Electrogenerated Chemiluminescence of CdSe Nanocrystals

Noseung Myung,[†] Zhifeng Ding,[‡] and Allen J. Bard*

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712

ABSTRACT

Electrogenerated chemiluminescence (ECL) was observed from TOPO-capped CdSe nanocrystals dissolved in CH_2Cl_2 containing 0.1 M TBAP. The solution of monodisperse nanocrystals with an absorption maximum at 537 nm was synthesized at 330 °C using TOPO (trioctylphosphineoxide) and TOP (trioctylphosphine) as capping agents and Cd-acetate and Se powder as precursors. The photoluminescence (PL) spectrum showed an emission maximum at 545 nm. Cyclic voltammetry and differential pulse voltammetry of this solution displayed no distinctive features, but light emission was observed through the annihilation of oxidized and reduced forms electrogenerated during cyclic potential scans or steps. The oxidized species was somewhat more stable than the reduced form. The ECL spectrum was substantially red shifted by ~200 nm from the PL spectrum, suggesting that surface states play an important role in the emission process.

Introduction. Semiconductor nanocrystals (NCs) or quantum dots (QDs) with dimensions smaller than the bulk exciton Bohr radius exhibit unique quantum size effects and strongly size dependent electronic, magnetic, optical, and electrochemical properties.[1−7] Extensive studies on synthesis, characterization, and applications of NCs have been reported over the past two decades.[8−13] Several reviews are available in this area.[1−10] CdSe NCs have been extensively studied, following Murray and co-workers successful synthetic method using a hot trioctylphosphineoxide (TOPO) as a capping agent.[8] CdSe NCs can be synthesized with a narrow size distribution and high crystallinity by this method. Moreover, the desired particle size (and band gap) can be achieved by changing the reaction temperature or reaction time. Bulk CdSe has a direct band structure, and studies of quantum confinement effects on the light emission are of practical and fundamental interest.

Recently, Peng and co-workers developed an alternative route for the synthesis of CdSe NCs using CdO or Cd acetate instead of the toxic, pyrophoric, and unstable $Cd(CH_3)_2$.[14−16] Monodisperse NCs were obtained by this method without any post-synthesis separation for size selection. This simple and reproducible method can also be used for the synthesis of CdS and CdTe NCs.[14]

Electrogenerated chemiluminescence (ECL) has been extensively used to investigate the nature of an emitting state, the mechanism by which it is produced, and electron transfer theory.[17−19] ECL has also been used to probe the mechanisms of organic reactions involving radicals, and there has been some interest in bioanalytical fields such as immunoassays and DNA analysis.[17] Although ECL has been observed in many systems, reports concerning ECL from semiconductor NCs are scarce mainly due to their low solubility and the instability of oxidized and reduced forms.[20] The electrogenerated reactants must be sufficiently energetic to generate light upon reaction, but must also be moderately stable. In some cases, limited stability in an ECL can be accommodated by the use of a coreactant. Recently, a report from this lab described ECL from the Si NCs and found that the oxidized Si NC species were more stable than reduced ones.[20] The ECL spectrum showed a maximum significantly red shifted from the photoluminescence (PL) maximum. As opposed to elemental semiconductors such as Si, NCs of compound semiconductors such as CdS and PbS are chemically unstable upon electron transfer.[21,22] To date, ECL from solutions of compound semiconductors such as CdS and CdSe NCs has not been reported.

In this report, we describe for the first time ECL from CdSe NCs synthesized by Peng's method using Cd-acetate as a Cd precursor.[23] We also discuss the stability of both oxidized and reduced forms that were electrogenerated when the electrode potential was cycled between positive and negative values. Finally, the difference in the ECL and the PL spectra is explained by involvement of surface states of the CdSe NCs in the emission process, similar to that previously invoked for Si NCs.

Experimental Section. CdSe nanocrystals were synthesized by the procedure developed by Peng et al. without any

