Electrogenerated chemiluminescence of CdS spherical assemblies

Ting Ren a, Jin-Zhong Xu a, Yi-Feng Tu b, Shu Xu a, Jun-Jie Zhu a,*

a Department of Chemistry, Key Laboratory of Analytical Chemistry for Life Science, Nanjing University, Nanjing 210093, PR China
b Department of Chemistry, Suzhou University, Suzhou 215006, PR China

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Abstract

We report the first observation of electrogenerated chemiluminescence (ECL) from CdS spherical assemblies in both nonaqueous system and aqueous system. The CdS spherical assemblies consist of CdS nanocrystals about 5 nm in diameter. Four ECL peaks were found under cyclic voltammetric conditions. According to the annihilation mechanism and two-equivalent adsorbed surface state theory, the mechanism for ECL peaks was proposed. The morphology of the CdS spherical assemblies is proved to play an important role in maintaining the stability of partial electrogenerated species to generate the ECL light.

Keywords: Electrochemistry; Electrogenerated chemiluminescence; CdS spherical assemblies

1. Introduction

Nanometer-sized semiconductor particles have been extensively studied with optical and electrical techniques [1–3]. Electrogenerated chemiluminescence (ECL) is proved to be useful for analytical applications including organic analysis, ECL based immunoassays, DNA-probe assays and enzymatic biosensors [4]. Recently, there has been a growing interest in ECL studies of semiconductor nanomaterials. Bard and co-workers [5–7] have reported ECL of semiconductor nanocrystals (NCs) in organic solvent, such as Si, CdSe and Ge. In these cases, the NCs adsorbed capping ligands are chemically stable and maintain their charged states long enough to transfer charge upon colliding with oppositely charged NCs and then give the excited state to generate the luminescence. However, ECL of thioglycerol-capped CdS NCs has not been observed because of the instability of electrogenerated reactants [5,6].

Herein, for the first time, we describe ECL from CdS spherical assemblies consisting of 5 nm CdS NCs. Four ECL peaks corresponding to their respective voltammetric peaks were observed in both nonaqueous system and aqueous system. Correlating ECL curve with the cyclic voltammogram (CV), we discuss the emission mechanism for the CdS spherical assemblies. The appearance of ECL peaks implies that the as-prepared CdS assemblies can maintain the stability of partial electrogenerated species in the process of the decomposition to allow the formation of the excited states. We propose that the morphology of CdS spherical assemblies plays an important role in generating the luminescence.

2. Experimental

In a typical procedure, 0.46 g of cadmium chloride hydrate and 2.8 g of ammonium citrate were added to 80 ml distilled water. The pH of the solution was adjusted to 10 using sodium hydroxide. After adding 0.15 g of thioacetamide, the mixture solution was irradiated with a high-intensity ultrasonic horn (Sonic Co.,
Ti-horn, 20 kHz, 50 W/cm²) under ambient 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.

CVs and ECL curves were recorded simultaneously using a Model MPI-A electrochemiluminescence analyzer systems (Xi’An Remax Electronic Science & Technology Co. Ltd., Xi’An, China). The bandwidth of the photomultiplier tube (PMT) used in Model MPI-A electrochemiluminescence analyzer was in the range of 200–800 nm and the voltage of the PMT was set at 800 V in the process of detection. A conventional three-electrode configuration was used in the experiments. An Ag/AgCl reference electrode and a platinum wire counter electrode were used for all measurements. All potentials were reported relative to the Ag/AgCl reference electrode. Different working electrode was used, respectively, in the study of nonaqueous and aqueous system.

The electrochemical and ECL studies of CdS assemblies in nonaqueous organic solvent were performed using a Pt disk working electrode (0.03 cm²). CVs and ECL curves were obtained from the as-prepared CdS assemblies dispersed in an acetonitrile solution containing 0.1 M tetra-n-butylammonium perchlorate (TBAP) as a supporting electrolyte.

