Electrochimica Acta 54 (2008) 733–737

Contents lists available at ScienceDirect

Electrochimica Acta

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

Cathodic electrochemiluminescence behavior of norfloxacin/peroxydisulfate system in purely aqueous solution

Wu Yao [a,b], Lun Wang [a,*], Haiyan Wang [a,*], Xiaolei Zhang [a]

[a] Anhui Key Laboratory of Chemo-Biosensing, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, PR China
[b] Department of Chemistry, Huangshan University, Huangshan 245041, PR China

ARTICLE INFO

Article history:
Received 29 May 2008
Received in revised form 25 June 2008
Accepted 28 June 2008
Available online 6 July 2008

Keywords:
Cathodic electrochemiluminescence
Peroxydisulfate
Norfloxacin
Fluoroquinolone
Cyclic voltammogram

ABSTRACT

A novel cathodic electrochemiluminescence (ECL) behavior of the norfloxacin (NFLX)/peroxydisulfate ($S_2O_8^{2-}$) system in purely aqueous solution at a glassy carbon electrode (GCE) was firstly reported in this paper. The NFLX/$S_2O_8^{2-}$ system could produce a very strong ECL signal under the potential scan from 0 to −1.8 V in 0.1 M phosphate buffer solution (pH 7.0) containing 0.24 mg/mL NFLX and 10 mM $S_2O_8^{2-}$, which was about 350 times higher than that of $S_2O_8^{2-}$ alone, while NFLX did not produce ECL in the absence of $S_2O_8^{2-}$. The effects of pH value, $S_2O_8^{2-}$ and NFLX concentration on the ECL intensity were investigated and the possible mechanism for the ECL behavior of NFLX/$S_2O_8^{2-}$ system was proposed.

1. Introduction

In the past several decades, a number of electrochemiluminescence (ECL) reaction systems have been discovered and studied [1,2], by which the nature of an emitting state has been extensively investigated, and the related theory has been developed [3,4]. Among the different ECL types that have been classified, the kind of cathodic ECL reaction systems involving peroxydisulfate ($S_2O_8^{2-}$) plays an important role [2,5–12]. Peroxydisulfate can be electrochemically reduced to sulfate radical anion ($SO_4^{\bullet -}$), a strongly oxidizing intermediate, and be used as co-reactant in many ECL systems. Generally, cathodic ECL of peroxydisulfate system was divided into three types. First, in the inorganic/$S_2O_8^{2-}$ cathodic ECL system, the strong oxidant $SO_4^{\bullet -}$ undergoes an electron transfer reaction with the reduced species of an inorganic ECL luminophore such as $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ to generate light [2,9–12]. Second, in the case of semiconductor nanoparticles (NPs), such as Si, Ge, CdS, CdSe, CdTe, ZnS, CdSe/CdS, light emission occurs at cathode with $S_2O_8^{2-}$ as the co-reactant due to the hole injection into the reduced intermediates of these nanomaterials by $SO_4^{\bullet -}$ [13–19]. Third, the ECL phenomenon of the organic such as hydrocarbon with $S_2O_8^{2-}$ was discussed by Bard's group, and the ECL emission produced from the excited state of organic, which were formed by interaction of reduced organic with the strong oxidant $SO_4^{\bullet -}$ [2,20–23]. However, the ECL of organic/$S_2O_8^{2-}$ system was restricted in purely or mixed organic solvent due to the poor solubility of organic species in aqueous solution, which limits the wide application of this system. Therefore, it is important to investigate the ECL of such system in purely aqueous solution.

Fluoroquinolones is an important organic species, exhibiting high activity against Gram-positive and Gram-negative bacteria by inhibiting the activity of their DNA gyrase [24,25] and is widely used as anti-bacteria drugs. Now, studies on the fluoroquinolones have attracted more and more attention [26–30].

In this present work, we selected norfloxacin (NFLX, the chemical structure shown in Fig. 1) as a representative of the fluoroquinolones to study the cathodic ECL behavior of NFLX/$S_2O_8^{2-}$ system in purely aqueous solution at a glassy carbon electrode (GCE). It was found that NFLX could catalyze the reduction of peroxydisulfate and the NFLX/$S_2O_8^{2-}$ system could produce a very strong ECL signal under the potential scan from 0 to −1.8 V in 0.1 M phosphate buffer solution (pH 7.0). A possible mechanism for the ECL behavior of NFLX/$S_2O_8^{2-}$ system was proposed.

