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Electrochemiluminescence in the $S_2O_8^{2-}$ system: Pt–Cd electrodes

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Abstract

The electrochemiluminescence (ECL) in the $S_2O_8^{2-}$ system occurs under conventional cyclic voltammetry, when the Pt working electrode was coated with Cd elementary substance. The ECL mechanism was proposed, due to the reaction between the strongly oxidizing intermediate $SO_4^{\cdot-}$ and the transitory production, CdO, generated by oxidation of Cd with $SO_4^{\cdot-}$. Moreover the ECL behavior was studied in different pHs and concentrations of $S_2O_8^{2-}$solution. It was showed that the ECL signal was strongest at pH 8.0, and its intensity increased with $S_2O_8^{2-}$. The experimental results verified well with the proposed ECL mechanism.

Keywords: Electrochemiluminescence; $S_2O_8^{2-}$ system; Cd elementary substance; CdO

1. Introduction

As a valuable detection method ECL is becoming more important in analytical chemistry [1]. Since the mid-1960s, a number of reaction systems have been discovered and studied about electrochemiluminescence (ECL) [2], by which the nature of an emitting state has been extensively investigated, and the related theory has been developed [3–5]. ECL can convert electrical energy into radiative energy, in which the reaction between strong reductants and strong oxidants is usually involved. The reduction of $S_2O_8^{2-}$ produces $SO_4^{\cdot-}$, a strongly oxidizing intermediate, so light emission can occur in some systems including peroxydisulfate [6–12]. For example, in the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system, $SO_4^{\cdot-}$ undergoes an electron transfer reaction with the luminophore to generate light [11–13]. In the cases of n-type semiconductors, light emission occurs due to the hole injection into these materials by $SO_4^{\cdot-}$ at the reduction process [14]. In recent years, the ECL of semiconductor nanocrystals (NCs, also referred to as quantum dots) is reported and attracts interest [15–19].

In this work, we described a novel ECL phenomenon in the peroxydisulfate system, not that of NCs. The ECL is generated in persulfate solutions when the Pt electrode with Cd deposit is as the working electrode. To our knowledge, this is the first example for ECL of Cd elementary substance. A reasonable mechanism is proposed, that the light is emitted from CdO semiconductor, generated by the reaction between Cd and the strong oxidant of $SO_4^{\cdot-}$. The ECL mechanism is consistent with the dependence of the ECL intensity on the concentrations of $S_2O_8^{2-}$ and pHs.

2. Experimental procedure

$CdCl_2$ was obtained from Shanghai Chemical Reagent Company (China). Na_2TeO_3 was purchased from Aldrich Chemical Company (USA). $(NH_4)_2S_2O_8$, NaH_2PO_4, Na_2HPO_4, and NaOH were all purchased from Beijing Chemical Reagent Company (China). All chemicals and reagents were of analytical grade and used without additional purification. And all solutions were prepared with deionized water ($18.2\ M\Omega \cdot cm$) processed with Milli-Q

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ultra-high purity water system (Millipore, Bedford, MA, USA).

The CdTe NCs were prepared according to a previously reported method [20], a one-pot aqueous synthesis of CdTe. The ECL behavior of the CdTe NCs was studied under conventional cyclic voltammetry (CV) at a naked Pt disk electrode with a 3-mm diameter.

In our work, two methods were adopted to deposit Cd elementary substance on the Pt electrode. One was from CdTe NCs. The CdTe was added into the mixture of 20 mmol/L $(NH_4)_2S_2O_8$ and 50 mmol/L phosphate (pH 8.2). Then the cycling potential between 0 and −2.5 V was set for about 20 min at a scan rate of 100 mV/s. And Cd was deposited on the electrode surface. The second method was simple, in which $CdCl_2$ solution was directly electroreduced into Cd in 50 mmol/L phosphate (pH 8.2) when repetitive cycling from 0 to −2.5 V at 100 mV/s scan rate.

