Electrogenerated chemiluminescence of near-infrared-emitting
CdSe@CdSe nanorods in aqueous solution

Yafeng Zhuang^{a, b,*}, Yilong Zheng^b, S. Scott Saavedra^b, Nicholas G. Pavlopoulos^b,
Jeffrey Pyun^b

^a Department of Chemical Engineering, School of Chemical Engineering and
Materials, Changzhou Institute of Technology, Changzhou, Jiangsu 213022, P. R.
China

^b Department of Chemistry and Biochemistry, University of Arizona, Tucson, Arizona
85721, United States

^c World Class University Program for Chemical Convergence for Energy and
Environment, School of Chemical and Biological Engineering, Seoul National
University, Seoul 151-744, Korea

Electrogenerated chemiluminescence (ECL) was observed from TOPO-capped CdSe@CdSe nanorods (NRs) depositing on a metal electrode in phosphate buffer solution (PBS). Two ECL peaks at -1.05 and -1.33 V in pH 9.2, 0.1 M PBS were found under cyclic voltammetric conditions. Cyclic voltammetry of this solution displayed no distinctive features, on the other hand, light emission was observed during cyclic potential scans. The photoluminescence (PL) spectrum showed an emission maximum at 692 nm. The spectrum of ECL possesses one peak which coincides very well with the PL spectrum of the nanorods film. The mechanism for ECL peaks was proposed. Electron transfer reactions between charged nanorods and molecular redox-active coreactants such as dissolved oxygen and H₂O₂ or between positively and negatively charged nanorods occurred that led to electron and hole annihilation, producing light.

Keywords: Electrochemiluminescence, CdSe@CdSe Nanorods, Near-infrared-emitting, Aqueous solution

^{*}Corresponding author. *E-mail address:* zhuangyf@czu.cn.

Electrogenerated chemiluminescence or electrochemiluminescence (ECL), the process whereby species generated at electrodes undergo high-energy electron-transfer reactions to form excited states that emit light, has been extensively exploited in analytical applications including organic analysis, immunoassays, enzymatic biosensors and DNA-probe assays^{1,2}. Semiconductor nanocrystals (NCs), especially quantum dots (QDs), have attracted considerable attention due to their unique optical properties, including high quantum yield, low photobleaching, high photochemical stability, size-tunable emission and simultaneous excitation of multiple fluorescence colors^{3,4}. Furthermore, their emission positions are tunable in a wide emission range from ultra violet (UV) to near-infrared (NIR) due to changing the size of the NC (the quantum size effect) and composition^{5,6}. Since the ECL emission of SiNPs was reported in 2002⁷, many NC-based ECL emitters (e.g., II-VI, III-V and IV-VI NCs) with different sizes, shapes and compositions have been used for analysis and bioanalysis.

Cadmium selenide (CdSe) QDs are attractive for applications in optical devices, bioanalysis and bioimaging because of their optical properties, and have been employed luminescence probes in a large variety of bio-detection schemes⁸⁻¹². For biological analysis, the near-infrared region (NIR)- window (650–900 nm) is appealing due to the low tissue absorption and scattering effects in this range¹³, and thus NIR NCs have been an attractive research objective. To date, research on NIR NCs has mostly focused on cadmium telluride (CdTe) QDs or telluride alloyed QDs¹³⁻¹⁵. It is reported that the CdSe-based NCs can only reach typically 650 nm in emission, which is just below the optimal near-infrared range for imaging^{13,16}. In this paper, we describe the photoluminescence and ECL of CdSe@ CdSe nanorods (NRs) with strong emission about 692 nm, which is in the optimal NIR region. We also discuss the emission mechanism for the CdSe@ CdSe NRs assemblies, correlating PL and ECL curves with

the cyclic voltammogram (CV). In particular, because of the close correspondence of the ECL and PL spectra, we suggest that the CdSe@CdSe NRs surface sites are passivated efficiently **due to the** core/shell structure.

