

Environmental Effects on Photoluminescence of Highly Luminescent CdSe and CdSe/ZnS Core/Shell Nanocrystals in Polymer Thin Films

Amjad Y. Nazzal,[†] Xiaoyong Wang,[†] Lianhua Qu,[‡] William Yu,[‡] Yunjun Wang,[§] Xiaogang Peng,^{*,‡} and Min Xiao^{*,†}

Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701,

Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701, and

Nanomaterials and Nanofabrication Laboratories (NN-Labs), Fayetteville, Arkansas 72704

Received: May 16, 2003; In Final Form: February 26, 2004

We report our systematic studies of the environmental effects on the photoluminescence (PL) from colloidal CdSe nanocrystals (NCs) embedded in polymer thin films. The highly luminescent bare-core CdSe NCs were significantly more robust than the core/shell CdSe/ZnS NCs against photoannealing under inert environments, while the core/shell NCs are more resistant to photooxidation. For the case of bare-core NCs, we show the importance of the initial photoactivation as the proper treatment for subsequent studies, a step that is basically irrelevant in the case of core/shell NCs. By measuring the PL wavelength shift, PL line width, and PL intensity, we investigated the dynamic changes of the emission properties of these NCs under different environments, including argon, oxygen, air, water vapor, and wet oxygen, and under different excitation conditions to reveal the photoinduced nature of the interactions between the nanocrystal surface and the environment. Mechanisms related to photoactivation, photooxidation, and PL enhancement are briefly discussed.

I. Introduction

Colloidal semiconductor nanocrystals (NCs) have attracted a lot of interest recently in the fields of physics, chemistry, biology, and engineering. The ability to control the optical properties of these NCs (through their size and shape) has made this field of material science very interesting for fundamental understanding and technological applications. Most importantly, such engineered NCs with controlled optical properties will impact applications that employ the emission properties of these NCs such as biological labeling,¹ optical and optoelectronic devices (such as optical switches, solar cells, LEDs, and lasers),^{2–10} and gas sensing.¹¹ Incorporating these NC structures in such devices and applications requires the understanding of their PL behaviors under different environmental and photoexcitation conditions.

The surface of colloidal semiconductor NCs and the immediate surroundings (environment) are very important in determining their PL properties.^{12–15} Previous investigations performed on NC systems dispersed in solutions have shown evidence for the important roles of reagent adsorption on the surface of the colloidal NCs and on their emission properties in the photoelectron-transfer processes.^{16–18} Many applications require the NCs to be dispersed on thin films. Investigations of the effects of the adsorption of different gaseous analytes (on the surface of the colloidal NCs) on the emission properties of colloidal NCs in polymer thin films are also of great importance and have attracted some interest recently.^{19–23}

These reports provide a good deal of scientific insight into the effect of different gaseous environments on the PL properties of different systems of CdSe NCs dispersed onto thin films.

These investigations include studying the effect of water molecules and other gases on the PL from CdSe NC monolayers,¹⁹ studying the influence of the surrounding atmosphere on the PL and blinking behavior and the effect of photooxidation and photobleaching of CdSe and CdSe/ZnS NCs embedded in polymer thin films,^{20–22} and the study of the photooxidation of monolayers of CdSe NCs by time-resolved PL spectroscopy.²³ However, these studies did not provide decisive conclusions on some of the important issues. For example, it is not clear whether the highly luminescent CdSe bare-core NCs are good candidates for fabricating LEDs, lasers, and other optoelectronic devices, in comparison to the commonly used CdSe/CdS and CdSe/ZnS core/shell NCs.^{8,12,13,24,25} Also, we recently reported that CdSe bare-core NCs embedded in polymer thin films showed significant photoactivation, brighter and sharper PL upon above-band gap photoradiation.¹¹ In this report, we will show that omitting photoactivation could be the actual reason behind the apparent discrepancies in the literature dealing with environmental effects of the PL of semiconductor NCs.^{11,19–23}

In general, the dynamic properties of the PL signals have not been thoroughly and systematically investigated previously, and such detailed studies are necessary for research in colloidal NCs, at least for the purposes of comparison between different NC systems and for potential applications.

In this work, we report our systematic studies of the PL properties, such as wavelength shift, PL line width, and PL intensity, from colloidal CdSe NCs embedded in acoustic and electronic highly insulating polymer thin films. We use two kinds of NCs, i.e., bare-core CdSe NCs and CdSe/ZnS core/shell NCs, and study their PL properties under different atmospheric environments, such as vacuum, air, Ar, O₂, and H₂O, and under different photoirradiation conditions. We first characterize the photoactivation stage,¹¹ which is needed to precede the PL-based investigations for these colloidal bare NCs. We demonstrate the photostability of the NCs under inert

* Corresponding authors. E-mail: mxiao@uark.edu, xpeng@uark.edu.

[†] Department of Physics, University of Arkansas.

[‡] Department of Chemistry and Biochemistry, University of Arkansas.

[§] Nanomaterials and Nanofabrication Laboratories (NN-Labs).

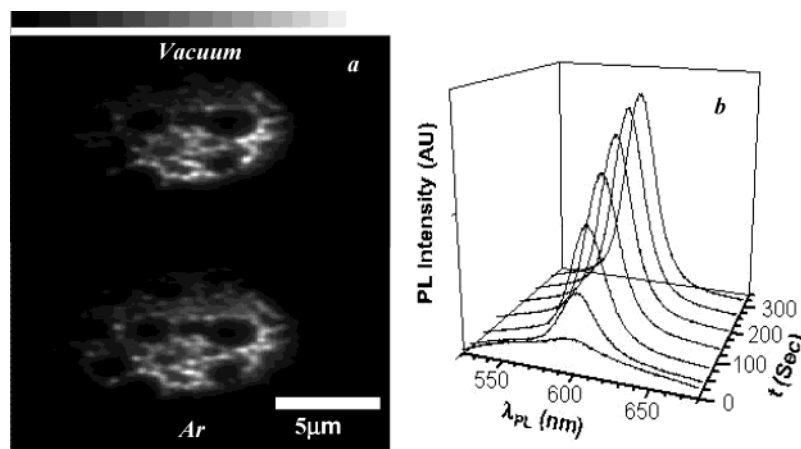


Figure 1. (a) CCD images of PL from a chosen spot of the CdSe NC film taken under vacuum (top) and under Ar gas (bottom), respectively. These images indicate high mechanical stability achieved in the experiments. (b) Evolution of the PL spectrum from NCs of sample A in the first 5 min during photoradiation under vacuum with an excitation intensity of 80 kW/cm² at 514.5 nm.

environments. Next, we show the dynamical evolutions of the PL signals during two photochemical processes, namely photo-oxidation due to exposure to oxygen molecules and photo-induced emission enhancement due to water molecules adsorbed onto the surfaces of NCs. We will also discuss effects under different photoexcitation conditions and their relevance to different photoinduced processes.