* Corresponding author. E-mail: ajbard@mail.utexas.edu.
† Permanent address: Department of Applied Chemistry, Konkuk University, Chungju Campus, Chungju, Chungbuk, 380-701 Korea.
‡ Present address: Department of Chemistry, University of Western Ontario, London, Ontario, N6A 5B7 Canada.
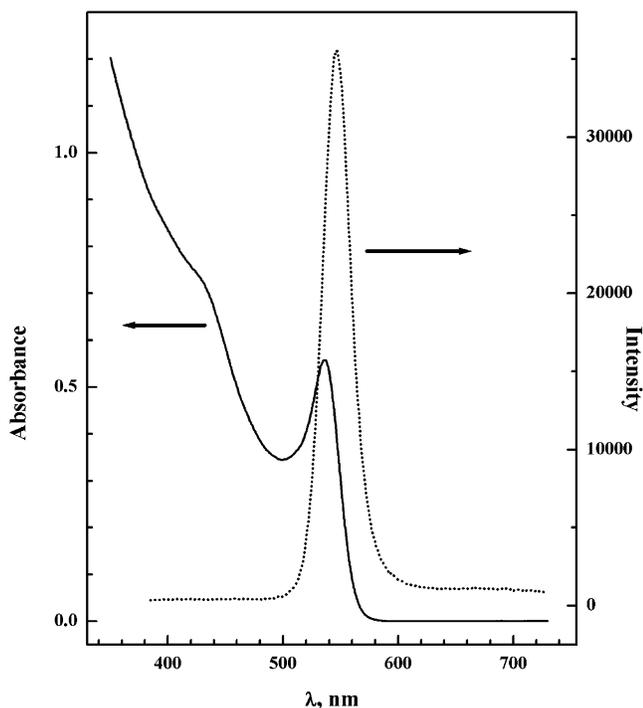
Figure 1. Room-temperature absorption (—) and emission (- - -) spectra of CdSe nanocrystals dispersed in CHCl₃. Excitation wavelength: 370 nm.

Figure 2. Cyclic voltammograms and ECL curves of (A) CdSe nanocrystals in 0.1 M TBAP CH₂Cl₂ electrolytes and (B) the blank supporting electrolyte (scan rate: 1 V/s).

significant modifications.[23] Typically, a Se solution was prepared by mixing 0.16 g of Se powder, 4 g of trioctylphosphine (TOP), and 80 μL of toluene. 12 g of technical grade trioctylphosphineoxide (TOPO) and 0.1 g of cadmium acetate hydrate were placed into a three-neck round-bottom flask and heated to ∼140 °C. After degassing with argon for about 1 h at this temperature, the solution in the flask was heated to 330 °C. At this temperature, a Se solution was quickly injected into the reaction vessel through the rubber septum. The instant color change indicated the formation of CdSe nanocrystals. Heat was removed immediately and the resulting solution was cooled to ∼50 °C. After addition of 10 mL of CHCl₃, the solution was kept in the dark. All chemicals were purchased from Aldrich and used with no further purification.

The NCs were precipitated with a copious amount of methanol and collected by centrifugation and decantation. The precipitate was dissolved in CHCl₃ and centrifuged again to remove any elemental Cd and Se. This solution was vacuum-dried and the resulting powder was used for the electrochemistry and ECL experiments.

Cyclic voltammograms (CVs) and ECL curves were obtained simultaneously using an Autolab electrochemical workstation (Eco Chemie, The Netherlands) coupled with a photomultiplier tube (PMT, Hamamatsu R4220p) held at −750 V with a high-voltage power supply series 225 (Bertan High Voltage Corp., Hicksville, NY). The ECL signal, measured from the PMT as a photocurrent, was transformed into a voltage signal by an electrometer (Model 6517, Keithley, Cleveland, OH) and fed into the external input channel of the Autolab. All fluorescence spectra were

measured with an ISA Spex Fluorolog-3 (JY Horiba, Edison, NJ) with an excitation wavelength of 370 nm and slit width of 1 nm. Absorption spectra were acquired with a Milton Roy Spectronic 3000 array spectrophotometer. CdSe NCs were dissolved in CHCl₃ and this solution was used for absorbance and fluorescence measurements. ECL spectra were recorded using a charge coupled device (CCD) camera (CH260, Photometrics, Tucson, AZ) cooled below −110 °C with liquid N₂. The camera was focused with a 100 nm lens (Pentax) on the output of grating spectrometer (Chemspec 100S, American Holographics Inc., Littleton, MA). The recorded spectra were calibrated with a Hg−Ar vapor lamp. The cell was pulsed between fixed potentials at 10 Hz frequency using a PAR model 175 universal programmer and model 173 potentiostat-galvanostat during the measurement of ECL spectra.

An electrochemical cell consisted of a Pt disk working electrode (0.06 cm²), a Pt wire counter electrode, and an Ag wire quasi-reference electrode. All CdSe NC solutions containing about 50∼60 mg of NCs with 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as a supporting electrolyte were prepared with Sure Sealed CH₂Cl₂ (∼2 mL) and loaded into a airtight cell in a He filled drybox (Vacuum/ Atmospheres Corporation, Los Angeles, CA).

