Talanta 101 (2012) 362–367

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Hot electron-induced cathodic electrochemiluminescence at oil film-covered carbon paste electrode and application to nano-molar determination of catechol

Xiao-Yan Chen [a,b], Rui-Juan Zheng [a,c], Su-Fang Qin [a], Jian-Jun Sun [a,]*

[a] *Key Laboratory of Analysis and Detection for Food Safety, Ministry of Education, Fujian Provincial Key Laboratory of Analysis & Detection Technology for Food Safety, College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou 350108, China*
[b] *Fujian Metrology Institute, Fuzhou 350003, China*
[c] *Department of Chemistry and Materials Engineering, Longyan University, Longyan, Fujian 364000, China*

ARTICLE INFO

Article history:
Received 18 April 2012
Received in revised form
18 September 2012
Accepted 22 September 2012
Available online 28 September 2012

Keywords:
Carbon paste electrode
Cathodic electrochemiluminescence
$Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system
Catechol

ABSTRACT

Hot electron-induced cathodic electrochemiluminescence of the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system was investigated at an oil film-covered carbon paste electrode (CPE) under cathodic pulse polarization for the first time. Compared with other electrodes, the CPE is of lower background, better stability and reproducibility. The method is also applied to the determination of catechol. Under the optimum conditions, the linear correlation between the quenched ECL intensity (ΔI) and the logarithm of catechol concentration ($\log C_{catechol}$) was observed over the range of 2.0×10^{-10} mol/L–4.0×10^{-9} mol/L and 4.0×10^{-9} mol/L–4.0×10^{-7} mol/L with the limit of detection (LOD) of 2.0×10^{-10} mol/L, which is lower than the other reported methods. The proposed method is applied to determine catechol in reservoir water. The mean recoveries of 83.3%–99.0% and the relative standard deviations (RSDs) of 0.8%–2.2% were obtained.

1. Introduction

Compared with common electrogenerated chemiluminescence, hot electron-induced cathodic electrochemiluminescence (cathodic ECL) owns a wider potential window and higher sensitivity. These advantages is attributed to the special manner of polarization (polarization potential can be set more negative than −10.0 V) and the insulating-film covered electrodes [1]. The injection of hot electrons tunneled through the insulating film into the aqueous electrolyte solution, resulting in the generation of hydrated electrons as reducing mediators; and then the redox reactions successively occurred between the reducing mediators and fluorescein, leading to fluorescence emission. The cathodic ECL can also be enhanced by adding coreactants [2]. The Al/Al_2O_3 [3–6], Ta/Ta_2O_5 [7–10], Si/SiO_2 [11], Mg/MgO [12] and other composite electrodes [13] are commonly used for cathodic ECL in previous studies. Kulmala *et al.* reported the cathodic electroluminescence at an oxide-coated aluminum electrode in the early age, and put forward the theory [3–6]. Bard developed the cathodic ECL at oxide-covered tantalum electrode [7–10]. These electrodes suffer from their own drawbacks, such as strong background luminescence, poor stability of insulating film, and the complicated preparing processes. Therefore, different kinds of new electrode materials which are suitable for cathodic ECL have been studied recently [14–17]. For example, a C/C_xO_{1-x} electrode [16] was fabricated by oxidizing a glassy carbon electrode and used as a reagentless DNA biosensor based on the quenching effect of intrinsic cathodic ECL. Such electrodes possess excellent biocompatibility, a wide pH range and high sensitivity.

The carbon paste electrode (CPE) was first introduced by Adams in 1958, which is made simply by direct mixing of graphite powder with a pasting liquid (e.g. liquid paraffin, silicone) and can be regenerated by polishing or cutting [18–21]. Since then, it has attracted a great deal of attention and been widely used for electrochemical analysis [22–24] due to its low cost, easy fabrication and good reproducibility. In 1999, CPE was used for electrochemiluminecence of the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system in purely aqueous solution for the first time [25]. The luminescence was quite bright and clearly visible to the non-dark-adapted eye in solution.

In this work, a CPE is used for the hot electron-induced cathodic ECL with extremely low background under cathodic pulse polarization, while here the paraffin oil was used as an insulating film. The cathodic ECL of the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system at the CPE exhibited excellent sensitivity and perfect stability. Phenol, resorcinol, catechol and hydroquinone have various degrees

---

* Corresponding author. Tel./fax: +86 591 22866136.
E-mail address: JJSun@fzu.edu.cn (J.-J. Sun).

0039-9140/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2012.09.042

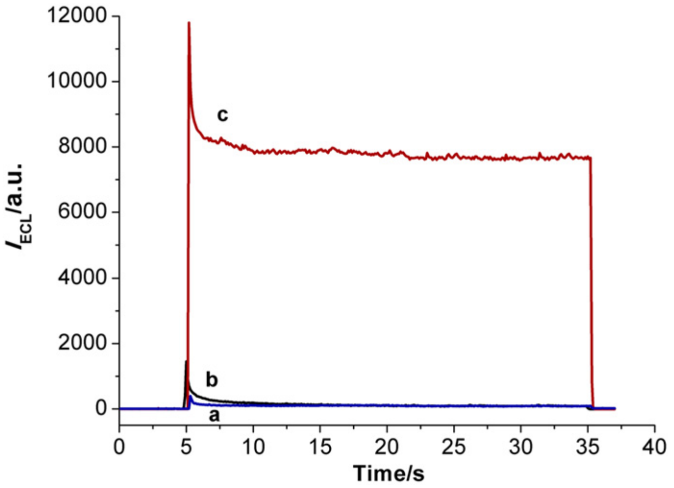

Fig. 1. Cathodic ECL at: (a) graphite electrode in 10.0 mM $Ru(bpy)_3^{2+}$; (b) CPE in 0.0 mM $Ru(bpy)_3^{2+}$ and (c) CPE in 10.0 mM $Ru(bpy)_3^{2+}$ with 0.2 M borate buffer solution (pH 9.0) containing 0.1 M Na_2SO_4. Pulse amplitude: −20.0 V (vs. Ag/AgCl), pulse width: 0.2 ms, pulse period 10 ms.