II. Experimental Description

We have investigated many samples of the high-quality plain (bare-core) CdSe NCs—synthesized using the alternative schemes^{12,13}—with different sizes and batches of synthesis as well as core/shell CdSe/ZnS NCs. Results presented in this paper are mainly from three sets of plain CdSe NC samples (labeled as A, B, and C, respectively) and core/shell CdSe/ZnS NCs (labeled as D).

The detailed synthesis procedure for sample A is discussed in ref 13. This sample was isolated at the bright PL point with a quantum yield of 85% at room temperature. The as-prepared solution of the sample has the first absorption peak at 598 nm and PL peak position at 609 nm with a PL line width of 28 nm.

For the detailed synthesis procedure of the CdSe NC core samples B and C, a different route^{12,13} was followed. Typically, 0.018 g of cadmium oxide and 0.160 g of stearic acid were put into a 25-ml flask and heated to 150 °C under Ar flow. After cadmium oxide was totally dissolved, the mixture was cooled to room temperature. Then, 1.940 g of trioctylphosphine oxide and 1.940 g of hexadecylamine were loaded into the flask and heated to 310 °C under Ar flow to obtain a clear solution. A selenium solution containing 0.056 g of selenium, 0.168 g of tributylphosphine, and 1.776 g of dioctylamine was swiftly injected into the hot solution. After the injection, the temperature was set as 285 °C for the growth of CdSe NCs. Aliquots (samples) were removed from the flask at the desired time (for obtaining certain size) and diluted by chloroform (CHCl₃). The as-prepared solution of sample B (C) has the first absorption peak at 598 (584) nm and the PL peak position centered at 610 (595) nm with PL-fwhm (full-width-at-half-maximum) of 24 (25) nm.

The core/shell NCs were synthesized as follows. First, CdSe core NCs were synthesized using the protocol by Qu et al.¹³ After reaction, the remaining precursors were removed using methanol/hexane extraction. The growth of the ZnS shell was achieved using a recently developed method, SILAR.²⁵ The CdSe core concentration was first measured by using Beer's

law with the reported extinction coefficients of CdSe NCs.²⁴ The Zn and S injection solution (zinc stearate, and S dissolved in ODE) were injected in an alternating fashion at 200 °C. The amount of shell precursors added into the growth solution for each monolayer was calculated on the basis of the size and concentration of the core NCs. The as-prepared core/shell CdSe/ZnS NC solution was purified via hexane/methanol extraction and is found to have its first absorption peak at 593 nm and PL peak position at 602 nm with line width of 23 nm.

All optical measurements were performed on thin film samples using a standard far-field microscopic setup. The thin film samples were prepared by mixing the diluted NCs solution (typically 1/10 of the as-prepared solution concentration) with 1% PMMA (poly(methyl methacrylate))—dissolved in the same solvent of the NCs solution, e.g., chloroform or toluene—and then spin-casting a drop of this mixture onto a UV-grade and pre-cleaned fused silica substrate. This will produce a thin PMMA film with NCs embedded on the polymer film with an average distribution of a few NCs/μm² of the film. The AFM (atomic force microscope) images of the film further reveal an average height of the film of about 300–500 nm. The 514.5 nm line of an argon-ion laser was used as an excitation source. A laser beam was directed normally, through a high-magnification microscope objective (50×, NA = 0.55, and a working distance of 13 mm) used for spatial resolution, onto the sample, and emitted light was collected by the same objective (reflection mode). The scattered laser light was blocked by a notch filter. PL light is directly projected into the spectrometer, and then detected by a liquid nitrogen-cooled CCD camera. The PL images were obtained using a flat mirror in place of the grating inside the spectrometer. All the PL images and spectra were taken at room temperature.

For optical characterizations under vacuum (typically 10^{−3} Torr) and under different gases, the sample was mounted tightly in a sealed flow chamber with an optical window. Gases could be bubbled through a sealed flask that contained deionized and degassed water, carrying its vapor into the chamber at a flow rate that will maintain one atmosphere of pressure inside the chamber. The chamber is mounted on a micro-movement-controlled XYZ translation stage for sample positioning. High mechanical stability has been achieved, as shown in Figure 1a. Upon gas purging or evacuating the chamber, the maximum shift in the (in-plane) position of the sample was less than 1 μm (typically 0.3 μm). CCD images (integration time 1–5 s, typically) were taken every time the chamber was vented or

evacuated to make sure that the spot under investigation has not moved. Integration time used for the PL spectra was typically in the order of 100 ms. An argon-laser-pumped dye laser was used for exciting the samples with wavelengths below the band gaps of the NCs.

We observed initial blue-shifts of PL peak positions of around 10, 4, and 2 nm in the thin film samples when cast with plain NC samples of A, B, and C, respectively, compared to their PL peaks in solution. This blue-shift was found to vary from sample to sample, and from one size to another (even within the same synthesized batch). However, the results described below are generally valid for all samples tested. Such a blue-shift was not observed for the core/shell NCs when cast onto the solid film.

III. Results and Discussions

In the following, we describe the experimental measurements performed on these thin film samples of CdSe NCs under different environments. Figure 1a, shows the high mechanical stability of our mounting platform and flow chamber. Achieving this was very crucial to ensure that changes observed on the PL signal, when the atmosphere was altered, are arising from the same NCs under consideration. To closely monitor this significant issue, CCD images were taken whenever the flow chamber was evacuated or vented, as demonstrated in Figure 1a.

The first step was to establish a well-defined reference point (NCs in a vacuum) for the subsequent measurements. This was achieved by pre-photoactivation, to bring the NCs to a stable state of emission.

Photoactivation and Photostability under Inert Environments. PL properties of highly luminescent CdSe plain core NCs show significant photoactivation, e.g., brighter and sharper PL spectra upon photoradiation with the photon energy above band gap of the NCs.¹¹ Here, we further deal with this important issue, to shed some light into this interesting phenomenon. To provide a complete picture for this, a small portion of this section will be used to provide some information similar to what we reported previously.¹¹

In preparing samples for optical measurements, we maintained a medial level of average concentration of CdSe NCs on films (a few NCs/ μm^2), as shown in Figure 1a. We first place the sample in a vacuum environment (10^{-3} Torr) and excite the sample with an intensity of 80 kW/cm² ($\lambda_{\text{excitation}} = 514.5$ nm). In the case of plain CdSe NCs, the PL signal (sample A) changes after the excitation laser is first turned on, as shown in Figure 1b, which starts weak with a broad profile, then it becomes narrower in width and higher in intensity during continuous photoradiation.

Figure 2 plots changes in the PL peak shift, PL fwhm, and PL intensity. As one can see clearly, all these quantities are stabilized after about 60 s. These stabilized values can serve as reference points for the subsequent studies under different environments (with possible photochemical processes). We consider this process as the photoactivation stage,¹¹ a necessary step before all other optical measurements.