2. Experimental

2.1. Chemicals

Norfloxacin (98%) and $K_2S_2O_8$ were purchased from Institute of Medical Biotechnology (Beijing, China) and Shanghai Chemical

---

* Corresponding authors. Tel.: +86 553 3869303; fax: +86 553 3869303.
E-mail addresses: wanglun@mail.ahnu.edu.cn (L. Wang), hywang@mail.ahnu.edu.cn (H. Wang).

0013-4686/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2008.06.067

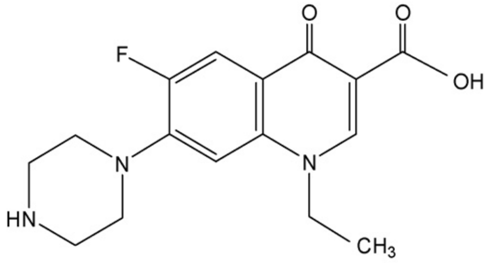

Fig. 1. The chemical structure of NFLX.

Reagent Company (Shanghai, China), respectively. A 4 mg/mL stock solution of NFLX was prepared by dissolving it in 0.01 M NaOH and the standard solutions were obtained by diluting them to the designed concentration with doubly distilled water and stored at 4 °C. A 0.1 M stock solution of peroxydisulfate was also prepared by dissolving 6.7533 g $K_2S_2O_8$ and diluting to 250 mL with double-distilled water. Other reagents were of analytical grade or better, double-distilled water was used throughout the experiments.

2.2. *Apparatus and procedures*

Electrochemiluminescence studies were performed using a BPCL-2-KIC mode Ultra-Weak Chemiluminescence Analyzer controlled by a personal computer with BPCL program (Institute of Biophysics, Chinese Academy of Science) in conjunction with a CH Instruments model 760c Electrochemical Analyzer (Shanghai Chenhua Instrument Co., China).

A conventional three-electrode system was used, which was composed of a glassy carbon electrode (φ = 3 mm) as the working electrode, a platinum wire as the counter electrode and an Ag/AgCl (sat. KCl) electrode as the reference electrode. A commercial cylindroid's glass cell was used as an ECL cell, and it was placed directly in the front of the photomultiplier tube (PMT) which was biased at 900 V. Before each measurement, the working electrode was pretreated by polishing the surface with aqueous slurries of 0.3 and 0.05 μm alumina powders and rinsed with water, then washed with distilled water in an ultrasonic bath to give a smooth electrode surface. After that, 15 cyclic scans were carried out in the potential range from 0 to −1.8 V in the 0.1 M phosphate buffer solution (pH 7.0) to get stable signals. The cyclic voltammograms (CVs) and ECL of NFLX, $S_2O_8{}^{2-}$, and NFLX/$S_2O_8{}^{2-}$ system were then simultaneously performed in air saturation condition at room temperature. The photoluminescence (PL) spectrum of NFLX was obtained by a Hitachi F-4500 spectrofluorometer (Tokyo, Japan).

3. Results and discussion

3.1. *Electrochemical and ECL behaviors of NFLX/$S_2O_8{}^{2-}$ system*

The electrochemical property of norfloxacin and $S_2O_8{}^{2-}$ in 0.1 M phosphate buffer solution (pH 7.0) was studied with cyclic voltammograms. As shown in Fig. 2, it was evident that the electrode processes for the reductions of NFLX and $S_2O_8{}^{2-}$ were irreversible and the reduction peak potentials were −1.48 and −1.42 V, respectively. For the NFLX/$S_2O_8{}^{2-}$ mixture system, the reduction peak potentials of NFLX and $S_2O_8{}^{2-}$ shifted to −1.54 and −1.26 V, respectively. The obvious positive shift of the reduction peak potential of $S_2O_8{}^{2-}$ in the presence of NFLX suggested that the NFLX could catalyze the reduction of $S_2O_8{}^{2-}$. In addition, the effect of scan rate on the NFLX reduction peak current was also considered and shown in Fig. 3. It can be seen that the peak currents of NFLX in the NFLX/$S_2O_8{}^{2-}$ mixture system was linearly increasing with the square root of scan rate in the range of 0.05–0.30 V/s with correlation coefficients of 0.9994 (inset, Fig. 3), which suggested that the electrochemical reduction of NFLX at the GCE was diffusion-controlled, i.e., NFLX was not adsorptive or weakly adsorptive at the glassy carbon electrode [3].

