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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-

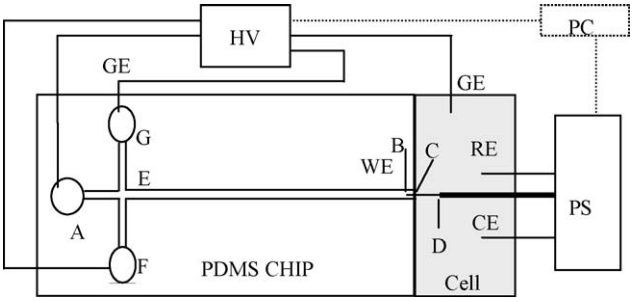

Fig. 1. Schematic diagram of the PDMS/PDMS microanalysis system. WE: working electrode (the carbon fiber cylindrical electrode); CE: counter electrode; RE: reference electrode; GE: ground electrode; PS: potentiostat; HV: high voltage; PC: personal computer; A: running buffer reservoir; B: the tip of 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.

aration of analytes, sampling and waste cells were filled with running buffer. While in the separation procedure, both cells were kept floating.

2.4. Detection

2.4.1. The single carbon fibre cylindrical electrode preparation

Firstly, a glass capillary with inner diameter of 0.5 mm was pulled under a multifunctional glass microelectrode puller (Shanghai Biological Institute, China) to form a fine tip. Then a single carbon fibre was carefully mounted into the tip and fixed with epoxy. A copper wire was connected with the carbon fibre through carbon powder on the other end of capillary and then fastened with epoxy. Prior to use, the tip of the carbon fibre was cut with a clean scalpel to form a 1.5 mm long cylindrical electrode under the microscope.

2.4.2. In-channel electrochemical detection

Detection was performed with the carbon fibre cylindrical electrode. An Ag/AgCl reference electrode, a Pt auxiliary and a Pt ground electrode, were placed in contact with the solution in the detection cell. The carbon fiber cylindrical electrode was activated at a constant detection potential of 1.5 and −1.0 V for 200 s, respectively. Under the microscope, the carbon fibre cylindrical electrode was placed in the end of the separation channel with a distance ca. 40 μm from the tip of the working electrode to the channel exit. Electrochemical detection was performed using "amperometric *i–t* curve" mode with a CHI 660A electrochemical workstation (CHI Co., Shanghai, China) at a detection potential of 1.4 V. All experiments were performed at room temperature.

2.4.3. Measurement of EOF

EOF was simply detected as our previous report [37]. Briefly, the separation channel and detection cell were firstly filled with running buffer. Then the separation and injection sample channels were rinsed with running buffer for 10 min in sequence, respectively. A diluted buffer (buffer:water = 8:2) was placed in the sample reservoir. The signal of the diluted buffer was monitored at 0 V with a single carbon fibre cylindrical electrode, which was placed in-channel. Migration time of EOF can be obtained from electropherograms.

2.5. Preparation of gold nanoparticles and its modification on microfluidic channels

Gold nanoparticles were prepared according to literature [38]. Briefly, 0.5 mL of 100 mM $HAuCl_4$ solution was added to a 50 mL boiling trisodium citrate (4.0 mM). The size of gold nanoparticles was about 13 nm through transmission electron microscopy (TEM) experiments. The obtained nanoparticles were stored in brown glass bottle at 4 °C.

Running buffer containing a polyelectrolyte was pumped through the microchip for 5 min by vacuum pump. After the polymer adsorbed, the microchip was flushed with PBS for 10 min. Then, gold nanoparticles solution was pumped through the chip for 60 min. Finally, the microchip was flushed with running buffer for 10 min.

3. Results and discussion

3.1. Effect of the first coated polyelectrolyte layer

As well known, the PDMS/PDMS devices have lower separation efficiency than those of fused silica or glass microchips. To control EOF and enhance the separation efficiency, gold nanoparticles were used to modify PDMS/PDMS microchannels after pre-coating with a layer of polyelectrolyte. Fig. 2 depicted the modification procedures. Coating with polyelectrolyes formed a cationic surface once it became ionically adsorbed onto the channel surface, which supported a reverse EOF. EOF directed to anode and no analytes reached the detector. The interactions between gold nanoparticles and polyelectrolye coated channel surface altered the electroosmotic velocity and also changed its direction. In the experiments, it was found that the polyelectrolyte played an important role in separation efficiency. Some polyelectrolytes including PDDA, LPEI, PAH and chitosan were investigated, which strongly adsorbed on