The PL peak wavelength, as shown in Figure 2a, fluctuates slightly (within 1 nm) at the beginning before reaching its final value of around 600 nm for this specific sample. However, the temporal evolutions of the PL fwhm and PL intensity during the photoactivation stage were very dynamic and can typically be best fitted by multiple exponential functions. In Figure 3, the dependences of the major (shortest) time constants for PL fwhm and PL intensity during the photoactivation stage are

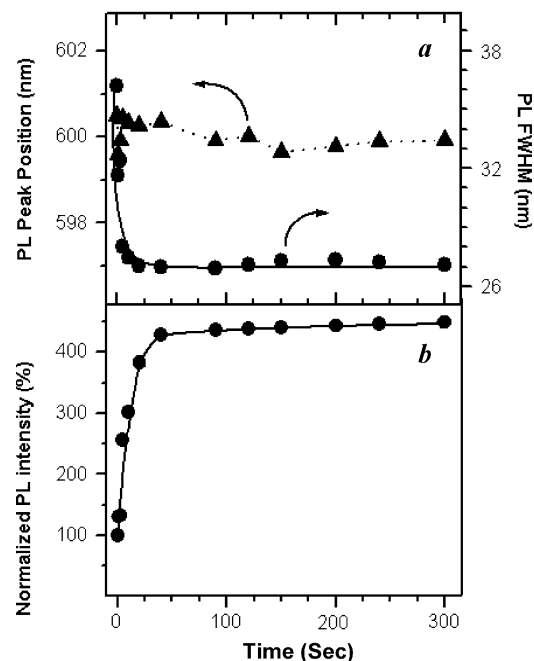


Figure 2. Dynamic evolutions of PL properties from NCs (cast from sample A) during the photoactivation process in a vacuum. The sample is continuously irradiated by a 80 kW/cm² of 514.5 nm laser light. Changes of (a) PL peak position (left axis), PL fwhm (right axis), and (b) PL peak intensity as a function of exposure time.

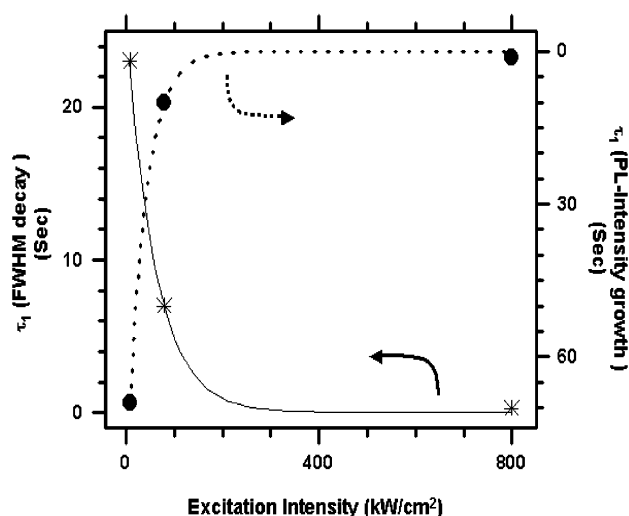


Figure 3. Shortest (and dominate) time constants of dynamic multi-exponential changes of PL fwhm (left axis) and PL intensity (right axis) as a function of excitation intensity at 514.5 nm. The measurements were done in the photoactivation process on the NC thin film sample cast from sample C.

plotted for different excitation powers. The other (longer) fitted time constants show similar trends and one can easily see that the NCs will activate faster if they are excited by a higher light intensity. The results in Figures 2 and 3 suggest that the narrowing and brightening of the PL of CdSe NCs are closely related.

A simple model, considering the different environments for the NCs in the solution and when embedded in the polymer film, can be used to explain this photoactivation process. This model is in the context of the position optimization of the surface ligands due to excited LO phonons that eventually lead to an optimized bonding state between the ligands and the surface atoms of the NCs. The decrease of the line width during

photoactivation to eventually mimic that in solution supports this suggestion.

Heating effect is not thought of as playing a significant role in discussing this photo-activation process. This is so for the following two reasons. First, heating is known to hinder the PL efficiency of NCs.²⁶ Second, leaving an activated (or partially activated) sample of NCs in the dark for a few hours does not change their state of emission.

To further investigate the nature of the photoactivation process in our CdSe NCs, we used a dye laser to provide a continuous excitation source. When the NCs were irradiated with below-the-band gap radiation, they could still be photoactivated, but with a much slower rate compared to the case of using an above-the-band gap excitation. For example, photoactivating a NC spot with below-the-band gap excitation (for PL intensity to reach 500% of the initial value) takes about 10 min, while it only takes less than one minute to fully photoactivate the NCs ($\sim 500\%$ of the initial value) with an above-the-band gap excitation (the same laser power and focusing spot were used). However, our simple model cannot explain why a below-the-band gap light can carry out such an activation process. Further investigations are needed to fully understand the roles of phonons in bonding optimization of the ligands and surface atoms of the NCs in a solid polymer film.

For all optical measurements described below, the plain CdSe NC spots under study were all photoactivated first for about 15 min under vacuum, to account for the variations observed in the activation time among different NC samples, except when noted otherwise. In this way all the measured data under different environmental conditions can be directly compared with a common reference point, which is essential for our systematic studies.

Those photoactivated plain NCs in the polymer thin films are extremely stable in a vacuum or in an inert atmosphere, such as Ar. As was shown in Figure 2 of ref 11, the PL peak position, PL fwhm, and PL intensity emitted from the NCs in a selected spot (from sample A) do not show any significant changes in an Ar atmosphere under continuous photoradiation for about 2 h (80 kW/cm² of 514.5 nm excitation laser). The PL peak position shifts to the blue side about 0.3 nm, the PL intensity fluctuates within $\pm 2\%$ of the saturation (activated) level, and the PL-fwhm shows to be extremely stable. In Ar or under vacuum, we have not noticed any significant variations of the PL properties for all plain core samples that we have tested. This fact indicates the unique behavior of these NCs in terms of being highly sensitive (as will be shown later) to the surrounding environment, yet at the same time, they are proven to be robust and very resistant to aging and bleaching effects even with extreme photoexcitation conditions under chemically inert environments.

This result is in agreement with a previous observation by Cordero et al.,¹⁹ where the inert environments such as Ar and N₂ had no influence on the fluorescence intensity, although our results on O₂ and water vapor (see below) are different from their observations.

