

Spectroelectrochemistry of hollow spherical CdSe quantum dot assemblies in water

Bo Liu^a, Ting Ren^a, Jian-Rong Zhang^a, Hong-Yuan Chen^a,
Jun-Jie Zhu^{a,*}, Clemens Burda^{b,*}

^a Key Laboratory of Analytical Chemistry for Life Science, Department of Chemistry, Nanjing University, Nanjing 210093, PR China

^b Department of Chemistry, Case Western Reserve University, Cleveland, OH 44106, USA

Received 16 September 2006; received in revised form 14 October 2006; accepted 16 October 2006

Available online 16 November 2006

Abstract

The hollow spherical CdSe QD assemblies were synthesized via a sonochemical approach that utilizes β -cyclodextrin as a template reagent in aqueous solution. The hollow nanospheres have an average diameter of 70 nm and are found to consist of an assembly of monodispersed 5 nm sized CdSe quantum dots. Following an electrochemical reaction with persulfate ions, strong electrogenerated chemiluminescence (ECL) was observed from the CdSe nanoassemblies suspended in an aqueous solution of $\text{pH} \leq 7.95$. The study indicates that the morphology of the 70 nm nanoassembly plays an important role in generating the stable ECL since individually dispersed quantum dots did not exhibit any significant ECL. The unique ECL intensity and stability of the synthesized spherical nanoassemblies could allow for potential sensor applications of CdSe quantum dots in water.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Spectroelectrochemistry; Electrogenerated chemiluminescence; CdSe hollow sphere

1. Introduction

CdSe quantum dots (QDs) have been the subject of intense study because of their unique optical properties [1–7]. Their strong and tunable absorption and luminescence properties make them ideal systems for bioimaging, sensor, and assay applications [8–10]. However, these nanomaterials are usually prepared with organic capping that makes them soluble in nonpolar solvents and it requires a rather lengthy procedure to make them retain their good optical properties in aqueous media. Particularly water is found to be a very efficient luminescence quencher for CdSe QDs [11]. In this paper we report an alternative way of generating strong and stable luminescence from CdSe QDs in aqueous solution through electro-

generated chemiluminescence (ECL). ECL is a radiative charge recombination originating from emitting excited states of electrogenerated species [12]. During the past decades, ECL has been used in a wide range of analytical applications including organic analysis, immunosensors, DNA-probe assays and enzymatic biosensors [13,14]. Recently, a growing interest in ECL studies of semiconductor nanomaterials has emerged because of the unique size-dependent electrochemical and optical properties of these nanomaterials [15,16]. Current studies have demonstrated that semiconductor nanocrystals can be electrically excited in both non-aqueous media [17–21] and aqueous systems [22]. Furthermore, the ECL behavior of semiconductor nanocrystals was found to be dependent and more sensitive to the particle surface states as compared to the bulk counterpart [18–21].

In order to generate ECL, the electrogenerated reduced and oxidized species have to be stable enough to be able to form excited state complexes [17,18]. In addition, some co-reactants such as persulfate ions are usually added to the

* Corresponding authors. Tel.: +86 25 83594976; fax: +86 25 83594976 (J.-J. Zhu).

E-mail addresses: jjzhu@mail.nju.edu.cn (J.-J. Zhu), burda@case.edu (C. Burda).

system to promote good luminescence efficiencies [17]. In recent studies, the ECL arising from spherical assemblies of CdS nanocrystals has been demonstrated [23]. The aggregated surface morphology of the nanostructures was found to play an important role in the ECL emission. In this paper we have extended our work towards optimizing the stability of the ECL generated from quantum dot nanoassemblies. The control of size, shape, and surface properties are critical in order to create or enhance specific optical and electronic properties [24]. Along this line, we have synthesized hollow spherical CdSe QD assemblies with narrow size distribution in order to generate highly stable ECL from these semiconductor nanomaterials.

