Sample Concentration by Asymmetry EOF flow in Micro/Nano channels with O2/H2O plasma Treated Channel Surfaces

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ABSTRACT

Sample pre-concentration is an important step in many high-performance separation techniques, such as liquid chromatography or capillary electophoresis, which determines the detection sensitivity of separated samples. However, they either need particular microdevices or special surface treatment in local area, posing system fabrication/operation complexity. In this study, we employ simple and rapid surface plasma processes to create an asymmetry electroosmotic flow (EOF) in micro/nano channels. By this way, the sample can be concentrated into one side of the channel induced by the non-uniform zeta potential variation. We demonstrate that the concentrating ability for neurotransmitter (1μM Dopamine) in the modified asymmetry surface treated channel (500nm and 30 μm channel depth) are 8.5 or 2.8 times larger than that in the channels with symmetrical surface treatment, respectively.

Keywords: asymmetry electroosmotic flow, sample concentration, plasma treatment, nano channel

1 INTRODUCTION

EOF control is a well-known technique to pump liquid inside a channel. EOF offers important advantages over other methods of microfluidic pumping, such as no moving parts and no sophisticated micromachining processes. Furthermore, EOF is easy to implement and operate, especially in micro or nano scale.

A typical EOF flow is generated in the outer boundary of the electro-double layer produces nearly flat velocity profile in micro channels. Any blockage at the channel outlet results in a pressure increment in the channel thus creates a pressure-driven back-flow (PDF) that can be linearly superposed with the EOF, as shown in Fig. 1. Maximum pressure is achieved when no net pumping occurs, that is, when the pressure-driven back flow rate through the channel is equal to the electroosmotic flow rate. Since the speed of pressure-driven back flow is proportional to the square of capillary diameter, electroosmotic forward flow can dominate over very large outlet-to-inlet pressure differentials when the capillary diameter is very small [1].

Electroosmosis is also an important component of capillary zone electrophoresis. Electroosmosis directly influence the efficiency, resolution, and reproducibility of most electro-kinetic separation techniques. Recently, many studies showed that the detection limit of CE can be improved by controlling electroosmotic flow (EOF) to generate special flow fields, such as mixing [2], EOF speed reduction [3], and flow focusing [4]. However, the maximum concentration ratios which those methods can obtain were less than 5 fold. In this study, we propose a new technique, by employing different surface treatments on the top and bottom of micro/nano channels to concentrate sample effectively. This treatment carries out different zeta-potentials on the opposite walls of micro/nano channels for generating asymmetry EOF flow to concentrate samples into one side of the channel. By employing this technique combined with nanochannel, the sample concentration and diffusion length for the sample to the electrochemistry detection site is greatly reduced, and near one order of magnitude signal enhancement has been achieved in this study.

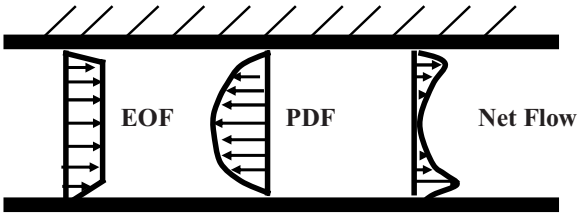


Fig.1. For a small Debye thickness, the electroosmotic flow (EOF) shows nearly flat velocity profile. The pressure-driven back flow (PDF) can be (mathematically) linearly superposed with the EOF flow solution to yield the flow profile at right

2 MATERIALS AND METHODS

2.1 Materials

Rhodamine B base dye was purchased from Sigma-Aldrich. For the fluorescence image measurements, the dye was further diluted to 50, 20, 10, 5, 2, 1 mM in 10 mM 4-(2 Hydroxyethyl)-piperazine-1-ethanesulphonic acid (HEPES, Sigma) buffer solution at pH 6.5. All buffer solutions were made by using deionized water. All

solutions were filtered before use with 0.2 mm syringe filters (Whatman, Fisher Scientific Canada, Ottawa, ON).

Microchannels were made using poly(dimethylsiloxane) (PDMS) prepared according to product information from a Sylgard 184 silicone elastomer (Dow Corning, Midland, MI)

2.2 Microfabricated devices

A 2-cm long channel of PDMS-glass microchip (Figure 2) was made from PDMS with sectional dimensions of 30μm or 500 nm in height and 50 μm in width. The process is briefly described as follows. Before bonding the PDMS layer to the glass substrate carrying the electrodes, The upper-surfaces of the channel walls (PDMS) were treated with either O_2 or H_2O plasma (100W, 30 or 300s) of less or equal process time than or to that of the lower-surfaces (Glass) (top/ bottom to be 10%/90% or 50%/50%). Seven different types of surface plasma treatments were studied in channels of 30 μm depth except the last one of a 500 nm deep channel, and the conditions are (a) without treatment, (b) O_2/O_2 (50/50%), (c) O_2/O_2 (10/90%), (d) O_2/O_2 (10/90%, tested after 20 days), (e) H_2O/H_2O (50/50%), (f) H_2O/O_2 (10/90%), and (g) H_2O/O2 (10/90%, 500 nm depth). By the plasma treatment processes, the PDMS and glass substrates can not only be bonded directly but also the channel inner surfaces are modified with asymmetry or symmetry zeta potentials, as shown in fig.2.