As for the case of core/shell NCs, under inert atmosphere and continuous illumination (light with photon energy below and above the NC's band gap), the PL signal from CdSe/ZnS NC polymer films did not show any intensity enhancement. In contrast to the plain core NCs, the PL from core/shell NCs quenches under extended continuous illumination time periods until the NCs are completely photobleached. As an example, Figure 4 displays typical behaviors of the PL signal from core/shell NCs under continuous illumination in a vacuum. As shown

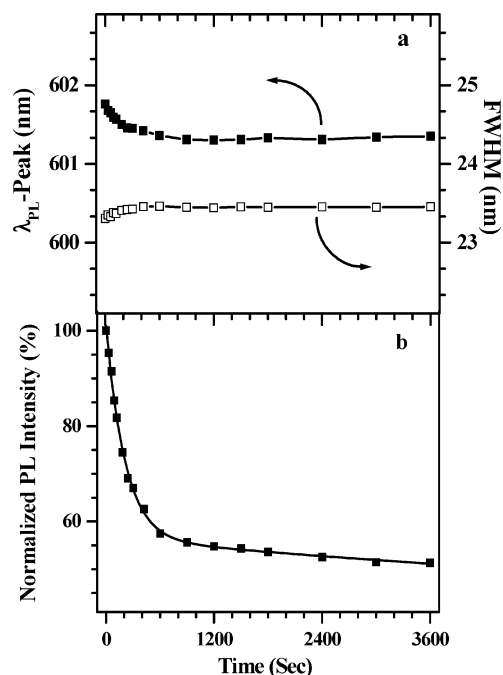


Figure 4. Dynamical evolutions of the PL properties from core/shell NCs (cast from sample D) in a vacuum under continuous irradiation by an 80 kW/cm² of 514.5 nm laser beam. Changes of (a) PL peak position (left axis), PL fwhm (right axis), and (b) PL peak intensity as a function of exposure time.

in Figure 4a, the PL peak position shifts insignificantly to the blue side (less than 0.4 nm) and similarly the line width widens (less than 0.2 nm) in the first 10 min and then stabilizes over the course of the experiment. As for the PL intensity, the dramatic change during the continuous exposure to light is depicted in Figure 4b, where, as can be seen, the intensity drops by more than 40% in the first 10 min of illumination and then continues to drop on a slower rate over the time of exposure. Monitoring the PL signal for a longer (hours) illumination period shows that the NCs will eventually be photobleached completely without showing any change over the line shape. These observations are in agreement with the results obtained by van Sark et al.,^{21,22} where it was found that single CdSe/ZnS NC would photobleach under N₂ without shifting to shorter wavelength of the PL peak position. The photobleaching time was found, as expected, to depend on the excitation intensity where NCs would photobleach faster if the excitation intensity was increased. This photobleaching in core/shell CdSe/ZnS NCs in thin films has been observed previously in single NCs both at room temperature^{21,22,27} and at cryogenic temperatures²⁸ with reported photobleaching times for single NCs on the order of few minutes. Still, the nature of this photoinduced quenching effect has not been explained.

Photooxidation under O₂. When either the plain core or core/shell NC film samples were placed in the O₂ atmosphere, the PL properties (peak position, fwhm, and intensity) behaved very differently when compared to the behavior under inert environments, as shown in Figure 5 for sample A with continuous laser irradiation (80 kW/cm² of 514.5 nm). The peak position shifts to the blue side following an exponential decay with a decay time constant of 29 s. Further irradiation makes the peak position reach a saturated value of around 570 nm eventually (not shown in Figure 5a). The second blue-shift regime of the PL peak position (from 580 to 570 nm) is found to be much slower and can be fitted well by a biexponential function, which makes the total fitting function for the PL peak

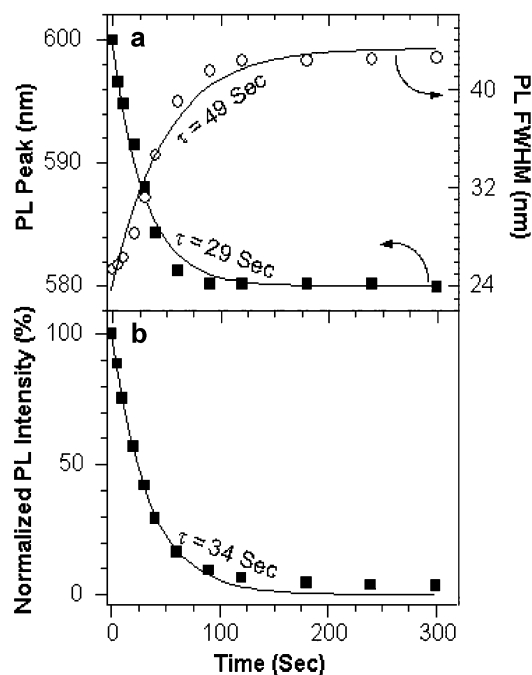


Figure 5. Dynamical evolution of the PL properties from NCs (cast from sample A) in O_2 under continuous irradiation by an 80 kW/cm^2 of 514.5 nm laser light. Changes of (a) PL peak position (left axis), PL fwhm (right axis), and (b) PL peak intensity as a function of exposure time, with shortest (and dominant) time constants of 29 s, 49 s, and 34 s, respectively.

position as a function of irradiation time to be triple-exponential with fitting time constants in the orders of 10, 100, and 1000 s, respectively.

A similar argument holds for the evolution of the PL fwhm, where it also follows an exponential growth route. The PL fwhm almost doubles to around 43 nm in the five minutes shown with an exponential growth time constant of 49 s. During irradiation, the line profile gets significantly distorted and loses its symmetry, which shows fluctuation of few nanometers as the line width starts to saturate before the NCs stop emitting light.

The evolution of the PL intensity under continuous irradiation also shows exponential decay behavior, as shown in Figure 5b, with a drop of 90% in the intensity reading in the first five minutes (with a decay time constant of 34 s). In general, under continuous irradiation in an O_2 environment, the PL peak position and intensity decrease in a multiexponential fashion with time constants in the orders of 10, 100, and 1000 s, respectively. The same orders of magnitude were found for the exponential increase of the PL fwhm.

In the present experiment, the nature of the photooxidation product has not been analyzed. Previous investigations have confirmed the formation of $CdSeO_x$ ($x = 2^{29,30}$ and $x = 3^{31}$) on the surfaces of the CdSe NCs as the outcome of their photooxidation. It has also been reported³² that the surfaces of CdSe NCs can be oxidized without the need of intense photoexcitation (ambient conditions) with the formation of SeO_2 as its product. Also XPS experiment³² has shown that O_2 , assisted by light, will bind to selenium atoms forming evaporating oxides. The formation of these oxides on the surface layers of the NCs will cause the effective core diameter of the NCs to decrease. It is estimated that such a blue-shift (30 nm) in the emission wavelength is attributed to about 1 nm decrease in the diameter, which corresponds to the oxidation of about 1 to 2 monolayers of CdSe from the surface of each NC.^{24,22}

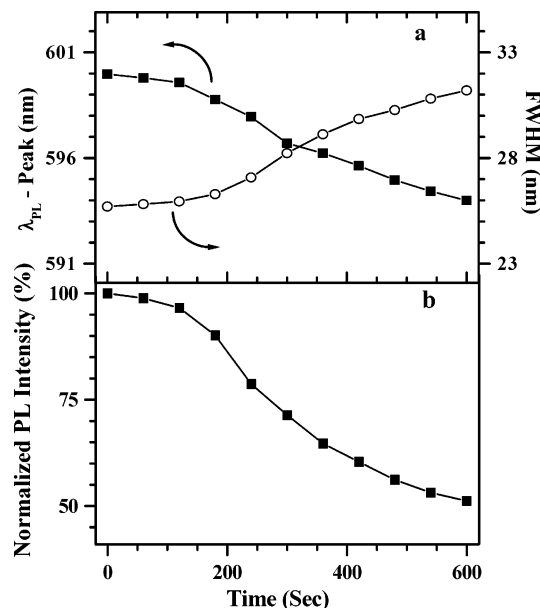


Figure 6. Dynamical evolutions of the PL properties from NCs (cast from sample A) in O_2 under dark-flow measurement conditions by an 80 kW/cm^2 of 514.5 nm laser light. Total light exposure time is about 20–30 s and total experiment time is 600 s. Changes of (a) PL peak position (left axis), PL fwhm (right axis), and (b) PL peak intensity as a function of exposure time.