In the experiment, three-electrode system was adopted, in which Pt wire was as a counter electrode, and Ag/AgCl (in saturated KCl solution) as a reference electrode. CVs and ECL curves were obtained using a CHI600b Electrochemical Analyzer (CH instruments, CO., Austin TX, USA) and a MCFL-A multifunctional chemiluminescent and bioluminescent analytical system with the voltage of the photomultiplier tube set at 600 V (Xi'an Rimax Electronics Co. Ltd., China), respectively. 50 mmol/L phosphate was as the background electrolyte. When Pt–Cd electrode was used as working electrode, the ECL performance was investigated with different $(NH_4)_2S_2O_8$ concentration (0.1–20 mmol/L) and pH values (5–9.5) of background electrolyte. Phosphate solutions were prepared by 50 mmol/L NaH_2PO_4 and 50 mmol/L Na_2HPO_4; and pHs were adjusted by 0.1 mol/L NaOH.

XPS analysis was performed by XPS instrument (ESCALABMK II, Thermo). And ECL spectrum with different wavelength was collected by the fluorescence instrument (Deltaram V).

3. Results and discussion

Originally, we had been trying to study the ECL of water-soluble CdTe NCs similar to the Ref. [19]. In our experiment, the ECL behavior of CdTe NCs was studied in the solution of 20 mmol/L $(NH_4)_2S_2O_8$ and 50 mmol/L phosphate (pH 8.2). When repetitive cycling between 0 and –2.5 V at a scan rate of 100 mV/s, it was found that ECL signals became stable after many cycles. But the CdTe fluorescence disappeared; this result implied that the NCs were destroyed. And some gray product was deposited on the surface of the working electrode. By XPS analysis, the deposit was mainly including Cd, and no Te (as Fig. 1a-2 and b). Considering the experimental condition with negative potential, the deposit was considered as Cd elementary substance, reduced from CdTe. To confirm this, an additional XPS analysis was carried out for the Cd elementary substance, reduced from $CdCl_2$, as Fig. 1a-1. The element analysis of Cd3d indicated that the deposit was ensured to be mainly Cd elementary substance (as Fig. 1a).

In the blank experiment, we found that ECL did not occur at the naked Pt electrode in the single peroxydisulfate system. However, when the Pt electrode with Cd (noted as Pt–Cd electrode) was used as the working electrode, ECL light was generated, that was quite novel and interesting. Fig. 2 depicted the ECL spectrum for 20 mmol/L $(NH_4)_2S_2O_8$ (pH 8.2) at the Pt–Cd electrode. It was shown that ECL was observed when the potential was more negative than –1.8 V. It was noteworthy that ECL for $S_2O_8^{2-}$

