JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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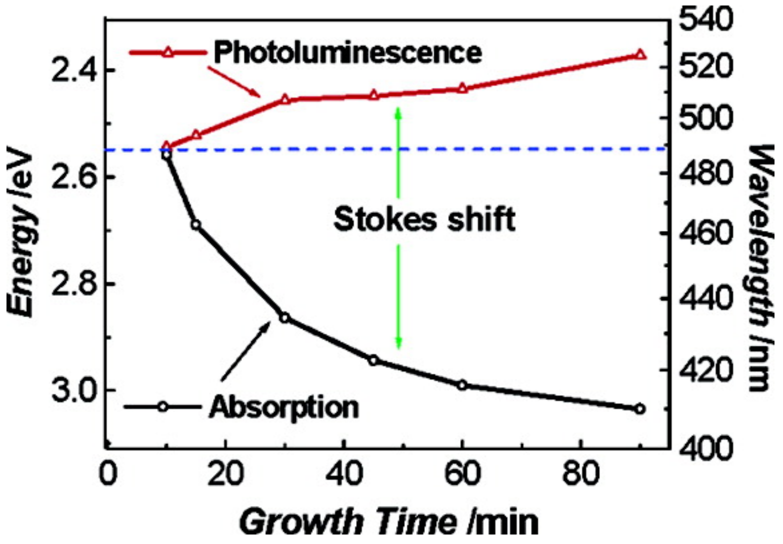
J. Am. Chem. Soc., **2005**, 127 (12), 4372-4375• DOI: 10.1021/ja0458219 • Publication Date (Web): 05 March 2005



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Published on Web 03/05/2005

Investigation of the Crystallization Process in 2 nm CdSe Quantum Dots

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Abstract: Investigation of the growth of CdSe nanocrystals (∼160 atoms) to the uniquely stable size of 2 nm allows the monitoring of the crystallization process in semiconductor quantum dots. By using a combination of optical techniques, high-resolution transmission electron microscopy (HRTEM), and powder X-ray diffractometry (XRD), new phenomena were explored during the CdSe nanocrystal growth process, which involved significant morphological reconstruction and crystallization of the initially formed amorphous nanoparticles. During the crystallization, the absorption onset of the CdSe quantum dots blue shifted toward higher energies at 3 eV (414 nm), while the photoluminescence red shifted to lower energies. Furthermore, an apparent increasing Stokes shift was observed during the formation of small CdSe nanoparticles. On the other hand, the photoluminescence excitation spectra showed constant features over the reaction time. Additionally, results from HRTEM and XRD studies show that the CdSe nanoparticles were amorphous at early reaction stages and became better crystallized after longer reaction times, while the particle size remained the same during the crystallization process. These observations demonstrate the important role of the surface on the optical properties of small CdSe quantum dots and facilitated the spectroscopic monitoring of the crystallization process in quantum dots.

Introduction

Quantum size confinement occurs as the size of materials is reduced to the nanometer regime. This phenomenon induces discrete electronic states and the increase or blue shift of the band edge transition energy in nanoparticles (NPs) as compared to the corresponding bulk materials.[1−4]Another important consequence is the manifestation of highly surface-related properties, from structural transformation to the emergence of unique optical properties,[1−3,5,6] due to the high surface-to-volume ratio in NPs. In the NP, the surface atoms usually have fewer adjacent coordinate atoms and more dangling bonds and can be treated as defects as compared to the bulk atoms.[1−4] These defects induce additional electronic states in the band gap, can mix with the intrinsic states to a substantial extent, and may also influence the spacing of the energy levels and optical properties of NPs.[1−4] At high densities of surface defects, a decrease in the observed transition energy and a red shifted emission band can be observed due to defect band formation,[3,7] which can be investigated by monitoring the photoluminescence (PL) of the NPs.[1−6] Theoretical studies suggested that there should be absorption peaks at lower energies in the band gap with considerable contributions from dangling surface orbitals, or mixed (intrinsic/surface) states.[8,9] However, such low energy features are usually, due to the low defect content in NPs[7] and the small transition dipole moments between intrinsic and surface states, not observed in absorption experiments[8] until the recent studies on ZnS NPs.[7]

