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Fabrication of a totally renewable off-channel amperometric platform for microchip electrophoresis

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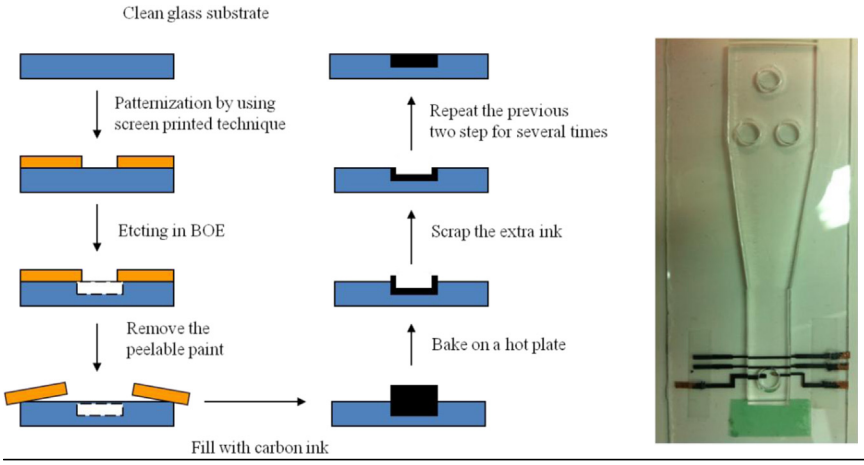
HIGHLIGHTS

- A novel method to construct an off-channel based EC device is demonstrated.
- All electrodes used in this device can be easily regenerated.
- Microscopy is unnecessary in assembling of the PDMS chip and the EC device.
- A low background with a noise level of 1.4 pA (peak to peak) is achieved.
- The LOQ of dopamine and catechol can be down to sub-micro molar level.

GRAPHICAL ABSTRACT



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ABSTRACT

In this approach, a novel method to fabricate an integrated amperometric platform used in off-channel electrophoresis has been introduced. A simple screen printed protocol combining a wet etching procedure was used to define the pattern on a glass substrate, and whole electrodes were constructed by filling the conductive carbon ink into the etched cavities. A simple Teflon tape was used to align this platform with the micro-channel, and the variation of reassembling of this device can be down to 2.2% without the assistance of microscope. This device was characterized by dopamine (DA) and catechol (CA), and the width of half peak is around 4 s, even a 100 μm double T shape injection design and a 550 μm working electrode were used in this work. Under the optimum condition, this device possesses a low background with a noise level of 1.4 pA (peak to peak). The linear range for DA and CA are 0.1–100 μM (R = 0.998) and 0.2–200 μM (R = 0.996) with a theoretical plate number of 1.57×10^4 and 3.46×10^4 (plate/m), respectively.

1. Introduction

Microchip capillary electrophoresis (MCE) has received a great interest in the past two decades due to its potential in the development of a portable device, fast analysis and reduces the operating reagent over than a conventional capillary electrophoresis or liquid chromatography. The major advantage of the MCE is

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its diversification, which makes the pretreatment, separation, and analysis be easily performed on a single microchip, simultaneously. Thus, its progress in biological and environmental applications, such as DNA sequencing [1], proteins [2], neurotransmitters [3], and nerve agent detections [4] has been widely reviewed in several journals. In addition, the diversification of the MCE also makes the design of the detection system as an interesting subject. Several optical detectors including photospectrometer, refractive index, Raman detection and laser induced fluorescence (LIF) have been widely employed in MCE devices. Among them, LIF is the most popular optical scheme due to its lowest detection limit and high selectivity. However, most of the important analytes do not possess a suitable chromophore moiety to absorb or emit the photon, therefore, an on-line or off-line derivative procedure is a common practice to overcome this drawback. Although the derivative design on a microchip has been well demonstrated in the prior reports, it still requires a bulky and expensive optical system to perform its high sensitivity.

Electrochemical (EC) schemes, especially for an amperometric detector, is another common approach used in MCE due to its low cost, ease to be miniaturized with a closed sensitivity toward to the LIF. Basically, MCE-EC devices can be divided into a separated electrode and integrated platform based on the design of the working electrode. The prior one mounts an individual working electrode at the sidewall of the micro-channel. However, since the sample plug would be quickly diluted when it runs out of the channel, controlling the relative position between the outlet of the channel and the electrode becomes one of the most challenges with this approach. In literatures, several useful strategies have been proposed to deal with this issue. Dou et al. used a *X–Y–Z* manipulator to adjust the rod electrode facing to the outlet [5]. Wang et al. mounted a replaceable screen printed ink electrode perpendicularly to the micro-channel, and used a tape as a spacer to fix the distance [6]. Zeng et al. inserted a cylinder electrode into a guiding tube which is just opposite to the outlet of the channel, and used a screw to move the electrode approaches to the channel [7]. The major advantage of these methods is that the working electrode could be replaced and/or polished easily; however, because the sample plug would be dispersed significantly after leaving the outlet of the channel, an extra equipment such as microscopy is required to secure the fine position of the electrode. Furthermore, it is obvious that the width of electrode used in these reports is larger than the width of the channel to prevent the high deviation from position mismatch, this compromise causes a larger ineffective area with high background level.

