

# Electrogenerated Chemiluminescence of Ge Nanocrystals

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## ABSTRACT

Organic layer capped Ge nanocrystals (NCs) were synthesized by an arrested-growth method within supercritical octanol. Electrogenerated chemiluminescence (ECL) from the Ge NCs dispersed in *N,N'*-dimethylformamide (DMF) containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) was observed during potential scans or pulses through the annihilation of electrogenerated oxidized and reduced species. The light emission intensity was higher during the oxidation scans and pulses, suggesting that the reduced forms were more stable than the oxidized ones. The ECL spectrum was obtained by potential stepping between the potentials for oxidation and reduction. The ECL spectrum was red-shifted from the photoluminescence spectrum by ~200 nm, which implied, in agreement with previous studies, ECL emission predominantly via surface states and the importance of the surface passivation on ECL.

**Introduction.** Semiconductor nanocrystals (NCs), or quantum dots (QDs), have been extensively studied due to their quantum confinement effects which exhibit unique size dependent electronic and optical properties.<sup>1,2</sup> The II–VI semiconductor NCs, such as CdSe and CdTe, have attracted particular attention following reports of successful methods to grow highly crystalline, monodisperse NCs using TOPO (trioctylphosphine oxide) as a capping agent.<sup>3</sup>

There has also been interest in NCs of indirect band gap, elemental semiconductors, such as Si and Ge, especially since these show useful levels of photoluminescence (PL) in the visible region and suggest possible applications in optoelectronics and microelectronics.<sup>4–8</sup> Compared to Si, Ge nanocrystals are of particular interest, because the Bohr radius is larger in Ge than Si, which consequently should lead to a more prominent quantum confinement effect. In addition, while Si nanocrystals remain an indirect band gap semiconductor even at sizes near 1.5 nm,<sup>9</sup> Ge nanocrystals are more likely to undergo a transition to a direct band gap semiconductor since Ge is nearly a direct band gap semiconductor in the bulk<sup>10</sup> and the lowest direct band gap for Ge is 0.8 eV, which is only about 0.1 eV above the indirect band gap, thus making it an interesting material for the photonic applications in the IR region.

Recently, a new synthetic method using a supercritical solvent to produce highly crystalline and monodisperse Si QDs passivated with a capping agent was described.<sup>9,11</sup> The

Si QDs clearly revealed quantum size effects, such as a substantial blue-shift in the UV absorbance and PL spectrum from the bulk band gap energy. Interesting features were observed from the electrochemical experiments. For example, the differential pulse voltammetry (DPV) and electrogenerated chemiluminescence (ECL) of Si NCs revealed a quantized charging effect and a significant red-shift (~220 nm) from the PL maximum, respectively.<sup>11</sup> A similar red-shift was observed from the ECL of CdSe NCs.<sup>12</sup>

In this article, we describe the ECL of Ge NCs in *N,N'*-dimethylformamide (DMF) containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP). The germanium NCs were synthesized for the first time in a supercritical fluid by an arrested-growth method in hexane with octanol as capping ligand.

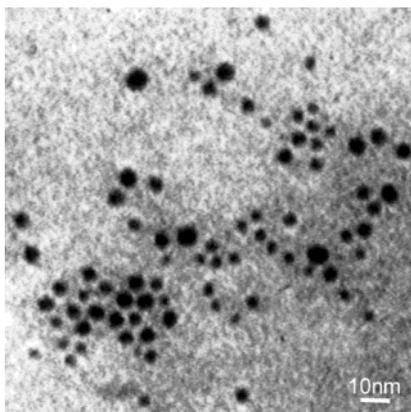
**Experimental Section.** The Ge NCs were synthesized by decomposing 62.5 mM Ge precursor, tetraethylgermane, in a supercritical mixture of hexane/octanol (v/v = 3:1) at 450 °C in a batch reactor.<sup>13</sup> They were polydisperse in nature with an average size of 4.0 nm and capped with an organic layer of C<sub>8</sub> hydrocarbon chains bound through an alkoxide layer (Figure 1).<sup>14</sup> The small particle diameter indicates that the capping layer was solvated sufficiently well by the supercritical fluid mixture to provide steric stabilization and arrest particle growth. In a supercritical solvent, the ability to synthesize nanocrystals at high temperatures, required for crystallization, with steric stabilization is an advantage not available in gas-phase synthesis. The ECL of Ge NCs in DMF containing 0.1 M TBAP was measured using Pt working, Pt counter, and Ag reference electrodes placed in

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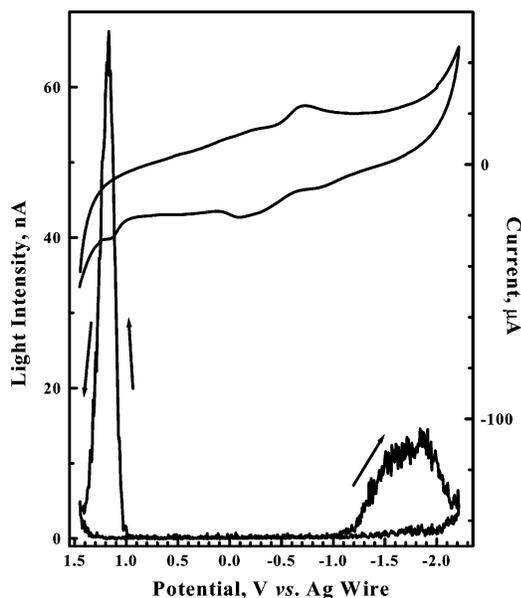
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**Figure 1.** TEM image of the Ge NCs made from tetraethylgermane in hexane/octanol at 450 °C.

