various dispersions, there was in general an enhancement after days of storage. Furthermore, during dilution, the dispersions exhibited a continuous decrease in the PL intensity; at the same time, on going from Hex to THF, the decrease percentage in the PL intensity was enhanced; after days of storage, the starting dispersions exhibited an enhancement in the PL efficiency, while very diluted ones exhibited a decrease but with a significant baseline uprising.

The CdSe nanocrystals used were prepared from the synthetic approach developed in our laboratories, which involves the addition of a TOPSe/TOP solution into a CdO/TOP solution and promotes a period of slow growth which can be inserted into the reaction scheme to promote a high-quality surface and large-scale production. Even with a slow growth in size, the surface quality of the growing nanocrystals changes during the entire growth periods; subsequently, it is necessary to study several nanocrystal ensembles with different growth periods rather than one ensemble, and it is necessary to provide the growth kinetics of the colloidal nanocrystals when investigating their PL properties, such as dispersing media affecting PL efficiency.

Supporting Information Available: Comparison of the growth kinetics of the CdSe nanocrystals from 0, 4, and 10% amine reaction media, as well as the dispersion media affecting PL intensity and efficiency. This material is available free of charge via the Internet at http://pubs.acs.org.

CM048457L