of quenching effect to the cathodic ECL of $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system. Typically, it is applied to the detection of catechol with a low LOD down to 2.0×10^{-10} M. Applied to the determination of catechol in water from reservoirs, the method is of high sensitivity. The mean recoveries of 83.3%–99.0% and the RSDs of 0.8%–2.2% were obtained, which are basically satisfactory.

2. Experimental

2.1. Chemicals and materials

0.2 M borate buffer solution (pH 9.0) containing 0.1 M Na_2SO_4 was used for ECL investigations. Tris(2,20-bipyridyl)ruthenium(II) chloride was purchased from Aldrich Chemical Co. (Milwaukee, WI). Graphite powder and paraffin oil were purchased from Shanghai Sinopharm Chemical Reagent Co. Ltd., China. The iron in water (GBW(E)080601), the manganese in water (GBW(E)08060), the copper in water (GBW(E)080605), the zinc in water (GBW(E)-080607), the lead in water (GBW(E)080581), the arsenic in water (GBW(E)080586), the cadmium in water (GBW(E)080608), the mercury in water (GBW(E)08617); standard materials, and the nitrites standard solution (GBW(E)080223), the nitrate standard solution (GBW(E)080264), the sulfate standard solution (GBW(E)-080266), the chloride standard solution (GBW(E)082048) were purchased from National Research Center for Certified Reference Material (NRCCRMS). All other reagents were of reagent grade. All solutions were prepared with Milli-Q water (resistivity of 18.2 MΩ·cm at 25 °C) from a Millipore system. The counter electrode was a platinum foil (area ca. 200 mm^2), and the reference electrode was an Ag/AgCl (3 M KCl) electrode.

The water samples were collected from Youxi section of Jiemian reservoir, Eyang section and zhanghu section of shuikou reservoir respectively.

2.2. Apparatus and measurements

A model VMP3 multichannel potentiostat (VMP3, Princeton Applied Research Co., Ltd., USA) was used as pulse generator. The cathodic pulse parameters are fixed unless specially mentioned, with amplitude of −17.0 V (vs. Ag/AgCl), pulse width of 0.2 ms, and pulse period of 10 ms. The ECL signal was recorded by an Ultra-weak Chemiluminescence Analyzer (BPCL-K, Institute of Biophysics, Academia Silica, Beijing, China). The time for collecting ECL signals was 30 s, PMT was operated at −900 V, and the PMT window was opened towards the working electrode only. ECL spectrum was obtained by a series of optical filters and was rectified to a fluorometer using a tungsten lamp.

2.3. Electrode preparation

The CPE was prepared by hand mixing of graphite powder with paraffin oil thoroughly in the proportion of 3:1 (W/W). The mixture was firstly ground fully and mixed uniformly, and then was packed firmly into the electrode cavity (2.5 mm diameter, 5 mm depth) of a PTFE sleeve with a copper lead. 1.0 μL of the paraffin oil was dropped on the surface of CPEs, and the surface of the resulting carbon paste electrodes were smoothed gently on weighting paper and dried in the air to obtain the CPEs.

3. Results and discussion

3.1. Dependence of cathodic ECL on the paraffin oil film covered on the CPE

To investigate the dependence of intensity of cathodic ECL (I_{ECL}) on the paraffin oil, the CPE covered with liquid paraffin (the CPE) and the graphite electrode were used for cathodic ECL of the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system respectively. As shown in Fig. 1, low I_{ECL} of the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system is detected at graphite electrode during cathodic pulse polarization (Fig. 1a), while strong intensity (Fig. 1c) and low background emission (Fig. 1b) are observed at the CPE. It is indicated that the ECL intensity of $Ru(bpy)_3^{2+}$ was enhanced dramatically with $S_2O_8^{2-}$ as a coreactant during the cathodic pulse potential of −20.0 V due to the paraffin oil on the CPE.

The CPE is made by direct mixing of graphite powder with paraffin oil, the liquid paraffin spread on the surface of the CPE, acting as a thin insulating film, which is essential for cathodic ECL [3]. The paraffin oil is an organic insulation material, it is electrically non-conductive. Under cathodic pulse polarization, the electrons are emitted and tunneled through the paraffin oil film into the conduction band of water. They gain energy from the insulating film, and become the hot electrodes (e_h). Some of the e_h turn into hydrated electrons (e_{aq}) after thermalization and hydration [26,27], and interact with $S_2O_8^{2-}$, forming SO_4^{*-}. Hence, $Ru(bpy)_3^{3+}$ and SO_4^{*-} are simultaneously achieved in the vicinity of the electrode surface, and cathodic ECL of $Ru(bpy)_3^{2+}$ occurred.