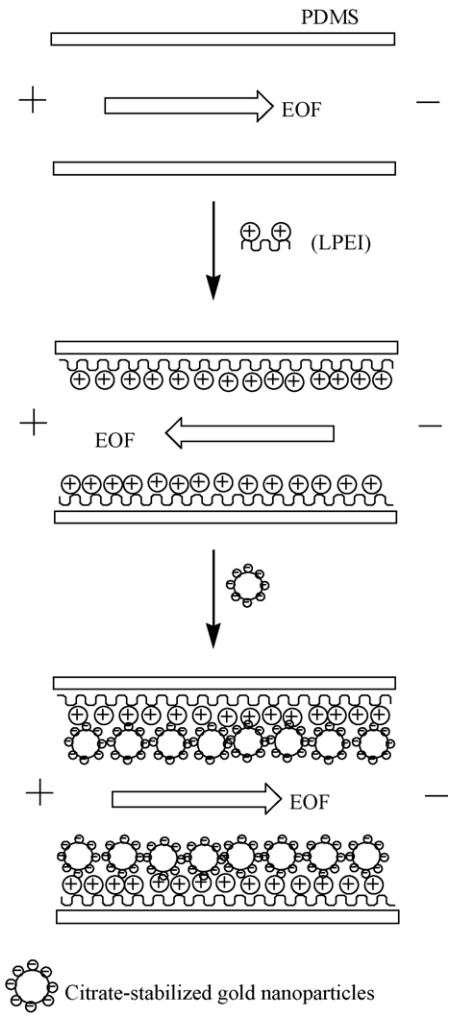

Fig. 2. The PDMS/PDMS microchip modification procedures.

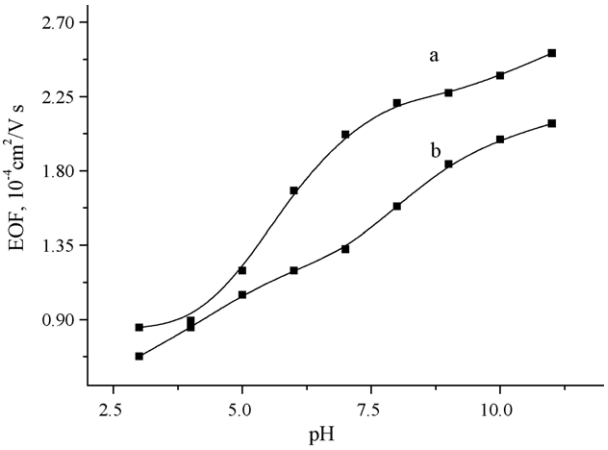

Fig. 3. Influence of the pH of running buffer on EOF: (a) native PDMS/PDMS microchip; (b) gold nanoparticles coated PDMS/PDMS microchip.

PDMS and were commonly used for anchoring gold nanoparticles. It was observed that when the channels were firstly coated with PAH or chitosan, peak shapes of dopamine and epinephrine were distortional. In contrast, LPEI or PDDA modified channels yielded more efficient separations with more symmetrical peaks. Since PAH or chitosan with a lot of amino groups has much stronger interactions with gold nanoparticles and PDMS than those of LPEI or PDDA, which has many imine and ammonium groups, respectively. The characteristics of PDMS surface and EOF were greatly affected by these interactions. Further experimental results showed that LPEI and PDDA modifications were stable within the pH range of 3.0–11.0, while chitosan modification was unstable at lower pH (<6.0) because chitosan's pK_a was 6.3. In the following experiments, LPEI was used to form the first layer modification.

