

Effect of Surface Passivation on the Electrogenerated Chemiluminescence of CdSe/ZnSe Nanocrystals

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ABSTRACT

The electrogenerated chemiluminescence (ECL) spectrum of CdSe/ZnSe nanocrystals (NCs) dispersed in a CH₂Cl₂ solution containing 0.1 M TBAP was obtained by stepping the potential between +2.3 and -2.3 V. Unlike the spectra from the ECL of Si or CdSe NCs, where the emission occurs in a single peak that is significantly red-shifted from the photoluminescence (PL) peak (attributed to emission from surface states), ECL from CdSe/ZnSe produced a spectrum containing two peaks: a sharp peak whose position was almost identical to that in the PL spectrum and another broader peak with a red shift of ~200 nm compared to that in the PL. This suggests emission from both surface states on the NCs and from the bulk in NCs where the surface states have been passivated.

Semiconductor nanocrystals (NCs) or quantum dots have been extensively studied because of their unique size-dependent electronic, optical, and electrochemical properties.^{1–3} Highly luminescent semiconductor NCs have gained increasing attention for use in light-emitting devices and tagging applications.^{4–6} Several methods have been developed for the synthesis of monodisperse and highly crystalline nanocrystals.^{7–9}

The photoluminescence (PL) efficiencies of NCs are known to be sensitive to the nature of the particle surface because of the large surface area and the possible presence of surface states caused by uncoordinated atoms.^{9,10} Such surface states act as quenchers of the luminescence, and the passivation of the surface is the key to the preparation of highly luminescent semiconductor NCs. Such surface passivation has been achieved using organic capping agents as well as the formation of inorganic core/shell systems such as CdSe/ZnSe.^{4,6,11–14}

In previous reports, we demonstrated the electrogenerated chemiluminescence (ECL) of semiconductor NCs such as Si and CdSe, where the excited states are generated by an electron-transfer reaction.^{9,10} In both cases, the ECL spectrum was red-shifted compared to the PL spectrum by hundreds of nanometers. We proposed that the PL is dominated by excitation and emission within the NC core and that electron transfer occurs at the NC surface so that the ECL emission is characteristic of surface energy levels, as depicted

schematically in Figure 1. If this model is correct, then highly passivated NCs should result in an ECL spectrum that is more like the PL spectrum. In this communication, we describe the ECL spectrum of CdSe NCs passivated with a shell of the wider band gap material, ZnSe, and show that this is indeed the case.

CdSe NCs were synthesized according to the procedure previously described.^{8,9} Highly luminescent CdSe/ZnSe core/shell NCs were fabricated following the synthetic method of Reiss and co-workers,⁴ except that dodecylamine (DDA) was used instead of hexadecylamine (HDA) to improve the solubility of the CdSe/ZnSe NCs in CH₂Cl₂ (see Supporting Information). Experimental details of ECL and PL procedures are described elsewhere.^{9,10}

The formation of a core/shell structure results in a dramatic enhancement of PL. Figure 2 shows PL and UV absorption spectra (inset) of CdSe/ZnSe NCs dispersed in CHCl₃. As shown, both the PL and UV spectra from the core/shell NCs essentially maintain their overall shape with a small red shift compared to those of CdSe NCs. The red shift is an indication of the formation of a core/shell structure, which has been described in detail by several authors.^{4,11,12} Although the experimental conditions have not been optimized, the PL peak intensity increased more than 10 times after passivation with a shell of ZnSe NCs, compared to that of CdSe, without significant modifications of the absorbance and PL features. In addition, the line width of the PL peak remained essentially unchanged during core/shell formation, indicating that the NCs remained substantially monodisperse.

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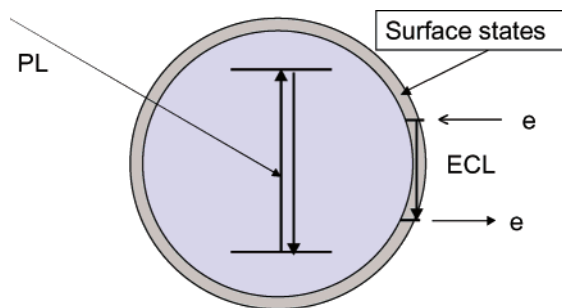


Figure 1. Schematic representation of PL and ECL in a semiconductor NC.