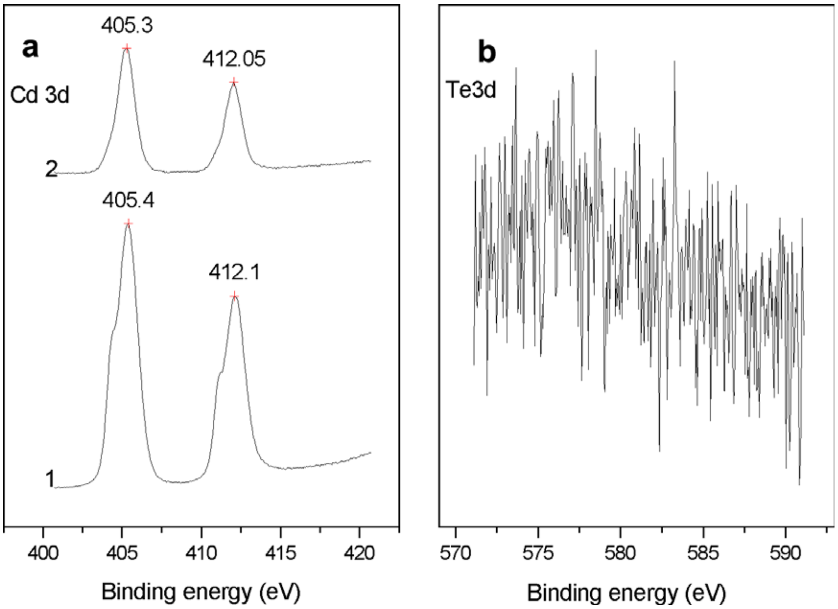

Fig. 1. XPS spectra. (a) Cd3d analysis, (1) Cd reducted from $CdCl_2$, (2) the gray product deposited on the working electrode surface; (b) Te3d analysis of the gray product deposited on the working electrode surface.

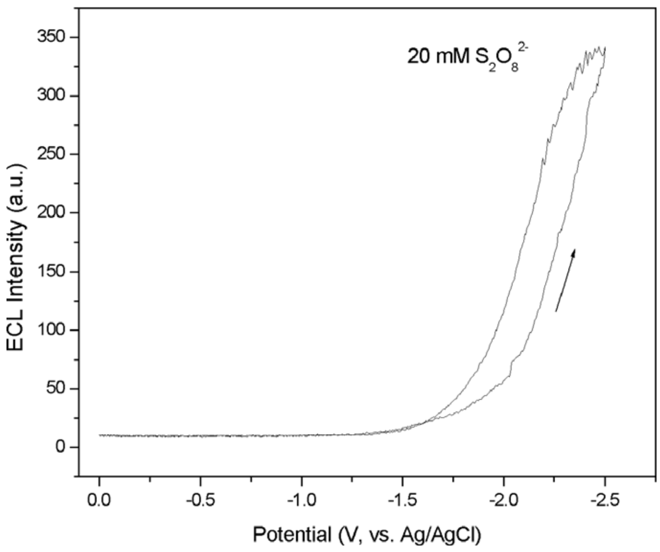

Fig. 2. ECL intensity-potential curve at a Pt–Cd electrode in 20 mmol/L peroxydisulfate. Background electrolyte, 50 mmol/L phosphate (pH 8.2); scan rate, 0.1 V/s; voltage of PMT, 600 V.

could only be obtained at a Pt–Cd electrode when the applied electrode potential was sufficiently negative.

And in a control experiment, the Cd elementary substance was electrodeposited on the naked Pt surface from a $CdCl_2$ solution, the ECL phenomenon can also occur. This corroborated that the Cd elementary substance on the Pt electrode was the only essential and prerequisite condition for ECL in the experiments.

Fig. 3 showed the relationship between the ECL intensity and wavelength of 20 mmol/L $(NH_4)_2S_2O_8$ (pH 8.2). In experiment, the potential set at Pt–Cd electrode was −2.3 V, and the ECL signal was recorded in the range of 400–800 nm. From the figure, the emission maximum is at about 593 nm.

To gain better insight into this phenomenon, we proposed the following mechanism [18].

$$\mathrm{S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{\cdot-}} \tag{1}$$

$$\mathrm{SO_4^{\cdot-} + Cd + 2OH^- \rightarrow CdO + SO_4^{2-} + H_2O} \tag{2}$$

$$\mathrm{SO_4^{\cdot-} \rightarrow SO_4^{2-} + h^+} \tag{3}$$

$$\mathrm{CdO + h^+ \rightarrow CdO^{*+}} \tag{4}$$

$$\mathrm{CdO^{*+} + e^- \rightarrow CdO +} h\nu \tag{5}$$

$$\mathrm{CdO + H_2O + 2e^- \rightarrow Cd + 2OH^-} \tag{6}$$

It was supposed that CdO semiconductor was generated with the strong oxidant of $SO_4^{\cdot-}$ at the electrode surface. The semiconductor was unstable and easy to be reduced, but it had an enough long life for the ECL process. When the formed sulfate radicals injected holes into the valence band of CdO, the semiconductor was excited; then the holes combined the electrons from the conduction band and the light emitted.

