Enhanced solid-state electrochemiluminescence of CdS nanocrystals composited with carbon nanotubes in H_2O_2 solution

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CdS nanoparticles composited with carbon nanotubes not only enhances their electrochemiluminescent intensity but also decreases their ECL starting potential; such a property would promote the application of quantum dots in fabricating sensors for chemical and biochemical analysis.

Electrochemiluminescence (ECL) concerning semiconductor nanocrystals (NCs) has attracted tremendous interest in recent years. Bard and co-workers reported that reduced and oxidized NCs, such as Si, CdSe, CdSe@ZnSe, Ge or CdTe,[1–5] generated at a certain electrochemical voltage, can react with some co-reactants to produce ECL.

It is interesting to study the ECL of CdS NCs. In previous work, Bard's group reported that ECL in thioglycerol-capped CdS NCs has not been found because of the instability of the electrogenerated reactants.[2] However, Zhu *et al.* observed ECL from CdS spherical assemblies in aqueous solution.[6] The investigation of ECL processes in CdS NCs is valuable both for the study of semiconductor NCs' ECL mechanisms and for searching for new ECL materials to accelerate the use of ECL in analytical fields.

ECL analysis has many advantages over photoluminescence due to the absence of background from unnecessary photoexcitation. In an ECL process, the electron transfer reaction between electrochemically formed nanocrystal species and co-reactants implies that semiconductor NCs have great potential for the development of novel ECL sensors for analytical applications. However, to our knowledge, only one ECL sensor based on CdSe semiconductor NCs has been reported.[7] The reasons are partially that the ECL intensity of semiconductor NCs is lower than that of conventional luminescent reagents such as luminal or $Ru(bpy)_3^{2+}$, and that the NCs in ECL processes with a high excited electrochemical potential are unstable. Thus, new semiconductor NCs and methods to enhance ECL are urgently needed for the development of novel ECL sensors. Recently, Poznyak *et al.* found that electron injection into CdSe/CdS core–shell nanocrystals *via* a negative potential can not only dramatically enhance the chemiluminescent intensity but also prevent nanocrystals from undergoing oxidative corrosion, and so obtain stable ECL.[8]

Due to their peculiar optical, electronic, magnetic and catalytic properties, nanomaterials have been widely applied in microelectronics, non-linear optics, catalysis, sensor science and other areas. For example, gold colloids have been used to enhance photoluminescence of CdSe@ZnS quantum dots.[9] Carbon nanotube (CNT)-modified electrodes exhibit an excellent electrocatalytic

The Key Lab of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China. E-mail: hychen@nju.edu.cn; Fax: +86 25-83594862; Tel: +86 25-83597294

ability in the reduction and oxidation of some compounds with decreasing overvoltages.[10]

In the present work, CdS NCs were prepared *via* an easy method using thioglycolic acid as a protective reagent. A CdS NC/CNT composite solid-state thin film modified electrode was fabricated using CdS NCs composited with CNTs. When negative potentials, such as −1.1 V, were applied to the modified electrode in H_2O_2 solution, efficient ECL was clearly visible in daylight. Compared with pure CdS NC thin films, a *ca.* 5-fold enhanced ECL of a CdS NC/CNT film has been found, and the ECL starting voltage shifts positively from −1.15 to −0.85 V. Meanwhile, the ECL intensities of CdS NCs and co-reactant H_2O_2 were very stable. All the above properties would promote the development of novel hydrogen peroxide ECL sensors based on CdS NCs doped with CNTs.

