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The use of poly(dimethylsiloxane) surface modification with gold nanoparticles for the microchip electrophoresis

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Abstract

Poly(dimethylsiloxane) (PDMS) microfluidic channels modified by citrate-stabilized gold nanoparticles after coating a layer of linear polyethylenimine (LPEI) were successfully used to separate dopamine and epinephrine, which were difficult to be separated from baseline in native and hybrid PDMS microchannels. In-channel amperometric detection with a single carbon fibre cylindrical electrode was employed. Experimental parameters of separation and detection processes were optimized in detail. The analytes were well separated within 100 s in a 3.7 cm long separation channel at a separation voltage of +800 V using a 30 mM phosphate buffer solution (PBS, pH 7.0). Linear responses of them were obtained both from 25 to 600 μM with detection limits of 2 μM for dopamine and 5 μM for epinephrine, respectively. The modified PDMS channels have a long-term stability and an excellent reproducibility within 2 weeks.

Keywords: Poly(dimethylsiloxane); Microchip electrophoresis; Gold nanoparticles; Dopamine; Epinephrine

1. Introduction

Micrototal analysis system (μ-TAS) has been established itself at the forefront of analytical chemistry since the 1990s [1]. Recently, soft polymer materials [2–4] appeared as a material of choice to design the multifunctional microfluidic devices instead of glass, quartz or silicon. Among them, poly(dimethylsioxane) (PDMS) [5,6] is one of the most successful examples, mainly due to easy handling, good sealing properties, and optical transparency. Additionally, PDMS has many other fascinating properties such as low cost, good electrical resistivity, adequate thermal conductivity, conveniently molding from the prepolymer and rapidly fabricating complex devices [7,8]. However, PDMS microchips have inherent defects in separation field. It is more difficult to wet the channels and easy to form air bubble in the channel for the extreme hydrophobicity of PDMS. Particularly, there exists strong tendency to adsorb other molecules onto the surface and some molecules even spontaneously penetrate into the polymer matrix [9,10]. Moreover, electroosmotic flow (EOF), which is unstable and poorly controlled, is greatly dependent on the ionic strength and pH of running buffer [10].

To control EOF and reduce adsorption of analytes, surface modifications are developed. Covalent modification to change the surface properties is an important strategy. Successful examples included radiation induced graft polymerization [11], cerium(IV) catalysis [12], silanization [13], atom-transfer radical polymerization [14], chemical vapor deposition [15], and sol–gel method [16], etc. Forming covalently linked coatings often require organic solvent and high temperature, and the fabricated procedures are tedious. While, dynamic coating is a simple and rapid strategy to cover the charged sites on the surface by physically adsorption with surfactants such as tetrabutylammoniumchloride [10], cetyltrimethylammonium bromide [17], sodium dodecyl sulfate, sodium deoxycholate and phosphatidic acid [18], 2-morpholinoethanesulfonic acid [19], and Brij-35 [20]. Besides, phospholipid and proteins were often used [21,22]. The adsorbed layer could shield analytes from the microfluidic channels surface and suppress EOF. But it is a great challenge for a long-term stability because the dynamic coating unavoidably degrades during electrophoresis separation. Recently, polyelectrolyte multilayers modification [23–25] has been developed to impart lasting hydrophilicity to the PDMS surface through introducing layer-by-layer assembly technique,

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which is widely used in functional materials [26] and bioelectrochemistry [27]. There is a good review about the art of surface modification of PDMS microchips by Makamba et al. [28].

Recently, gold nanoparticles have been introduced into microchips to enhance separation efficiency [29]. Two approaches are often adopted. One is that gold nanoparticles serve as additives in running buffer. For example, double-stranded DNA had been successfully separated on poly(methyl methacrylate)(PMMA) microchips using polymer solution containing gold nanoparticles [30,31]. The other is that they act as modifiers adsorbed on channel surface. Although many researches are related to gold nanoparticles modified interfaces [32–34], there are few reports on gold nanoparticles modified microfluidic channels. Only Pumera et al. reported that gold nanoparticles were used as channel modifiers to improve the separation of aminophenols isomers on glass microchip [34].

In this work, gold nanoparticles were used to modify PDMS/PDMS microfluidic channels via electrostatic assembly on a pre-layer of polyelectrolyte. Dopamine and epinephrine served as a model system to evaluate the effect of modification. It has been reported that they failed to be completely separated on hybrid PDMS/glass [35], PDMS/quartz microchips [36] and PMDS/PDMS microchip [37] due to their similar electrophoresis properties. Our results show that gold nanoparticles modification improves the separation efficiencies of dopamine and epinephrine, and the resolution for them is largely enhanced from 0.62 on native PDMS device to 1.14 on coated PDMS microchip in 30 mM phosphate buffer solution (PBS, pH 7.0). Moreover, the present microchip has a long-term stability and good reproducibility.