To confirm the need of photoexcitation for the induction of photooxidation, and to isolate this from other effects, like the other reported (dark) oxidation processes,³² we carried out the PL experiment under a dark environment. Basically, the NCs are exposed to the excitation light only for measuring the PL. Figure 6 shows the PL results of a spot that was kept under flowing O_2 for 10 min. PL data points on this figure represent exposure of the NCs to the laser beam (80 kW/cm^2 of 514.5 nm laser) for a couple of seconds to acquire the luminescent spectrum with the laser beam blocked immediately afterward. During this 10 min time period (the course of the experiment), the total exposure time was estimated to be between 20 and 30 s. As can be seen from Figure 6a, the PL peak position has blue-shifted by an amount of around 6 nm and the PL fwhm has increased also by around 6 nm. Figure 6b shows that the PL intensity has dropped to around 50% of its initial value after photoactivation under vacuum.

Comparing these to the results under continuous irradiation, like the ones shown in Figure 5, we find that 20–30 s of continuous exposure time will, on the average, cause the PL peak position to blue-shift by around 10 nm, the PL fwhm to increase by around 6 nm, and the PL intensity to drop to half. This agreement in the two equivalent photoexcitation measurements (continuous 20–30 s irradiation and pulsed irradiation with the same equivalent total exposure time) clearly implies that these dynamical changes in the PL signal are induced by the intense photoexcitation under the O_2 atmosphere, and confirms the occurrence of the photooxidation process. Our results also indicate that the photobleaching caused by photooxidation is irreversible, in agreement with previous report.²¹ Our results also contradict those of ref 19, where it was reported that the PL intensity from CdSe NCs was not affected in an O_2 environment.

As for the case of core/shell CdSe/ZnS NCs, the PL signal under O_2 shows similar behaviors as those of the plain core NCs although the dynamical behaviors are slightly different. Typical dynamic evolutions for the PL signal from a group of core/shell NCs (cast from sample D) in the polymer film under

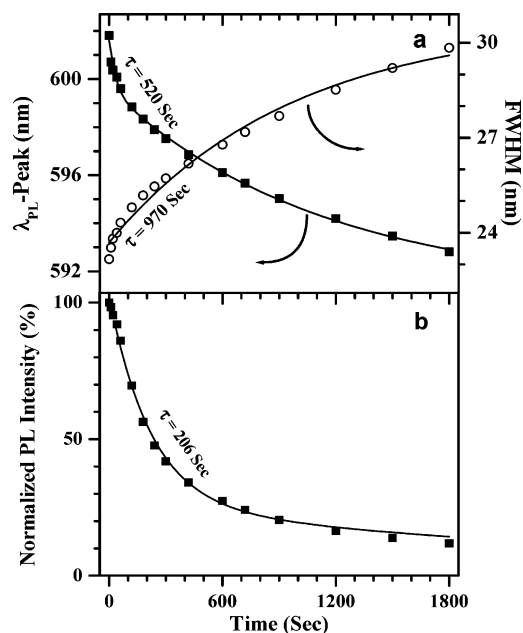


Figure 7. Dynamical evolutions of the PL properties from core/shell NCs (cast from sample D) in O_2 under continuous irradiation by an 80 kW/cm^2 of 514.5 nm laser light. Changes of (a) PL peak position (left axis), PL fwhm (right axis), and (b) PL peak intensity as a function of exposure time, with dominant time constants of 520 s, 970 s, and 206 s, respectively.

continuous illumination (using 80 kW/cm^2 of 514.5 nm laser light) in O_2 atmosphere are shown in Figure 7. Photooxidation is manifesting itself through the blue-shift in the PL peak position, the widening of the line width, and the quenching of the PL intensity. However, compared to the case of plain NCs and under the same conditions, the rate of photooxidation is much slower in the case of the core/shell NCs. The best fitting curves describing the exponential growth (of the fwhm) and the exponential decays (of the PL peak wavelength and PL intensity) are more complicated. However, single or double exponential curves can give reasonable fits to these curves, as shown in Figure 7. The fitting time constants are an order of magnitude larger than the case of plain NCs. Continuing to monitor (around 2 h) the PL signal of NCs from sample D under these conditions reveals that the NCs would completely photobleach with the PL peak at around 590 nm and line-width of around 31 nm. In addition to the slower oxidation rate and the smaller changes over the line shape in the case of core/shell NCs, the trace of the PL peak wavelength (fwhm) does not show a tendency of converging as the NCs are quenched, it just follows a much slower second exponential decay (growth) route ($\sim 10^5$ s).

Two main factors play significant roles in complicating the picture in view of these observations on PL properties of core/shell NCs. First, the photooxidation is evidently accompanied by photobleaching which was shown to affect only the PL intensity but not the line shape. How much each process contributes to the quenching of the PL intensity would be an important question to answer. Understanding the nature of photobleaching in these NCs would be the first step toward uncovering the underlying mechanism, which requires more detailed analysis beyond the current PL probe in order to clarify these observed phenomena. The second factor, which assumes that photooxidation is well understood in plain CdSe NCs, is related to the role of the inorganic ZnS capping layer. Recently, experimental evidence^{21,22} has confirmed the reduction of the photooxidation rate when the thickness of the capping layer is

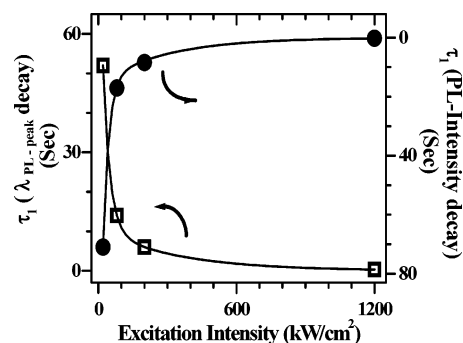


Figure 8. Shortest (and dominant) time constants of PL peak position (left axis) and PL intensity (right axis) dynamic multiple-exponential changes as a function of excitation intensity at 514.5 nm. The measurements were done in air on the NC thin film sample cast from sample B.

increased in CdSe/ZnS NCs. This could explain the slower oxidation rate in core/shell NCs compared to the plain ones. However, the mechanism of photooxidation and dark oxidation in core/shell NCs is still an unresolved issue that needs to be addressed.