Results and Discussion. As the particle size decreases, the absorption edges of CdSe are shifted to higher energies
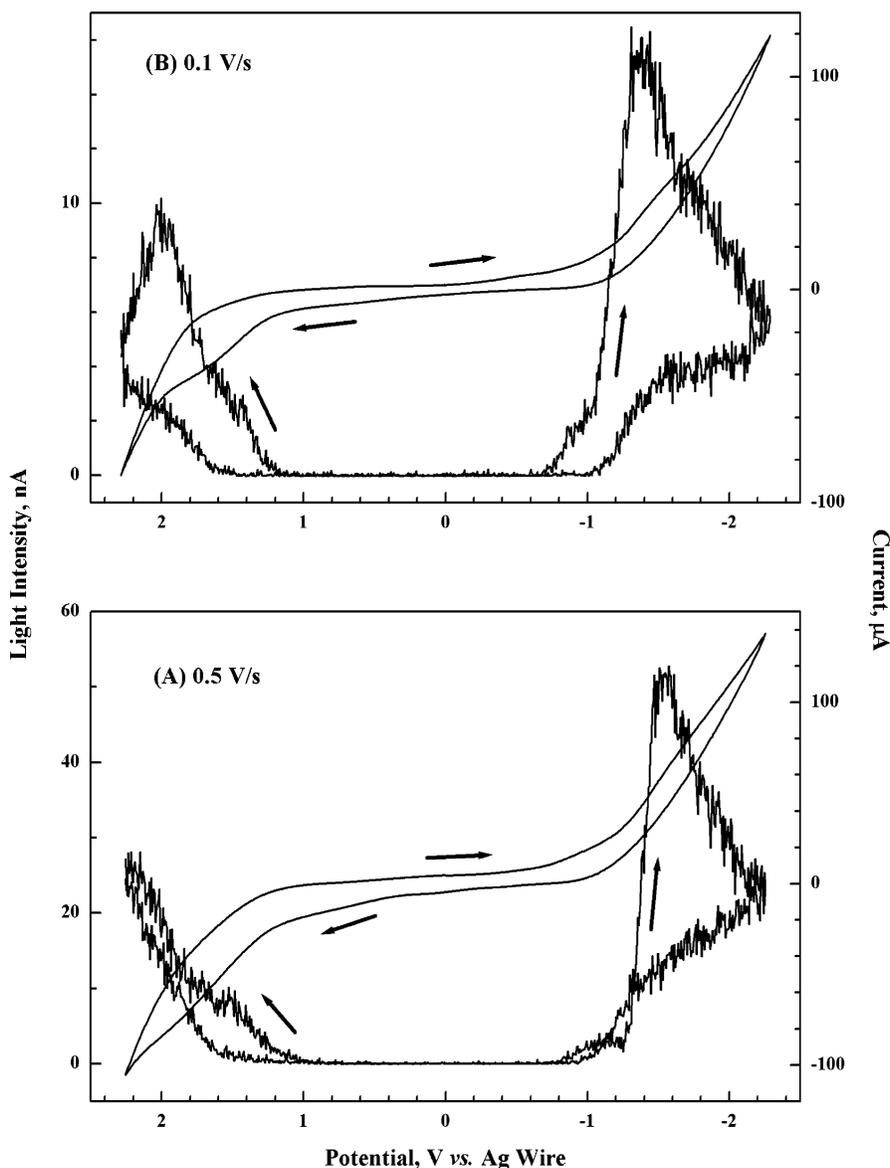
Figure 3. Cyclic voltammograms and ECL curves of CdSe nanocrystals in 0.1 M TBAP CH$_2$Cl$_2$ electrolytes with different scan rates. Scan rates are indicated in the figure.

from the bulk band gap of 1.7 eV (730 nm) due to the well-known quantum size effect. Figure 1 shows typical absorption and photoluminescence (PL) spectra of CdSe NCs in CHCl$_3$. The sharp UV and PL peaks indicate a highly monodisperse sample. The UV spectrum with the absorption maximum at 537 nm (gap, 2.3 eV) allows one to estimate the size of the CdSe nanocrystals as about 32 Å.[8] The PL spectrum shows a narrow line width comparable to the absorption line width, with the emission peak red shifted by ∼8 nm, reflecting the size distribution of the sample.[8] The PL spectrum shows a nonzero tail toward longer wavelength, suggesting the presence of surface traps as observed by others.[8,24]

