Electrochemistry Communications 38 (2014) 57–60

Contents lists available at ScienceDirect

Electrochemistry Communications

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

Short communication

One-step process for fabricating paper-based solid-state electrochemiluminescence sensor based on functionalized graphene

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ARTICLE INFO

Article history:
Received 15 October 2013
Received in revised form 5 November 2013
Accepted 5 November 2013
Available online 10 November 2013

Keywords:
Paper-based chips
One-step process
Functionalized graphene
Electrochemiluminescence sensor
Tetracycline hydrochloride

ABSTRACT

Taking advantage of simple manipulation of the screen printed electrodes, with the assistance of different functionalized graphene materials, a simple and time-saving one-step process was developed for fabricating solid-state electrochemiluminescence (ECL) sensors on paper-based chips (PCs). The solid-state $Ru(bpy)_3^{2+}$ or co-reactant ECL sensors could be facilely obtained by screen-printing the mixture of $Ru(bpy)_3^{2+}$/poly(sodium 4-styrenesulfonate) functionalized graphene nanosheets (PSSG)/carbon paste or branch poly(ethylenimine) (BPEI)-functionalized graphene nanosheets (BPEIG)/carbon paste through one-step process on the PCs, respectively. The ECL behavior of $Ru(bpy)_3^{2+}$ ECL sensor was investigated using tripropylamine (TPA) and detection limit (S/N = 3) of 5.0 nM was obtained. It also exhibited excellent reproducibility and linear relationship with the concentration of TPA ($R = 0.991$). In addition, the ECL behaviors of the coreactant sensor were measured for tetracycline hydrochloride (TCH) by inhibition method. A linear relationship between the ECL intensity and logarithm of the concentration of TCH was gained in a range of 1×10^{-8} to 1×10^{-6} M and the detection limit was as low as 2.22 nM. Therefore the one-step process for fabricating paper-based ECL sensor was confirmed with the advantages of simplicity, high efficiency and potential applicability.

1. Introduction

Since Whitesides' group raised the concept of utilizing patterned paper substrate as microfluidic platform for analyte assays [1], paper-based chips (PCs) have been attracting increasing attention recently because of their cost-effectiveness, simpleness, portability, etc. [2,3]. Now it has been applied to detect medical materials such as glucose and uric acid [4,5]. The advantages of screen printing are low-cost, easy manipulation, etc. [4,6]. It offers a convenient way to transfer the carbon ink or other printable materials onto PCs to receive desired images such as electrodes [4], and therefore makes the PCs be feasible in establishing electrochemical [4] and electrochemiluminescence (ECL) sensing platforms [7]. In addition, because tris(2,2′-bipyridyl) ruthenium(II) ($Ru(bpy)_3^{2+}$) can be regenerated in situ at the electrode surface during the ECL process due to the oxidation–reduction reaction mechanism [8], regenerable solid-state ECL sensors could be constructed by immobilizing $Ru(bpy)_3^{2+}$ on the electrode surface by various ways such as ion-exchanging, π–π interaction, etc. [9,10]. Moreover, highly efficient solid-state ECL sensors on PCs could be developed at the screen printed electrodes (SPEs) by using the composite films of Nafion and functionalized graphene materials [11]. These confirmed the good compatibility between the solid-state ECL sensor and the PCs.

Despite of the results obtained, several steps such as film formation, ion-exchanging, etc. had to be taken in previous ways for solid-state ECL sensor fabrication both at traditional electrodes and SPEs on PCs [9–11]. While simpleness is the initial intent and development trend of both solid-state ECL sensor and PCs, much more convenient and efficient ways are still in urgent need.

Herein, a much more convenient, time-saving and efficient one-step-process technology was developed to fabricate the solid-state ECL sensors on PCs. Either $Ru(bpy)_3^{2+}$, or its coreactant could be ingeniously immobilized on PCs by directly screen-printing the mixture of carbon paste, functionalized graphene materials (or with $Ru(bpy)_3^{2+}$) on the PCs. Through the characterization of their cyclic voltammograms (CVs) and ECL behaviors, the sensors displayed good reproducibility and high efficiency. Detection for tripropylamine (TPA) or tetracycline hydrochloride (TCH) showed excellent reproducibility, good linear relationship and sensitive results, respectively.