The crystallization process during particle growth involves structural reconstructions and surface relaxations, which have been proposed theoretically[8,11] and experimentally[10] due to the surface strain in nanocrystals[6,10] and the minimization of the total free energy.[8] The surface can induce reversible structural transformation in different environments due to the different interfacial free energies assumed by the surface of the NPs.[13] Surface reconstruction and structural relaxation can also reduce the permanent dipole moment in CdSe nanocrystals,[11,12] thus changing the optical properties of the nanocrystals. Reversely,

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(1) (a) Alivisatos, A. P. *J. Phys. Chem.* **1996**, *100*, 13226−13239. (b) Alivisatos, A. P. *Endeavour* **1997**, *21*, 56−60.

(2) (a) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706−8715. (b) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545−610.

(3) (a) Nirmal, M.; Brus, L. *Acc. Chem. Res.* **1999**, *32*, 407−414. (b) Bawendi, M. G.; Carroll, P. J.; Wilson, W. L.; Brus, L. E. *J. Chem. Phys.* **1992**, *96*, 946−954.

(4) (a) Peng, Z.; Peng, X. *J. Am. Chem. Soc.* **2001**, *123*, 183−184. (b) Peng, X. *Adv. Mater.* **2003**, *15*, 459−463. (c) Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2002**, *124*, 3343−3353. (c) Qu, L.; Yu, W. W.; Peng, X. *Nano Lett.* **2004**, *4*, 465−469. (d) Qu, L.; Peng, X. *J. Am. Chem. Soc.* **2002**, *124*, 2049−2055.

(5) (a) Burda, C.; Link, S.; Mohamed, M.; El-Sayed, M. *J. Phys. Chem. B* **2001**, *105*, 12286−12292. (b) Landes, C.; Braun, M.; Burda, C.; El-Sayed, M. A. *Nano Lett.* **2001**, *1*, 667−670.

(6) Chen, X.; Lou, Y.; Samia, A. C.; Burda, C. *Nano Lett.* **2003**, *3*, 799−803.

(7) (a) Chen, W.; Wang, Z.; Lin, Z.; Lin, L. *J. Appl. Phys.* **1997**, *82*, 3111−3115. (b) Chen, W. *Handbook of Nanostructured Materials and Nanotechnology, Vol. 4: Optical Properties*; Nalwa, H. S., Ed.; Academic Press: New York, 2000; Ch. 5, pp 325−392.

(8) Leung, K.; Whaley, K. B. *J. Chem. Phys.* **1999**, *110*, 11012−11022.

(9) (a) Troparevsky, M. C.; Kronik, L.; Chelikowsky, J. R. *Phys. Rev. B* **2001**, *65*, 033311/1−033311/4. (b) Troparevsky, M. C.; Kronik, L.; Chelikowsky, J. R. *J. Chem. Phys.* **2003**, *119*, 2284−2287.

(10) McGinley, C.; Riedler, M.; Möller, T.; Borchert, H.; Haubold, S.; Haase, M.; Weller, H. *Phys. Rev. B* **2002**, *65*, 245308/1−245308/5.

(11) (a) Rabani, E. *J. Chem. Phys.* **2001**, *115*, 1493−1497. (b) Rabani, E.; Hetényi, B.; Berne, B. J.; Brus, L. E. *J. Chem. Phys.* **1999**, *110*, 5355−5369.

10.1021/ja0458219 CCC: $30.25

the change of the optical properties of nanocrystals can be used to investigate the crystallization process.