Experimental

Chemicals and Materials. — All reagents were of analytical grade, and the aqueous solutions were prepared with ultrapure water (Millipore Milli-Q water, 18.2 MΩ cm). CdSe@CdSe NRs were synthesized as described previously¹⁷. CdSe nanoparticles (NPs) were synthesized and used to seed the growth of CdSe@CdSe NRs based on a modified literature procedure for CdSe@CdSe NRs¹⁸. For the **nanorods** thin-film preparation, the CdSe@CdSe NRs were ultrasonically dispersed in chloroform to obtain a colloidal solution of CdSe@CdSe NRs, which was kept in a refrigerator at 4 °C. Soda lime glass coated with indium-tin oxide (ITO, ca. 100 nm thick) **and coated with** Au (ca. 100 nm thick) were purchased from Thin Film Devices (total thickness of 1.1 mm). Hydrogen peroxide **was** obtained from Jiangsu Yongfeng Chemical Reagent Co., Ltd (Danyang, Jiangsu, China).

Modified Electrode and NRs films on ITO, Au surface Preparations.—Platinum electrode, metal oxide (indium-tin oxide, ITO) and Au slides were used as a substrate for immobilizing CdSe@CdSe NRs. The platinum electrode (diameter of 3.0 mm) was polished with 1.0, 0.3 and 0.05 μm alumina powders, respectively, and rinsed thoroughly with ultrapure water between each polishing step. The electrode was then successively sonicated in ultrapure water, and then allowed to dry with N₂ at room temperature. A drop of 5.0 μL 5.8 mg/mL CdSe@CdSe NRs colloidal solution was placed onto the surface of platinum electrode and then let dry at room temperature under ambient pressure to form a thin film. ITO-coated planar electrodes and metal (Au) slides were cleaned by sonicating in detergent (1% Triton X-100), water, and ethanol

for 15 minutes for each step. Cleaned ITO or Au slides were stored in ethanol. Immediately before use, ITO or Au slides were dried under flowing nitrogen gas at room temperature. Then, a drop of 20.0 μL 5.0 mg/mL CdSe@CdSe NRs colloidal solution was placed onto the surface of cleaned ITO or Au slides and then let dry at room temperature under ambient pressure.

Apparatus.— Cyclic voltammograms (CVs) and ECL curves were obtained simultaneously using a CHI 760 electrochemical workstation (CH Instrument Company, Shanghai, China) coupled with a flow injection chemiluminescence analyzer (IFFL-E, Remex Electronic Instrument Limited Co., Xi'an, China) at room temperature, and the photomultiplier tube (CR-105, HAMAMATSU, Beijing, China) was biased at 800 V. All experiments were carried out with a conventional three-electrode system. A CdSe@CdSe NRs thin-film modified electrode, a platinum wire and a Ag/AgCl (saturated KCl) were used as working electrode, counter electrode, and reference electrode, respectively. Nitrogen was bubbled through the solution for different times and kept flowing over the solution during the ECL experiments. Fluorescence measurements and the ECL spectrum were obtained using a FL3-11 Fluorolog-3 Spectrofluorometer (Jobin Yvon-Spex Instruments SA Inc., Edison, NJ, USA) with emission slit widths of 10 nm. Fluorescence spectra from CdSe@CdSe NRs adsorbed or tethered to ITO surfaces were obtained using a fixed excitation wavelength of 490 nm. The ECL spectroscopy from CdSe@CdSe NRs on metal (Au) surfaces was carried out in the spectrometer within a fluorescence cell, while using the fixed potential -1.7 V controlled with a 263-A potentiostat/galvanostat (Princeton Applied Research, USA). UV-vis spectra were recorded for the CdSe@CdSe NRs dispersed in chloroform at room temperature using a UV-756 CRT UV/vis spectrophotometer (Shanghai Youke instrument Co., Ltd, Shanghai, China).