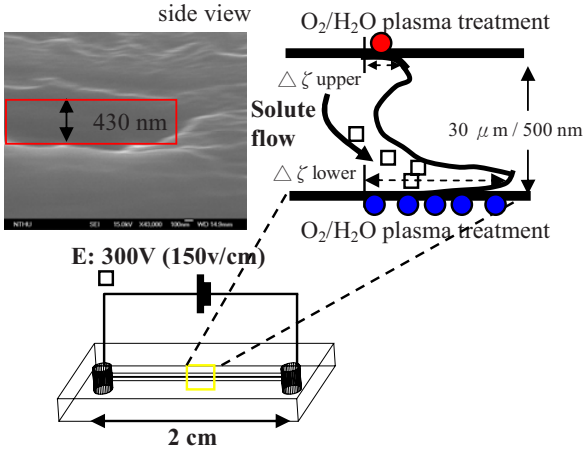


Fig.2. Schematic of asymmetry EOF flow induced by unbalanced zeta potentials on channel top and bottom surfaces, produced by different surface plasma treatments.

2.3 Experimental Setup

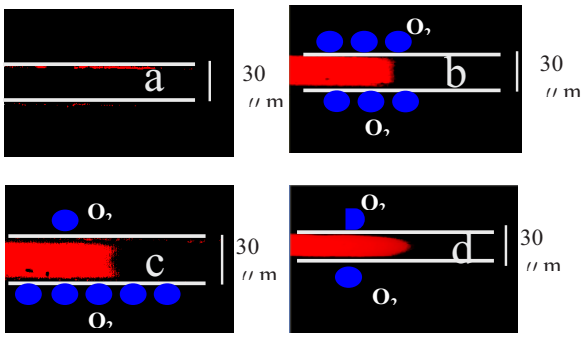
Before any fluorescence image test, the channel was filled with pure water, base (1 M NaOH), and pure water in order, for 30 min. Two platinum electrodes were placed in the solution in each of the reservoirs, and connected to a high-voltage DC power source (CZE1000R, Spellman, High-Voltage Corp., Plainview, NY). In the sample concentration experiment, the capillary and the upstream reservoir were filled with the solution of Rhodamine B base dye, and the downstream reservoir contained only pure buffer. Images were captured and saved on the computer at a rate of 15 Hz with individual exposure times of 1/60 s. A progressive scan CCD camera (CV-m30, JAI) was used to avoid image defects due to field-field interlacing. The data from the CCD camera was fed into a monitor for real-time image viewing and a PC-based frame grabber for data acquisition.

For an electrochemical detection system, the oxidation current of the analyte with a time resolution of 0.5 s was recorded while the detection potential was set at a constant potential of 700 mV versus the Ag/AgCl reference electrode. All results of electrochemical detection were recorded (CHI 760B, Bioanalytical Systems, West Lafayette, IN), processed, and stored directly in a computer.

3 RESULTS AND DISCUSSION

The top view of the generated EOF flow profiles are shown in figure 3, indicated by Rhodamine-B dye in a 5 mM or 2 mM buffer solution of 10mM HEPES. There is no any fluorescence image obtained in the microchannel without surface plasma treatment due to the surface tension is larger than the electrokinetic force to repress EOF in figure 3(a). The figure 3(b) shows the traditional EOF flow with flat profile in a channel treated with the same amount of O_2 plasma on the up and bottom channel walls.

Figure 3(c) and 3(d) are the comparison between the fresh state (1 day) and the long-time state (after 20 days) of non-equal O_2 plasma treatment on channel surfaces, and the difference in flow profiles (pull-back for 1day, and parabolic for 20days) could be clearly seen. The non-equal H_2O plasma treated channels have similar flow profiles in those by non-equal O_2 plasma treated channels, as shown in Fig. 3(e). In the Fig. 3(f) and 3(g), channel surfaces were treated with different types of plasmas, and the pull-back flow profile can also be observed for both micro and nano channels. Pull back flow is induced by very strong asymmetry zeta potion posing top part of the flow in opposite direction to the bottom one, while parabolic flow means a more pressure driven type flow in the same direction of EOF.