The growth and crystallization processes are highly important issues in the preparation of NPs. Highly crystalline CdSe NPs can be obtained at elevated temperatures, and several methods have been developed to improve the crystallinity of NPs.[2,5] Recently, the nucleation and growth of CdSe NPs have been investigated in situ.[4] Usually, the CdSe NPs sizes grow over time, which involves the simultaneous growth and crystallization process, and the optical properties of the NPs reflect mostly the size change of the NPs caused by the growth process.[2,4] In this paper, the crystallization process is observed separately from the growth process and investigated during the controlled synthesis of CdSe NPs toward a particle size of 2.0 nm, which is considered an especially stable size for CdSe NPs with an associated band edge absorption centered at 414 nm that has been observed earlier.[2,4] Specially stable sizes have been known for many years as certain electronic and geometric combinations of atoms yielding stable structures with unique atomic arrangements[2,4,5] that can prevent the growth of the NPs. This in turn facilitates the isolated observation of the crystallization process, during NP growth if the reaction is carefully controlled. During this process, new phenomena, including the blue shift of the absorption and the increasing Stokes shift over time, have been observed as the reaction proceeded.

Experimental Procedures

For a typical synthesis of the CdSe NPs, 0.1846 g of cadmium stearate (tech. 90%, Strem Chemicals) and 2.0588 g of TOPO (tech. 90%, Strem Chemicals) was loaded in a three-neck flask and heated to 240 °C for 2 h under Ar flow in a Schlenk line. Then, hot selenium stock solution (0.0213 g of Se (99.5%, Alfa Aesar) dissolved in 1.0294 g of TPP (99%, Strem Chemicals)) was quickly injected. After the injection, the temperature of the mixed solution dropped to 200 °C. This solution was quickly heated to 220 °C and reacted at this temperature for 90 min. As the reaction progressed, 0.1 mL fractions of the CdSe sample were taken out and quenched in 2 mL of cold toluene. Afterward, the fractions of CdSe NPs in toluene were placed in 1 cm quartz cuvettes, and the steady-state UV−vis absorption and PL spectra were collected at room temperature on a Varian Cary 50 and a Varian Eclipse Fluorescence spectrophotometer, respectively. High-resolution transmission electron microscopy (HRTEM) was obtained on a Tecnai F30 machine operated at 300 kV. Samples for TEM analysis were prepared by a drop of NP solution being deposited onto a copper grid supporting a film of amorphous carbon. The grid was dried in air prior to HRTEM measurements.

Results and Discussion

The temporal evolution of the UV−vis spectra of the CdSe NPs is shown in Figure 1. The reaction time was counted after the injection of the Se stock solution into the Cd TOPO mixture. Within the first 10 min of the reaction, no absorption was detected in the visible range. However, after 10 min of reaction time, a small absorption peak starting at 2.56 eV (486 nm) was observed. This absorption band then shifted to 2.86 eV (434 nm) after 30 min and was observed to move to 3.00 eV (414 nm) as the reaction was prolonged to 90 min. Overall, a blue shift of the absorption peak was observed as the reaction proceeded over time.

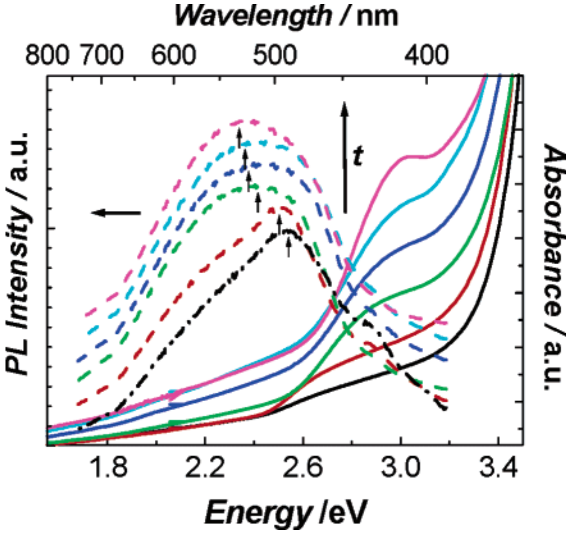

Figure 1. UV−vis (solid lines) and photoluminescence (PL) (dashed lines) spectra of CdSe NPs observed after 10 min (black), 15 min (red), 30 min (green), 45 min (blue), 60 min (cyan), and 90 min (magenta) reaction time.