3.2. Quenching effects of hydrated electron scavengers

Hydrated electron is another key to cathodic ECL. After tunneling through the insulating film, the hot electrons underwent a fast hydration reaction in the conduction band of water, and forming hydrated electrons partially. The hydrated electrons reacted with $S_2O_8^{2-}$ which acted as coreactant and the strong oxidants SO_4^{*-} were formed. Ultimately, the cathodic ECL results from the reaction between SO_4^{*-} and $Ru(bpy)_3^{2+}$.

The quenching effects of several common hydrated electron scavengers including NO_2^-, NO_3^-, and $Co(NH_3)_6^{3+}$ were illuminated in Fig. 2. I_{ECL} is reduced by all these scavengers and the degree depends on their scavenging concentration. The quenching capabilities are positive proportional to the second-order reaction rate constant of them reacting with hydrated electron [$k(e_{aq}^- + NO_2^-) = 4.1 \times 10^9$, $k(e_{aq}^- + NO_3^-) = 9.7 \times 10^9$, $k(e_{aq}^- + Co(NH_3)_6^{3+}) = 8.7 \times 10^{10}$ [28]. It is demonstrated that hydrated electron is so important to cathodic ECL at the CPE.

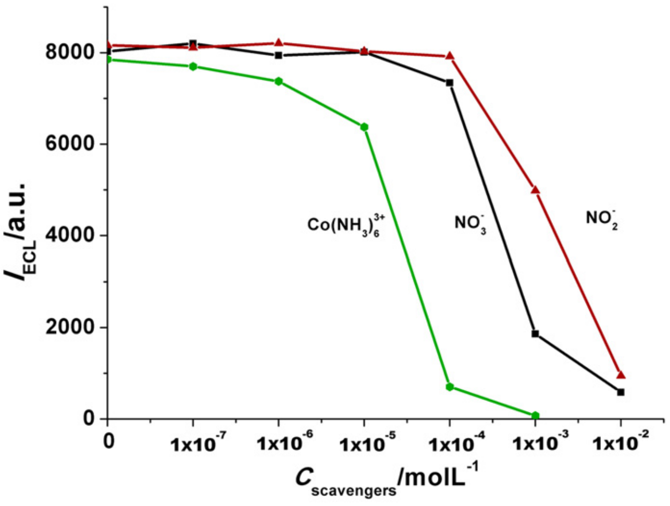

Fig. 2. Quenching effects of hydrated electron scavengers, NO_2^-, NO_3^-, $Co(NH_3)_6^{3+}$, in 0.2 M borate buffer solution (pH 9.0) containing 0.1 M Na_2SO_4 and 1.0 mM $K_2S_2O_8$ with 1.0×10^{-5} mol/L of $Ru(bpy)_3^{2+}$. Other conditions are as in Fig. 1.

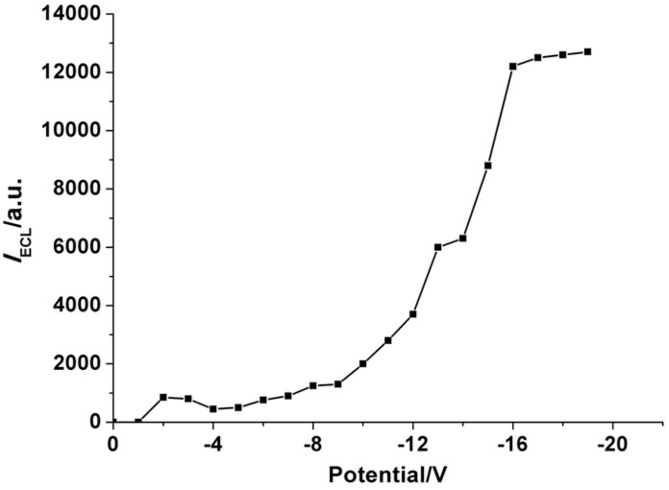

Fig. 3. Influence of cathodic pulse potential. 0.2 M borate buffer solution (pH 9.0) containing 0.1 M Na_2SO_4 and 1.0 mM $K_2S_2O_8$ with 1.0×10^{-5} mol/L of $Ru(bpy)_3^{2+}$, pulse width: 0.2 ms, pulse period 10 ms.

3.3. Influence of cathodic pulse polarization and pH

Similar to the potential voltage of the formation of hydrated electrons [29], the onset pulse potential induced ECL of the CPE is about -2.9 V, and the ECL intensity increases abruptly and reaches a plateau after -17.0 V (shown in Fig. 3).

As a type of thin insulating film-coated electrode [30], the primary step for the cathodic ECL of the CPEs has been suggested to be the injection of hot electrons from the insulating film to the conduction band of water during strong cathodic pulse polarization. The cathodic onset pulse potential is in accordance with those of several other luminophores as they share the same primary processes [31], during which the onset pulse is close to the conduction band edge of water [29] ($E^{\circ} = -2.9$ V vs. SCE). With the pulse potential increasing, the more electrons tunneled through the insulating film, the more hot electrodes engender with absorption of the energy. When the pulse potential is higher than -17.0 V, the process of generating hydrated electrons tends to be stabilized. To deliberate on all of this, -17.0 V was selected as the cathodic pulse potential.

While the -17.0 V was chosen as the optimal cathodic pulse potential, the influence of cathodic pulse width was investigated.

When the pulse width was 0.2 ms, the intensity of cathodic ECL was stable, and when the pulse width increased, the intensity was enhanced initially and decreased dramatically after 20 s for the electrode surface dissolved gradually. The decrease of the cathodic ECL could be accounted for the damage of the CPE by the increasing of the pulse width, and 0.2 ms was chosen as the optimum pulse width.