2. Materials and method

2.1. Chemicals and reagents

Chromatography paper (Whatman, No. 1) was obtained from Whatman International Ltd. (U.K.). SU-8 3025 negative photoresist was purchased from MicroChem Corp. (Newton, MA). Carbon ink and silver conductive ink were from Alfa Aesar (MA, USA). Tris(2,2′-bipyridyl)ruthenium(II) chloride hexahydrate ($Ru(bpy)_3Cl_2 \cdot 6H_2O$, 98%), TPA, and PSS (molecular weight = 1,000,000 Da) were obtained from Sigma Aldrich Chemical Co. (Milwaukee, WI). Branched poly

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http://dx.doi.org/10.1016/j.elecom.2013.11.007

(ethylenimine) (BPEI) (Mw = 25,000) was from Aldrich (St. Louis, USA) and used as received. Methanol, ethyl alcohol and tetrahydrofuran were from Beijing Chemical Works. (Beijing, China). TCH was obtained from Sangon Biotechnology Co., Ltd. (Shanghai, China). All the other reagents were of analytical grade and MilliporeMill-Q water (18.2 MΩ cm) deionized water was used throughout.

2.2. Apparatus

Cyclic voltammetric experiments were performed with a CH Instruments 800 voltammetric analyzer. ECL intensities were measured with a computer controlled capillary electrophoresis-ECL system (Xi'an Remex Electronics, Xi'an, China). The voltage of the photomultiplier tube (PMT) for collecting the ECL signal was set at 800 V during detection.

2.3. Synthesis of PSSG and fabrication of PCs

PSSG sheets and BPEIG sheets were prepared according to the previous methods [12,13]. The PCs were fabricated by photolithography on the basis of previously reported method [14]. Then, for easy operation counter electrode (CE, carbon, with the width of 1 mm) and reference electrode (RE, Ag, with the diameter of 4 mm) were screen-printed on the one side of PCs and working electrode as well as the $Ru(bpy)_3^{2+}$ sensor or coreactant ECL sensor was laid on the other side with the diameter of 4 mm. The electrodes were all printed on the hydrophilic circular zone of PCs with a diameter of 8 mm[14]. The $Ru(bpy)_3^{2+}$ sensor and coreactant sensor were fabricated as shown in Fig. 1. Typically, the $Ru(bpy)_3^{2+}$ sensor could be obtained by screen-printing a uniform mixture of 30 μL of 10 mM $Ru(bpy)_3^{2+}$, 30 μL of 0.30 mg/mL PSSG, 30 μL carbon paste and 40 μL cosolvent of tetrahydrofuran on the PCs. Similarly, the coreactant sensor was also gotten by screen-printing a uniform mixture of 30 μL 0.30 mg/mL BPEIG, 30 μL volume of carbon paste and 40 μL cosolvent of tetrahydrofuran. Then the prepared electrodes needed to evaporate the solvents under an infrared lamp heating for 180 s. After that, the electrodes were rinsed thoroughly with deionized water and 0.1 M phosphate buffer solution (PBS) (pH = 7.4) to remove the unimmobilized $Ru(bpy)_3^{2+}$ or coreactant. Then they should be covered to avoid dust and after each use. Owing to the opaqueness of the SPEs, the working side of the electrode was placed over against the photomultiplier tube (PMT) biased at 800 V to collect the utmost ECL signal.

3. Results and discussion

3.1. Characterization of the $Ru(bpy)_3^{2+}$ ECL sensor

It is known that PSSG possesses the characteristics of both PSS and graphene, so $Ru(bpy)_3^{2+}$ could be immobilized effectively on the SPEs of PCs and the fast electron transfer of $Ru(bpy)_3^{2+}$ could be ensured in the composite film of PSSG/Nafion [10]. Herein, PSSG is also used for fabrication of the solid-state $Ru(bpy)_3^{2+}$ ECL sensor. The difference is by screen-printing the mixture of PSSG, $Ru(bpy)_3^{2+}$ and carbon paste directly on the PCs to obtain the SPEs. Simultaneously, the solid-state $Ru(bpy)_3^{2+}$ ECL sensors could be obtained. It only took a few minutes to fabricate the sensors. Meanwhile, the stability and the electron transfer could also be ensured.