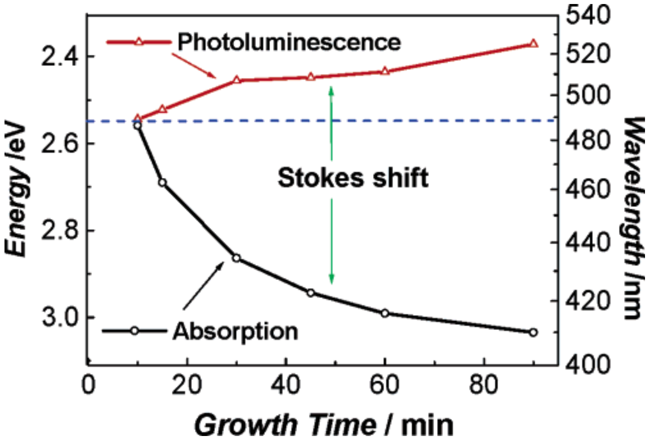

Figure 2. Evolution of the Stokes shift of the CdSe NPs during synthesis.

On the other hand, the emission spectra (Figure 1) recorded under 3.27 eV (380 nm) light excitation featured a broad band around 2.49 eV (500 nm) and a long tail up to 1.78 eV (700 nm). Unlike the blue shift of the absorption band, the emission spectra red shifted as the NPs formed. The emission peak was measured at 2.55 eV (488 nm) after 10 min and then shifted to 2.44 eV (508 nm) and 2.37 eV (523 nm) after 30 and 90 min reaction times, respectively. Furthermore, the emission spectra had initially an asymmetric shape, and as the CdSe NPs formed, the long wavelength tail of the emission became less pronounced.

Shown in Figure 2 is the temporal evolution of the Stokes shift, defined as the energy difference between the first peak of the absorption spectra and the emission peak of the CdSe NPs investigated in this study. From Figure 2, one can see that the Stokes shift increased from 0.014 to 0.409 and 0.663 eV as the CdSe NPs formed from 10, 30, and 90 min reaction time, respectively.

By performing photoluminescence excitation (PLE) measurements, one can gain insights as to the origin of the observed emission. Furthermore, it is also useful for revealing the purity

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(12) (a) Blanton, S. A.; Leheny, R. L.; Hines, M. A.; Guyot-Sionnest, P. *Phys. Rev. Lett.* **1997**, *79*, 865−868. (b) Empedocles, S. A.; Bawendi, M. G. *Science* **1997**, *278*, 2114−2117.

(13) Zhang, H.; Gilbert, B.; Huang, F.; Banfield, J. F. *Nature* **2003**, *424*, 1025−1029.

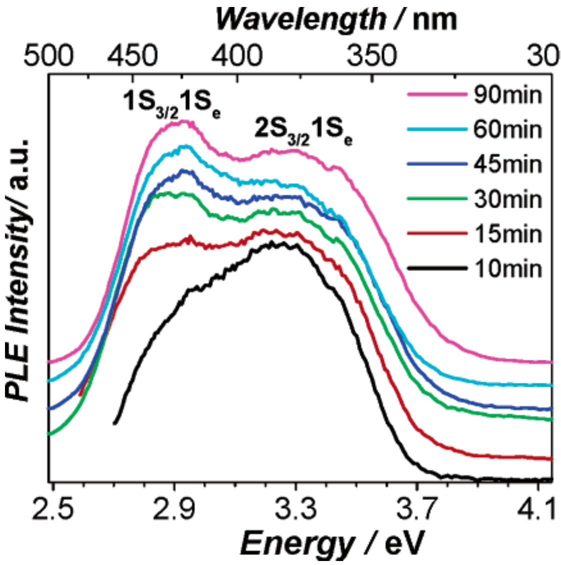

Figure 3. Temporal evolution of the PLE spectra of the CdSe NPs during the crystal formation. The emission wavelengths of the PLE spectra for the sample of 10 min (black), 15 min (red), 30 min (green), 45 min (blue), 60 min (cyan), and 90 min (magenta) reaction times are 474, 490, 500, 510, 510, and 525 nm, respectively. (For clarity, the spectra were normalized and offset.)