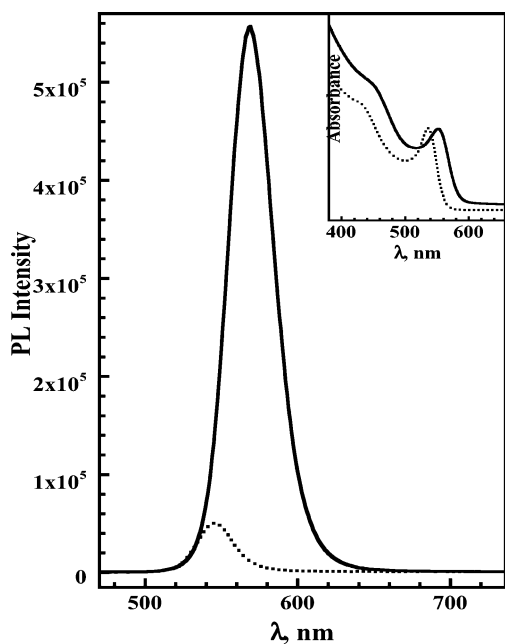


Figure 2. Photoluminescence and UV absorption (inset) spectra of CdSe (---) and CdSe/ZnSe (—) NCs dispersed in CHCl_3 . Excitation wavelength: 370 nm.

Unlike PL, the ECL emission is more sensitive and dependent on the surface properties and the presence of surface states.^{9,10} Therefore, the ECL with semiconductor NCs that have a large surface/volume ratio is dominated by surface effects. ECL has been widely used in a range of studies, such as those of organic reactions involving radicals, electron transfer theory, and immunoassays.^{15,16} Because ECL is more sensitive to surface states than PL, it can also be effectively used to elucidate the nature of the emitting state of semiconductor NCs.^{9,10,15,16} As described earlier, the ECL spectrum from Si NCs showed a significant red shift from the PL; the same result was observed for CdSe NCs, and these shifts were attributed to surface effects.^{9,10} Figure 3 shows an ECL spectrum from the CdSe/ZnSe NCs dispersed in a CH_2Cl_2 solution containing 0.1 M TBAP. This ECL spectrum shows one main peak at ~ 580 nm, which is almost identical to the one in the PL spectrum (Figure 2). In other words, no red shift from the PL is observed for this peak. This is the first observation of an ECL spectrum from semiconductor NCs where the peak position is very similar to the one in PL. This peak location suggests that the solution contains NCs whose surfaces have been largely passivated.

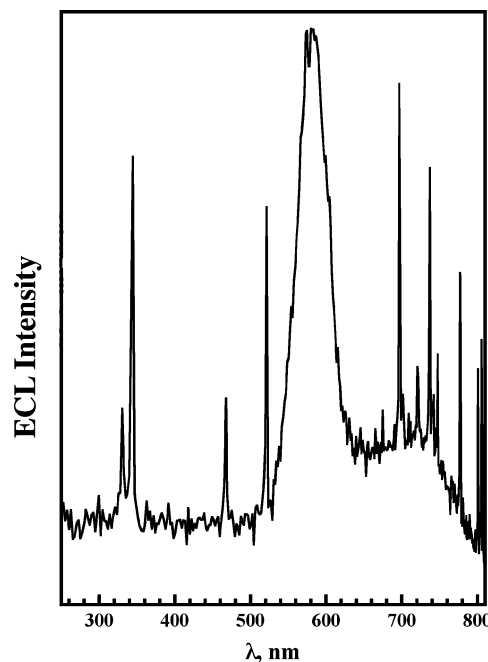


Figure 3. ECL spectrum of CdSe/ZnSe core/shell NCs in a CH_2Cl_2 solution containing 0.1 M TBAP. The spectrum was obtained by potential steps between +2.3 and -2.3 V at 10 Hz with an integration time of 30 min. The large, sharp peaks represent random cosmic ray events detected by the CCD camera.

There is another broad peak at ~ 740 nm that is red-shifted by ~ 200 nm from the PL peak. This is the same extent of red shift as found in the ECL spectra from CdSe and Si NCs.^{9,10} This broad and ill-defined peak thus results from the NCs whose surfaces are not passivated. In other words, this Figure suggests that largely passivated CdSe NCs are present with (partially) nonpassivated NCs. This ability to probe the surface states of NCs is an important advantages of ECL.

To summarize, CdSe NCs passivated with a shell of wider band gap ZnSe NCs were synthesized, and the CdSe/ZnSe core/shell nanostructure was confirmed with PL and UV absorption spectra. Also, an ECL spectrum was obtained from CdSe/ZnSe NCs dispersed in a CH_2Cl_2 solution containing 0.1 M TBAP. A peak whose position is almost identical to the one in the PL spectrum was observed along with a substantially red-shifted peak. The ECL spectrum implied that completely passivated NCs were present along with nonpassivated NCs, demonstrating that ECL is an effective probe of surface states on semiconductor NCs. Further studies on ECL and surface states are underway in this laboratory with other kinds of semiconductor NCs such as Ge and CdTe.

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Supporting Information Available: Synthesis of CdSe/ZnSe NCs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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