Fig. 3 showed EOFs of 30 mM PBS in the pH range of 3.0–11.0 on native and gold nanoparticles coated PDMS/PDMS microfluidic chips. Under the same ionic strength, EOFs in the modified microchip were lower values than those in the native microchip. After modification, EOF decreased from $(1.60 \pm 0.12) \times 10^{-4}$ cm^2 V^{-1} s^{-1} ($n = 5$, 95% confidence limit) in the native channel to $(1.31 \pm 0.05) \times 10^{-4}$ cm^2 V^{-1} s^{-1} ($n = 5$, 95% confidence limit) in the modified channel at pH 7.0. The more homogenous gold nanoparticles on the PDMS channel surface may weaken the effect of running buffer on EOF and stabilize EOF, giving a higher reproducibility. As observed in Fig. 4(A and B), dopamine and epinephrine failed to be baseline separated in native channels, however, they could be completely separated in the modified channels with gold nanoparticles. The resolutions and the analysis times for native and coated microchips were from 0.62 to 1.14 and from 55 to 100 s, respectively. The resolution was not obviously different without or with gold nanoparticles in running buffer. It indicated that incubation time of 60 min in the channel to electrostatic assembly for gold nanoparticles was sufficient to occupy the great majority of the available adsorption sites on the LPEI layer. Results also showed that peak currents of dopamine and epinephrine on the microchip modified with gold nanoparticles were actually higher than those on the native one. It was clearly evident that gold nanoparticles could greatly enhance the sensitivity and separation efficiency.

3.2. Effect of the buffer concentration

The chemical composition and the buffer concentration can affect the baseline stability, the peak shape and the separation selectivity. Based on our previous report [37], PBS (pH 7.0) was chosen as running buffer. It was found that the buffer concentration had a great influence on the separation efficiency. The influence of the buffer concentration on the separation of dopamine and epinephrine was investigated in the range of 10–40 mM. Fig. 5 indicated that with the buffer concentration increasing, migration times of two analytes increased accompanying with the increase of resolution. Dopamine and epinephrine can be realized baseline separation at 30 mM PBS. When the concentration reached 40 mM, the resolution achieved 2.07, while the peak currents decreased. Since variation of the ionic strength can affect the adsorption of polyelectrolytes and gold nanoparticles desorption, and even conglomeration of gold nanoparticles may be happened.

3.3. Effect of injection time and injection voltage

The volume of the sample plug can be controlled by sampling time and injection voltage. It greatly influences separation efficiency. The influence of sampling time from 1 to 7 s and injection voltage from 200 to 1400 V on the responses of dopamine and

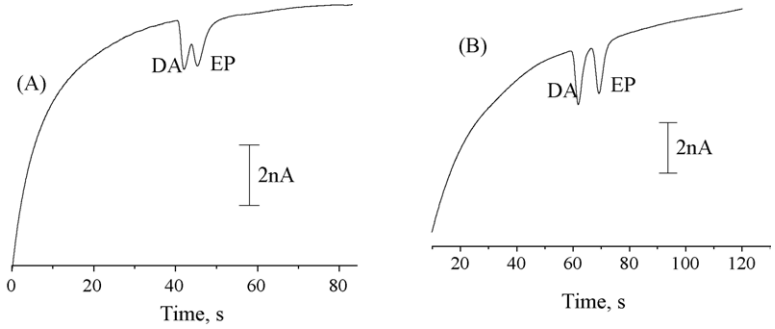

Fig. 4. Electropherograms showing the separations of 400 μM dopamine (DA) and 400 μM epinephrine (EP): (A) in native PDMS/PDMS microfluidic chip; (B) in coated PDMS/PDMS microfluidic chip. Conditions: 30 mM PBS (pH 7.0) as running buffer; sample injection at +800 V for 4 s; separation voltage, +800 V. The signals were recorded after quiet 20 s in coated PDMS/PDMS microchips.

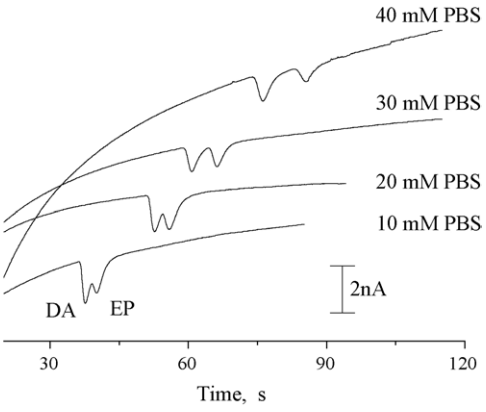

Fig. 5. Influence of the buffer concentration on the responses for 400 μM DA and 400 μM EP. Other conditions as in Fig. 4.

epinephrine were investigated, respectively. As expected, with increasing sampling time from 1 to 4 s and injection voltage from 200 to 800 V, peak currents of dopamine and epinephrine increased, respectively. However, when sampling time beyond 4 s and injection voltage over 800 V, peak currents were growing slowly and peak shapes became broad. Meanwhile, theoretical plate numbers gradually decreased. Considering the sensitivity, in the following experiments, an injection time of 4 s and an injection voltage of 800 V were chosen.