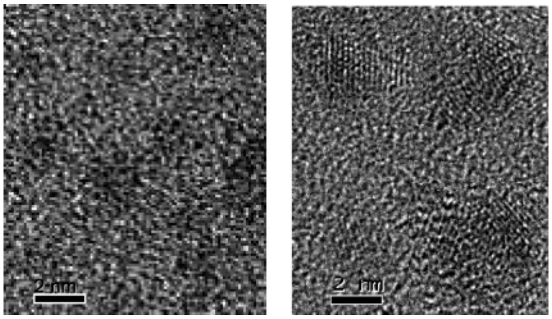

Figure 4. HRTEM images of CdSe NPs after 10 min (left) and 90 min (right) particle formation. Compared to the amorphous phase of the 10 min sample, the 90 min sample was well-crystallized.

and sizes of the samples.[7,14,15] As seen in Figure 3, all the samples have two peaks in their PLE spectra, one around 2.94 eV (423 nm) and the other around 3.28 eV (379 nm). Unlike the absorption and emission spectra, the energies of these two excitation peaks in the PLE spectra were independent of the formation time of the CdSe NPs. By taking a series of PL spectra at different excitation energies and a series of PLE spectra at different emission energies, one observes that the PL spectra as well as the PLE are consistent in shape and lack wavelength dependence, suggesting that the samples are of good homogeneity. From these measurements, evidence for narrow size distribution and a uniquely stable size was derived.

The HRTEM studies performed for the 10 and 90 min samples are shown in Figure 4, which displays that both these samples had similar sizes around 2.0 nm, consistent with results in the literature.[2] For the 10 min sample, no lattice fringes were observed in the HRTEM images of the randomly oriented NPs (Figure 4). Thus, the 10 min sample was suggested to be amorphous since from the statistical point of view, there should be a chance to resolve the lattice fringe at least for some NPs if the samples were well-crystallized and randomly oriented on the carbon grid. In contrast, the 90 min sample was well-crystallized, and the lattice structure could be resolved (Figure 4). This observation is consistent with the XRD results, where the 90 min sample had stronger diffraction pattern than the 10 min sample (see Supporting Information). The similar fwhms of the corresponding diffracting peaks suggested that the size of these CdSe NPs had similar size, which was estimated to be 2.1 ± 0.1 nm in diameter,[2] containing about a total of 160 atoms.[2,8,11] The similar sizes of these two samples suggested that the crystallization process is by far dominant over the growth process in the formation of CdSe NPs, at least between 10 and 90 min reaction time. From the HRTEM, well-crystallized CdSe nanocrystals were formed over time from the amorphous structures with similar sizes via a gradual crystallization process.

The slow crystallization was possible by using triphenylphosphine (TPP) instead of TOP as the capping material. The large steric demand of the TPP capping material can cause inefficient capping on the surface of CdSe NPs (coordinated to the Se atom) and thus can result in more surface defects. At the same time, the formation temperature was lowered to control the transformation rate of the CdSe NPs, thus allowing for a longer formation time for small CdSe NPs to extend the observation time window. In general, higher quality CdSe NPs can be obtained at higher formation temperatures and with longer formation times.[2,4] At lower temperatures, however, the CdSe NPs formed usually have many surface states at the initial stage, and the growth and crystallization rate is much slower, thus providing an opportunity to investigate the phenomena related to the growth and crystallization process of NPs. As observed in the HRTEM images and verified in the PLE measurements, the crystallization process is dominant over the growth process in the presented reaction. Thus, the growth process can be safely considered negligible, and the observed optical property changes of NPs can be attributed to the isolated crystallization process of the particularly stable 2.0 nm CdSe NPs.