NCs can be oxidized and reduced during the potential cycling or pulsing. Light emission occurs when electrogenerated reduced species (R$^{\cdot-}$) collide with oxidized species (R$^{\cdot+}$) in an annihilation process that produces excited states (R*).[19,20]

$$R^{\cdot-} + R^{\cdot+} \rightarrow R^* + R \qquad (1)$$

$$R^* \rightarrow R + h\nu \qquad (2)$$

In this case, electrogenerated species should be stable enough to allow reaction 1 to compete with any decomposition reaction. In a previous report, thioglycerol-capped CdS NCs showed no ECL light, mainly due to the instability of electrogenerated species.[21] Figure 2(A) shows light emission from TOPO-capped CdSe NCs in CH$_2$Cl$_2$ solution containing 0.1 M TBAP through the annihilation mechanism. Light emission was observed when the electrode potential was cycled between +2.3 V and −2.3 V at a scan rate of 1 V/s. Several points are noteworthy. First, electrogenerated oxidized forms are more stable, as indicated by the relative light intensity. The instability of reduced forms was clearly seen at a slow scan rate (Figure 3) and during successive runs. A similar observation was reported in previous experiments with Si NCs.[20] Second, ECL light was generated in the

potential region that corresponded to the band gap of CdSe NCs; the threshold voltage (~2.3 V) is almost same as the optical band gap estimated from the absorption maximum in Figure 1. Unlike the results with CdS NCs, the CV with CdSe did not show any significant features except a broad oxidation peak at ~1.0 V where the ECL light began. Similar behavior was observed with differential pulse voltammetry (DPV). This lack of good electrochemical behavior can be attributed to the low concentration of CdSe NCs resulting from the limited solubility in the solvents employed. Figure 2(B) shows the response with a blank electrolyte which shows higher currents compared to that in Figure 2(A). We attribute this unusual behavior to film formation or particle adsorption, which causes partial blocking of the electrode surface.

Figure 3 shows the effects of a scan rate on the light emission intensity. The intensity decreases as scan rate decreases, and this result implies some decomposition of the electrogenerated species. Slower scan rates are clearer in showing that the oxidized forms are more stable. The light emission upon reduction started a little earlier at slower scan rates, but the threshold voltage was the same.

Some ECL light was generated through a so-called preannihilation mechanism.[19] In Figure 4(A), the electrode potential was scanned from 0.0 V to +2.3 V, and therefore only oxidized species could be generated in this "half scan". The intensity of light emission also decreased during the "half scan" with continued scanning. Very similar behavior was found for a scan from 0.0 V to −2.3 V, Figure 4(B). The origin of this ECL is unclear, but may depend on the presence of impurities or reactions in products that can act as coreactants. Dotted lines in the figure show the responses from the blank electrolyte, indicating that the presence of CdSe was necessary to observe this emission.

ECL transients could also be obtained by switching the electrode potential between oxidation and reduction of CdSe. Figure 5(A) shows ECL transients for annihilation in a double potential step experiment. The potential was initially stepped from 0.0 V to −2.3 V and then stepped alternately between −2.3 V and +2.3 V at 10 Hz. As seen in Figure 4, an initial step from 0.0 V to −2.3 V shows a weak emission, which is consistent with the result in "half scan" experiments. Similar behavior was obtained when the electrode potential was stepped from 0.0 V to +2.3 V and then stepped alternately between +2.3 V and −2.3 V. The second step to +2.3 V (or −2.3 V) generated substantially higher light emission by the annihilation process. As in the potential scan experiments, the light intensity was higher in the potential region where reduced forms were electrogenerated, whereas light intensity in the anodic region decreased substantially with successive potential steps.