In the ECL experiments, the Cd layer on the Pt electrode was stable, and not easy to fall off, that was probably due to the similar reaction conditions between the ECL process and the electro-deposition one. Fig. 4 gave the ECL emission of 10 mmol/L $S_2O_8^{2-}$ under continuous potential scanning for 10 cycles. It showed that the repeatability was satisfied.

Also, we investigated the pH effect of phosphate solution on the ECL intensity. Considering that Cd was soluble in acid medias, the experiment was carried out from high pHs to low pHs. The observed dependence of the ECL intensity on pH was represented in Fig. 5a, and the plot exhibited a convex curve in the range between pH 5 and 9.5. At the pH of 8.0, the ECL intensity was about to the

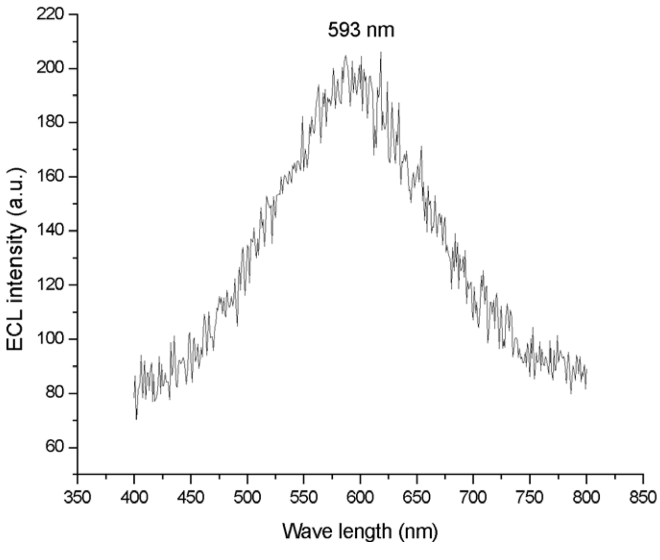

Fig. 3. ECL spectrum of 20 mmol/L peroxydisulfate at a Pt–Cd electrode. Background electrolyte, 50 mmol/L phosphate (pH 8.2); electrode potential, −2.3 V; integration time 10 min.

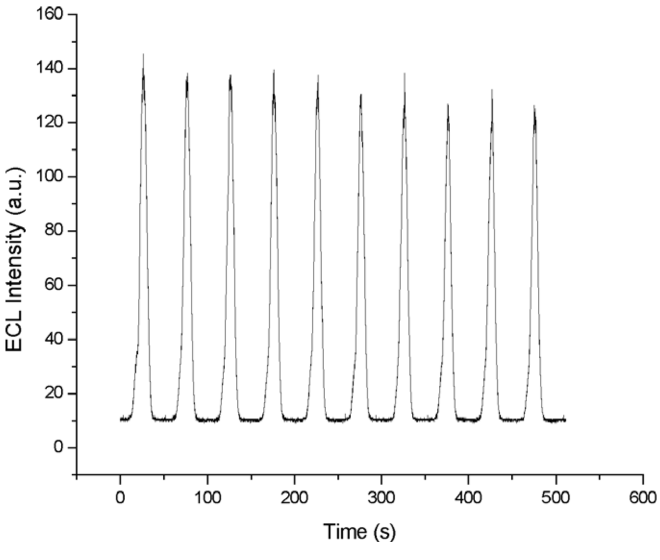

Fig. 4. ECL emission from Pt–Cd Electrode in 10 mmol/L $S_2O_8^{2-}$ under continuous cyclic voltammetry for 10 cycles. Experiment conditions as Fig. 2.