As the reaction proceeded, a blue shift in absorption and red shift in emission were observed with similar PLE features. These phenomena can be elucidated in light of the gradual removal of surface defects during the crystallization process. Usually as NPs grow, the intrinsic absorption, due to transitions from valence band to the conduction band levels, shifts to the red.[1−4] The absorption properties observed here can therefore be attributed to the transitions involving surface defects states (in 2 nm NPs, 70% of the atoms are on the surface). Theory predicts weak and broad surface-state absorption within the band gap with low oscillator strength[8,9] occurring as a long wavelength tail in the optical absorption spectrum. These transitions are likely to be coupled with intrinsic states.[8] In this study, the CdSe NPs formed at shorter times show deep trap states causing the long-wavelength absorption.[7,9] During the crystallization process of the CdSe NPs, surface atoms can be rearranged until a minimization in surface energy is reached.[8,13] The blue shift of the absorption, as the NPs develop, reflects the correspondingly gradual removal of the initial trap and surface states during the

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(14) (a) Norris, D. J.; Bawendi, M. G. *J. Chem. Phys.* **1995**, *103*, 5260−5268. (b) Norris, D. J.; Bawendi, M. G. *Phys. Rev. B* **1996**, *53*, 16338−16346. (c) Norris, D. J.; Sacra, A.; Murray, C. B.; Bawendi, M. G. *Phys. Rev. Lett.* **1994**, *72*, 2612−2615. (d) Nirmal, M.; Norris, D. J.; Kuno, M.; Bawendi, M. G.; Efros, Al. L.; Rosen, M. *Phys. Rev. Lett.* **1995**, *2001*, 3728−3731. (e) Nirmal, M.; Murray, C. B.; Bawendi, M. G. *Phys. Rev. B* **1994**, *50*, 2293−2300.

(15) (a) Soloviev, V. N.; Eichhöfer, A.; Fenske, D.; Banin, U. *J. Am. Chem. Soc.* **2001**, *123*, 2354−2364. (b) Soloviev, V. N.; Eichhöfer, A.; Fenske, D.; Banin, U. *J. Am. Chem. Soc.* **2000**, *122*, 2673−2674.

cystallization process. According to the model involving the focusing of the NP size distribution during the preparation of CdSe NPs,[4] the initially observed broad absorption could also be explained by an inhomogeneous size distribution, with subsequent focusing around 2.0 nm. However, this possibility is excluded since the blue shifted absorption would mean that the NPs significantly shrink with time, which is considered unlikely under these growth conditions.

In the assignment of the PL contributions, the band gap PL and the trap state PL should be considered. The band gap PL is narrow (width determined by the size distribution) and is only slightly Stokes-shifted from the absorption onset.[1−4] The trap state PL is broad and is substantially red shifted from the absorption onset (typically >0.2 eV).[1−4] The initial broad widths and large red shifts of the PLs are consistent with the characteristics of deep-trap emission in the NPs. This PL is thus assigned to transitions involving the trap states. The long tail emission suggests broad distribution of surface and defect states and relatively low density at each energy.[14,16] The change from a broad and asymmetric into a narrow and symmetric shape of the emission spectra of these CdSe NPs confirmed the conclusions from the UV−vis measurement that during the formation of these small CdSe NPs, the initial deep trap surface states were gradually removed. Moreover, the distribution of surface defect states became narrower as the surface gradually reconstructed and became more ordered. During this reconstruction, the NPs were gradually crystallized when the reaction proceeded over time.[1,17]

Previous work on larger NPs reported that the Stokes shift becomes smaller as the NPs grow.[1−4,14] In contrast, the Stokes shift of a molecule or small cluster is very small since it originates from the energy difference of the ground state vibrational levels. The increase in the Stokes shift is consistent with the gradual crystallization of NPs in that the NPs possessed mesostable structures with many defects (amorphous) in the beginning and they reconstructed and crystallized to minimize the total energy, thereby removing defects. The main contribution of the increased Stokes shift derives from the shift of absorption to the blue during the growth, with smaller contributions from the shift of PL to the red. This can be understood since the observation of the emission from surface-related states requires a much lower surface defect density, while the observation of surface-related absorption requires a high surface defect density. With a longer formation time (e.g., 90 min sample), the absorption quickly resembles the intrinsic transitions, while the emission is still quite affected by the surface defects. The Stokes shift of the CdSe sample after 90 min reaction was consistent with the extrapolated values from previous work.[14,16]