As shown in Fig. 4, the influence of pH on the ECL intensity was investigated in the range from pH 3.0 to pH 13.0. The cathodic ECL signals were weak when pH was lower than 3.0 for the conjugate reaction of hydrated electrons; in the range from pH 3.0 to pH 11.0, the intensity at the CPE was not relevant to the pH value. It is indicated that the CPEs' stability to the pH variation is superior to the other electrodes. The signals were decreased with pH above 11.0 and the surface of the CPE lost its luster, became coarse. Probably, under strong alkalic condition, the paraffin oil on the surface of the CPE was dissolved and the electrode structure was damaged, which ultimately resulted in the decrease of the ECL.

3.4. Calibration and stability of cathodic ECL at CPE

Under the optimized conditions selected above, the cathodic ECL spectrum of the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system at the CPE in Fig. 5A reveals that its emission maxima at about 630 nm, in accordance with traditional ECL spectrum of $Ru(bpy)_3^{2+}$ [32]. It is indicated that the mechanism of ECL of $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system is unchanged by cathodic pulse polarization, while the intensity is much stronger.

The intensity of the ECL was linearly increased with the concentration of $Ru(bpy)_3^{2+}$ in the range of 4.0×10^{-9} mol/L–4.0×10^{-7} mol/L (slope:2×10^{10}, intercept: 2168, $R^2 = 0.994$) with the LOD of 1.0×10^{-9} mol/L (S/N=3).

In addition, the reproducibility of the ECL at the CPE was shown in Fig. 6. The 9 parallel determinations of $Ru(bpy)_3^{2+}$ at a concentration of 1.0×10^{-5} mol/L gave a RSD of 0.82%. These results indicate that the CPE covered with paraffin oil have good stability and repeatability. This method is in the advantages of low cost, ease of fabrication, and good stability and reproducibility.

3.5. Determination of catechol

Catechol is widely used in many fields, such as chemical industry, pharmaceutical industry and dyes. However, it is also

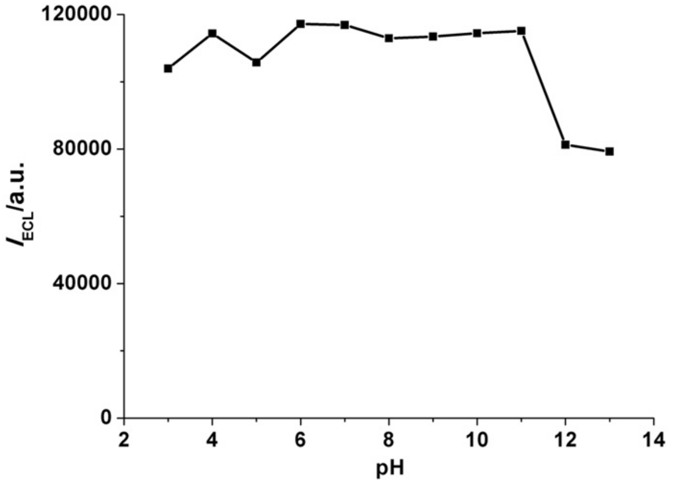

Fig. 4. Influence of pH. 0.2 M borate buffer solution containing 0.1 M Na_2SO_4 and 1.0 mM $K_2S_2O_8$ with $1 \times 10^{-5}$of $Ru(bpy)_3^{2+}$. Pulse amplitude: -17 V (vs. Ag/AgCl), pulse width: 0.2 ms, pulse period 10 ms.

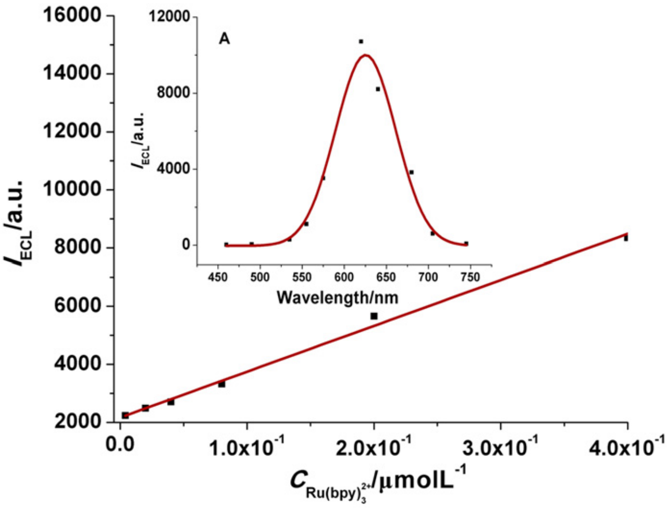

Fig. 5. Calibration curve of cathodic ECL of $Ru(bpy)_3^{2+}$. Inset*:* Cathodic ECL spectrum of the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system at the CPE. 0.2 M borate buffer solution (pH 9.0) containing 0.1 M Na_2SO_4 and 1.0 mM $K_2S_2O_8$. Pulse amplitude: − 17.0 V (vs. Ag/AgCl), pulse width: 0.2 ms, pulse period 10 ms.