CdS NCs were synthesized by the following procedure: 0.2 g of cadmium chloride hydrate and 50 μL thioglycolic acid were added to 50 mL distilled water. The pH of the solution was adjusted to 10 using sodium hydroxide. Then, 50 mL 0.2% thioacetamide aqueous solution was added with extensive stirring in air for 30 min. The yellow precipitate was centrifuged, washed and dried in air. The resulting powder was used for the electrochemistry and ECL experiments. Multi-walled CNTs (95%) (diameter 10 ∼ 20 nm), purchased from Shenzhen Nanotech. Port. Co. Ltd. (Shenzhen, China), were thoroughly oxidized according to existing procedures involving acidic potassium permanganate solution and hydrochloric acid.[11] 0.5 mg mL^{-1} CdS NC and CNT solutions were obtained *via* dispersing CdS NCs and CNTs in twice-distilled water under ultrasonication, respectively. The CdS/CNT composite was obtained by mixing the above CNT solution and the CdS NC solution in the volume ratio 2 : 3 under ultrasonication for 30 min.

The CdS NCs, CNTs and CdS/CNT composite were characterized by transmission electron microscopy (TEM, JEM-CX001). The TEM images show that the CdS NC sample prepared comprised of large clusters composed of many small nanocrystals, with an average size of 4–5 nm (A in Fig. 1). The dispersed CNTs obtained through the oxidation process were very pure (B in Fig. 1). From the CdS/CNT composite TEM (C in Fig. 1), the CNT surfaces were covered with CdS NC clusters. The side walls of the CNTs obtained *via* the oxidation procedure were coated with keto, carboxylic, aldehyde and alcoholic groups.[12] These functional groups may play an important role in anchoring CdS NCs capped with thioglycolic acid. UV-vis (UV-2401PC) and fluorescence (RF-5301PC) spectrophotometers were used to characterize the adsorption, emission and ECL spectra of CdS NC films. Scanning electron microscopy (SEM, Leo 1530 with a field emission column) was used to characterize the CdS NC and
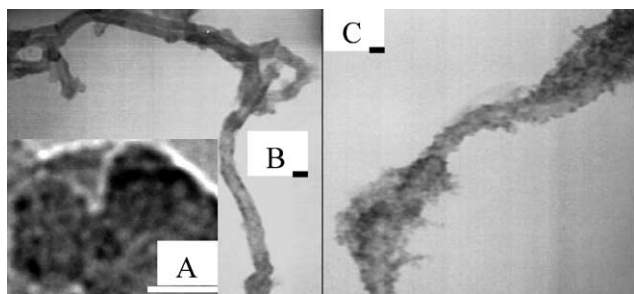
Fig. 1 TEM analysis for (A) CdS NCs, (B) CNTs and (C) CdS NC/CNT composite. The tool bars are 20 nm.

CdS/CNT composite films on a glassy carbon disk modified electrode (GCE). Electrochemical and ECL were performed with a MPI-A ECL analyzer (Xi'an Remax Electronic High-Tech Ltd.) using a three-electrode system. A GCE (diameter 4 mm), a platinum wire and a saturated calomel electrode (SCE) were applied as the working, auxiliary and reference electrodes, respectively. The photomultiplier tube (PMT) was biased at 500 V.

For investigating the ECL of CdS NC thin films, modified electrodes were applied. To ensure an equal quantity of CdS in the films, 6 µL of CdS NCs and 10 µL of the CdS/CNT (2 : 3 volume ratio) composite were used to fabricate the films on a GCE. In the present investigation, H_2O_2 was used as the ECL co-reactant. Only when applying a negative scan voltage was the ECL very stable. In this case, electrochemical n-doping of the particles *via* electron injection provides a "quantum confined cathodic protection" against nanocrystal oxidative corrosion upon hole injection, allowing the achievement of efficient and stable electrogenerated chemiluminescence.[8] However, if the upper limit of the scan potential was over 0.3 V, ECL decreased quickly and then disappeared due to the instability of CdS with respect to the $(EC)^n$ mechanism.[13]