In the PLE spectra, the energies of the two excitation peaks were independent of the formation time of the CdSe NPs. This suggested that these are the intrinsic state transitions and that these CdSe NPs were the same size during the formation. They can be assigned to the lowest two excited states: $1S_{3/2}1S_e$ and $2S_{3/2}1S_e$, respectively, which match quite well with the extrapolated values from the PLE and transient differential absorption (TDA) measurements.[14] This assignment is also consistent with the theoretical predictions that the excitonic energy is not sensitive to the surface relaxation and reconstructions.[8] In addition, the transition intensity at 2.94 eV (423 nm) increased faster than the $2S_{3/2}1S_e$ transition at 3.28 eV (379 nm). This suggests that the lower excited state $1S_{3/2}1S_e$ is more strongly coupled to the surface states than the higher excited state $2S_{3/2}1S_e$. The gradual change in relative intensities is due to changes in the coupling with the surface states. At the same time, the energies of the transitions are not affected, supporting further that the measurements presented here describe the gradual crystallization of the CdSe NPs at a given size of 2.0 nm.

Summary and Conclusions

Although in most studies the growth and crystallization of NPs occur simutaneously,[2,4] here the crystallization process was isolated and studied in the controlled crystallization of CdSe NPs at an especially stable size of 2.0 nm under suitable conditions. The combination of HRTEM, XRD, UV−vis absorption, PL, and PLE results suggest that the CdSe NP samples over different formation times had similar sizes and that the initially formed 2.0 nm CdSe NPs underwent gradual crystallization at this particularly stable size, for the following reasons. First, the similar fwhms of the XRD and the similar feature of the PLE spectra over time suggested that these NPs had similar sizes since the PLE are mostly due to the transitions between the intrinsic states in the bands.[3,7,14] Second, HRTEM and XRD revealed that the initially formed CdSe NPs had amorphous structures, while the later ones were better crystallized. Third, the changes in absorption and emission of these CdSe NPs over time further displayed this process. The size around 2.0 nm with absorption at 3.00 eV (414 nm) has been suggested as a very stable structure for CdSe NP.[2,4,5] The initially formed amorphous CdSe nanoparticles gradually crystallized in the way that the deeper surface defects are first removed followed by the shallower ones. This involved rearrangement and reconstruction toward thermodynamic stability.[4] Thus, the gradual crystallization of CdSe NPs involves a surface reconstruction, consistent with other reports.[8,13] The Stokes shift of the CdSe NPs increases from 0.014 to 0.663 eV as the particle formed due to the energy difference between surface and intrinsic states (PL peak).

In a summary, optical techniques were combined with HRTEM and XRD to investigate the crystallization of small CdSe nanocrystals toward a stable size of 2.0 nm. This involves the gradual removal of the surface defects and reconstruction of CdSe NPs. Thus, the crystallization process is also a surface related phenomenon. The unique stability of this size of NPs allows the separation of the crystallization process from the growth. While the optical properties from the intrinsic states (PLE) are not much affected by the crystallization process, other optical properties, which are related to defects changes, are strongly influenced in this crystallization process.

Acknowledgment. The authors gratefully acknowledge financial support from NSF (CHE-0239688) and Provost's Opportunity Fund at Case Western Reserve University (PRI-3420700).

Supporting Information Available: XRD patterns of patterns of the CdSe nanoparticles formed for 10 and 90 min. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0458219

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(16) Efros, Al. L.; Rosen, M.; Kuno, M.; Nirmal, M.; Norris, D. J.; Bawendi, M. *Phys. Rev. B* **1996**, *54*, 4843−4956.

(17) Zhang, J.; Wang, X.; Xiao, M.; Qu, L.; Peng, X. *Appl. Phys. Lett.* **2002**, *81*, 2076−2078.