It has been well established that ultrasonic irradiation causes a number of physical and chemical effects deriving from acoustic cavitation [25,26]. Such cavitation behavior, i.e. the formation, growth and implosive collapse of gas bubbles, has been discovered to have a strong effect on the aggregation of nanoparticles [27–30]. Here, we demonstrate that the sonication of nanomaterials can be an effective assembly route for the controllable synthesis of slightly more complex, spatially structured and functional nanomaterials. To this end, the high-intensity ultrasonic irradiation was used to induce the formation of hollow spherical CdSe nanoassemblies using β -cyclodextrin as a template reagent. The synthesized nanospheres are ~ 70 nm in diameter and are composed of small 5 nm sized CdSe quantum dot assemblies. ECL from dispersed CdSe quantum dots and CdSe nanocrystal films has been previously reported [18,22]. However, either non-aqueous systems or strong alkali aqueous solutions were required for the generation of ECL emission to occur efficiently, which limited its applications to physiological environments. Here, we present hollow spherical CdSe nanoassemblies with strong and stable ECL in aqueous solution of pH 7.95, which allows for a broader range of applications. The observed highly efficient and stable ECL can be attributed to the self-assembled structure and correspondingly to the unique surface properties of the synthesized semiconductor nanoassemblies.

2. Experimental

2.1. Chemicals and materials

All reagents used were of analytical grade, and were used as purchased without further purification. β -cyclodextrin was purchased from Shanghai Chemical Reagent Corporation (China) and selenium powder was purchased from Acros Organics. The sodium selenosulfate stock solution (0.2 M) used in the experiment was prepared by stirring sodium sulfite (0.5 M) and elemental selenium (0.2 M) at ca. 70 °C for 24 h, using distilled water as solvent.

The structure of the synthesized products was studied by means of powder X-ray diffractometry (XRD) using a Philips X^{pert} X-ray diffractometer at a scan rate of 4°/min in the 2θ range of 20°–80° using Cu K α radiation ($\lambda = 1.5418$ Å). The investigation of the morphology and

microstructure of the synthesized CdSe nanostructures was carried out by transmission electron microscopy (TEM) (JEOL JEM-200CX) and scanning electron microscopy (SEM) (JEOL-4000EX) studies. Specimens for TEM investigation were prepared by dispersing a drop of the suspension in ethanol, followed by deposition of the nanoparticles onto a copper grid with a layer of amorphous holey carbon.

2.2. Spectroscopy and spectroelectrochemistry

The UV–vis absorption spectra were measured with a Ruili 1200 spectrophotometer (Peking Analytical Instrument Co.). The electrogenerated chemiluminescence was recorded on a MPI-A Electrochemiluminescence Analyzer (Xi'An Remax Electronic Science & Technology Co. Ltd. Xi'An, China). A CHI 660 electrochemical workstation was used in all the electrochemical experiments and all potentials were recorded relative to an Ag/AgCl reference electrode. The ECL spectrum was recorded on a fluorescence scanning spectrometer (AMINCO Bowman Series 2 SLM Inc., USA). The ECL spectroscopy was carried out in the spectrometer within a fluorescence cell, while continuously stepping the potential between 0.1 and -1.5 V.

2.3. Preparation of hollow spherical CdSe nanoassemblies

Cadmium chloride hydrate ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, 0.23 g, 0.0010 mol) and β -cyclodextrin (2.0 g, 0.012 mol) were dissolved in 40 ml distilled water. Afterwards, ammonia (30% NH_3) was added dropwise to the solution to adjust the pH to 10. Following this step, sodium selenosulfate (5 ml, 0.2 M) was added to the reaction mixture and the solution was irradiated with a high-intensity ultrasonic titanium horn (Sonic, 20 KHz, 75 W/cm²) under ambient conditions. Following a 20 min. ultrasonication step, a red precipitate was obtained and the precipitate was centrifuged and washed with distilled water and absolute ethanol, and then air-dried for the succeeding experimental measurements. Individually dispersed CdSe QDs were prepared in an analogous way, however without the β -cyclodextrin.

2.4. Electrochemical experiments

A three-electrode system was employed in all the electrochemical experiments, whereby a platinum wire was used as a counter electrode, Ag/AgCl as a reference electrode, and a carbon–paste electrode was used as the working electrode. The carbon–paste electrode was fabricated by mixing graphite powder and the as-prepared hollow spherical CdSe QD assemblies (6:1 mass ratio) in ethanol. After drying, a homogenized graphite/CdSe mixture was achieved. Subsequently, paraffin oil was added into the mixture (oil:mixture = 1:4 mass ratio) and thoroughly mixed until a homogeneous paste was obtained. The prepared paste was packed into a glass tube with a 4 mm inner diameter and electrical contact was established with a copper rod through

the back of the electrode. Afterwards, the electrode surface was polished with smooth paper. All potentials were recorded relative to an Ag/AgCl reference electrode.