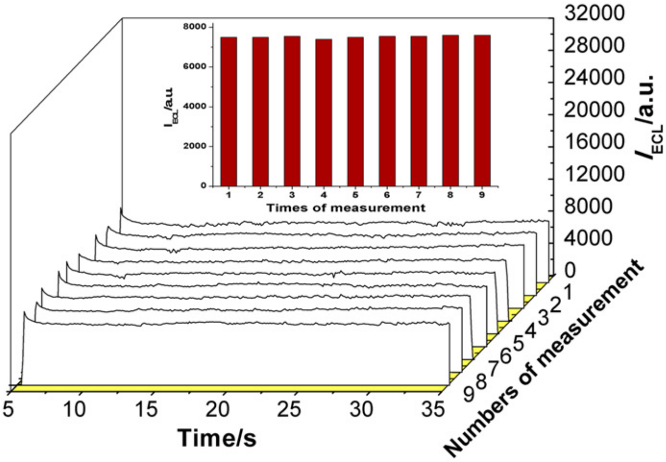

Fig. 6. Stability of CPE. 0.2 M borate buffer solution (pH 9.0) containing 0.1 M Na_2SO_4 and 1.0 mM $K_2S_2O_8$ with 1×10^{-5} mol/L of $Ru(bpy)_3^{2+}$. Pulse amplitude: −17.0 V (vs. Ag/AgCl), pulse width: 0.2 ms, pulse period 10 ms.

a widespread contaminant in the environment, and it is hazardous to human health and difficult to degrade. It has been included in the lists of priority pollutants to be monitored in the aquatic environment by international body [33].Various methods [32–36] for quantification of catechol have been described earlier. Here catechol is determined based on its competitive consuming oxidized radicals with $Ru(bpy)_3^{2+}$.

Quenching effect of phenols on the cathodic ECL was investigated and the results are shown in Fig. 7. As known, phenols are good antioxidants, and they would react with the strong oxidant radical SO_4^{*-}, forming quinoidal products. The possible mechanism was shown in Fig. 8. Phenol, catechol, hydroquinone exhibited strong quenching effect of the cathodic ECL due to their excellent deoxidization ability. While the quenching effect of resorcinol is weaker because it is difficult to be oxidized to quinone. As an example, the cathodic ECL method for the determination of catechol was performed.

The effects of pH and concentration of $S_2O_8^{2-}$ on the determination of catechol were investigated and the results are shown in Figs. 9 and 10 respectively. Fig. 9 manifested that the quenching

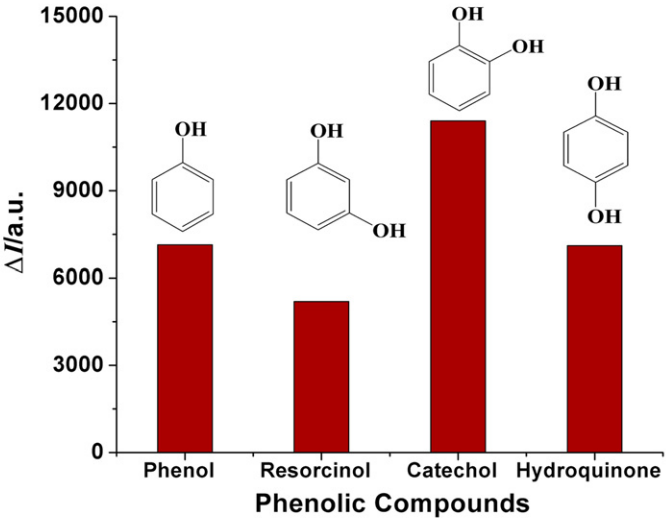

Fig. 7. Quenching effect of phenols on the cathodic ECL. 8.0×10^{-9} mol/L of phenol, resorcinol, catechol, hydroquinone were respectively added into 0.2 M borate buffer solution (pH 9.0) containing 0.1 M Na_2SO_4 and 1.0 mM $K_2S_2O_8$ with 1×10^{-5} mol/L of $Ru(bpy)_3^{2+}$.Pulse amplitude: −17.0 V (vs. Ag/AgCl), pulse width: 0.2 ms, pulse period 10 ms. (*I* was an abbreviation for the intensity of cathodic ECL of the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system, *I′* was for the ECL intensity after adding phenols into the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system, the quenching effect of intensity was abbreviated to Δ*I*, $\Delta I = I - I'$).

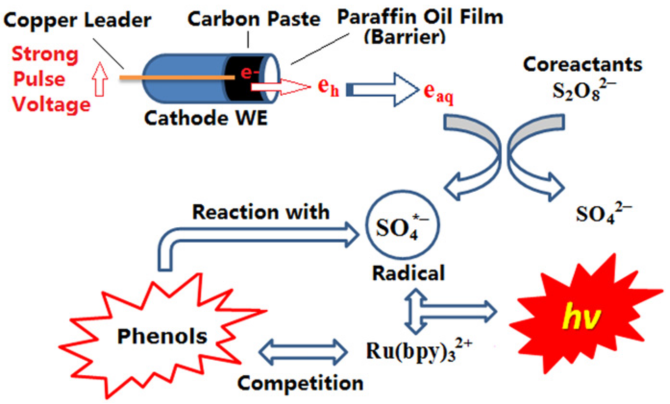

Fig. 8. The quenching effect of phenols.

effect of catechol was most evident at pH 4.0. With the increase of pH value, the quenching effect decreased, it is probably because catechol is easier to react with SO_4^{*-} in acidic environment, so pH 4.0 was chosen. As shown in Fig. 10, the fluorescence quenching value of catechol increased with the increase of the concentration of $S_2O_8^{2-}$ ($CS_2O_8^{2-}$) until the $CS_2O_8^{2-}$ reaches 5.0×10^{-5} mol/L, which might be correlated with the concentration of $Ru(bpy)_3^{2+}$. When too much $S_2O_8^{2-}$ added into buffer solution, the catechol will react with surplus $S_2O_8^{2-}$, the competition between catechol and $Ru(bpy)_3^{2+}$ will be eliminated.