Fig. 2 shows the (a) UV spectrum, (b) photoluminescence (PL) spectrum with an excitation wavelength of 355 nm, and (c) the ECL spectrum of CdS NC films. The UV and PL spectra of the CdS NC film were measured on quartz glass. The ECL spectrum of CdS NCs was measured by fluorescence spectroscopy (RF-5301PC), where the CdS NC modified GCE working electrode was biased at −1.1 V in 0.1 mol L^{-1} (pH 9.0) phosphate buffered saline (PBS) with 10 mmol L^{-1} H_2O_2 in a conventional three-electrode system. As the particle size decreases, the absorption edges of CdS are shifted to higher energies from the bulk band gap due to the well-known quantum size effect. Experimental results showed that the maximum wavelength of the adsorption spectrum was 440 nm, according to the equation of Peng *et al.*[14] The matching value of the particle diameter should be 4.85 nm, which is coincidental with the TEM experimental results. The sharp PL peaks indicate a highly monodisperse sample. The PL spectrum shows a narrow line width, comparable to the absorption line width, with the emission peak red-shifted by 28 nm compared to the maximum wavelength of the adsorption spectrum. This shift is the result of a combination of relaxation into trap states and the size distribution.[15] The PL spectrum shows a non-zero tail towards longer wavelengths, suggesting the presence of surface traps.[2] Meanwhile, the observed maximum wavelength of the ECL spectrum at 650 nm was red-shifted by almost 200 nm from the PL emission maximum wavelength. The difference in light emission spectra between ECL and PL most likely results from a major contribution of the surface states in the ECL emission, which is consistent with the results of the ECL behaviors of Si and CdSe nanocrystals obtained by Bard *et al.*[1,2] This result suggests that ECL spectra are more important tools than PL spectra when studying the surface states of NCs.

Fig. 3 shows the ECL–potential (*E*) curves for the CdS/CNT composite and pure CdS films in pH 9.0 PBS solution containing 10 mmol H_2O_2. It has been mentioned that the quantities of CdS are equal in both films. The integral luminescence intensity was recorded simultaneously with the cathodic current as the potential was scanned in the negative direction from 0 to −1.5 V. The possible ECL mechanisms of the CdS NCs reacted with H_2O_2 can be expressed as follows (eqn. (1), eqn. (2) and eqn. (3)):[1,7]

$$CdS\ NCs + ne^- \rightarrow nR^- \tag{1}$$

$$2R^- + H_2O_2 \rightarrow 2R^* + 2\ OH^- \tag{2}$$

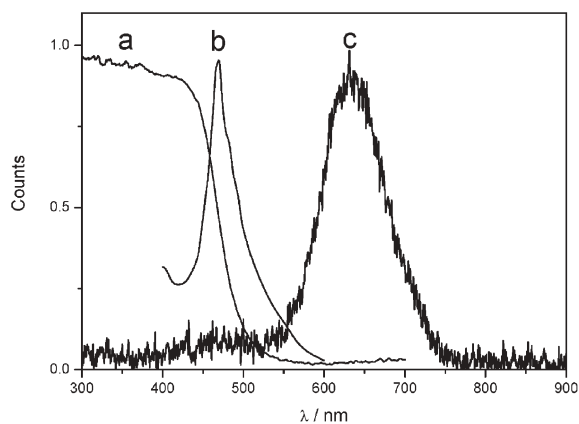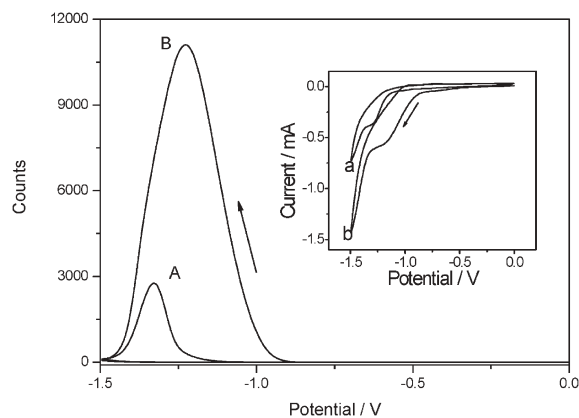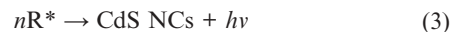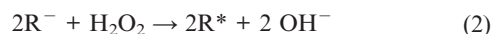$$nR^* \rightarrow CdS\ NCs + h\nu \tag{3}$$

Fig. 2 Normalized spectra of a CdS NC film. (a) Adsorption spectrum on quartz glass, (b) emission spectrum on quartz glass with a 355 nm excitation wavelength and (c) ECL spectrum on a GCE working electrode biased at −1.1 V in 0.1 mol L^{-1} PBS (pH 9.0) with 10 mmol L^{-1} H_2O_2.