3. Results and discussion

3.1. Synthesis and characterization

The hollow spherical CdSe QD assemblies were synthesized under ultrasonic irradiation, using β -cyclodextrin as a templating reagent. Transmission electron microscopy (TEM) studies show that the synthesized particles have the uniform and regular hollow spherical morphology with an average diameter of 70 nm (Fig. 1a).

The corresponding selected area electron diffraction (SAED) pattern (inset of Fig. 1a) indicates that the nanoassemblies are polycrystalline with diffraction rings corresponding to the (111), (220), and (311) lattice planes of a cubic CdSe crystallographic phase, respectively. In order to analyze the surface morphology of the nanoassemblies, scanning electron microscopy (SEM) was used and the SEM image (Fig. 1b) shows that these hollow nanospheres consist of an assembly of spherical quantum dots with an average size around 5 nm. This observation was further confirmed from powder X-ray diffraction studies on the hollow nanospheres.

Shown in Fig. 2 is the powder X-ray diffraction pattern obtained from the synthesized nanospheres. All the diffraction peaks can be indexed to the cubic phase of CdSe (JCPDS No. 19–191) and no characteristic peaks of other impurities were detectable. The broadening of the peaks indicates small nanocrystals that compose the spherical nanoassemblies. An average size of the CdSe particles of ~ 5 nm was confirmed by using the Debye–Scherrer equation as calculated from the half-width of the diffraction peaks.

The UV–vis absorption spectrum of the CdSe nanoassemblies was measured and is shown in Fig. 3. According to the direct conversion method [31] the band gap is found to be 2.24 eV, which is larger than the reported value of bulk CdSe ($E_g = 1.74$ eV). This band gap value can be attributed to the small size of CdSe quantum dots of which the spheres are made up and allows one to confirm an average size of about 5 nm for the individual quantum dots that form the spherical assembly [31].

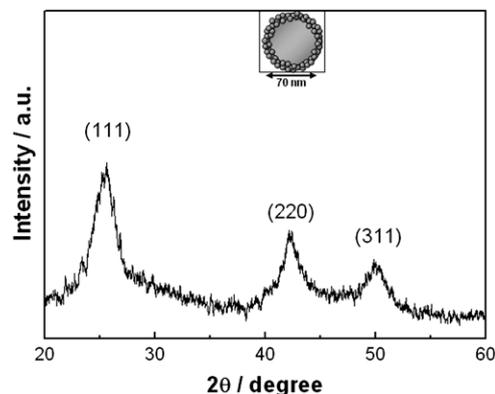


Fig. 2. The XRD pattern of the hollow spherical CdSe QD assemblies.

In the self-assembly process of the hollow CdSe nanospheres, aggregates of β -cyclodextrin are used to serve as a soft template for the particle formation. β -cyclodextrin is a cyclic oligosaccharide consisting of seven 1,4-linked D-glucopyranose units, which have a characteristic hydrophilic exterior and a hydrophobic interior [28]. In an aqueous solution with a high enough concentration, cyclodextrin undergoes self-association to form aggregates [32–37]. This process of cyclodextrin nanosphere formation has already been reported [38] and seems to play an important role in the formation of the CdSe assemblies.

3.2. Electrogenerated chemiluminescence

Nanocrystals can be oxidized and reduced by charge injection during the potential cycling at the electrodes [23]. Here, ECL occurs through radiative electron–hole recombination when electrochemically oxidized species collide with reduced quantum dots [14]. The addition of co-reactants can help overcome either a limited potential window of a solvent or the poor stability of electrogenerated oxidized or reduced species [39]. In the presented ECL experiments, persulfate ions were used as the co-reactant. In this case, the reduction of persulfate produces a strong oxidant species, SO_4^- . This intermediate can react with the negatively charged CdSe nanocrystals to generate chemiluminescence according to the following reaction scheme.