Photooxidation in Air. Under continuous irradiation in normal air environment, the PL signal from plain CdSe NCs shows similar dynamic behaviors as observed under O_2 , but with larger fitting time constants. Both the PL peak position shift and PL intensity decrease follow triple-exponential function with time constants in the orders of tens, hundreds, and thousands of seconds, respectively. The same orders of magnitude were also found for the exponential increase of the PL fwhm. For example, for NCs cast from sample A, the shortest and dominant time constants for the PL peak position, PL intensity, and PL fwhm are obtained to be 48, 81, and 78 s, respectively, and show a slower (around 50% on average) photooxidation dynamics under air ambient than that under pure O_2 environment, as expected.

We also measured the dependence of the photooxidation process on the excitation intensity (at 514.5 nm) and found that the higher the excitation intensity is, the faster the NCs would be photooxidized and photobleached. The shortest (and dominant) time constant of both, the PL peak position and PL intensity decays, decreases exponentially as the excitation intensity increases, as shown in Figure 8.

In an attempt to study the relation between photooxidation and the photon energy used to irradiate the NCs, we scanned the tunable dye laser from below to above the band gap of the NCs. We found that light with photon energy below the band gap *does not* induce photooxidation. For example, when irradiating plain CdSe NCs (cast from sample B) with 625 nm light at an intensity of 200 kW/cm^2 for an hour, the PL signal shows no sign of photooxidation compared to the initial state (fully photoactivated under vacuum). On the contrary, the PL intensity gets a little further enhanced after such a long exposure to such intense radiation, probably due to the further photoactivation by the radiation.

The kinetics of the PL properties under air are in good agreement with previous investigations,¹⁹ where similar behaviors and fitting time constants were obtained. However, in the previous report,¹⁹ a significant initial increase (decrease) in the PL intensity (fwhm) was observed, which must be due to the lack of pre-photoactivation. At the beginning of illumination, there is a competition between photoactivation and photo-oxidation, which could cause a misrepresentation of the PL kinetics. We can get the same PL dynamics as that of ref 19 by simply skipping the photoactivation stage.

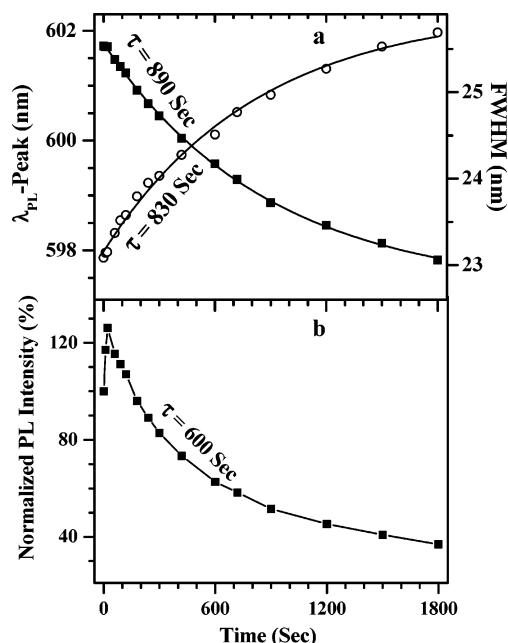


Figure 9. Dynamical evolutions of the PL properties from NCs (cast from sample D) in air under continuous irradiation by an 80 kW/cm^2 of 514.5 nm laser light. Changes of (a) PL peak position (left axis), PL fwhm (right axis), and (b) PL peak intensity as a function of exposure time, with shortest (and dominant) time constants of 890 s, 830 s, and 600 s, respectively.

The dynamics of the PL signal from core/shell NCs under continuous illumination (above the band gap light) in air shows another complication, as shown in Figure 9. The PL peak emission wavelength and fwhm follow the same trends as those observed in a pure O_2 atmosphere with similar fitting curves but much slower rates (larger time constants), an indication of slower photooxidation in air. However, the PL intensity shows an initial increase (20–50%) before it starts to decay down, following the exponential decay route that was observed during the photooxidation process in the pure O_2 atmosphere. This behavior cannot be explained with the previous arguments. We believe that slower photooxidation rate and this initial PL enhancement are an indication of a competition with another photoinduced interaction. As will be discussed in the following, such a behavior can be understood if we consider the interaction between the NCs and the H_2O molecules existing in air.

PL Enhancement by H_2O Molecule Passivation. One of the important active components of the ambient atmosphere is water vapor. Understanding the effect of water molecules on the luminescent properties of CdSe NCs with different chemistry surfaces would be of great importance toward better understanding the role of NC surfaces on the optical properties. It was reported^{33,34} that PL from bulk CdSe surface could be enhanced by an order of magnitude when electron-donating molecules (Lewis basis) get adsorbed on the surface, in contrast to the Lewis acids, which cause a reduction in PL yield.³⁵ Recently, there have been some efforts toward enhancing the luminescent quantum yield in CdSe NCs by adsorbed water molecules on their surfaces.¹⁹ The proposed model suggests that the adsorbed water molecules can passivate the surface trap states and, hence, improve the luminescence efficiency.

To study the effect of water molecules on the PL properties, the chamber under vacuum was vented to Ar gas that was bubbled through deionized and degassed water. Typical results of this experiment are shown in Figure 10, where the selected spot of plain CdSe NCs was illuminated (with 80 kW/cm^2 of 514.5 nm laser light) under H_2O vapor for 5 min. As can be

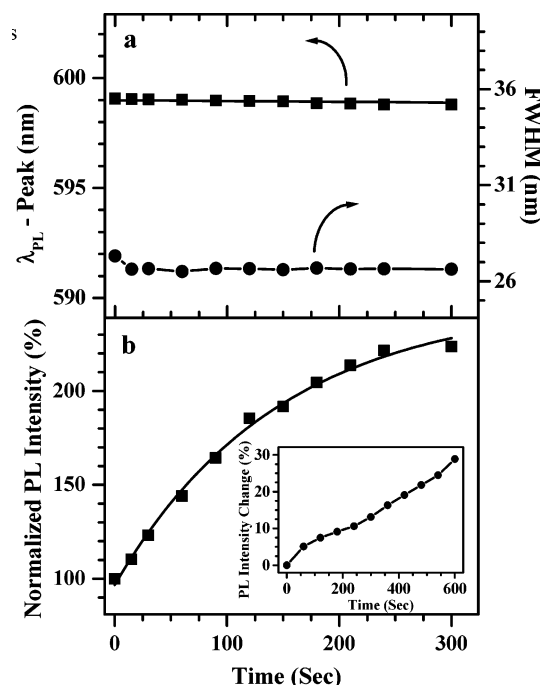


Figure 10. Dynamical evolutions of the PL properties from NCs (cast from sample A) in H_2O under continuous irradiation by an 80 kW/cm^2 of 514.5 nm laser light. Changes of (a) PL peak position (left axis), PL fwhm (right axis), and (b) PL peak intensity as a function of exposure time. Inset of (b): PL intensity change of the same sample in H_2O under dark flow measurements. Total light exposure time is about 20–30 s, and total experiment time is 600 s.