Fig. 3 ECL–*E* curve of (A) CdS NCs and (B) CdS NC/CNT composite film modified electrodes in 0.1 M phosphate buffer (pH 9.0) with 10 mmol L^{-1} H_2O_2. Inset: The cyclic voltammograms corresponding to (a) CdS NCs and (b) CdS NC/CNT composite film modified electrodes in 10 mmol L^{-1} H_2O_2. Scan rate: 100 mV s^{-1}.
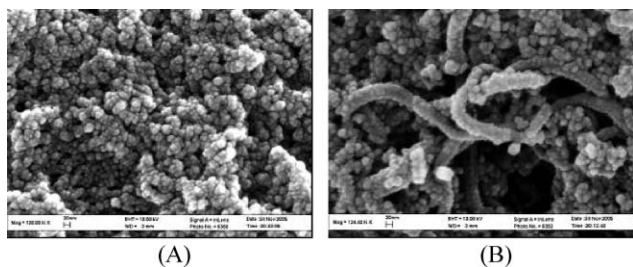
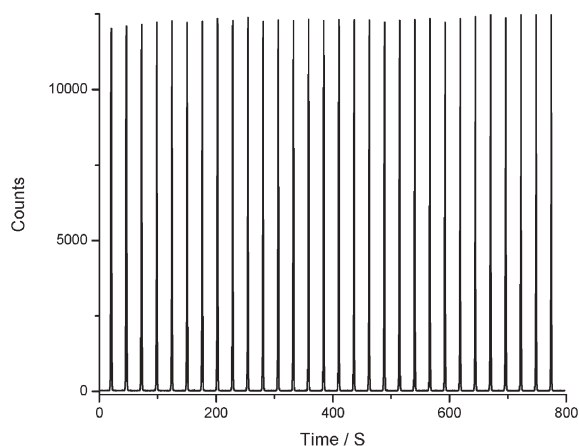**Fig. 4** FE-SEM of (A) CdS NC and (B) CdS NC/CNT composite films.

Fig. 6 Dependence of the ECL intensity of CdS NC/CNT composite modified GCE on the concentration of H_2O_2. (a) 1.0, (b) 5.0 and (c) 10.0 mmol L^{-1} in 0.1 mol L^{-1}, pH 9.0 PBS with a scan rate of 100 mV s^{-1}.

Fig. 5 ECL emission from the CdS NC/CNT composite film in 0.1 mol L^{-1} phosphate buffer (pH 9.0) containing 10 mmol L^{-1} H_2O_2 under continuous cyclic scans from 0 V to -1.45 V for 30 cycles. The PMT was biased at 500 V. Scan rate: 100 mV s^{-1}.

In this case, R^- and R^* refer to the reduced species and excited states of CdS NCs, respectively.

The cathodic current–potential (inset to Fig. 3) and the ECL intensity–potential dependencies, measured for the films of CdS NCs with and without CNTs, show the effect of CNTs on the cathodic current, the ECL intensity and the ECL onset voltage. It can be seen that the cathodic peak current and ECL intensity of CdS NC/CNT composite film is, respectively, *ca.* 2-fold and *ca.* 5-fold higher than that observed for the pure CdS NC film, where the ECL onset voltage of the composite film is about -0.85 V while the ECL onset voltage of the pure CdS film is about -1.15 V. In order to identify the function of CNTs in ECL processes, we studied the electrochemical behaviors of CdS and CdS CNT composite modified electrodes in 0.1 mol L^{-1} PBS solution without H_2O_2 and O_2. Cyclic voltammograms demonstrated that the onset reduction potential of CdS NCs also shifted positively and the cathodic peak current was enhanced in the composite film (not shown). These phenomena indicate that the presence of CNTs obviously decreased the potential barriers of eqn. (1). On the other hand, the more porous structure of the composite film (see the FE-SEM in Fig. 4) facilitated the diffusion of H_2O_2 into the membrane and resulted in ECL occurring not only at the interface but also in the bulk of the nanocrystal film.