3.4. Effect of separation voltage

The influence of separation voltage on the amperometric responses and separation efficiency was shown in Fig. 6. As expected, increasing separation voltage from 400 to 1200 V dramatically decreased migration times from 184.8 to 56.2 s for dopamine and from 203.9 to 61.9 s for epinephrine, respectively.

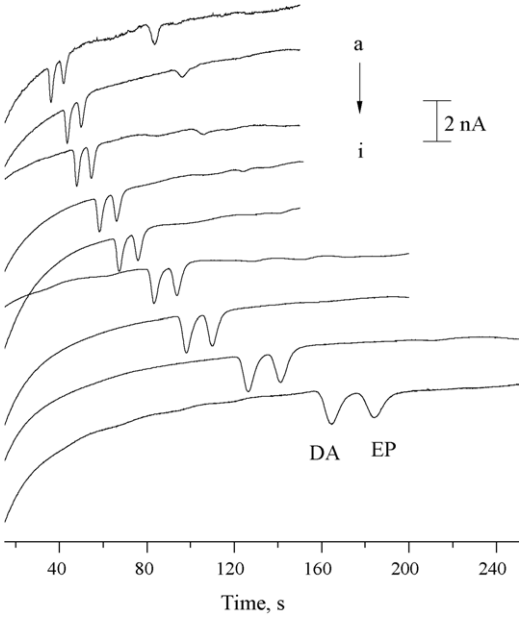

Fig. 6. Influence of separation voltage on the responses for 500 μM DA and 500 μM EP: (a) 1200 V; (b) 1100 V; (c) 1000 V; (d) 900 V; (e) 800 V; (f) 700 V; (g) 600 V; (h) 500 V; (i) 400 V. Other conditions as in Fig. 4.

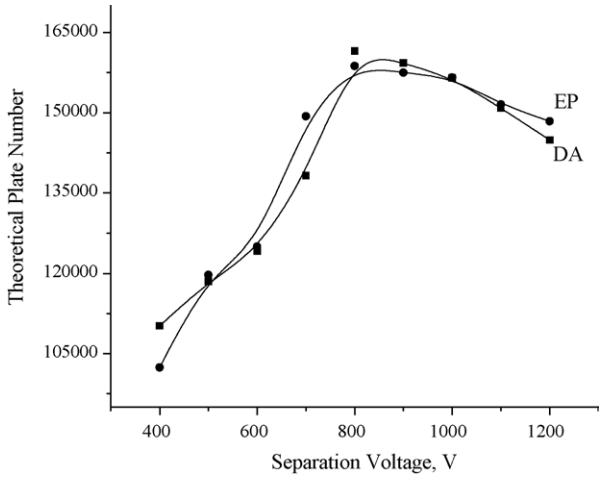

Fig. 7. Influence of separation voltage on the theoretical plate numbers. DA: 500 μM; EP: 500 μM. Other conditions as in Fig. 4.

The peak width (at half height) of dopamine and epinephrine decreased from 6.8 and 7.8 s at 400 V to 1.8 s and 1.9 s at 1200 V, respectively. Fig. 7 showed the effect of separation voltage on the separation efficiency, i.e. on theoretical plate number (the number of plates per meter, $N\,m^{-1}$). The theoretical plate numbers reached maximum values of $1.61 \times 10^5\,N\,m^{-1}$ for dopamine and $1.59 \times 10^5\,N\,m^{-1}$ for epinephrine at the separation voltage of 800 V, respectively. The higher separation voltage had much effect on the background noise level. Flat baselines were observed at lower separation voltages (<900 V).