Under the optimal condition, The relationship between the decrease of the ECL intensity (Δ*I*) and the logarithm of catechol concentration ($\log C_{catechol}$) exhibited satisfactory linearity over the concentration range of 2.0×10^{-10} mol/L–4.0×10^{-9} mol/L (slope:5545, intercept:58340, $R^2=0.979$) and 4.0×10^{-9} mol/L–4.0×10^{-7} mol/L (slope:897, intercept:18931, $R^2=0.976$) with LOD of 2.0×10^{-10} mol/L. The standard deviation of 9 parallel determination of catechol at each concentration is also shown in Fig. 11. Compared with other methods including electrochemical,

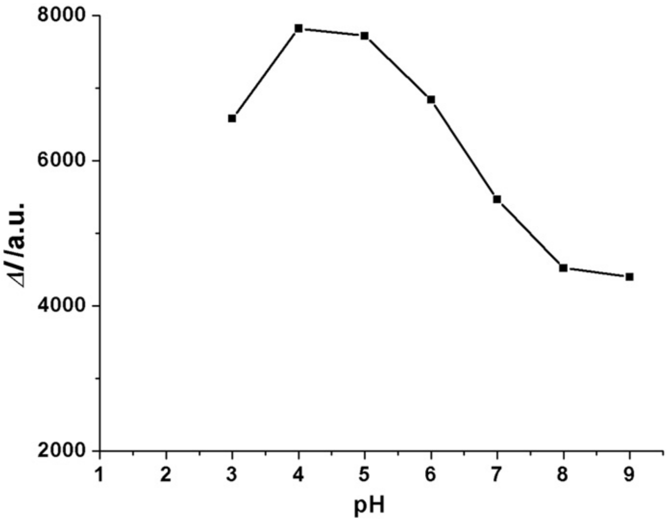

Fig. 9. The effect of pH on determination of catechol. 0.2 M borate buffer solution containing 0.1 M Na_2SO_4 and 1.0 mM $K_2S_2O_8$ with 1×10^{-5} mol/L of $Ru(bpy)_3^{2+}$. Pulse amplitude: -17.0 V (vs. Ag/AgCl), pulse width: 0.2 ms, pulse period 10 ms.

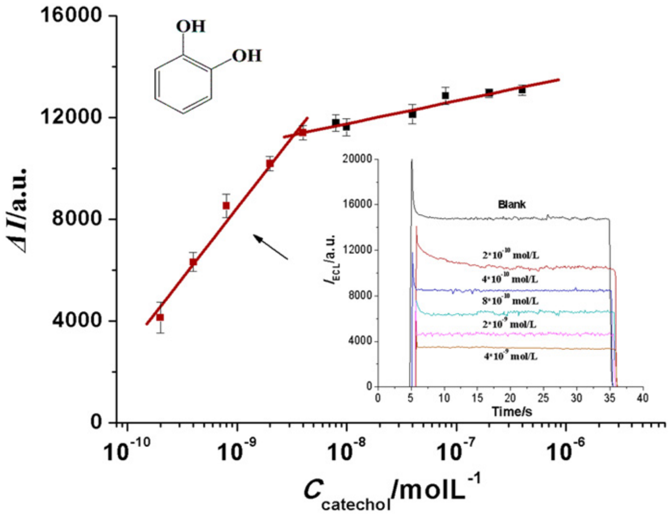

Fig. 11. Calibration curve for catechol detection. 0.2 M borate buffer solution (pH 4.0) containing 0.1 M Na_2SO_4 and 5.0×10^{-5} mol/L $K_2S_2O_8$ with 1.0×10^{-5} mol/L of $Ru(bpy)_3^{2+}$. Pulse amplitude: -17.0 V (vs. Ag/AgCl), pulse width: 0.2 ms, pulse period 10 ms.

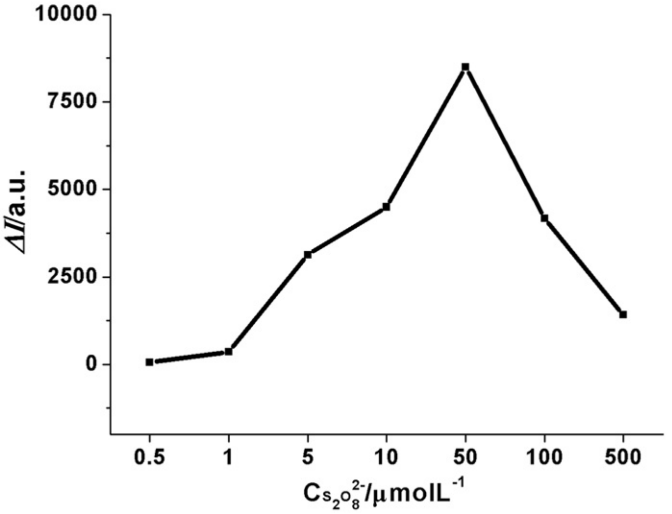

Fig. 10. The concentration of $S_2O_8^{2-}$ on determination of catechol. 0.2 M borate buffer solution (pH 4.0) with 1×10^{-5} mol/L of $Ru(bpy)_3^{2+}$. Other conditions are as in Fig. 9.

Table 1
Various methods for quantification of catechol.