A carbon-paste electrode was used as the working electrode in aqueous solution. Because of their broad potential window, low background current, chemical inertness, carbon-paste electrodes are more favorable for the study of aqueous system compared with platinum electrodes. The carbon-paste electrode was fabricated as follows: 75 mg graphite powder and 25 mg the as-prepared CdS spherical assemblies were thoroughly mixed in ethanol solvent by ultrasonic dispersion. After drying under stirring, a homogenized graphite/CdS mixture was achieved. Subsequently, the paraffin oil was added in the mixture (oil:mixture = 1:4 by weight) and mixed fully until a homogeneous paste was obtained. The prepared paste was packed into a glass tube with 4 mm inner diameter and electrical contact was established with a copper rod through the back of the home-made electrode. The electrode surface was polished with smoothing paper. Electrochemical and ECL measurements of the fabricated carbon-paste electrode were performed in a 0.1 M aqueous NaOH solution containing 0.1 M KNO₃.

3. Results and discussion

Fig. 1 shows a typical TEM image of the CdS spherical assemblies. In the synthetic process of the CdS assemblies, there is no capping material addition. The particles are secondary particles aggregated by small CdS NCs, due to their extremely small dimensions and high surface energy. The size of these small CdS NCs is about 5 nm according to TEM observation. The absorption of the CdS spherical assemblies is showed in Fig. 2. The UV spectrum with the absorption maximum at 406 nm (Band gap, 3.05 eV) allows one to estimate the size of the CdS NCs as about 5 nm [8], which supports the sizes observed from the TEM image.

Bard and co-workers [9] have reported electrochemistry of thioglycerol-capped CdS NCs in N,N-dimethylformamide (DMF). The electrochemical process of CdS NCs can be proposed an (EC)n reaction, where the decomposition of the cluster occurs and can be viewed as the trapping of electron (e.g., as Cd⁰) on the particle surface. Because of this, thioglycerol-capped CdS NCs showed no ECL light [5,6]. Here, employing the as-prepared CdS spherical assemblies, we observe the ECL emission.

Fig. 3(a) shows the CV and ECL curve of the as-prepared CdS assemblies in nonaqueous system. The potential sweeps were started at 0 V and initially went in the cathodic direction. Light emission was observed when
the electrode potential was cycled between −2.5 and +2.5 V at a scan rate of 100 mV/s.

As shown in the Fig. 3(a), reduction and oxidation peaks appear at −2.05 V (C1) and +1.38 V (A1), which can be correlated, respectively, to electron transfer at LUMO and HOMO [9]. The electrochemical band gap between C1 and A1 is 3.43 V, a value comparable to the 3.05 eV obtained spectroscopically. Due to the nature of charge transfer to CdS assemblies (EC)n, the electrochemical band gap will increase with increasing scan rate, which has also been observed in thioglycerol-capped CdS NCs. In the case of thioglycerol-capped CdS NCs with different sizes, the difference of electrochemical band gap between 100 and 10 mV/s is from 0.3 to 0.5 V. Moreover, the CV peaks at 10 mV/s are not well defined when the particle size is 4.5 nm [9]. In our experiments, the lack of good electrochemical behavior at 10 mV/s can be attributed to the bigger particle size of 5 nm. Thus, it is possible that the electrochemical band gap at 100 mV/s is greater than the optical band gap.

Electrogeneated reduced species (CdS−) can collide with oxidized species (CdS+) in an annihilation process to produce excited states (CdS*), which generated the luminescence [5,10].

CdS− + CdS+ → CdS* + CdS

CdS* → CdS + hv

In Fig. 3(a), reduced and oxidized ECL peaks (I and II) corresponding to these two voltammetric peaks (C1 and A1) were observed through the annihilation mechanism. Unlike the results with thioglycerol-capped CdS NCs, the appearance of ECL-I and ECL-II implies that the CdS spherical assemblies, despite the decomposition, can maintain the stability of partial electrogenerated species to allow the formation of the excited states.

Additional cathodic and anodic peaks in the middle of the potential window (C2, C3, A2, and A3) can be assigned to CdS/Cd0 and CdS/S0 couple [9,11]. As illustrated in Fig. 3(a), the appearance of cathodic peaks (C2 and C3) is due to the reduction of oxidation products of CdS at A1, and C1 reduction products are reoxidized at A2 and A3. Because of this decomposition, Cd0 will be formed in the electrochemical process. With two-equivalent species (species with an intermediate valence) adsorbed on a semiconductor surface, surface state theory must be modified to consider two surface states −X+/X and X+/X. Fig. 4(a) shows the energy level diagram of two-equivalent adsorbate with stable forms X and X++ [12].
\[ X^{++} + e = X^+ \]
\[ X^+ + e = X \]