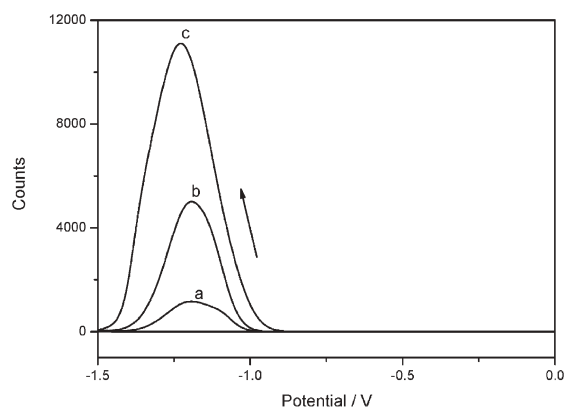Fig. 5 shows that the ECL of the CdS/CNT composite is stable. When consecutive scans from 0 to -1.45 V were performed for 30 cycles in 10 mmol H_2O_2 solution, no obvious change was observed. The effect of hydrogen peroxide concentration on the ECL intensity of the CdS NC/CNT composite modified GCE is shown in Fig. 6. By increasing the concentration of H_2O_2, the corresponding ECL increased. The accurate and rapid determination of hydrogen peroxide is of essential importance in bioanalytical and environmental fields. All the results mentioned above would not only promote the development of novel hydrogen peroxide ECL sensors based on CdS NCs doped with carbon nanotubes but also accelerate the use of semiconductor NCs' ECL in analytical fields.

Notes and references

1 Z. Ding, B. M. Quinn, S. K. Haram, L. E. Pell, B. A. Korgel and A. J. Bard, *Science*, 2002, **296**, 1293–1297.
2 N. Myung, Z. Ding and A. J. Bard, *Nano Lett.*, 2002, **2**, 1315–1319.
3 N. Myung, Y. Bae and A. J. Bard, *Nano Lett.*, 2003, **3**, 1053–1055.
4 N. Myung, X. Lu, K. P. Johnston and A. J. Bard, *Nano Lett.*, 2004, **4**, 183–185.
5 Y. Bae, N. Myung and A. J. Bard, *Nano Lett.*, 2004, **4**, 1153–1161.
6 T. Ren, J.-Z. Xu, Y.-F. Tu, S. Xu and J.-J. Zhu, *Electrochem. Commun.*, 2005, **7**, 5–9.
7 G. Zou and H. Ju, *Anal. Chem.*, 2004, **76**, 6871–6876.
8 S. K. Poznyak, D. V. Talapin, E. V. Shevchenko and H. Weller, *Nano Lett.*, 2004, **4**, 693–698.
9 O. Kulakovich, N. Strekal, A. Yaroshevich, S. Maskevich, G. Gaponenko, I. Nabiev, U. Woggon and M. Artemyev, *Nano Lett.*, 2002, **2**, 1449–1452.
10 X.-L. Luo, J.-J. Xu, J.-L. Wang and H.-Y. Chen, *Chem. Commun.*, 2005, **16**, 2169–2171.
11 H. Hiura, T. W. Ebbesen and K. Tanigaki, *Adv. Mater.*, 1995, **7**, 275–276.
12 A. M. Bond, W. Miao and C. Raston, *Langmuir*, 2000, **16**, 6004–6012.
13 S. K. Haram, B. M. Quinn and A. J. Bard, *J. Am. Chem. Soc.*, 2001, **123**, 8860–8861.
14 W. W. Yu, L. Qu, W. Guo and X. Peng, *Chem. Mater.*, 2003, **15**, 2584–2560.
15 C. B. Murray, D. J. Norris and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706–8715.