seen in Figure 10a, over the course of the experiment, the PL peak position shows no sign of blue-shift and, similarly, the PL fwhm also maintains a stable value. These results indicate that oxidation did not occur, which is reasonable since all oxygen molecules were removed from the system prior to the measurements. However, Figure 10b shows that the PL intensity has enhanced by more than 100% over the continuous light exposure period. These results are common for all samples measured in our experiments. These changes in the PL signal are not due to the photooxidation process, as was reported earlier.¹⁹

The need for light irradiation to enhance the PL intensity of the CdSe NCs under H_2O environment is demonstrated by performing the dark flow measurements. First, the vacuum chamber was vented to wet Ar, which was flowing in the chamber and, then, the spot of NCs under investigation was exposed to the excitation laser (80 kW/cm^2 of 514.5 nm light) only for measurement purpose. As in the measurement discussed in Figure 6, the total time of exposure to the excitation light was around 20–30 s in a total dark flow time of 10 min. Our results show that the PL peak position and PL fwhm do not show any changes, as in Figure 10a. The PL intensity, on the other hand, shows an enhancement by a factor of 30%, as shown in the inset of Figure 10b. Comparing this result to the continuous radiation case (Figure 10b), we see that a continuous irradiation of 20–30 s under H_2O leads to around 30–40% enhancement in the PL yield. Such an agreement demonstrates that this PL emission enhancement is a light-assisted process.

Our data further reveal a semi-reversible behavior in the effects caused by water molecules when the NCs were brought to vacuum again. Our results suggest that the bonding of water molecules to the CdSe NC surfaces is strong. With the vacuum capabilities that we had (10^{-3} Torr), we could only partially remove some of the water molecules from the NC surfaces, which is evident from the PL intensity drop seen during and

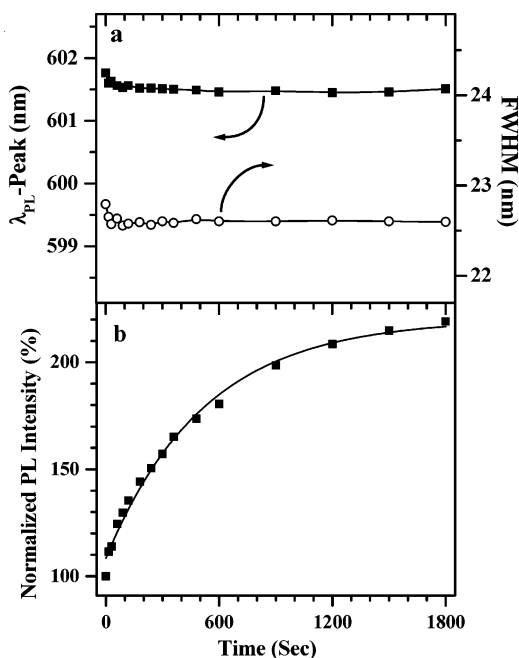


Figure 11. Dynamical evolution of the PL properties from NCs (cast from sample D) in H_2O under continuous irradiation by an 80 kW/cm^2 of 514.5 nm laser light. Changes of (a) PL peak position (left axis), PL fwhm (right axis), and (b) PL peak intensity as a function of exposure time.

after bringing the NCs to vacuum again. This semi-reversible behavior of the PL intensity under H_2O agrees with a previous report¹⁹ and suggests the need for further surface analysis.

As for the PL behaviors of the core/shell NCs in an H_2O vapor atmosphere, typical responses are presented in Figure 11. The general behaviors are very similar to the case of plain NCs. Under continuous illumination with 80 kW/cm^2 of 514.5 nm laser light, the PL peak position has a very small blue-shift (around 0.3 nm) initially and then stabilizes. Similarly, the PL fwhm decreases by around 0.2 nm at the beginning of the light exposure and then approaches a constant value, as shown in Figure 11a. However, in a manner similar to the case of the plain NCs, the PL intensity gets enhanced by more than 100% over the exposure period (half an hour). This is an indication that even core/shell NCs can be passivated by water molecules as they adsorb on the surface of the NCs, reducing the quenching surface trap states and hence enhancing the PL emission. As expected, the existence of the ZnS layer plays the role of a barrier by slowing down this interaction. This is clear from Figure 11 since it takes more than five times longer for the core/shell NCs to show the same amount of intensity enhancement, compared to the plain NCs under the same conditions. With this observation, it becomes easier to interpret the response of the PL signal from these core/shell NCs in air atmosphere (Figure 9b). Under air atmosphere the NCs interact with both O_2 and H_2O molecules. It is likely that the adsorption of the water molecules has a faster rate initially than O_2 adsorption, causing the initial enhancement of the PL intensity. Later, the adsorption rate of O_2 molecules increases and photooxidation becomes the dominant process. In addition to that, the strong resistance of the core/shell NCs to photooxidation may play an important role in such competition.

Photooxidation under Wet O_2 . To put the above-mentioned two processes under the test, we placed the thin film sample of plain CdSe NCs in an environment where only wet O_2 was present (O_2 bubbled through deionized water). As expected, the dynamics induced by photooxidation dominate the changes in

the PL signal, which shows similar dynamics behaviors as in the case of photooxidation under air and dry O_2 environments. Our results indicate that the dynamical changes of the PL signal and the photobleaching induced under the wet O_2 environment were, as expected, slower than under the dry O_2 environment, which can simply be attributed to the resistance arising from the enhancement induced by the adsorbed water molecules. When comparing the dynamical changes of the PL signal under wet O_2 to the case under ambient air, we found that, generally, the dynamical evolutions under air are slower. This might be expected since there are less O_2 concentrations available in air than in the wet O_2 mixture.

IV. Conclusion

In summary, the PL properties of highly luminescent plain CdSe NCs and core/shell CdSe/ZnS NCs, incorporated into polymer thin films, were investigated. In comparison to the core/shell NCs, the plain core NCs were found to be extremely stable against photoannealing in inert environments even under intense, above-the-band gap photoradiation for a long exposure time. To make optical studies more consistent and reproducible, these NCs need to be photoactivated in an inert environment or vacuum prior to the optical measurement. This continuous illumination will recover part of the emission quantum efficiency of the NCs, which was quenched as the NCs are transferred from the solution to the solid film. For the core/shell NCs, such a step is not necessary and, on the contrary to the plain NCs, the core/shell NCs show a photobleaching effect under inert environments.