Results and discussion

Characterization of CdSe@CdSe NRs.— CdSe@CdSe NRs (length (L) $\approx$ 40 nm; D $\approx$ 9-10 nm)¹⁷ were synthesized by **growth from** CdSe NPs (diameter (D) = 2.7-3.2 nm) as seeds. UV photoemission spectroscopy and waveguide-based spectroelectrochemistry **were used** to measure conduction and valence band energies (E_{CB} , E_{VB}) for CdSe@CdSe NRs. Both approaches show E_{VB} = 5.9-6.1 eV and E_{CB} = 4.1-4.3 eV¹⁷. Figure 1a shows **the** photoluminescence (PL) spectrum from CdSe@CdSe NRs film deposited on ITO. The PL of CdSe@CdSe NRs exhibits a peak at 692 nm when excited at 490 nm. The absorbance spectrum from CdSe@CdSe NRs (Figure 1b) shows broad absorbance in the visible region. Absorption bands are observed at about 555 nm (band gap, 2.2 eV) and 680 nm (band gap, 1.8 eV) (marked by arrows). CdSe@CdSe NRs could be a useful semiconductor in photovoltaic cells and electrooptic modulators, because its band gap is in the visible light region. The PL emission peak is red shifted about **10 nm** from the lowest energy band in the absorbance spectrum. The red shift **indicative** of the formation of a core/shell structure; the same results for core/shell NCs have been reported in details by several authors^{19,20}.

As described earlier, ideal QDs will produce a narrow and sharp PL spectra and the QDs band gap width can be deduced from the central PL wavelength position **in the absence of** surface defects. On the other hand, **non-ideal** QDs will produce a broad, asymmetric, and red-shifted PL peak with a nonzero background tail attributed to their surface defects; these surface energetic states **can** trap the excited electrons/holes that migrate from the conduction band /valence band, resulting in the surface-state-related e-h recombination and transition (emission)^{21,22}. The PL spectrum from CdSe@CdSe NRs in Figure 1a **lacks a** background tail **which** indicates that there is no significant luminescence from surface defects.

Electrochemical and ECL Behaviors of CdSe@CdSe NRs Thin Film. — A 5.0 ml volume of phosphate buffer solution (0.1 M, pH = 9.2) and the required amount of hydrogen peroxide was added to a 10 ml ECL cell. The electrodes were immersed into the cell that was placed in the dark chamber. A cyclic potential from 0 to -2.0 V (versus Ag/AgCl) was applied to the working electrode. When the potential was applied to the working electrode, ECL was generated and the ECL signal was recorded. Figure 3 shows the cyclic voltammograms and ECL curves of the CdSe@CdSe NRs assemblies at 100 mV/s in PBS. The bare Pt electrode showed low background current (Figure 2a), and no light emission was observed in an air-saturated solution (Figure 2b). At the CdSe@CdSe NRs thin-film modified Pt electrode, a scan between 0 and -2.0 V in air-saturated solution, there is a broad shoulder around -1.3 V (Figure 3a). On the other hand, a large ECL signal was observed at -1.05 V (ECL-I) and a smaller ECL signal at -1.33 V (ECL-II) when the electrode potential was cycled at a scan rate of 100 mV/s (Figure 3b). ECL-I might result from the reaction between co-reactants and individual reduced nanorods species and ECL-II could be explained by an electron transfer reaction between reduced and oxidized NRs. The ECL-I observed at the first negative potential region is not explained with annihilation of redox species of NRs because there are only reduced rods without the oxidized ones acting as an electron acceptor⁶.²³. The CVs in Fig. 2 and 3 also showed a broad shoulder around -1.3 V due to the reduction of O₂/H₂O₂. So, there might be oxidized species such as HO₂⁻ or OH[·] to accept electrons from the anion NR radicals and to form the emitter. The lack of good electrochemical behavior at 100 mV/s may be due to the bigger size of nanorods (length (L) ≈ 40 nm; D ≈ 9-10 nm). Similar results were observed for CdS nanocrystals²⁴. The CV peaks at 10 mV/s are not well defined when the particle size is 5 nm which can be attributed to the limited solubility of the particles¹. The solubility of the particles in the