Finally, an ECL spectrum was obtained of the TOPO-capped CdSe nanocrystals dispersed in a CH_2Cl_2 solution containing 0.1 M TBAP to compare with the PL spectrum. Figure 5(B) shows an ECL spectrum obtained using a double potential step between +2.3 V and −2.3 V at a 10 Hz rate integrated over 30 min. The observed maximum wavelength at ~740 nm is red-shifted by almost 200 nm from that in
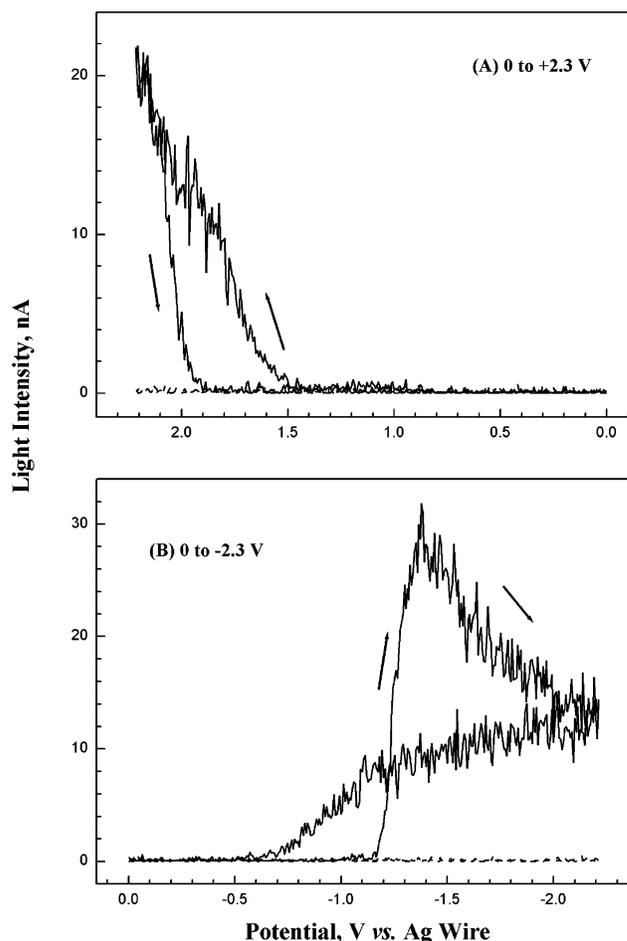
Figure 4. ECL curves of CdSe nanocrystals in 0.1 M TBAP CH_2Cl_2 electrolytes with a different potential window ("half scan") between (A) 0.0 V and +2.3 V, and (B) 0.0 V and −2.3 V (scan rate: 1 V/s). Dotted curves are the ECL responses from the blank electrolyte.

Figure 1. This substantial red shift between the PL and ECL emission was also observed in the previous experiment with Si NCs.[20] Because of the high surface-to-volume ratio of NCs, surface properties have significant effects on the structural and optical properties such as emission efficiency and spectrum.[24,25] For example, adatoms and surface vacancies can provide localized surface states within the band gap.[26] In addition, ECL depends more sensitively on surface states than PL, which mainly occurs through excitation and emission within the NCs core.[20] NC cores have band gaps greater than the energy separation of surface states. Considering all of these factors and the nonzero tail in the PL spectrum shown in Figure 1, the difference in light emission spectra between ECL and PL most likely results from a major contribution of the surface states in ECL emission. This result suggests the importance of surface passivation studies on ECL.

In summary, the electrochemical behavior of NC CdSe could not be elucidated due to the low solubility of the material. An ECL spectrum was obtained from the TOPO-capped CdSe NCs dispersed in a CH_2Cl_2 solution containing 0.1 M TBAP. A substantially red-shifted ECL spectrum compared to the PL spectrum suggested that surface states
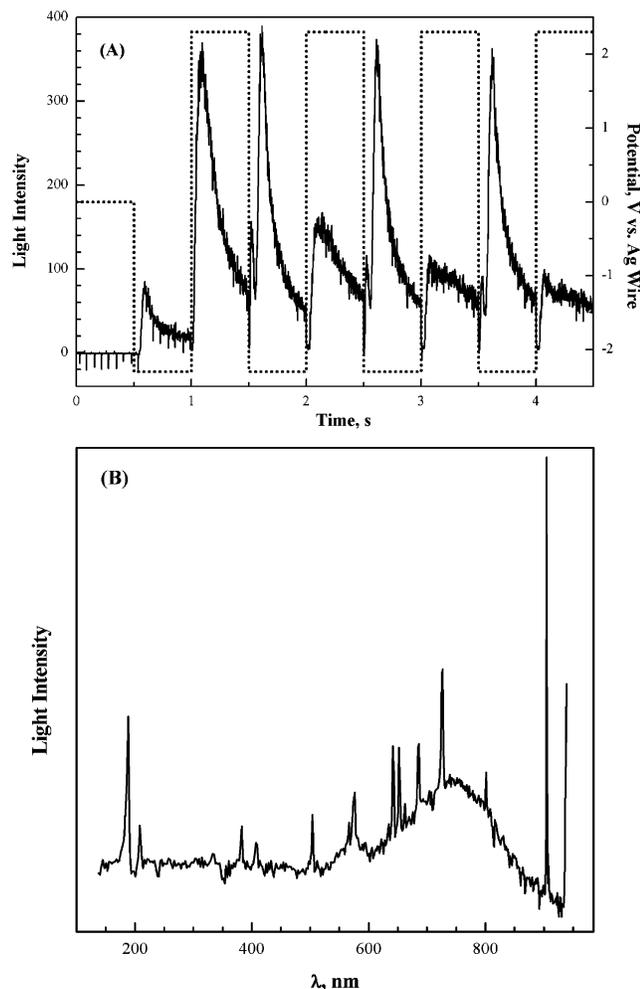
Figure 5. (A) ECL transients (solid curve) applied potential steps between +2.3 V and −2.3 V (dotted lines). (B) ECL spectrum obtained by stepping same potential as in (A) at 10 Hz with an integration time of 30 min.