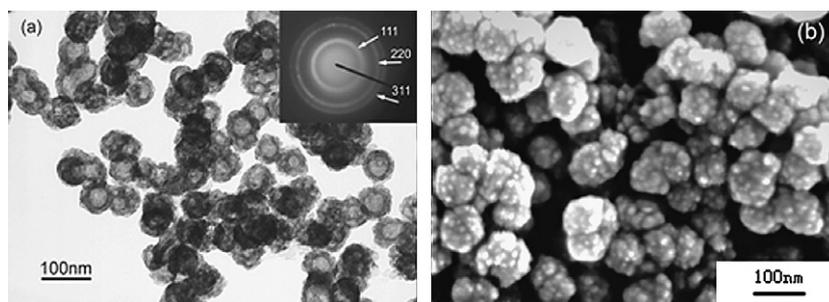


Fig. 1. (a) TEM and (b) SEM images of the hollow spherical CdSe QD assemblies.

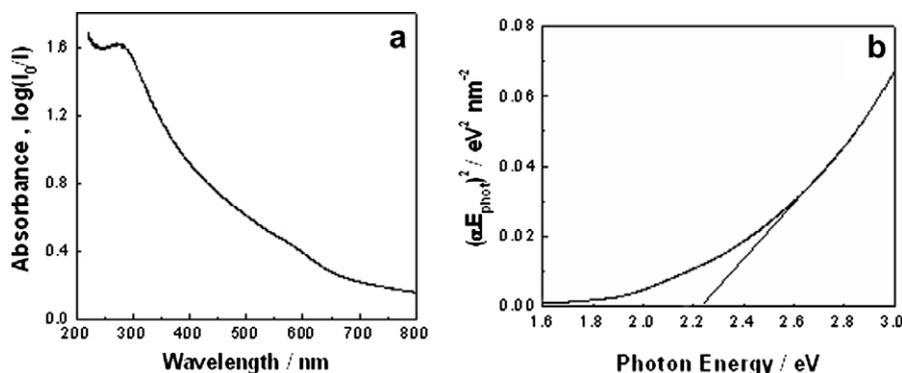
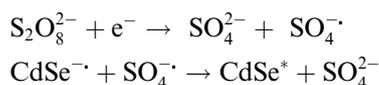


Fig. 3. (a) The UV-vis absorption spectrum of the hollow spherical CdSe QD assemblies (in EtOH) (b) Plots of $(\alpha E_{\text{phot}})^2$ vs. E_{phot} for a direct transition.



Differential pulse voltammetry (DPV) was used to investigate the electrochemical behavior of the hollow spherical CdSe QD assemblies. As shown in Fig. 4a, in the presence of $\text{S}_2\text{O}_8^{2-}$, two cathodic peaks were observed at -0.8 V and -1.1 V, respectively (curve 3). The peak at -1.1 V did not appear in blank carbon-paste electrode (curve 2). This implies that the cathodic peak at -1.1 V correlated to the reduction of CdSe nanocrystals. On the other hand, the peak at -0.8 V appearing in both curves 2 and 3 can be assigned to the reduction of peroxydisulfate ions, because this peak cannot be found in the absence of $\text{S}_2\text{O}_8^{2-}$ (curve 1). Fig. 4b shows the ECL-potential curve of the hollow spherical CdSe QD assemblies in the presence of peroxydisulfate ions ($\text{S}_2\text{O}_8^{2-}$) under cyclic voltammetric (CV) conditions. As the potential is cycled between 0.1 V and -1.2 V at 0.1 V/s scan rate, strong ECL signal is detected around -1.1 V, which is in good agreement with the cathodic DPV peak potential of CdSe nanocrystal reduction [22]. All these phenomena support the emission mechanism using persulfate ions as the co-reactant.

Fig. 5 shows the electrochemiluminescence spectrum of the CdSe nanoassembly obtained by stepping the potential between 0.1 V and -1.5 V. The envelope over the fluores-

cence spikes resembles the emission spectrum of a typical CdSe quantum dot with emission maximum at ~ 640 nm, which is red shifted from 5 nm QD emission. The emission spectrum is also relatively broad with a FWHM of 230 meV. This inhomogeneous broadening is not due to a broad size distribution, rather from surface states involved. In addition, the slight red-tailing of the spectrum towards 700 nm reveals a significant contribution from band gap states to the emission. The self-assembly seems therefore to have a protective function for these lower electronic states, which might well be localized surface or interface states.