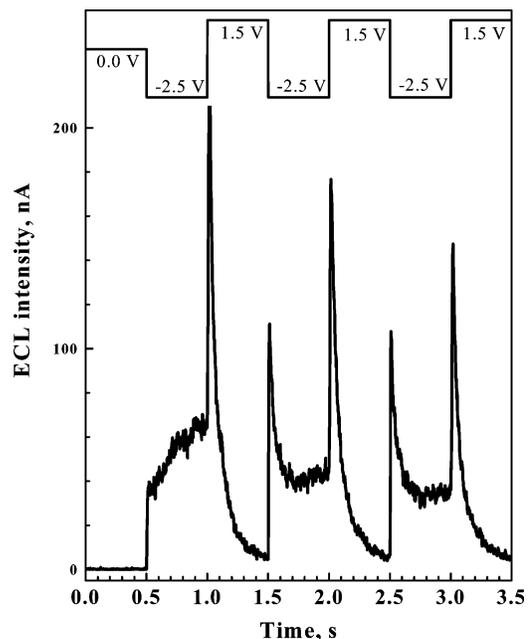


**Figure 2.** Cyclic voltammogram and ECL emission as a function of electrode potential curve of Ge NCs in DMF containing 0.1 M TBAP (scan rate/ 1.0 V/s).

a cylindrical Pyrex vial. Experimental methods are described in detail elsewhere.<sup>11,12</sup>

**Results and Discussion.** NCs can be oxidized and reduced by charge injection during electrode potential cycling or potential steps between the potentials for oxidation and reduction. Light emission occurs through an annihilation (electron transfer) process when electrochemically oxidized species collide with reduced species. Therefore, to observe ECL, electrogenerated charged NCs must be stable enough to show electron transfer upon colliding with an oppositely charged species.<sup>11,12,15</sup>

Figure 2 shows light emission from the Ge NCs in a DMF solution containing 0.1 M TBAP. ECL was observed through the annihilation mechanism when the electrode potential was cycled between +1.5 V and -2.3 V at a scan rate of 1.0 V/s. As shown in the figure, ECL light was not observed within the potential gap that corresponded to the threshold voltage (~2.1 V). Several important features were observed. First, the electrogenerated reduced species are more stable

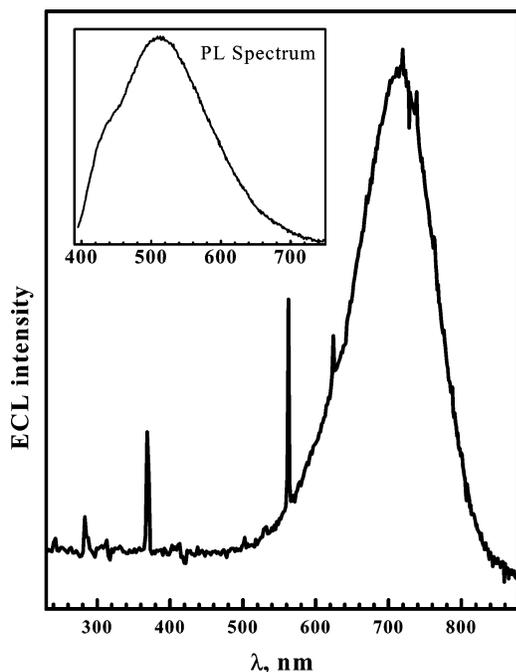


**Figure 3.** ECL transients in DMF containing 0.1 M TBAP obtained by potential steps between +1.5 V and -2.5 V.

than oxidized ones, as indicated by the relative ECL light intensities at positive and negative potentials. In other words, electrogenerated reduced forms produced in the negative potential region are stable enough to maintain their states until the electrode potential is sufficiently positive to generate oxidized species. This results in the light emission through an annihilation mechanism. On the other hand, the light emission upon reduction is lower and broader in intensity, suggesting some decay of the oxidized forms during the time the potential moves to the reduction region. Unlike the Si QDs, poor electrochemical behavior was observed from the Ge NCs with cyclic voltammetry and differential pulse voltammetry, so that well-defined peaks were not observed. This behavior is similar to the case of CdSe NCs.<sup>12</sup>

ECL transients for annihilation of the oxidized and reduced forms were obtained by switching the electrode potential between oxidation and reduction of Ge NCs. The potential was stepped from 0.0 V to -2.5 V and then pulsed between -2.5 V and +1.5 V in 0.5 s steps. As seen in Figure 3, an initial step from 0.0 V to -2.5 V generated weak and broad ECL light, although only reduced species were generated during this potential step. Similar behavior, a so-called preannihilation process, was observed and discussed before.<sup>12,15</sup> The next step to 1.5 V generated substantially sharp and intense light emission through the annihilation mechanism. The ECL light intensity was higher when the potential was stepped to the oxidation potential, suggesting again that the reduced forms of Ge NCs are more stable. However, ECL light generated upon oxidation decayed faster than the light generated upon reduction, and this may be related to the similar peak shape in Figure 2.