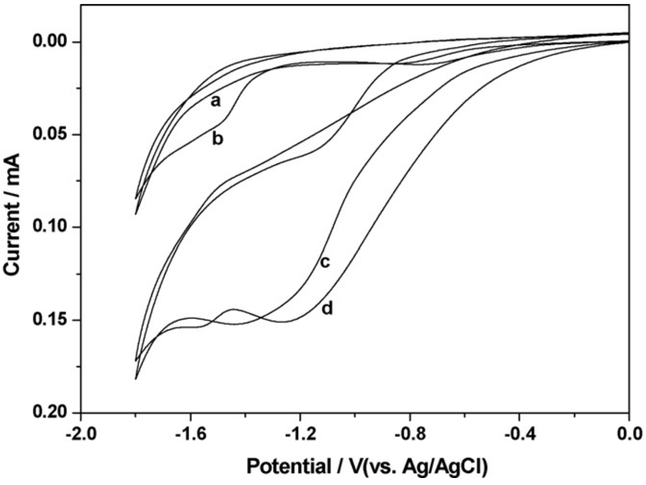

Fig. 2. Cyclic voltammograms of (a) blank PBS solution (pH 7.0), (b) 0.24 mg/mL NFLX, (c) 10 mM $S_2O_8{}^{2-}$ and (d) 10 mM $S_2O_8{}^{2-}$ and 0.24 mg/mL NFLX in 0.1 M PBS (pH 7.0); scan rate, 0.1 V/s.

The corresponding ECL behavior of NFLX/$S_2O_8{}^{2-}$ mixture system was simultaneously recorded when the CV was performed, as shown in Fig. 4. The primary experiment showed that NFLX did not give ECL at GCE in the absence of peroxydisulfate (Fig. 4, curve a), whereas peroxydisulfate alone produced weak ECL (Fig. 4, curve b). Moreover, the ECL intensity of peroxydisulfate increased with the oxygen saturation of solution and obviously decreased after the solution was deoxygenated with pure nitrogen for 20 min. Koval'chuk and coworkers [31–33] observed similar ECL behavior of peroxydisulfate in aqueous solution at magnesium, silver or platinum electrodes and proposed that the light-emitting species containing $^1O_2$, $^1(^1O_2)_2$ and $^3(^1O_2)_2$ were formed by interaction of water with the strong oxidant $SO_4{}^{\bullet-}$, which were generated during the electrochemical reduction of peroxydisulfate. Therefore, the ECL of $S_2O_8{}^{2-}$ alone at GCE in our work produced in a way similar

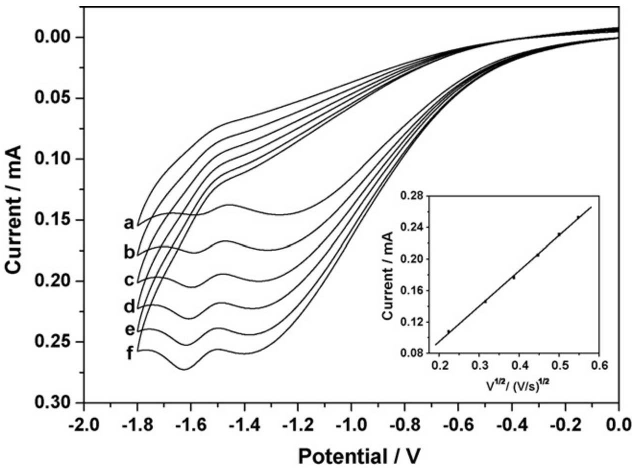

Fig. 3. Cyclic voltammograms of NFLX/$S_2O_8{}^{2-}$ system in 0.1 M PBS (pH 7.0) at the different scan rates. (a) 0.05 V/s, (b) 0.10 V/s, (c) 0.15 V/s, (d) 0.20 V/s, (e) 0.25 V/s, and (f) 0.30 V/s. [$K_2S_2O_8$] = 10 mM; [NFLX] = 0.24 mg/mL. Inset: plot of cathodic peak current of NFLX vs. square root of scan rate ($\nu^{1/2}$).