The above two equations represent, respectively, electron capture or injection from the surface state designated as \( X^{++}/X^+ \) and \( X^+/X \). It is clear that the electron captured by \( X^+ \) will occupy a stable orbital, because the chemical species providing the surface state is in the zero-valent form \( X \). Therefore, the energy of the surface state \( X^+/X \) is quite different to the energy level \( X^{++}/X^+ \) at which the unstable electron is captured by \( X^{++} \). Such two-equivalent behavior can lead to an increase of anodic current termed “current doubling”. This phenomenon can also be observed in the CV of the CdS spherical assemblies (A3 in Fig. 3(a)). Thus, it is considered that the surface state of the CdS spherical assemblies during ECL process is similar to the two-equivalent adsorbed surface state.

According to such surface state theory, we suggest the proposed mechanism for the other two ECL peaks (ECL-III and ECL-IV). As the electrode potential is negative, an electron will be captured by the \( \text{Cd}^{2+}/\text{Cd}^+ \) level:

\[ \text{Cd}^{2+} + e \rightarrow \text{Cd}^{+*} \]

The formed \( \text{Cd}^{+*} \) will inject an electron into the LUMO of the CdS NC, which can generate the luminescence (ECL-III corresponding to C2 in Fig. 3(a)) by reacting with the electrogenerated oxidized species (Fig. 4(b)):

\[ \text{CdS}^{+*} + \text{CdS}^{+*} \rightarrow \text{CdS}^+ + \text{CdS} \]
\[ \text{CdS}^+ \rightarrow \text{CdS} + \text{hv} \]

Similarly, when the electrode potential is made positive, the holes will be injected into the \( \text{Cd}^+/\text{Cd}_0 \) level:

\[ p + \text{Cd}_0 \rightarrow \text{Cd}^{+*} \]

The light emission (ECL-IV in Fig. 3(a)) will be observed through the surface electron–hole recombination between electrogenerated reduced species \( \text{CdS}^{+*} \) and the resulting \( \text{Cd}^{+*} \) (Fig. 4(c)):

\[ \text{CdS}^{+*} + \text{Cd}^{+*} \rightarrow \text{CdS}^+ + \text{Cd} \]
\[ \text{CdS}^+ \rightarrow \text{CdS} + \text{hv} \]

In the first cycle of the CV, because the decomposition of the cluster does not occur, \( \text{Cd}_0 \) will not be formed. Hence, In the ECL curve corresponding to the first cycle (Fig. 3(b)), ECL-III and ECL-IV are not observed, which supports this proposed mechanism. The appearance of ECL-III and ECL-IV can be considered as the evidence to indicate that the morphology of the CdS assemblies, which is quite different from that of thioglycerol-capped CdS NCs, provides the possibility for the stability of partial electrogenerated species. Fig. 5 shows the ECL spectrum obtained from the CdS spherical assemblies in 0.1 M TBAP acetonitrile electrolytes. The ECL spectrum shows only a maximum wavelength of 700 nm. This further indicates that the excited state, by which generates the ECL emission at the different potentials, is \( \text{CdS}^* \).

With the purpose of making ECL of semiconductor NCs valuable for analytical applications, we also further studied the behavior of CdS ECL in aqueous solution. Fig. 6 shows the CV and ECL curve of the CdS spherical assemblies. The potential sweeps were also started at 0 V and initially went in the cathodic direction. Light emission was observed when the electrode potential was cycled between \(-2.0\) and \(+2.0\) V at a scan rate of 100 mVs. We notice that there are similarity between CVs and ECL curve in nonaqueous solution and in aqueous solution. It is possible that the emission mechanism of
aqueous system is similar to that of nonaqueous system, which is still in exploration.

4. Conclusion

In summary, ECL emission from the CdS spherical assemblies in both nonaqueous and aqueous solutions was found under CV conditions. We have successfully correlated the CV with the ECL for the CdS spherical assemblies. Corresponding to the electrochemical behavior of the as-prepared CdS assemblies, four ECL peaks were observed in both nonaqueous system and aqueous system. According to the annihilation mechanism and two-equivalent adsorbed surface state theory, the mechanism for ECL peaks was proposed. The CdS spherical assemblies were proved effective to maintain the stability of partial electrogenerated species in the process of the decomposition. We will next make further investigations on the ECL of other semiconductor assemblies in aqueous solution and analytical applications of it.

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