Based on the structure of the β -cyclodextrin template reagent, the Cd(II) ions likely coordinate to the hydroxy groups in the glucose sub-units, which are enriched on the surface of the *in situ* assembled template. The application of ultrasonic irradiation in turn facilitates the release of Se ions, which subsequently react with the Cd(II) ions to form CdSe nuclei around the β -cyclodextrin aggregates. The formed CdSe nuclei can then undergo crystal growth and form a nanoshell-type structure consisting of small CdSe quantum dots. With this spherical nanoassembly strong electrogenerated chemiluminescence (ECL) can be observed.

The intensity of the ECL in the presence of peroxydisulfate ions shows great dependence on the pH of the solution. As illustrated in Fig. 6, the ECL intensity decreases with

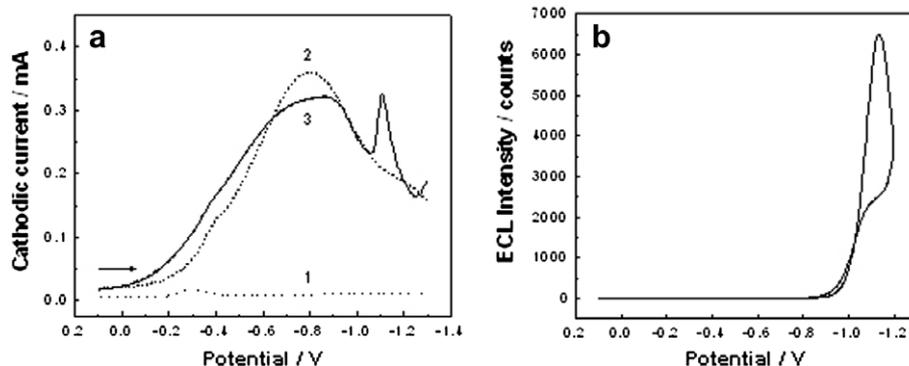


Fig. 4. (a) Differential pulse voltammograms of (1) blank carbon-paste electrode in 0.1 M KCl aqueous solution, (2) blank carbon-paste electrode in 0.1 M $\text{K}_2\text{S}_2\text{O}_8$ with 0.1 M KCl aqueous solution and (3) the hollow spherical CdSe nanoassemblies in 0.1 M $\text{K}_2\text{S}_2\text{O}_8$ with 0.1 M KCl aqueous solution. The arrow indicates the starting potential and the scan direction and (b) cyclic voltammetric ECL potential curve of the hollow spherical CdSe assemblies in 0.1 M $\text{K}_2\text{S}_2\text{O}_8$ with 0.1 M KCl aqueous solution (scan rate 100 mV/s).

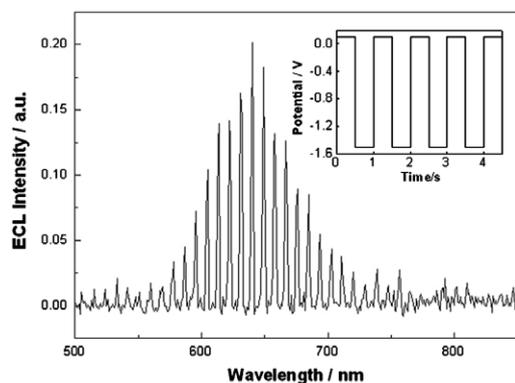


Fig. 5. Electrochemiluminescence spectrum of the hollow spherical CdSe QD assemblies obtained in 0.1 M $K_2S_2O_8$, 0.1 M KCl and 0.1 M KOH aqueous solution. Inset: potential steps curve between 0.1 V and -1.5 V (step time: 0.5 s).

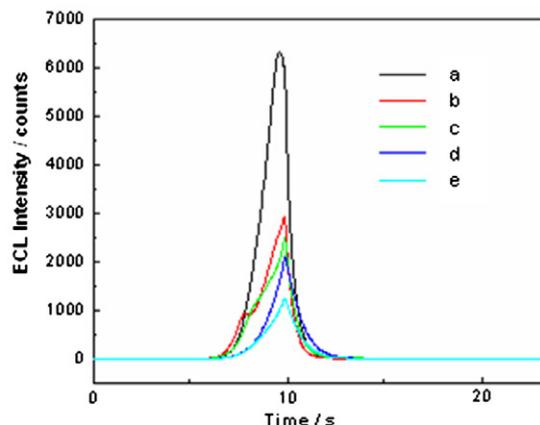


Fig. 6. Effect of different pH on ECL of the hollow spherical CdSe QD assemblies. The ECL curves were obtained in 0.1 M $K_2S_2O_8$ and 0.1 M KCl aqueous solution adjusted to the desired pH with potassium hydroxide. (a) pH 7, (b) pH 8, (c) pH 9, (d) pH 10, and (e) pH 11.