In contrast to the separated electrode design, the integrated detection platform assembles the working electrode and other assisted ones on a chip, which offers a potential to overcome the drawbacks of a separated design as discussed in the aforesaid section. By covering a plastic or glass based microchip on the upper side of the sheet, both the relative position and the dispersion effect can be controlled. In addition, the effective area of the working electrode is also restricted by the width of the micro-channel, which suppresses the noise level efficiently. However, in order to obtain a tightly sealed MCE-EC device, an ultra thin electrode is required to prevent the chip lift from the flat surface. Most reports adopt a photolithography coupled with a sputtering technique to deposit the metal layer such as gold, platinum [8], and palladium [9] on the substrate, however, an expensive process is required to fabricate their device. Several efforts have been proposed to substitute this procedure to fabricate the thin film electrode. Yan et al. used an electroless deposition process by sequentially chemical replacing of Sn, Ag, and Cu to fabricate a gold electrode on a glass substrate [10]. Kong et al. immersed a polycarbonate plate in a 1-(3-dimethyl-aminopropyl)-3-ethyl-carbodiimide solution, the amine-derivatized moiety provides a good adhesion to create an electroless plating gold electrode [11]. Except these metals based thin film electrodes, a carbon based one has been proposed by Hebert et al. who pyrolyzed the patterned photoresistor at 1000 °C to form a carbon thin film electrode on a fused quartz plate [12]. These thin film electrodes obtained from the aforementioned schemes have been shown their feasibility in microchip electrophoresis, however, a tedious fabrication steps and a fragile electrode remains a critical issue.

In contrast to the fabrication of a thin film electrode, creating a space which used to place these electrodes is another useful strategy in MCE-EC system. Vickers et al. designed two channels at the end of the polydimethylsiloxane (PDMS) microchip, which provide an extra space to place the gold and palladium wires ($\Phi = 25\ \mu m$) as the working electrode and decoupler on the top PDMS sheet [13]. Similar practices have been reported by placing a carbon fiber [14] and carbon ink coated gold microwire [15] in the PDMS channel as the working electrode. However, because the dimension of the microwire can not totally match with the channel, a small cavity would be exited in this system, which seems to cause a fluctuate background [16].

In the previous reports, Rossier et al. reported a new method to construct a carbon based micro band electrode by filling carbon ink in a laser ablated micro channel on a polyethylene sheet, and its application in microchip electrophoresis has been roughly demonstrated by the same group [17]. However, this method has rarely been extended in the past decade, in addition, the polymer based substrate is easy to be damaged and possesses very low tolerance to the solvent. In this approach, a mass production, cost efficient method is introduced to fabricate the carbon based amperometric platform. A simple screen printed method is used to substitute the photolithography or laser ablation to define the etching area on a glass substrate. By filling the carbon ink in the etching channel, all the essential elements for construction of an off-channel amperometric detector are integrated in this glass substrate. This device possesses a low noise level around 1.4 pA, which makes the limit of quantification (LOQ) for dopamine and catechol of this device can be down to sub-micro molar level with a theoretical plate number of 1.57×10^4 and 3.46×10^4 (plate/m), respectively. Since the carbon ink can be dissolved in the acetone solution, this microchip can be easily renewed. The detail characteristics and advantages of this device are illustrated in this approach.

2. Experimental

2.1. Chemicals

The following chemicals were used for the photolithographic processes. Negative photoresist, model Su-8 GM1060, and its developer were purchased from Gersteltec Sarl (Switzerland). Acetone and isopropanol for microelectronic use were purchased from J.T. Baker (NJ, USA). Nitrogen gas was purchased from logical supplier. All other chemicals were of analytical reagent grade. Dopamine, catechol, 2-(4-morpholino) ethanesulfonic acid (MES), were purchased from Sigma–Aldrich (MO, USA). Sodium hydroxide was purchased from Riedel-deHaën (Seelze, Germany). A peelable masking paint and screen printed mask were obtained from Faithful Printing Equipment & Supply Co. (Taiwan).

2.2. Instrument

High voltage power supply, model SL 300 and E833, from Spellman (New Jersey, USA) and Consort (Parklaan, Belgium) were employed to perform sample injection and separation in the electrophoresis process, high voltage switches were employed to