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Modification of poly(dimethylsiloxane) microfluidic channels with silica nanoparticles based on layer-by-layer assembly technique

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Abstract

A hydrophilic poly(dimethylsiloxane) (PDMS) microchip with stable electroosmotic flow (EOF) was prepared by a simple and reproducible coating procedure with silica nanoparticles. The microchannel wall of PDMS chip was coated with a layer of poly(diallyldimethylammonium chloride) (PDDA) and then collected silica nanoparticles. The assembly was followed by contact angle, charge-coupled device (CCD) imaging, electroosmotic flow (EOF) measurements and electrophoretic separation experiments. Contact angle measurements revealed the coated surface was hydrophilic; the water contact angle for coated chips was 64° compared with a water contact angle for native PDMS chips of 113°. CCD images indicated a substantially more hydrophilic microchannel than native PDMS. We carried out a comparison and concluded that the EOF values on the coated PDMS chip were close to those values on the glass chip above pH 7.0. The coated channel had an excellent stability and reproducibility, RSD of EOF values ($n = 6$) on native and coated PDMS microchip was 1.58 and 0.57%, respectively. Separation of dopamine and epinephrine was performed on the coated chip generated 1.40×10^5, 1.39×10^5 theoretical plates/m compared with the native PDMS chip of 0.79×10^5, 0.88×10^5, high resolution of 1.7 was achieved with a channel of 3.60 cm length.

Keywords: Microchip capillary electrophoresis; Poly(dimethylsiloxane) (PDMS); Silica nanoparticles; Layer-by-layer

1. Introduction

Silica-based substrates have traditionally been used in microfluidics because of their excellent optical properties and well-documented surface properties [1]. However, the fabrication of glass microchips is time-consuming, somewhat dangerous and relatively expensive. Interest has shifted to polymeric materials for microdevices due to the versatility, reduced cost and potential for large-scale manufacturing [2,3].

Of the polymers employed in fabricating these devices, poly(dimethylsiloxane) (PDMS) is one of the most utilized [4]. The intrinsic properties of PDMS can be both beneficial and disadvantageous, depending on the intended purpose of the device. The mechanical and optical properties of PDMS lend themselves to a variety of uses in microfluidics. There are also several disadvantages to the use of PDMS. Analyte absorption into PDMS has been well documented for nonpolar hydrophobic species [5–7]. In addition, PDMS is known to absorb organic solvents, which limits buffer systems to water and some alcohols. One common problem with polymer devices, including PDMS, is poorly defined electroosmotic flow (EOF) [7]. This is a significant disadvantage because the EOF typically dominates the linear flow velocity of both the run buffer and the analytes being separated.

To meet the specific requirements in applications, the surface of PDMS can be chemically modified or physically masked by adsorption [8–20]. Anionic, neutral, and cationic surfaces can be generated in this way and are useful for minimizing analyte adsorption as well as controlling EOF direction and magnitude.

Nanodispersions have attracted increasing attention in chemical separation. Nanoparticles always served as additives in running buffer or acted as modifier coated on the channel surface. A few researchers have adopted polymer-based nanoparticles to

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enhance separation [21–26]; gold nanoparticles were used both as additive and modifier in capillary electrophoresis (CE) and microchip CE [27–33]. Silica nanoparticles [34–36] and carbon nanotubes [37] were also employed as additives in CE. Recently, Roman et al. [38] reported on the use of sol-gel method for fabricating PDMS microchips with SiO_2 particles homogeneously distributed within the PDMS polymer matrix. Layer-by-layer technique has been widely used for inorganic and polymer surface modification [27,28,39–42]; PDDA is commonly employed as the polycation due to the property of strong cationic polyelectrolyte, so it can be tightly absorbed on the polymer surface by both ionic and hydrophobic interactions. Silica nanoparticles can also be combined on the polyelectrolyte surface by layer-by-layer technique [43–45].

In this work, a stable hydrophilic PDMS microchip was prepared by a simple method for coating microchip capillary channels using the successive multiple-ionic-layer approach. This method utilizes a cationic polymer, poly(diallyldimethylammonium chloride) (PDDA), coating, followed by a layer of anionic silica nanoparticles to generate and control EOF. To the best of our knowledge, this modification is the first time report that coating the PDMS channel surface with silica nanoparticles by layer-by-layer assembly technique. The surface modification brought the advantages for microfluidic-based separations: generation of stable EOF, enhanced surface hydrophilicity, long lifetime, and improved peaks resolution.