Method	LOD (μmol L^{-1})	Linear range (μmol L^{-1})	Reference
Quenching effect on cathodic ECL	2.0×10^{-4}	2.0×10^{-4}–4.0×10^{-3} 4.0×10^{-3}–0.40	This work
Chemiluminecence	0.010	0.010–0.2	32
Voltammetric sensor	0.032	2–100	33
Fluorescence quenching method	0.10	0.50–1000	34
GC–MS	0.18	0.9–980	35
On-line molecularly imprinted solid phase extraction	0.81	2.7–100	36

fluorescent, GC–MS method listed in Table 1, this result is the lowest one over other reported methods.

As shown in Fig. 7, phenols exhibited strong quenching effect of the cathodic ECL. So the method also can be used for determination of other phenols. But at the same time, when the method used to determine the analyses coexisting with various phenols, other phenols would affect the accuracy of the measurement of catechol. Applied to determination of catechol in reservoir water, the proposed method is of high sensitivity. The interfering effects of $(1.0\times10^{-9}$–$1.0\times10^{-5})$ mol/L of the metal ions and anions common in water from reservoirs were investigated to make a synthetic consideration of interference factors. If the concentration was less than 1.0×10^{-6} mol/L, the quenching effect of these pollutants would not be found. And when the concentration is higher than 1.0×10^{-6} mol/L, Fe, Pb, Hg and NO_3^-, NO_2^-, SO_4^{2-} showed obvious quenching effect as shown in Figs. 12 and 13. To sum up, the interfering effects on the determination of catechol would become obvious, only when the concentration of those disturbing substances is higher than 1.0×10^{-6} mol/L.

It is found that the water sample of shuikou reservoir both from eyang section and zhanghu section exhibited very low-level quenching effect on the cathodic ECL, while the water sample in the Youxi section of Jiemian reservoir shows faint strengthening effect on the cathodic ECL. Moreover, 10.0 nmol/L and 1.0 nmol/L of catechol were added into the water of reservoirs respectively to investigate the recovery rate. As shown in Table 2, the mean recoveries of 83.3%–99.0% and RSDs of 0.8%–2.2% were obtained.

4. Conclusions

The hot electron induced cathodic ECL of the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system at the CPEs were investigated for the first time. The signals of cathodic ECL were sensitive, stable and reproducible, and its ECL intensity of $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system exhibited satisfactory linearity over the concentration range of about three orders of magnitude. It is concluded that the CPE is an effective electrode to realize the cathodic ECL of the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system. At the same time, the determination of catechol at trace level were realized successfully based upon its decreasing effect on the

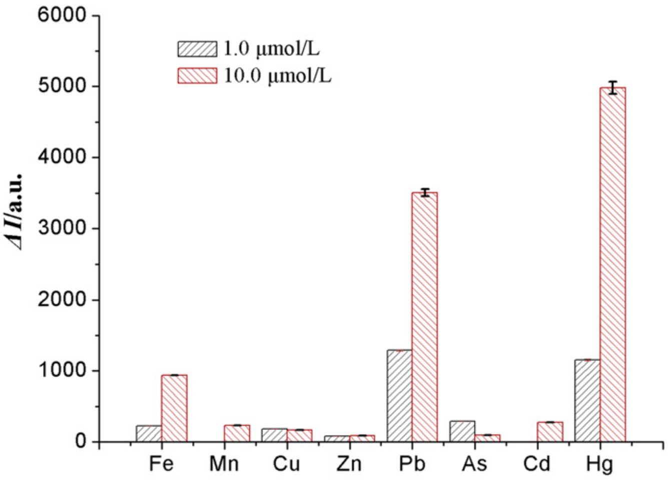

Fig. 12. The interfering effect of the metal ions. Other conditions are as in Fig. 11.

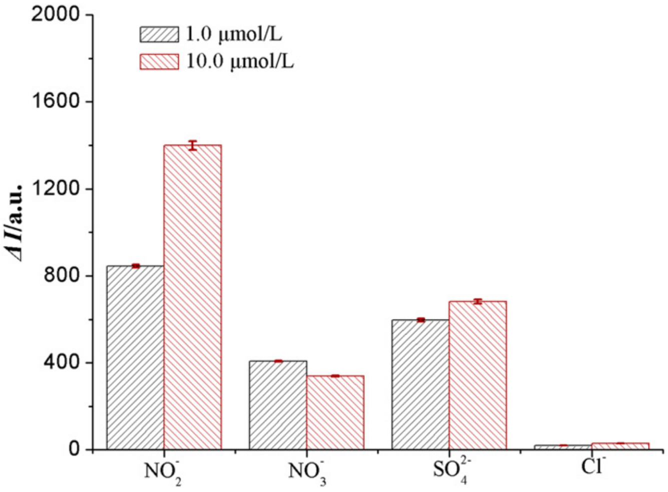

Fig. 13. The interfering effect of the anions. Other conditions are as in Fig. 11.

Table 2
Recovery of catechol in water of reservoirs.

	The water of Shuikou reservoir (Eryang section)		The water of Shuikou reservoir (Zhanghu section)		The water of Jiemian reservoir (Youxi section)	
Added/ nmol L^{-1}	10.0	1.0	10.0	1.0	10.0	1.0
Determined/ nmol L^{-1}	9.76	0.87	9.90	0.86	9.21	0.83
Recovery/%	97.6	86.6	99.0	86.3	92.1	83.3
R.S.D/%	1.0	1.6	0.8	1.5	1.3	2.2

cathodic ECL of the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system. The method is applied to the determination of catechol in the water of reservoirs. And the results are basically satisfactory.