Figure 4 shows the ECL spectrum obtained from the Ge NCs dispersed in a DMF solution containing 0.1 M TBAP using alternating potential steps between +1.5 V and -2.5 V at a 10 Hz rate for 30 min. The ECL spectrum shows a



**Figure 4.** ECL spectrum of Ge NCs in 0.1 M TBAP DMF electrolyte by stepping electrode potential between +1.5 V and -2.5 V at 10 Hz rate for 30 min. Inset: PL spectrum obtained from the Ge NCs dispersed in  $\text{CHCl}_3$ . Excitation wavelength: 380 nm. The large spikes represent the effect of cosmic ray events on the CCD.

maximum wavelength, which is  $\sim 200$  nm red-shifted compared with the PL spectrum (inset). This substantial red-shift was also observed in the previous experiments with Si and CdSe NCs and it was attributed to the strong role of surface states on the NCs in electrochemical and ECL processes.<sup>11,12</sup>

Charge injection into the NCs generally occurs via surface states, so ECL should be more sensitive to the surface state energetics than PL, which occurs mainly from the interior of the NC. Thus, completely passivated NCs should show an ECL spectrum that is very similar to the PL spectrum. In fact, such an ECL spectrum is seen with CdSe NCs passivated with the wider band gap ZnSe in a core/shell structure, suggesting an important advantage of ECL to probe surface states.<sup>16</sup> In addition, an ECL spectrum from the Si NCs, which were size selected by column chromatography,

showed a similar red-shift.<sup>11</sup> Therefore, we believe that the red-shift cannot be attributed to the size distribution or polydispersity of the NCs, although the broad PL spectrum in the inset reflects the size distribution of the Ge NCs. Based on the above explanations, the red-shift implies ECL emission from surface states of the Ge NCs.

Finally, a new synthetic method for generating Ge NCs using a supercritical solvent revealed quantum confinement effects from the control of the particle size with the capping ligands. Size-controlled and band-gap engineered semiconductor NCs, including Ge NCs, have a potentially wide range of applications, so light emission through PL or ECL in the visible region may find possible applications in optoelectronics and microelectronics.

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## References

- (1) Alivisatos, A. P. *Science* **1996**, *271*, 933.
- (2) Alivisatos, A. P. *J. Phys. Chem.* **1996**, *100*, 13226.
- (3) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.
- (4) English, D. S.; Pell, L. E.; Yu, Z.; Barbara, P. F.; Korgel, B. A. *Nano Lett.* **2002**, *2*, 681.
- (5) Lin, C.-W.; Lin, S.-H.; Lee, S.-C. *J. Appl. Phys.* **2002**, *91*, 1525.
- (6) Wu, Y.; Yang, P. *Adv. Mater.* **2001**, *13*, 520.
- (7) Wilcoxon, J. P.; Provencio, P. P.; Samara, G. A. *Phys. Rev. B* **2001**, *64*, 035417.
- (8) Niquet, Y. M.; Allan, G.; Delerue, C.; Lannoo, M. *Appl. Phys. Lett.* **2000**, *77*, 1182.
- (9) Holmes, J. D.; Ziegler, K. J.; Doty, R. C.; Pell, L. E.; Johnston, K. P.; Korgel, B. A. *J. Am. Chem. Soc.* **2001**, *123*, 3743.
- (10) (a) Peng, C. S.; Huang, Q.; Cheng, W. Q.; Zhou, J. M.; Zhang, Y. H.; Sheng, T. T.; Tung, C. H. *Phys. Rev. B* **1998**, *57*, 8805. (b) Okamoto, S.; Kanemitsu, Y. *Phys. Rev. B* **1996**, *54*, 16421.
- (11) Ding, Z.; Quinn, B. M.; Haram, S. K.; Pell, L. E.; Korgel, B. A.; Bard, A. J. *Science* **2002**, *296*, 1293.
- (12) Myung, N.; Ding, Z.; Bard, A. J. *Nano Lett.* **2002**, *2*, 1315.
- (13) Lu, X.; Ziegler, K. J.; Ghezelbash, A.; Johnston, K. P.; Korgel, B. A., submitted.
- (14) Ziegler, K. J. Ph.D. Dissertation, University of Texas, Austin, TX, 2001.
- (15) Faulkner, L. R.; Bard, A. J. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1977; Vol. 10, p 1.
- (16) Myung, N.; Bae, Y.; Bard, A. J. *Nano Lett.* **2003**, *3*, 1053.

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