Sensors and Actuators B 216 (2015) 255–262

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Open bipolar electrode-electrochemiluminescence imaging sensing using paper-based microfluidics

Rui Liu, Chunsun Zhang*, Min Liu

MOE Key Laboratory of Laser Life Science & Institute of Laser Life Science, College of Biophotonics, South China Normal University, Guangzhou 510631, China

ARTICLE INFO

Article history:
Received 28 January 2015
Received in revised form 22 March 2015
Accepted 1 April 2015
Available online 16 April 2015

Keywords:
Open bipolar electrode
Electrochemiluminescence
Paper-based Microfluidics
Visual detection
Wax-screen-printing
Small-batch manufacturing

ABSTRACT

A novel paper-based open bipolar electrode-electrochemiluminescence (P-*o*-BPE-ECL) sensing has been developed for visual detection. Wax-screen-printing was employed to make microfluidic channels on filter paper, and the carbon ink-based BPE and driving electrodes were screen-printed on paper. An inexpensive CCD camera was used as a detector for imaging sensing. In this study, two P-*o*-BPE-ECL imaging sensing platforms were demonstrated. For the first one, a hydrophilic paper channel was used to host a single "band"-shaped BPE. Under optimal conditions, this P-*o*-BPE-ECL platform successfully fulfilled the imaging sensing of tri-*n*-propylamine (TPA) with a linear range from 10 to 1000 μM with a detection limit of 8.7 μM. In addition, the determination of H_2O_2 using this platform could be performed in the linear range of 50 μM to 5000 μM with a detection limit of 46.6 μM. For the second platform, an open BPE array configuration has been proposed for P-*o*-BPE-ECL sensing, where eleven BPEs were stridden across the two legs of the "U"-shaped paper channel. On this prototype, a simple screening application has been performed. These results show that the proposed strategy offers great promise in providing a simple, low-cost, rapid and environment-friendly solution for biochemical applications.

1. Introduction

Since the first patterned paper was introduced by Whitesides and co-workers [1], the microfluidic paper-based analytical devices (or paper-based microfluidics) have recently gained considerable interest and wide attention from many researchers [2–5]. Due to its high sensitivity, low cost, small footprint, portability, easy operation, shorter time of analysis and integration of multiple functions in a chip, paper-based microfluidics has been used widely for molecular analysis, environmental detection, health monitoring and food quality control. In addition, various detection methods that are compatible with paper-based microfluidics have been reported, including colorimetry, electrochemistry, fluorescence, electrochemiluminescence (ECL), chemiluminescence, etc. [2–5]. Among these methods, ECL is one of the most useful methods due to its simple instrumentation, low or zero background signal, high specificity and good sensitivity.

Manz and co-workers first introduced bipolar electrode-electrochemiluminescence (BPE-ECL) to the microfluidic electrophoresis system in 2001 [6]. Since that time, BPE-ECL has gained increasing interest and attention especially in recent years. Various analytical applications, where BPE-ECL was coupled with a microfluidic or large-size system, have been reported [7,8]. Different from conventional three-electrode ECL (including paper-based three-electrode ECL [9–18]), a unique aspect of BPE-ECL is that it only needs one conductor with opposite polarity on two ends to allow for direct coupling of electrochemistry and ECL reactions. In addition, a BPE-ECL system is usually simple, easy to operate, and suited for performing a simultaneous screening. So far, two types of BPE-ECL systems have been used [7,8]: closed and open. For a closed BPE-ECL system, the solutions containing the BPE cathode and anode are physically separated from each other, and the current path between the two half cells is only through the BPE. Currently, some interesting applications of closed BPE [19–23] or BPE-ECL [24–30] systems have been reported. At the same time, electroanalytical studies involving open BPE systems have also been widely reported [7,8,31–34]. A typical open BPE-ECL system uses a fluidic channel to host a conductor. A voltage is applied to a pair (or more) of driving electrodes, and two coupled electrochemistry and ECL reactions occur at each pole of the BPE. It is noteworthy, however, that a new kind of BPE-ECL based on the wireless energy transmission technique without using driving electrodes has been recently introduced by Xu and co-workers [35]. Over the past years, the applications on open BPE-ECL system have been expanded