2. Experimental

2.1. Reagents

Sylgard 184 (PDMS) was from Dow Corning (Midland, MI, USA). The carbon fibre ($d = 8\,\mu m$) was purchased from Goodfollow, Co., Oxford, UK. Poly(diallyldimethylammonium chloride) (PDDA, 20 wt.% in water, $M_w = 200{,}000$–$350{,}000$), linear polyethylenimine (LPEI, $M_w = 25{,}000$), poly(allylamine hydrochloride) (PAH, $M_w = 70{,}000$), chitosan ($M_w = 200{,}000$), dopamine (DA) and epinephrine (EP) were purchased from Sigma–Aldrich. Na_2HPO_4, KH_2PO_4, $HAuCl_4$ and trisodium citrate were obtained from Nanjing Chemical Reagents Factory (China). PBS served as running buffer. PDDA and LPEI solutions were prepared a 1:2500 dilution of the original material with 30 mM PBS, respectively. PAH solution (0.05%) was prepared by dissolving it in 30 mM PBS. Chitosan (0.05%) was dissolved in acetic acid and then diluted with 30 mM PBS. All the solutions were passed through a 0.22 μm cellulose acetate filter (Xinya Purification Factory, Shanghai, China). The stock solutions of samples (20 mM) were prepared by dissolving analytes in doubly distilled water. Before use, they were diluted with corresponding running buffer. All other chemicals were of analytical grade and used without further purification. All the solutions were prepared with doubly distilled water.

2.2. Apparatus

PDMS microchip was fixed on a plexiglass holder with a precisely three-dimensional system (Shanghai Lian Yi Instrument Factory of Optical Fibre and Laser, China). A homemade power supply provides a voltage ranging from 0 to 5000 V. Separation parameters can be set up and automatically switched via RS232 communication port of personnel computer through a homemade program. The separation current can be monitored graphically in real time.

2.3. Procedure

2.3.1. Microfabrication and electrophoresis procedures

The PDMS/PDMS microanalysis system was shown in Fig. 1. The corresponding As–Ga master was fabricated as described [19,20]. Sylgard 184 PDMS prepolymer was mixed thoroughly with its curing agent at 10:1, w/w, and then degassed by vacuum pump. The mixture was cured against the As–Ga mold at 70 °C for 150 min. After the replica was peeled from the mold, holes ($d = 3$ mm) were punched. Flat PDMS substrate (0.2–0.4 mm height) was obtained by casting and cured the prepolymer mixture on a large flat glass slide. The PDMS layer with microchannel and the PDMS flat were ultrasonically cleaned, subsequently with water, acetone, methanol, water, and then dried under infrared lamp. They were sealed together to form a reversible PDMS microchip.

After the microchip was held on the holder, the working electrode was inserted into the electrode hole on the platform with silicon grease to prevent leaking of the detection cell. In all cases, the buffer was introduced into the reservoirs and flushed through the channels via vacuum before adjustment of the location of the working electrode in channel under the stereoscopic microscope (XTB-1; Jiangnan Optical Instrument Factory, Nanjing, China). A homemade program for the power supply was used to control the voltage switching from sampling to separation. Sampling mode was simple crossing without pinch. Before sep-

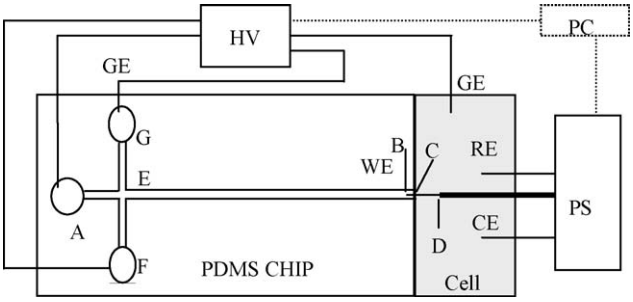

Fig. 1. Schematic diagram of the PDMS/PDMS microanalysis system. WE: working electrode (the carbon fiber cylindrical electrode); CE: counter electrode; RE: reference electrode; GE: ground electrode; PS: potentiostat; HV: high voltage; PC: personal computer; A: running buffer reservoir; B: the tip of the WE in channel; C: channel outlet; D: the tip of glass capillary; E: the crossing position of sample channel and separation channel; F: sample reservoir; G: waste sample reservoir; BC = 40 μm; BD = 1.5 mm; AE = EG = EF = 1 cm; EC = 3.7 cm. All channels were 18 μm deep; sampling channel was 30 μm wide and separation channel was 50 μm wide. CE and GE were platinum wires; RE was Ag/AgCl.