increasing pH value. The decrease of ECL intensity in basic solutions is assigned to the consumption of $SO_4^{\cdot -}$ by the scavenging reaction with OH^- [40]. This pH effect of the persulfate co-reactant on ECL intensity further supports the emission mechanism described above.

From Fig. 6, the best ECL measurements on the hollow CdSe QD assemblies were performed in aqueous solutions with pH around 7. This is important for potential applications since the pH environment in biological systems is ~ 7.4 . Shown in Fig. 7 is the ECL emission from the hollow CdSe QD assemblies in a 0.1 M, pH 7.95 phosphate buffer solution (PBS) containing 0.1 M $K_2S_2O_8$ and 0.1 M KCl, which was obtained under continuous potential cycling. Stable ECL emission from the hollow spherical CdSe QD assemblies was obtained during the course of the voltammetric cycling.

For comparison purposes, ECL measurements on dispersions of individually dispersed CdSe quantum dots were also carried out. A nanoparticle mean size of ~ 5 nm is estimated from the absorption of the CdSe quantum dots used in the analysis (Fig. 8a), based on the first absorption peak

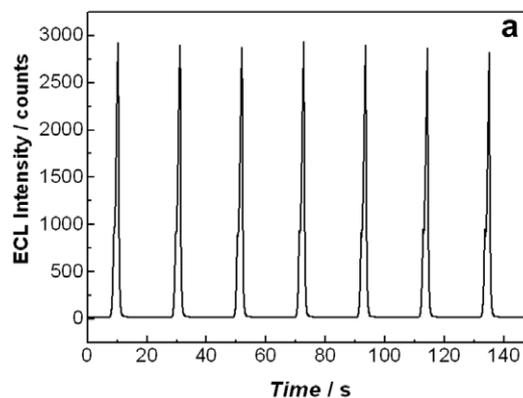


Fig. 7. ECL emission from the hollow spherical CdSe QD assemblies under continuous CVs for 7 cycles in 0.1 M pH 7.95 PBS with 0.1 M $K_2S_2O_8$ and 0.1 M KCl.

wavelength at 575 nm [31]. This size range coincides well with the one of the small CdSe quantum dots that compose the CdSe nanosphere assemblies. Fig. 8b shows the weak ECL emission signal from the individually dispersed CdSe quantum dots under cyclic voltammetric conditions. This weak emission increases as the cathodic potential decreases to more negative values. However, compared with the nanoassembly the ECL intensity of the CdSe quantum dots is extremely weak. As shown in curves 1–4 of Fig. 8b, a broader potential window is needed to obtain higher ECL intensity from the CdSe quantum dots. When the potential is cycled between 0.1 V and -1.2 V, which is the same as the potential window of the hollow spherical CdSe QD assemblies, no ECL emission is observed (curve 1). In all cases a reduction potential of ≤ -1.1 V versus Ag/AgCl indicates a significant quantum confinement effect compared to the bulk reduction potential of CdSe, which is attributed to the small 5 nm quantum dots comprising the hollow nanosphere assembly. Clearly, large 70 nm crystals would lack any observable quantum confinement effect on the energy level structure, which shows that the ECL must derive from the quantum dot-based hollow nanospheres. Moreover, the presented aggregation seems to be crucial for generating intense and stable ECL from CdSe quantum dots in water. Addition of cyclodextrin to the aqueous CdSe solution after QD formation did not increase the ECL intensity, which clarifies that the observed luminescence properties are not promoted because of a simple ligand exchange.