However, for the plain NCs under environments containing O_2 (dry O_2 , wet O_2 , and air), the continuous irradiation with intense, above-the-band gap light makes the PL peak position to blue-shift, PL fwhm to broaden, and PL intensity to decrease, all resulted from photooxidation. Intense light with photon energy below the band gap *does not* induce photooxidation, although it does photoactivate the NCs (slower than light with photon energy above the band gap). The photooxidation of the plain NCs shows a faster dynamics than the core/shell NCs, indicating the insulating nature of the inorganic layer to oxidation.

Our experiments also confirmed that the adsorbed water molecules on the surfaces of the NCs could enhance the luminescence dramatically without causing any oxidation in both types of NCs. The enhancement rate can be more than 5 times faster in plain NCs than in core/shell NCs.

According to our measurements, and in the case of NCs being embedded in solid films, colloidal NCs with different surface chemistries (bare and inorganic over coated) show different responses to photoexcitation under different environments. The ability to producing plain CdSe NCs that show a high luminescent yield and yet are more robust to photobleaching effects compared to core/shell NCs under inert environments, shows the need of re-addressing the role of the inorganic capping vitality to the stability of optical properties in these colloidal NCs. Understanding the surface properties and surface interactions with environment is crucial and will lead to great impacts for potential optoelectronic, biological, and emission-based applications.

Acknowledgment. Funding support of this work was provided by the National Science Foundation.

References and Notes

- (1) Jaiswal, J. K.; Mattoussi, H.; Mauro, J. M.; Simon, S. M. *Nature Biotechnology* **2003**, *21*, 47–51.

- (2) Bawendi, M. G.; Carroll, P. J.; Wilson, W. L.; Brus, L. E. *J. Chem. Phys.* **1992**, *96*, 946–954.
- (3) Empedocles, S.; Bawendi, M. G. *Acc. Chem. Res.* **1999**, *32*, 389–396.
- (4) Heath, J. R. *Science* **1995**, *270*, 1315–1316.
- (5) Tittel, J.; Göhde, W.; Koberling, F.; Basché, T.; Kornowski, A.; Weller, H.; Eychmüller, A. *J. Phys. Chem. B* **1997**, *101*, 3013–3016.
- (6) Colvin, V.; Schlamp, M.; Alivisatos, A. P. *Nature* **1993**, *370*, 354–357.
- (7) Brus, L. *Appl. Phys.* **1991**, *53*, 465–474.
- (8) Collier, C. P.; Vossmeier, T.; Heath, J. R. *Annu. Rev. Phys. Chem.* **1998**, *49*, 371–404.
- (9) Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013–2016.
- (10) Peng, X.; Schlamp, M. C.; Kadavanich, A. V.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1997**, *119*, 7019–7029.
- (11) Nazzal, A. Y.; Qu, L.; Peng, X.; Xiao, M. *Nano Lett. (Communication)* **2003**, *3*, 819–822.
- (12) Qu, L.; Peng, Z. A.; Peng, X. *Nano Lett.* **2001**, *1*, 333–337.
- (13) Qu, L.; Peng, X. *J. Am. Chem. Soc.* **2002**, *124*, 2049–2055.
- (14) Malý, P.; Kudrna, J.; Trojáněk, F.; Mikeš, D.; Němec, P.; Maciel, A. C.; Ryan, J. F. *Appl. Phys. Lett.* **2000**, *77*, 2352–2354.
- (15) Aldana, J.; Wang, Y. A.; Peng, X. *J. Am. Chem. Soc.* **2001**, *123*, 8844–8850.
- (16) Dannhauser, T.; O’Neil, M.; Jhonson, K.; Whitten, D.; McLendon, G. *J. Phys. Chem.* **1986**, *90*, 6074–6076.
- (17) Horváth, O.; Fendler, J. H. *J. Phys. Chem.* **1992**, *96*, 9591–9594.
- (18) Bavykin, D. V.; Savinov, E. N.; Parmon, V. N. *Langmuir* **1999**, *15*, 4722–4727.
- (19) Cordero, S. R.; Carson, P. J.; Estabrook, R. A.; Strouse, G. F.; Buratto, S. K. *J. Phys. Chem. B* **2000**, *104*, 12137–12142.
- (20) Koberling, F.; Mews, A.; Basché, T. *Advanced Materials (Weinheim: Germany)* **2001**, *13*, 672–676.
- (21) van Sark, W. G. J. H. M.; Frederix, P. L. T. M.; Van den Heuvel, D. J.; Gerritsen, H. C.; Bol, A. A.; van Lingen, J. N. J.; de Mello Donega, C.; Meijerink, A. *J. Phys. Chem. B* **2001**, *105*, 8281–8284.
- (22) van Sark, W. G. J. H. M.; Frederix, P. L. T. M.; Bol, A. A.; Gerritsen, H. C.; Meijerink, A. *Chem. Phys. Chem.* **2002**, *3*, 871–879.
- (23) Wang, X.; Zhang, J.-Y.; Nazzal, A.; Xiao, M. *Appl. Phys. Lett.* **2003**, *83*, 162–164.
- (24) Yu, W.; Qu, L.; Guo, W.; Peng, X. *Chem. Mater.* **2003**, *15*, 2854–2860.
- (25) Li, J. J.; Wang, Y. A.; Guo, W.; Keay, J. C.; Mishima, T. D.; Johnson, M. B.; Peng, X. *J. Am. Chem. Soc.* **2003**, *125*, 12567–12575.
- (26) 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.
- (27) Nirmal, M.; Dabbousi, B. O.; Bawendi, M. G.; Macklin, J. J.; Trautman, J. K.; Harris, T. D.; Brus, L. E. *Nature* **1996**, *383*, 802–804.
- (28) Blanton, S. A.; Hines, M. A.; Guyot-Sionnest, P. *Appl. Phys. Lett.* **1996**, *69*, 3905–36907.
- (29) Dabbousi, B. O.; Rodriguez-Viejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, K. F.; Bawendi, M. G. *J. Phys. Chem. B* **1997**, *101*, 9463–9475.
- (30) Hines, M. A.; Guyot-Sionnest, P. *J. Phys. Chem.* **1996**, *100*, 468–471.
- (31) Henglein, A. *Top. Curr. Chem.* **1988**, *143*, 113–180.
- (32) Bowen Katari, J. E. B.; Colvin, V. L.; Alivisatos, A. P. *J. Phys. Chem.* **1998**, *98*, 4109–4117.
- (33) Brainard, R. J.; Ellis, A. B. *J. Phys. Chem. B* **1997**, *101*, 2533–2539.
- (34) Kepler, K. D.; Lisensky, G. C.; Patel, M.; Sigworth, L. A.; Ellis, A. B. *J. Phys. Chem.* **1995**, *99*, 16011–16017.
- (35) Neu, D. R.; Olson, J. A.; Ellis, A. B. *J. Phys. Chem.* **1993**, *97*, 5713–5716.