* Corresponding author. Tel.: +86 20 85217070 8501; fax: +86 20 85216052.
E-mail addresses: zhangcs@scnu.edu.cn, zhangcs_scnu@126.com (C. Zhang).

http://dx.doi.org/10.1016/j.snb.2015.04.014
0925-4005/

significantly [7,8,31–34]. To the best of our knowledge, however, no reports on establishing open BPE-ECL using paper-based microfluidics have been published.

In the present work, disposable paper-based open BPE-ECL (P-*o*-BPE-ECL) sensing device was explored, where an inexpensive CCD camera was applied for simple visual detection. The paper-based sensor was fabricated by using the newly demonstrated wax-screen-printing technology [36]. For the electrode system of the paper-based sensor, the BPE and driving electrodes were screen-printed in-house using carbon ink. The performance of the P-*o*-BPE-ECL system with a single "band"-shaped BPE was optimized and then simply applied for the determination of tri-*n*-propylamine (TPA) or H_2O_2 coreactant (analyte) in an ECL system. Finally, a newly-designed open BPE array configuration was proposed for P-*o*-BPE-ECL imaging sensing using the $Ru(bpy)_3{}^{2+}$/TPA system, in which a BPE array was stridden across the two legs of the "U"-shaped paper-channel. The reaction mechanism of the production of ECL using $Ru(bpy)_3{}^{2+}$ and TPA was proposed as follows [37]:

$$Ru(bpy)_3{}^{2+} - e^- \rightarrow Ru(bpy)_3{}^{3+} \quad (1)$$

$$TPA - e^- \rightarrow TPA^{\bullet+} \rightarrow TPA^{\bullet} + H^+ \quad (2)$$

$$Ru(bpy)_3{}^{3+} + TPA^{\bullet} \rightarrow Ru(bpy)_3{}^{2+*} + \text{products} \quad (3)$$

$$Ru(bpy)_3{}^{2+*} \rightarrow Ru(bpy)_3{}^{2+} + h\nu \quad (4)$$

And, the possible reaction mechanism for the luminol-H_2O_2 ECL system was as follows [38]:

$$\text{Luminol} - e^- - H^+ \rightarrow \text{Diazoquinone} \quad (5)$$

$$H_2O_2 + \text{Diazoquinone} \rightarrow \text{Luminolendoperoxide} \quad (6)$$

$$\text{Luminolendoperoxide} \rightarrow N_2 + \text{3-aminophthalate}^* \quad (7)$$

$$\text{3-aminophthalate}^* \rightarrow \text{3-aminophthalate} + h\nu \quad (8)$$

2. Experimental

2.1. Chemicals and materials

Whatman chromatography paper #1 (200.0 mm × 200.0 mm, pure cellulose paper) was purchased from GE Healthcare World-wide (Shanghai, china) and used with further adjustment of size. The conductive carbon ink (model number CNB-7, <60 Ω $square^{-1}$), which was used as fabrication material of the driving/working electrodes, was obtained from Xuzhou Bohui New Materials Technology Co., Ltd. (Xuzhou, China). $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (98%, Ru > 13.5, article number: 50525-27-4) was bought from Beijing Greenchem Technology Co., Ltd. (Beijing China). TPA (≥98%, article number: 102-69-2) was from Sigma–Aldrich (St. Louis, MO, USA). Phosphate buffer solution (PBS), universal pH test paper, luminol (97%, article number: 521-31-3) and H_2O_2 (>30%, article number: 7722-84-1) were purchased from Sangon Biotech Co., Ltd. (Shanghai, China). Deionized water was prepared by a water purification system (≥18 MΩ, ELGA PURELAB® Option-R15, London, UK) and was used in all the experiments. Solid wax (Detong Co., Ltd., Guangzhou, China) and smooth spoon-like metal utensil were obtained from a local department store. All the chemical reagents used were of analytical reagent grade without any further purification.