played an important role in ECL. Light emission was observed with potential cycling and pulsing between oxidation (+2.3 V) and reduction potentials (−2.3 V) at a scan rate of 1 V/s. A lower level of preannihilation ECL was also observed. The electrogenerated oxidized species were more stable than the reduced ones. Surface passivation and the fabrication of core/shell NC structures should help elucidate the surface effects on the ECL spectra, and investigations toward this goal are underway in this lab.

References

(1) Alivisatos, A. P. *Science* **1996**, *271*, 933.
(2) Alivisatos, A. P. *J. Phys. Chem.* **1996**, *100*, 13226.
(3) Weller, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 41.
(4) Henglein, A. *Chem. Rev.* **1989**, *89*, 1861.
(5) Wang, Y.; Herron, Y. *J. Phys. Chem.* **1991**, *95*, 525.
(6) Bawendi, M. G.; Steigerwald, M. L.; Brus, L. E. *Annu. Rev. Phys. Chem.* **1990**, *41*, 477.
(7) Steigerwald, M. L.; Brus, L. E. *Acc. Chem. Res.* **1990**, *23*, 183.
(8) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.
(9) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545.
(10) Trindade, T.; O'Brien, P.; Pickett, N. L. *Chem. Mater.* **2001**, *13,* 3843.
(11) Chan, W. C. W.; Nie, S. *Science* **1998**, *281*, 2016.
(12) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. *Science* **2002**, *295*, 2425.
(13) Wang, C.; Shim, M.; Guyot-Sionnest, P. *Science* **2001**, *291*, 2390.
(14) Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2001**, *123*, 183.
(15) Qu, L.; Peng, Z. A.; Peng, X. *Nano Lett.* **2001**, *1*, 333.
(16) Peng, X. *Chem. Eur. J.* **2002**, *8*, 335.
(17) Bard, A. J.; Debad, J. D.; Leland, J. K.; Sigal, G. B.; Wilbur, J. L.; Wohlstadter, J. N., "Chemiluminescence, Electrogenerated," in *Encyclopedia of Analytical Chemistry: Applications, Theory and Instrumentation*, R. A. Meyers, Ed., John Wiley & Sons: New York, 2000; Vol. 11, p 9842 and references therein.
(18) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, 2nd ed., Wiley: New York, 2001; p 736.
(19) Faulkner, L. R.; Bard, A. J. In *Electroanalytical Chemistry*; Bard, A. J., Ed., Marcel Dekker: New York, 1977; Vol. 10, p 1.
(20) Ding, Z.; Quinn, B. M.; Haram, S. K.; Pell, L. E.; Korgel, B. A.; Bard, A. J. *Science* **2002**, *296*, 1293.
(21) Haram, S. K.; Quinn, B. M.; Bard, A. J. *J. Am. Chem. Soc.* **2001**, *123*, 8860.
(22) Chen, S.; Truax, L. A.; Sommers, J. M. *Chem. Mater.* **2000**, *12*, 3864.
(23) Aldana, J.; Wang, Y. A.; Peng, X. *J. Am. Chem. Soc.* **2001**, *123*, 8844.
(24) Hines, M. A.; Guyot-Sionnest, P. *J. Phys. Chem.* **1996**, *100*, 468.
(25) Danek, M.; Jensen, K. F.; Murray, C. B.; Bawendi, M. G. *Chem. Mater.* **1996**, *8*, 173.
(26) Brus, L. *New J. Chem.* **1987**, *11*, 123.

NL0257824