In order to prove the feasibility, sensitivity and stability and reproducibility of the $Ru(bpy)_3^{2+}$ ECL sensor, TPA was applied to investigate its ECL behaviors. Fig. 2(A) shows the ECL intensity-potential curve of $Ru(bpy)_3^{2+}$ sensor in the presence and absence of 15 μL of 200 μM TPA in 0.1 M PBS (pH = 7.4) which was dropped on the sensor at the scan rate of 100 mV/s. It can be clearly seen that the presence of TPA caused the anodic peak current increasing clearly while the cathodic peak current decreasing (the inset of Fig. 2A), which was consistent with the electrocatalytic reaction mechanism [10,11].

3.2. Stability and reproducibility of $Ru(bpy)_3^{2+}$ sensor

Subsequently, the ECL intensity of $Ru(bpy)_3^{2+}$ sensor at different concentrations of TPA from 10 nM to 200 μM was measured (the inset of Fig. 2B). The ECL intensity was correlated with the TPA concentrations ranging from 10 nM to 200 μM ($R = 0.991$) (Fig. 2B) and the detection limit (S/N = 3) was estimated to be 5.0 nM. In addition, the CVs of $Ru(bpy)_3^{2+}$ sensor at different scan rates from 25 mV/s to 200 mV/s were also tested by dropping 15 μL of 0.1 M PBS (pH = 7.4) on the sensor, the anodic peak currents and the square root of the scan rates were in good linearity and the linearly dependent coefficient was $R = 0.997$, which indicated that the $Ru(bpy)_3^{2+}$ was diffusion controlled. Moreover, the ΔE_p between anodic peak and cathodic peak was 0.086 V at the scan rate of 100 mV/s, compared with our previous work [10] of Nafion/PSSG modified electrodes ($\Delta E_p = 0.27$ V), the lower ΔE_p indicated much higher conductivity of the proposed sensor herein. Fig. 2(C) shows the ECL behavior of the solid-state $Ru(bpy)_3^{2+}$ ECL sensor in the absence and presence of 100 μM TPA under continuous CV for 12 cycles. The RSDs of the ECL peaks in the presence and absence of TPA are 1.50% and 1.45%, respectively. This means good stability and reproducibility of the sensor. This result demonstrated that $Ru(bpy)_3^{2+}$ had been immobilized effectively by the one-step process.

3.3. ECL of the coreactant sensor

BPEI could be used as both the stabilizer and the reducing agent in the preparation of long-term stable BPEIG [13], moreover, BPEI is one advanced materials containing abundant amino groups, so it could be used as a coreactant to increase the ECL signal of $Ru(bpy)_3^{2+}$ effectively [15]. The prepared materials BPEIG also possess the properties of high conductivity. Therefore, by screen-printing the blend of BPEIG and carbon paste through the one-step process, sensors with immobilization of ECL coreactant could be obtained.

ECL intensities of different concentrations of $Ru(bpy)_3^{2+}$ all at 10 μL were studied on the coreactant sensor or pure SPEs on the PCs,

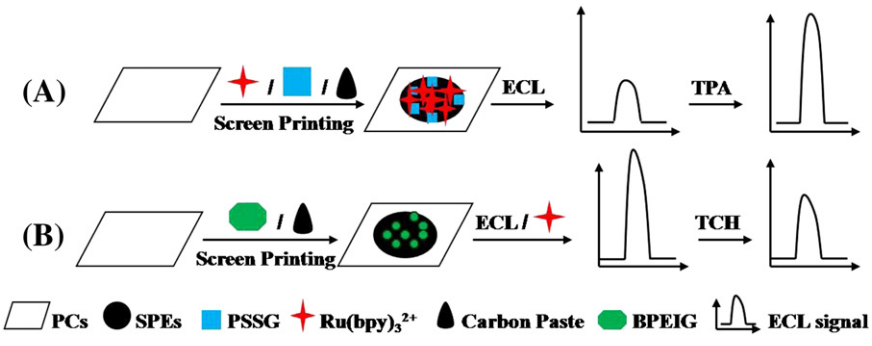

Fig. 1. Schematic illustration of preparation and application for solid-state (A) $Ru(bpy)_3^{2+}$ and (B) coreactant ECL sensors.