3.5. Reproducibility and stability

Reproducibility of the modification can be investigated according to the relative standard deviation (R.S.D.) of migration times and separation efficiencies [39]. Here the reproducibility was examined by EOF, migration time and peak current. A good reproducibility was obtained with coated microchips. R.S.D.s of EOF were 0.9% for day-to-day and 1.3% for chip-to-chip ($n = 5$), respectively. The chip-to-chip reproducibilities of migration times were also good. R.S.D.s of peak currents and migration times were 2.5% and 1.6% for dopamine ($n = 5$), 2.6% and 1.4% for epinephrine ($n = 5$), respectively. In addition, it should be pointed out that when gold nanoparticles modified PDMS/PDMS microchip was filled with running buffer after using, the channel coatings were found to be quite stable within 2 weeks. R.S.D.s of migration times and peak currents within 2 weeks on the same coated PDMS/PDMS microchip were 1.7%, 4.2% for dopamine ($n = 14$) and 2.2%, 4.0% for epinephrine ($n = 14$), respectively.

3.6. Linear range and detection limit

The amperometric detection displayed well-defined concentration dependence. Fig. 8 showed electropherograms of different concentrations of dopamine and epinephrine. On the optimized conditions, the linear responses of dopamine and epinephrine were both from 25 to 600 μM. The cal-

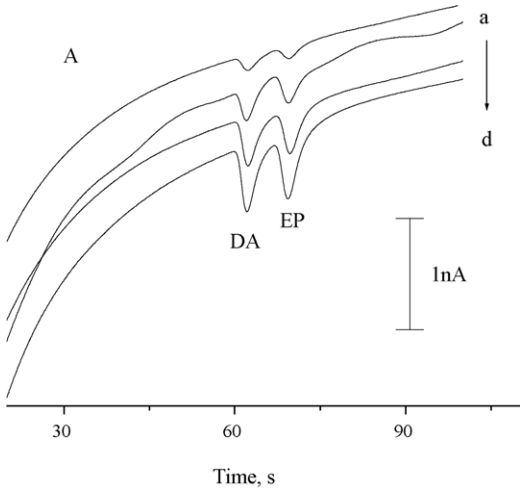

Fig. 8. Electropherograms of different concentrations of DA and EP: (a) 25 μM DA and 25 μM EP; (b) 50 μM DA and 50 μM EP; (c) 100 μM DA and 100 μM EP; (d) 200 μM DA and 200 μM EP. Other conditions as in Fig. 4.

ibration equation of dopamine was I (nA) = (0.02265 ± 0.00019) + (0.00451 ± 0.00008) × C_{DA} (C_{DA}: μM, 95% confidence limit, n = 3) with the correlation coefficient (r) to be 0.9994 and the calibration equation of epinephrine was I (nA) = (0.04018 ± 0.00023) + (0.00440 ± 0.00007) × C_{EP} (C_{EP}: μM, 95% confidence limit, n = 3) with the correlation coefficient to be 0.9986. The limits of detection (LOD) were 2 μM for dopamine and 5 μM for epinephrine (S/N = 3), respectively.

4. Conclusions

In this work, gold nanoparticles modified PDMS microfluidic channels have been successfully fabricated through electrostatic layer-by-layer assembly technique. In the coated PDMS/PDMS microchip, dopamine and epinephrine can be separated with baseline resolution. The modified PDMS channels have a long-term stability and an excellent reproducibility. It might be applied to establish new modification method for other kinds of analytes and detection modes. Moreover, it might be promising for the enzymatic reactor and immunoassays due to the excellent biocompatibility of gold nanoparticles.