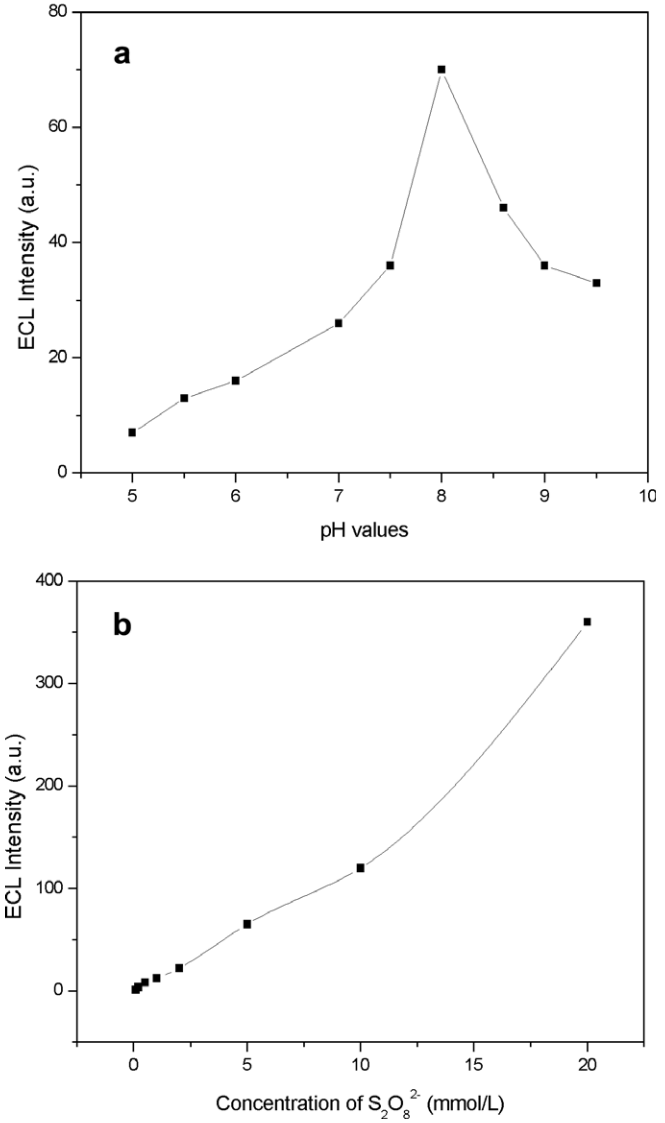

Fig. 5. Dependence of the ECL intensity (a) on the pH value ($S_2O_8^{2-}$ concentration 10 mmol/L), and (b) on the $S_2O_8^{2-}$concentrations (pH 8.0). Other experiment conditions as Fig. 2.

maximum. As the reaction scheme, pHs affected the Reaction (2). When pH < 7, the production of CdO was inhibited, so the ECL signals were poor. In the basic solutions of pH > 8, the ECL intensities were decreased, that was attributed to the consumption of $SO_4^{\cdot -}$ by the scavenging reaction with OH^- [21]. On the other hand, CdO was less created in the strong basic solutions, that was another factor to decrease the ECL intensity.

Furthermore, we studied the relationship between the ECL intensity and the peroxydisulfate concentration at the optimized pH. In Fig. 5b, it was shown that the ECL signals were increasing with the concentration of $S_2O_8^{2-}$ (0.1–20 mmol/L). The result agreed well with the proposed mechanism. As shown in the Reactions (1)–(3), amounts of CdO and holes would be increasing with the $S_2O_8^{2-}$ concentration. Then more excited semiconductor, $CdO*^+$, would be produced as Eq. (4). Finally the observed luminescence became stronger (as Fig. 5b).

4. Conclusion

In conclusion, we have studied a novel ECL phenomenon in the peroxydisulfate solution at a Pt–Cd electrode. And a reasonable mechanism was proposed. It was investigated that the ECL intensities depended on the pHs and the concentrations of peroxydisulfate. These results indicated that the formation of CdO played a key role in the ECL process. The difference of Pt–Cd electrode from that of Pt substance would result with its potential applications.

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