Acknowledgments

The authors thank for the financial support from the National Science Foundation of China (No. 20975022, 21275030), the National Key Technologies R & D Program of China during the 12th Five-Year Plan Period (Key technology of quality and safety control during aquatic product processing, No. 2012BAD29B06), the State Key Laboratory Breeding Base of Photocatalysis (Fuzhou University), the Program for Changjiang Scholars and Innovative Research Team in University (No. IRT1116).

References

[1] S. Kulmala, J. Suomi, Anal. Chim. Acta 500 (2003) 21–69.
[2] Johanna Suomi, Tiina Ylinen, Markus Håkansson, J. Electroanal. Chem. 586 (2006) 49–55.
[3] J.J. Kankare, D.E. Ryan, B.J. Fürst, Can. J. Chem. 55 (1977) 1193–1198.
[4] K. Haapakka, J. Kankare, S. Kulmala, J. Lumin. 31–32 (1984) 966–968.
[5] K. Haapakka, J. Kankare, S. Kulmala, Anal. Chim. Acta 171 (1985) 259–267.
[6] K. Haapakka, J. Kankare, S. Kulmala, Anal. Chim. Acta 209 (1988) 165–174.
[7] K. Haapakka, S. Kulmala, Anal. Chim. Acta 208 (1988) 69–79.
[8] Y.E. Sung, F. Gaillard, A.J. Bard, J. Phys. Chem. B 102 (1998) 9797–9805.
[9] Y.E. Sung, A.J. Bard, J. Phys. Chem. B 102 (1998) 9806–9811.
[10] F. Gaillard, Y.E. Sung, A.J. Bard, J. Phys. Chem. B 103 (1999) 667–674.
[11] Qinghong Jiang, Hanna Ketamo, Antti J. Niskanen, Electrochim. Acta 51 (2006) 3332–3337.
[12] Q. Jiang, M. Kotiranta, K. Langel, Anal. Chim. Acta 541 (2005) 171–177.
[13] M. Håkansson, Q. Jiang, S. Kulmala, Electrochim. Acta 51 (2005) 289–296.
[14] A.H. Wu, J.J. Sun, Y.M. Fang, Talanta 82 (2010) 1455–1461.
[15] A.H. Wu, J.J. Sun, Y.M. Fang, R.J. Zheng, G.N. Chen, Electroanalysis 22 (2010) 2702–2707.
[16] A.H. Wu, J.J. Sun, R.J. Zhen, H.H. Yang, G.N. Chen, Talanta 81 (2010) 934–940.
[17] A.H. Wu, J.J. Sun, X.L. Su, Y.W. Lin, Z.B. Lin, H.H. Yang, G.N. Chen, Analyst 135 (2010) 2309–2915.
[18] T. Kuwana, W.G. French, Anal. Chem. 36 (1964) 241–242.
[19] K. Ravichandra, R.P. Baldwin, J. Electroanal. Chem. Interface Electrochem. 126 (1981) 293–300.
[20] K. Kalcher, J.M. Kauffmann, J. Wang, I. Svancara, K. Vytras, C. Neuhold, Z. Yang, Electroanalysis 7 (1995) 5–22.
[21] R.N. Adams, Anal. Chem. 30 (1958) 1576–1581.
[22] J. Parellada, A. Narvaez, E. Dominguez, I. Katakis, Biosens. Bioelectron. 12 (1997) 267–275.
[23] J. Kulys, Biosens. Bioelectron. 14 (1999) 473–479.
[24] S. Shahrokhian, M. Ghalkhani, M.K. Amini, Sens. Actuators B 137 (2009) 669–675.
[25] Shaojun Dong Guobao Xu, Electroanalysis 12 (2000) 583–587.
[26] T. Ala-Kleme, S. Kulmala, M. Latva, Acta Chem. Scand. 51 (1997) 541–546.
[27] M. Håkansson, Q. Jiang, M. Helin, M. Putkonen, A.J. Niskanen, S. Pahlberg, T. Ala-Kleme, L. Heikkilä, J. Suomi, S. Kulmala, Electrochim. Acta 51 (2005) 289–296.
[28] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, J. Phys. Chem. Ref. Data 17 (1988) 513.
[29] S. Kulmala, A. Kulmala, T. Ala-Kleme, J. Pihlaja, Anal. Chim. Acta. 367 (1998) 17–31.
[30] S. Kulmala, T. Ala-Kleme, H. Joela, A. Kulmala, J. Radioanal. Nucl. Chem. 232 (1998) 91–95.
[31] S. Kulmala, T. Ala-Kleme, L. Heikkil, L.V. Rare, J. Chem. Soc. Faraday Trans. 93 (1997) 3107–3113.
[32] B. Haghighi, R. Dadashvand, J. Anal. Bioanal. Chem. 384 (2006) 1246–1253.
[33] Y. Kong, X.H. Chen, C. Yao, M.J. Ma, Z.D. Chen, Anal. Methods 3 (2011) 2121–2126.
[34] Wen Juan Dong, Jin Ping Song, Chuan Dong, Martin M.F. Choi, Chin. Chem. Lett. 21 (2010) 346–348.
[35] E.L.B. Lourenço, A. Ferreira, E. Pinto, M. Yonamine, S.H.P. Farsky, Chromatography 63 (2006) 175–179.
[36] Eduardo Costa de Figueiredo, César Ricardo Teixeira Tarley, Lauro Tatsuo Kubota, Susanne Rath, Marco Aurélio Zezzi Arruda, Microchem. J. 85 (2007) 290–296.