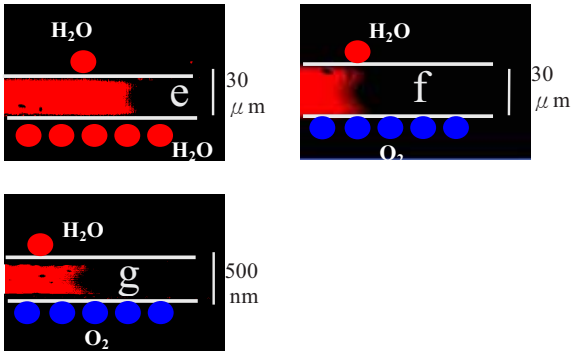


Fig 3. The flow profile of sample front under different surface plasma treatment conditions: (a) without treatment, (b) O_2/O_2 (up/bottom=50/50%), (c) O_2/O_2 (10/90%), (d) O_2/O_2 (10/90% after 20 days), (e) H_2O/H_2O (10/90%), (f) H_2O/O_2 (10/90%), and (g) H_2O/O_2 (10/90%). Conditions: g is 20:80 solutions in the 500 nm deep channel, others are 50:50 solution.in 30μm deep channel.

The time sequences of continuous EOF flow profiles in different channels are shown in figure 4. Very strong asymmetry EOF flows were observed in Fig. 4 (f), and (g), and both are under extreme conditions for surface treatment on opposite walls. From the top view of the sample profiles for these two cases, there is not only a much more intensive fluorescence but also a significant concave curve in the sample front owing to the strong asymmetry EOF effect.

The fluorescence intensities in Fig. 4 (c), (e) are similar,suggested that the asymmetry zeta potential throughout the whole channel inducing streaming flow (back flow) and the streaming potential is opposite to the EOF flow. In addition, the EOF flow for channels treated with similar gas plasma would not be very strong. As a result, the suppressed EOF flow would have weak concentration ability resulting in the similar fluorescence intensity for those channels [5].

Table 1 shows the electrophoresis mobility and flow profile of different channels. In micro-sized channels, the equal O_2 plasma treated cases have the maximum flow velocity owning to the balanced strong EOF on both surfaces, while the non-equal O_2 plasma treated cases (after 20 days) have the minimum velocity due to the unbalanced and weak EOF force on different side of surfaces.

The detected fluorescence and electrochemistry signals are analyzed in Fig. 5 and 6. The fluorescence intensities are calibrated by five different concentrations (1, 2, 5, 10, 20, and 50 mM, respectivley), and the linear calibration curve (the linear range is 1-20 mM) is showed in the inset of figure 5. Among the five different channel cases, only surfaces treated with non-equal and heterogeneous surface plasmas on the opposite channel walls carry out the strongest sample concentration ability, as shown in Fig. 5 (f) and (g). However, In Fig. 5(b), (c), (e), all are with the same type of surface plasma treatment on opposite wall surfaces, and their fluorescence intensities have similar time curve and much lower fluorescence intensities than that of the aforementioned ones.

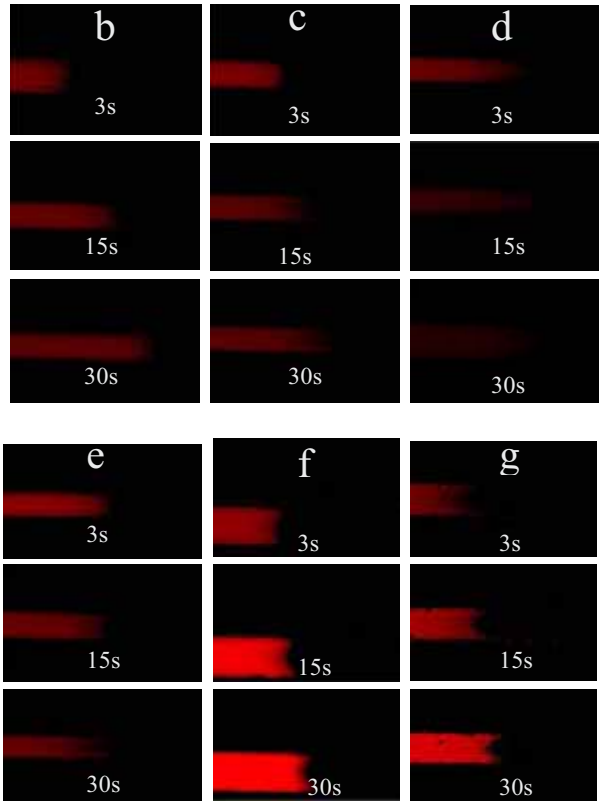


Fig 4. Time sequences of continuous EOF flow profiles in different channels. The experiment condition is the same as for Figure 2.