2. Experimental

2.1. Reagents and solutions

All reagents were of analytical grade. Sylgard 184 (PDMS) silicone elastomer and curing agent were obtained from Dow Corning (Midland, MI, USA). Silica gel (GS-30, 30%, w/w in water, diameter 15 nm) was obtained from Zhejiang Yuda Chemical Co., Ltd. (China). Poly(diallyldimethylammonium chloride) (PDDA, 20%, w/w in water, Mw = 200,000–350,000), dopamine and epinephrine were purchased from Sigma–Aldrich, Disodium hydrogen phosphate(Na_2HPO_4), Potassium dihydrogen phosphate(KH_2PO_4), Sodium hydroxide (NaOH) were obtained from Nanjing Chemical Reagents Factory (China). PDDA solution (0.04 wt.% in water), Silica nanoparticles solution (3%, w/w in water), phosphate buffer saline (PBS) (25 mM pH range from 4.0 to 11.0, 40 mM pH 7.0), 0.5 mM dopamine, 0.5 mM epinephrine. All solutions were prepared with doubly distilled water and passed through a 0.22 μm cellulose acetate filter (Shanghai Bandao Factory, Shanghai, China).

2.2. Microchips

2.2.1. Fabrication of PDMS microchips

The master with a positive relief structure of AsGa for the channels was made using microphotolithographic technique. A cross-type channel of PDMS chip with a 3.90 cm long separation channel (effective separation length, 3.60 cm) and 1.0 cm long injection channel (shown in Fig. 1) and a flat substrate were fabricated from PDMS as the previously described procedure

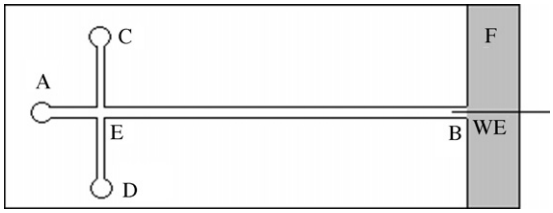

Fig. 1. Schematic diagram of PDMS microchip. A: running buffer reservoir; B: separation channel outlet; C: sample reservoir; D: waste sample reservoir; E: the crossing position of sample channel and separation channel; F: waste buffer reservoir; AE = 0.3 cm; EB = 3.6 cm; CE = ED = 0.5 cm. WE: working electrode.

[19,20]. Briefly, a mixture of elastomer precursor and its curing agent (ratio of 10:1) (sylgard 184) were degassed, poured over the GaAs master, and cured for 150 min at 80 °C. After the replica was peeled from the mold, holes (3 mm diameter) were punched. A flat PDMS substrate (0.3 mm thick) was obtained via casting and curing the prepolymer mixture in a large flat glass box (5 cm × 5 cm). The PDMS layer with microchannels and the PDMS flat were ultrasonically cleaned subsequently with acetone, ethanol, and water, then dried under infrared lamp. Finally, they were sealed together to form a reversible PDMS microchip. The sampling channel's width and depth were 30 and 18 μm, respectively; the separation channel's width and depth were 50 and 18 μm, respectively.

2.2.2. Glass microchip

The glass chip used in this study with a cross-type channel was fabricated by Zhejiang University based on our custom design using standard photolithography and chemical wet etching techniques. The outline of glass chip is the same as PDMS but the parameters are different. The sampling and separation channels' width and depth were all 60 and 20 μm. The total length of the separation and injection channels were 4.60 cm (effective separation length, 4.20 cm) and 1.0 cm, respectively.

2.3. Preparation of nanoparticle-coated PDMS channels

PDMS channels were coated with PDDA and silica nanoparticles according to the conventional CE procedures developed by Katayama et al. [9]. Briefly described, the channels were rinsed with 0.1 M NaOH and deionized water, respectively, for 10 min each. Once preconditioned, the channels were sequentially filled with PDDA solution (0.04%, w/w) and silica nanoparticle solution (3%, w/w) for 30 min each. This procedure of successive coating resulted in a bilayer of PDDA/silica nanoparticle on the channel walls. All rinsing was performed by applying vacuum to the buffer waste reservoir with the other three reservoirs filled with the respective rinsing solution.

2.4. CCD image

A nanoparticle-coated structured PDMS plate was peeled from the coated channel. 0.1–0.2 μL of water droplet was placed carefully on the structured PDMS plate with pipette and allowed to rest on the surface for 10 s. The chip was then imaged using