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References

[1] A. Manz, N. Graber, H.M. Widmer, Sens. Actuators B 1 (1990) 244.
[2] S.K. Sia, G.M. Whitesides, Electrophoresis 24 (2003) 3563.
[3] M. Pumera, J. Wang, F. Opekar, I. Jelinek, J. Feldman, H. Lowe, S. Hardt, Anal. Chem. 74 (2002) 1968.
[4] S.L.R. Barker, M.J. Tarlov, H. Canavan, J.J. Hickman, L.E. Locascio, Anal. Chem. 72 (2000) 4899.
[5] C.S. Effenhauser, G.J.M. Bruin, A. Paulus, M. Ehrat, Anal. Chem. 69 (1997) 3451.
[6] J.C. McDonald, G.M. Whitesides, Acc. Chem. Res. 35 (2002) 491.
[7] J.C. McDonald, D.C. Duffy, J.R. Anderson, D.T. Chiu, H. Wu, O.J.A. Schueller, G.M. Whitesides, Electrophoresis 21 (2000) 27.
[8] J.M.K. Ng, I. Gitlin, A.D. Stroock, G.M. Whitesides, Electrophoresis 23 (2002) 3461.
[9] D.C. Duffy, J.C. McDonald, O.J.A. Schueller, G.M. Whitesides, Anal. Chem. 70 (1998) 4974.
[10] G. Ocvirk, M. Munroe, T. Tang, R. Oleschuk, K. Westra, D.J. Harrison, Electrophoresis 21 (2000) 107.
[11] S. Hu, X. Ren, M. Backman, C.E. Sims, G.P. Li, N. Allbritton, Anal. Chem. 74 (2002) 4117.
[12] B.E. Slentz, N.A. Penner, F.E. Regnier, J. Chromatogr. A 948 (2002) 225.
[13] A. Papra, A. Bernard, D. Juncker, N.B. Larsen, B. Michel, E. Delamarche, Langmuir 77 (2001) 4090.
[14] D. Xiao, T.V. Le, M.J. Wirth, Anal. Chem. 76 (2004) 2055.
[15] J. Lahann, M. Balcelis, L. Hang, T. Rodon, K.P. Jensen, T. Langer, Anal. Chem. 75 (2003) 2117.
[16] G.T. Roman, T. Hlaus, K.J. Bass, T.G. Seelhammer, C.T. Culbertson, Anal. Chem. 77 (2005) 1414.
[17] J.S. Buch, P.C. Wang, D.L. DeVoe, C.S. Lee, Electrophoresis 22 (2001) 3902.
[18] C.D. García, B.M. Dressen, A. Henderson, C.S. Henry, Electrophoresis 26 (2005) 703.
[19] Y.H. Dou, N. Bao, J.J. Xu, H.Y. Chen, Electrophoresis 23 (2002) 3558.
[20] Y.H. Dou, N. Bao, J.J. Xu, F. Meng, H.Y. Chen, Electrophoresis 25 (2004) 3024.
[21] K.S. Phillips, Q. Cheng, Anal. Chem. 77 (2005) 327.
[22] E. Eteshola, D. Leckband, Sens. Actuators B 72 (2001) 129.
[23] Y. Liu, J.C. Fanguy, J.M. Bledsoe, C.S. Henry, Anal. Chem. 72 (2000) 5939.
[24] D. Wu, Y. Luo, X. Zhou, Z. Dai, B. Lin, Electrophoresis 26 (2005) 211.
[25] H. Makamba, Y.Y. Hsieh, W.C. Sung, S.H. Chen, Anal. Chem. 77 (2005) 3971.
[26] F. Mallwitz, A. Laschewsky, Adv. Mater. 17 (2005) 1296.
[27] L. Coche-Guerente, P. Labbe, V. Mengeaud, Anal. Chem. 73 (2001) 3206.
[28] H. Makamba, J.H. Kim, K. Lim, N. Park, J.H. Hahn, Electrophoresis 24 (2003) 3607.
[29] E. Guihen, J.D. Glennon, Anal. Lett. 36 (2003) 3309.
[30] Y.W. Lin, M.J. Huang, H.T. Chang, J. Chromatogr. A 1014 (2003) 47.
[31] Y.W. Lin, H.T. Chang, J. Chromatogr. A 1073 (2005) 191.
[32] C.X. Luo, Q. Fu, H. Li, L.P. Xu, M.H. Sun, Q. Ouyang, Y. Chen, H. Ji, Lab Chip 5 (2005) 726.
[33] K. Hosokawa, K. Sato, N. Ichikawa, M. Maeda, Lab Chip 4 (2004) 181.
[34] M. Pumera, J. Wang, E. Grushka, R. Polsky, Anal. Chem. 73 (2001) 5625.
[35] N.A. Lacher, S.M. Lunte, R.S. Martin, Anal. Chem. 76 (2004) 2482.
[36] N.E. Hebert, B. Snyder, R.L. McCreery, W.G. Kuhr, S.A. Brazill, Anal. Chem. 75 (2003) 4265.
[37] J.J. Xu, N. Bao, X.H. Xia, Y. Peng, H.Y. Chen, Anal. Chem. 76 (2004) 6902.
[38] M.F. Huang, C.C. Huang, H.T. Chang, Electrophoresis 24 (2003) 2896.
[39] F.B. Eric, A. Cifuentes, H. Poppe, J.C. Kraak, J. Chromatogr. A 708 (1995) 356.