Surface modify state	**mobility**	**Flow Profile**
(b) O_2(165s)-O_2 (165s)	666 μm/s	flat
(c) O_2(30s)-O_2(300s) for 1 day	580 μm/s	pull-back
(d) O_2(30s)-O_2 (300s) for 20 days	312 μm/s	parabolic
(e) H_2O(30s)-H_2O(300s)	600 μm/s	pull-back
(f) O_2(30s)-H_2O (300s)	500 μm/s	pull-back
(g) O_2(30s)-H_2O(300s) 500nm	720 μm/s	pull-back

Table 1. The surface modify state, electrophoresis mobility and flow profile are listed. The asymmetry zeta potential could induce the flow to develop the pull-back proflie.

Moreover, under the similar surface treatment and operation condition, the 500 nm nano-channel demonstrated a 2.25 times higher concentration ability than that of 30 μm channels by the ratio of the concentrated times (for 500nm: 2mM to 18mM; for 30μm: 5mM to 20 mM) as shown in Fig. 5(f), (g). As a result, treating opposite surface by heterogeneous plasmas and shrink the channel height from micro to nano scale can effectively induce strong unbalanced EOF flow and dramatically improve sample concentration. The linear calibration curve (the linear range is 1-20 mM) was showed in the illustration of figure 5.

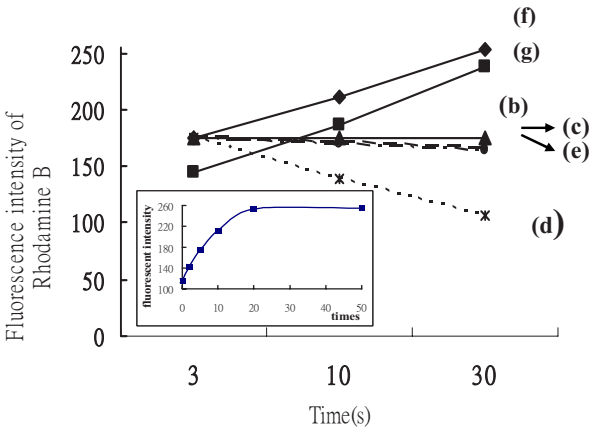


Fig 5. The analyzed Rhodamine-B fluorescence intensity for EOF flow under different channel conditions in different time. (inset: fluorescence calibration curve).

To demonstrate the concentrating ability of neurotransmitter in the modified channels, amperometric detections were performed and results are shown in Fig. 6. 1 μM dopamine (DA) running in three different surface treatment channels (solid line: without plasma, 30μm ; dotted line: non-equal O_2-H_2O plasma, 30μm ; black dotted line: non-equal O_2-H_2O plasma, 500nm) under a electrical filed of 166 V/cm. For amperometric detection, the working electrode was setting at the oxidative potential (+0.8V) vs. palladium pseudoreference electrode.

Asymmetry surface treated micro/nano channels (30μm and 500 nm in depth) have signal intensity (total Coulomb numbers) 2.8and 8.5 times larger than that of symmetry surface treated micro channel (30 μm in depth), respectively. Furthermore, the maximum oxidation current of the asymmetry surface treated nanochnnel (500 nm in depth) is the 4.2 times larger than that symmetry surface treated micro channel (30 μm in depth), this result may from the sample could be concentrated and carried closely into the diffusion layer that dramatically decreases the mass diffusion time and then to enhance the detection limit.

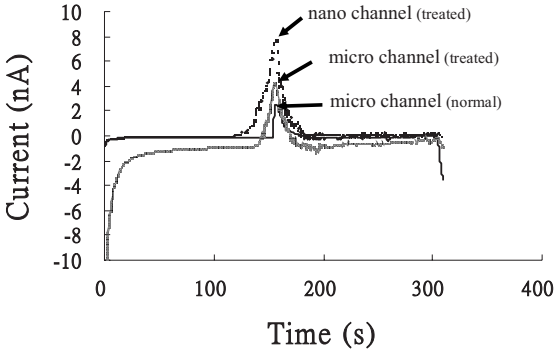


Fig 6. Electropherograms of 1 μM dopamine (DA) running in three channels under 166 V/cm. Conditions: amperometric detection at +0.8V vs. palladium pseudoreference electrode.

4 CONCLUSIONS

We demonstrate that sample pre-concentration in micro/nano channel can be performed by asymmetry EOF flow though surface treament. The plasma treatment process can also be applied to CE-chip bonding at the same time. Sample preconcentration up to 8.5 times has been successfully demonstrated by the application of both heterogenenious and asymmetry surface treatment in a channel of 500 nm deep on a electrochemical detector. Further optimization of this system has a potential to improve the sample concentration rate more than one order of magnitude. Such a novel approach should advance the miniaturization and realization of a CE-EC microchip based on the concept of lab-on-a-chip.

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