solvents employed was found to be inversely proportional to their size^{21,24}. CdSe@CdSe NRs in the thin film could be reduced to produce nanorods species ($R^{\bullet-}$) that then reacted with some co-reactants to produce excited states (R^*) and to emit light in an aqueous system. When dissolved oxygen was further removed by bubbling high-purity nitrogen for 20 min, the ECL emission disappeared. Thus, dissolved oxygen or its reduced product OOH^- participated in the ECL reactions. The addition of H_2O_2 to the deoxygenated solution by bubbling high-purity nitrogen for 20 min and kept flowing over the solution could reversibly enhance ECL intensity (Figure 4b). There were also no obvious electrochemical signals (Figure 4a). As shown in Figure 4b, another ECL signal (ECL-III) is observed by applying reverse sweeping from -2.0 to 0 V. Electron-transfer annihilation of electrogenerated anion and cation radicals result in the production of excited states for the ECL emission. The ECL-III signal is not often detected even in ECL transients.

Under optimized experimental conditions, the pH value of the PBS buffer showed an effect on the ECL emission. With an increasing solution pH from pH 5.0 to 10.0, the ECL intensity of the CdSe@CdSe NRs modified Pt electrode in the presence of 0.20 mM H_2O_2 increased greatly and then trended to a constant value at pH 9.2. So, pH 9.2 electrolyte solutions were used in our experiment. The enhancement in ECL emission in the presence of H_2O_2 was mainly due to the adsorption of Lewis bases, which changed the surface states of CdSe@CdSe NRs film²⁵.

The ECL property of QDs correlates to both the band gap transition and surface-state, thus it is rational to classify ECL of QDs into two basic types: the band gap type and the surface-state type^{22,26}. It is also believed that the ECL emission is not sensitive to NC size and capping agent used but depends more sensitively on surface properties and the presence of surface states^{1,7}. 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. Because ECL depends more sensitively on surface states than PL, it can also be effectively used to elucidate the nature of the emitting state of semiconductor NCs¹⁹.

The ECL spectrum was red-shifted compared to the PL spectrum by hundreds of nanometers such as CdSe NCs; and these shifts were attributed to surface effects¹. Figure 5 shows the ECL spectrum obtained from the CdSe@CdSe NRs modified Au slide in air-saturated 0.1 M pH 9.2 PBS containing 2.0 mM H₂O₂. The ECL spectrum shows a main peak at ~691 nm, which is virtually identical to the one in the PL spectrum (Figure 1a). This is the observation of an ECL spectrum where the peak position is very similar to the one in PL. This peak location suggests that NRs surfaces have been largely passivated. In CdSe@CdSe NRs, as other core/shell structures QDs, the shell can serve a physical barrier between the optically active core and the surrounding medium to stabilize its optical properties. The shell also provides an efficient passivation of surface trap states¹³. The same result was observed for CdSe/ZnSe NCs¹⁹. CdSe/ZnSe core shell NCs that were well-passivated with a shell of ZnSe showed an ECL peak at the wavelength of band-edged PL. To support the high surface passivation of CdSe@CdSe NRs, as shown in Figure 1, the PL went down to the background level at longer wavelengths without any PL tail. These data further indicate that the excited state, by which the ECL emission is generated at different potentials, is CdSe@CdSe*. H₂O₂ molecules can be catalytically decomposed at the Pt substrate. The dissolved oxygen can be electrochemically reduced to H₂O₂ and then works as a co-reactant to react with individual reduced nanorod species. The reaction

between co-reactants and assembly of CdSe reduced nanorods species to produce ECL emission. Thus, the ECL process can be expressed as follows:

From Figure 3, CdSe@CdSe NRs in the thin film could be reduced to produce nanorods species, dissolved oxygen in PBS solution could be reduced to $\text{HOO}^{\cdot-}$, and dissolved oxygen also could be further reduced to $\text{OH}^{\cdot}$. Thus, reactions 1-3, 6, 8 produced ECL-I emission and reactions 1, 5, 7, 8 produced ECL-II emission. From Figure 4, reactions 1, 4, 6, 8 produced ECL-I emission and reactions 1, 5, 7, 8 produced ECL-II emission. Compared with dissolved oxygen, hydrogen peroxide could be reduced to less product $\text{HOO}^{\cdot-}$. Figures 3 and 4 showed the difference sensitivity of ECL-I and ECL-II, indicating the reactions between $\text{HOO}^{\cdot-}$ and reduced nanorods species was faster than those between $\text{OH}^{\cdot}$ and the reduced nanorod species; also indicating the reaction between $\text{OH}^{\cdot}$ and nanorod species (the reaction 5) was faster than those between $\text{OH}^{\cdot}$ and the reduced nanorod species. During the potential reverse sweep from -2.0 to 0 V, a small number of nanorod holes was produced. According to the reactions 7 and 8, ECL-III was produced (Figure 4). The appearance of ECL peaks

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3 implies that the CdSe@CdSe NRs assemblies provide the possibility for the stability of
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5 partial electrogenerated species to allow the formation of the excited states. The ECL
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7 spectrum further indicates that the excited state is CdSe NRs*.
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10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

ECL emission from CdSe@CdSe NRs films in aqueous solutions was found under cyclic voltammetric conditions. Upon a negative potential scan, two ECL peaks were observed, corresponding to the electron-transfer reaction between co-reactants and individual reduced CdSe@CdSe NRs species and the annihilation mechanism of reduced NRs species. The CdSe -based core/shell systems exhibit electrochemiluminescence far-visible near-infrared region. These features may significantly broaden the possibility of using CdSe NCs for analysis, display and tagging applications. We will next make further investigations on the ECL of other near-infrared-emitting semiconductor NRs in aqueous solution and analytical applications of it.

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Legends:

Fig. 1. (a) The PL spectrum of CdSe@CdSe NRs on ITO in air-saturated 0.1 M pH 9.2 PBS (b) The UV-vis absorption spectrum of CdSe@CdSe NRs (dispersed in chloroform).

Fig. 2. (a) Cyclic voltammogram of bare Pt electrode in air-saturated 0.1 M pH 9.2 PBS. (b) ECL curve corresponding to the cyclic voltammogram.

Fig. 3. (a) Cyclic voltammogram of the CdSe@CdSe NRs modified Pt electrode in air-saturated 0.1 M pH 9.2 PBS. (b) ECL curve corresponding to the cyclic voltammogram.

Fig. 4. (a) Cyclic voltammogram of the CdSe@CdSe NRs modified Pt electrode in 0.1 M pH 9.2 PBS bubbled with N₂ for 20 min + 0.20 mM H₂O₂. (b) ECL curve corresponding to the cyclic voltammogram.

Fig. 5. ECL spectrum of CdSe@CdSe NRs modified Au slide in air-saturated 0.1 M pH 9.2 PBS containing 2.0 mM H₂O₂ obtained using the fixed potential -1.7 V.

Figure 1

Fig. 1. (a) The PL spectrum from CdSe@CdSe NRs on ITO in air-saturated 0.1 M pH 9.2 PBS (b) The UV-vis absorption spectrum from CdSe@CdSe NRs (dispersed in chloroform).

Figure 2

Fig. 2. (a) Cyclic voltammogram of bare Pt electrode in air-saturated 0.1 M pH 9.2 PBS. (b) ECL curve corresponding to the cyclic voltammogram.

Figure 3

Fig. 3. (a) Cyclic voltammogram of the CdSe@CdSe NRs modified Pt electrode in air-saturated 0.1 M pH 9.2 PBS. (b) ECL curve corresponding to the cyclic voltammogram.

Figure 4

Fig. 4. (a) Cyclic voltammogram of the CdSe@CdSe NRs modified Pt electrode in 0.1 M pH 9.2 PBS bubbled with N₂ for 20 min + 0.20 mM H₂O₂. (b) ECL curve corresponding to the cyclic voltammogram.

Figure 5

Fig. 5. ECL spectrum of CdSe@CdSe NRs modified Au slide in air-saturated 0.1 M pH 9.2 PBS containing 2.0 mM H_2O_2 obtained using the fixed potential -1.7 V.