2.2. Instrumentation

The YH-946B heating board was purchased from Guangzhou Yihua Electronic Equipments Co., Ltd. (Guangzhou, China). The MC15 CCD camera, the M1614-MP macro lens (Computar, Japan), the S7650 movable mechanical stage (Taiwan, China), the focus-adjustable bracket and the black box were obtained from Guangzhou Mingmei Technology Co., Ltd. (Guangzhou, China). The DHG-9035A oven was purchased from Shanghai Tensuc Experimental Instrument Manufacturing Co. Ltd. (Shanghai, China). The DC power supply (Model LW-6403KDS) was bought from Longwei Instrument Meter Co. Ltd. (Hongkong, China).

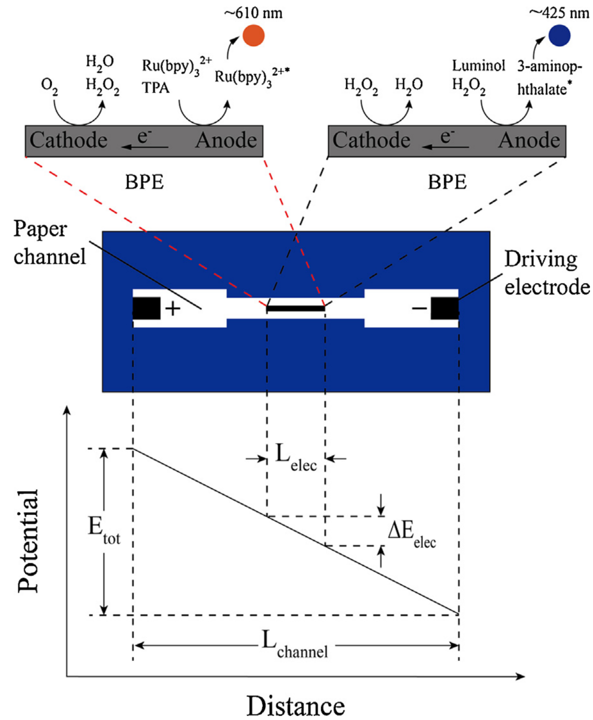

Fig. 1. Schematic description of the design and principle of P-*o*-BPE-ECL sensing platform.

2.3. Design principle for the present P-o-BPE-ECL sensing

The design principle of the present device for the P-*o*-BPE-ECL sensing of TPA or H_2O_2 is shown schematically in Fig. 1. For this sensing platform, the electric field between the driving electrodes essentially depends on the channel geometry and the conductivity of the electrolyte solution. In some cases, a linear electric field is generated by restricting the cross-section area of the solution between the driving electrodes. In our system, it can be achieved by embedding the BPE in a paper channel containing a small cross-section area. Thus, the potential difference (ΔE_{elec}) across the BPE can be simply estimated using the following equation [7]:

$$\Delta E_{elec} = E_{tot} \quad (L_{elec}/L_{channel}) \quad (9)$$

Here, E_{tot} represents the voltage applied between the two driving electrodes, while L_{elec} and $L_{channel}$ represent the length of the BPE and the channel, respectively. If ΔE_{elec} is sufficiently high, faradaic electrochemical reactions are triggered at both poles of the BPE. Taking the $Ru(bpy)_3{}^{2+}$/TPA ECL system as an example, after the reagents are injected into the paper channel, an appropriate driving voltage can activate simultaneous oxidation of the $Ru(bpy)_3{}^{2+}$/TPA and reduction of O_2. As a result, ECL signal generated at the anodic pole is captured by the CCD for visual detection.

2.4. Device fabrication

The screen-printing fabrication process for P-*o*-BPE-ECL microfluidic devices is shown in Fig. 2. A wax-screen-printing process was used for fabrication of hydrophilic paper channels, while the screen-printing using carbon ink was utilized to fabricate the