From previous studies we found that the aggregation of CdS quantum dots plays an important role in maintaining the stability of ECL [23]. As the applied electrode potential reaches the reduction potential, electrons are injected into the nanostructure to generate negatively charged CdSe quantum dots. The aggregated character of the hollow CdSe nanospheres provides some level of protection to the individual quantum dot as it is reduced. The formed $SO_4^{\cdot -}$ radical injects a hole across the nanosphere surface and efficient chemiluminescence can be observed accompanying electron–hole recombination. Therefore, it is likely

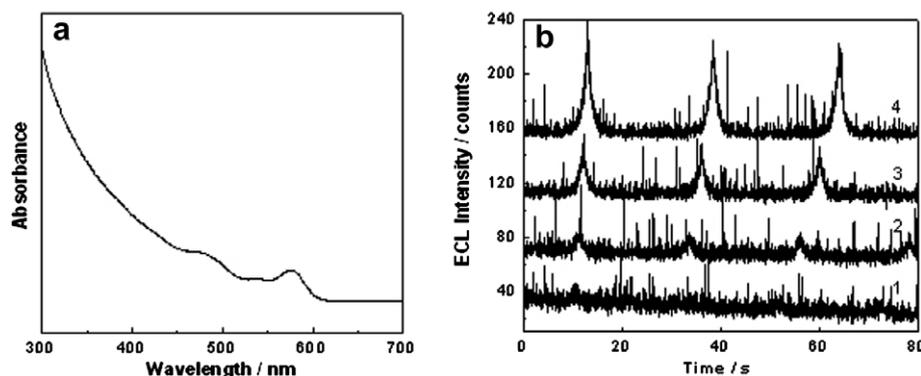


Fig. 8. (a) Absorption spectrum of CdSe nanoparticles in CHCl_3 . (b) ECL emission from CdSe nanoparticles in 0.1 M $\text{K}_2\text{S}_2\text{O}_8$ and 0.1 M KCl aqueous solution with different potential cycles between (1) 0.1 V and -1.2 V, (2) 0.1 V and -1.3 V, (3) 0.1 V and -1.4 V, and (4) 0.1 V and -1.5 V (scan rate: 100 mV/s). The fabrication of the carbon-paste electrode is the same as that of the CdSe hollow spheres, except that the hollow spherical CdSe nanoassembly solution was replaced with CdSe quantum dots.

that the spherical aggregation of the CdSe quantum dots has a protection effect on the electrogenerated negatively charged quantum dots, making the electrogenerated reduced species (CdSe^-) stable against destruction before hole injection occurs and therefore allowing ECL.

4. Conclusions

In summary, the hollow spherical CdSe nanoassemblies of 5 nm quantum dots were successfully prepared by using β -cyclodextrin as a templating agent. The hollow structure is formed under ultrasonic irradiation and the nanoassembly is shown to exhibit strong electrochemical luminescence (ECL) in the presence of persulfate as a co-reactant. The spherical nanoassembly structure and the addition of the co-reactant overcome the otherwise poor radical anion and cation stability and allow for enhanced ECL through radiative charge recombination. This approach allows the observation of uniquely intense and stable ECL of CdSe QDs in aqueous solution, which could well be beneficial for a broad range of potential sensor applications.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (Grant Nos. 20325516, 20575026, 20635020). This work is also supported by NSFC for Creative Research Group (20521503). CB gratefully acknowledges the support by NSF through a Career Grant (CHEM-0239688). We also thank the help of Professor Daiwen Pang from Wuhan University, China.

References

- [1] M.L. Steigerwald, L.E. Brus, *Annu. Rev. Mater. Sci.* 19 (1989) 471.
- [2] M.G. Bawendi, M.L. Steigerwald, L.E. Brus, *Annu. Rev. Phys. Chem.* 41 (1990) 477.
- [3] H. Weller, *Angew. Chem. Int. Edit.* 32 (1993) 41.
- [4] C.B. Murray, D.J. Norris, M.G. Bawendi, *J. Am. Chem. Soc.* 115 (1993) 8706.
- [5] A.P. Alivisatos, *J. Phys. Chem.* 100 (1996) 13226.
- [6] A. Henglein, *Top. Curr. Chem.* 143 (1998) 113.
- [7] M. Hines, P. Guyot-Sionnest, *J. Phys. Chem.* 100 (1996) 468.
- [8] M. Bruchez Jr., M. Moronne, P. Gin, S. Weiss, A.P. Alivisatos, *Science* 281 (1998) 2013.
- [9] Y.T. Lim, S. Kim, A. Nakayama, M.G. Bawendi, J.V. Frangioni, *Mol. Imaging* 2 (2003) 50.
- [10] W.C.W. Chan, S. Nie, *Science* 281 (1998) 2016.
- [11] S.F. Wuister, C. de Mello Donegá, A. Meijerink, *J. Phys. Chem. B* 108 (2004) 17393.
- [12] L.R. Faulkner, A.J. Bard, *Electroanal. Chem.* 10 (1977) 1.
- [13] K.A. Fährlich, M. Pravda, G.G. Guilbault, *Talanta* 54 (2001) 531.
- [14] M.M. Richter, *Chem. Rev.* 104 (6) (2004) 3003.
- [15] A.P. Alivisatos, *Science* 271 (1996) 933.
- [16] C.R. Kagan, C.B. Murray, M.G. Bawendi, *Phys. Rev. B* 54 (1996) 8633.
- [17] Z. Ding, B.M. Quinn, S.K. Haram, L.E. Pell, B.A. Korgel, A.J. Bard, *Science* 296 (2002) 1293.
- [18] N. Myung, Z. Ding, A.J. Bard, *Nano Lett.* 2 (2002) 1315.
- [19] N. Myung, Y. Bae, A.J. Bard, *Nano Lett.* 3 (2003) 1053.
- [20] N. Myung, X. Lu, K.P. Johnston, A.J. Bard, *Nano Lett.* 4 (2004) 183.
- [21] Y. Bae, N. Myung, A.J. Bard, *Nano Lett.* 4 (2004) 1153.
- [22] S.K. Poznyak, D.V. Talapin, E.V. Shevchenko, H. Weller, *Nano Lett.* 4 (2004) 693.
- [23] T. Ren, J.Z. Xu, Y.F. Tu, S. Xu, J. Zhu, *J. Electrochem. Commun.* 7 (2005) 5.
- [24] C. Burda, X. Chen, R. Narayanan, M.A. El-Sayed, *Chem. Rev.* 105 (2005) 1025.
- [25] K.S. Suslick, *Ultrasound: Its Chemical, Physical, and Biological Effects*, VCH Verlagsgesellschaft, Weinheim, 1988.
- [26] K.S. Suslick, G. Price, *J. Annu. Rev. Mater. Sci.* 29 (1999) 295.
- [27] Y.C. Zhu, H.L. Li, Y. Koltypin, Y.R. Hachoen, A. Gedanken, *Chem. Commun.* 24 (2001) 2616.
- [28] X. Zheng, Y. Xie, L. Zhu, X. Jiang, A. Yan, *Ultrason. Sonochem.* 9 (2002) 311.
- [29] S. Xu, H. Wang, J.J. Zhu, X.Q. Xin, H.Y. Chen, *Eur. J. Inorg. Chem.* 23 (2004) 4653.
- [30] S. Tsunekawa, T. Fukuda, A. Kasuya, *J. Appl. Phys.* 8 (2000) 1318.
- [31] W.W. Yu, L. Qu, W. Guo, X. Peng, *Chem. Mater.* 15 (14) (2003) 2854.
- [32] W. Saenger, J. Jacob, K. Gessler, T. Steiner, D. Hoffmann, H. Sanbe, K. Koizumi, S.M. Smith, T. Takaha, *Chem. Rev.* 98 (1998) 1787.
- [33] K.A. Connors, *Chem. Rev.* 97 (1997) 1325.
- [34] S. Polarz, B. Smarsly, L. Bronstein, M. Antonietti, *Angew. Chem. Int. Ed.* 40 (23) (2001) 4417.

- [35] G. González-Gaitano, P. Rodríguez, J.R. Isasi, M. Fuentes, G. Tardajos, M. Sánchez, J. Incl. Phenom. Macro. 44 (2002) 101.
- [36] D. Duchêne, A. Bochot, S.C. Yu, C. Pépin, M. Seiller, Int. J. Pharm. 266 (2003) 85.
- [37] T. Loftsson, M. Másson, M.E. Brewster, J. Pharm. Sci. 93 (2004) 1091.
- [38] E. Lemos-Senna, D. Wouessidjewe, D. Duchêne, L. Sylviane, Colloid. Surface. B 10 (1998) 291.
- [39] A.J. Bard, L.R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, 2nd ed., Wiley, New York, 2001.
- [40] K. Yamashita, S. Yamazaki-Nishida, Y. Harima, A. Segawa, Anal. Chem. 63 (1991) 872.