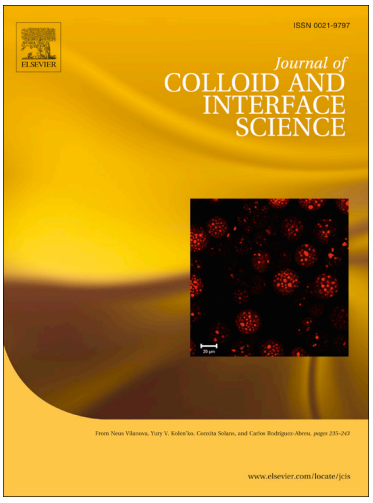

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Jun Li, Dongqing Li

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Electroosmotic flow velocity in DNA modified nanochannels

Jun Li and Dongqing Li*

Department of Mechanical and Mechatronics Engineering

University of Waterloo

Waterloo, Ontario, Canada N2L 3G1

*Corresponding author, Email: dongqing@uwaterloo.ca

Abstract

Electroosmotic flow (EOF) is systematically investigated in DNA grafted hard PDMS (h-PDMS) channels with size ranging from 50 nm to 2.5 μm by using the current-slope method. The effects of the DNA types, the incubation time in the process of surface modification, and the pH value, ionic concentration of electrolyte solutions, and the UV (ultraviolet) illumination on the velocity of electroosmotic flow are experimentally studied. It is found that the DNA type and the incubation time of DNAs affect the grafting density and the surface charge on the channel walls, thus influencing the EOF velocity. In the DNA modified channels, the pH effects on EOF velocity become less prominent compared with that in the pristine channels. On the contrary, UV illumination can increase the EOF velocity significantly in the DNA modified channels, whereas takes unapparent effects on EOF velocity in the pristine channels. The effects of ionic concentration on EOF are also studied in this paper. It is observed that EOF velocity is dependent on the channel size when the ionic concentration is low even without overlapped electric double layer (EDL) and is essentially independent of the channel size when the ionic concentration is high. Furthermore, with high ionic concentration and thin EDL, the EOF velocity can be enhanced by the coated DNA brushes on the channel surface.

Keywords:

Electroosmotic flow; Nanochannel; Surface modification; Electric double layer

1. Introduction

Microfluidic devices have attracted a lot of attention during the past decades and been widely used in the fields of biomedical analysis and chemical reaction because of their competitive advantages[1–5]. Typically, these microfluidic devices and nanofluidic devices are fabricated with polymers, glass, silicon, and combinations of these materials. Among various microfluidic systems, the polymer-based devices have been gaining popularity because of the advantages of low cost, optical transparency, and easy fabrication. The Polydimethylsiloxane (PDMS) is a far more dominant polymeric material used for making microfluidic devices and nanofluidic devices. Liquid flows in nanochannels and microchannels generally can be generated by pressure or external electric field, i.e., pressure-driven flow or electroosmotic flow (EOF)[6]. When an aqueous solution is brought into contact with the channel walls that have electrostatic charges, free ions in the liquid rearrange and form an electric double layer (EDL). The structure of EDLs includes a Stern layer comprised of immobile counterions attached on a charged solid surface and a diffuse layer of mobile ions whose thickness is characterized by the Debye-Huckel length [7,8]. Under the externally applied electrical field, the bulk liquid flow is generated by the movement of excess counter-ions in the diffuse layer due to the viscous effects. This is the so-called electroosmotic flow (EOF). With the advancement of lab-on-a-chip technology, EOF is widely employed as a method of transporting liquids in microfluidic devices and nanofluidic devices due to its many advantages, such as ease control and high reliability[9]. In most of the microfluidic devices, the thickness of EDL is much smaller than the dimensions of the channel, and the EOF has a plug-like velocity profile. Helmholtz-Smoluchowski theory provides a way to calculate the EOF velocity in microchannels. As the channel size decreases to the nanoscale, EDLs from different channel walls may become overlapped, and the actual thickness of the EDL estimate by the Debye-length is not accurate any more[10]. Recently, Wang et al. proposed modified models of EDL to analyze the effects of ionic concentration and pH on the electrokinetic transport in small channels with overlapped EDL[11–14]. Their results showed that the surface charge density varies according to the changes in pH and ionic concentration.

However, many aspects of the physics of EOF in small nanochannels are not well-understood, such as ion size effects on the distribution of EDL[15–17], and the effects of surface roughness[18–20].

Significant attention has been paid on EOF modulation in recent years. In EOF modulation, the surface coating is one of the most popular methods to effectively control EOF in microchannels[21–25] and nanochannels[26–30]. The effects of the coated layer on electrokinetic transport have been investigated extensively. Theoretically, Harden et al.[31] set up a model to predict the qualitative features of EOF velocity in channels with end-grafted polyelectrolytes and reported that the EOF mobility is essentially determined by the electrokinetic properties of the polymer in channels with densely grafted polymers. Adiga and Brenner[28] studied the EOF velocity distribution in a nanopore grafted with polymer brush by using molecular dynamics simulation method and showed that the EOF velocity depends on the coupling effects of polymer conformational dynamics induced by the drag force of fluid flow and electrohydrodynamics. Huang et al.[27] also investigated the electric properties of the surface on which polyelectrolyte brushes are grafted and report that the surface charge is dependent on the grafting density, pH, electrolyte concentration and the thickness of the brush layer. Cao et al.[29] stated that the maximum EOF velocity in the polymer-grafted nanochannel center region depends on the grafting density and solvent quality. Experimentally, the polymer or DNA chains can be irreversibly grafted onto the surface by covalent bonds[32–38], or reversibly adsorbed on the surface. Xia et al.[39] fabricated a pH-regulated smart nanochannel by coating DNA brushed onto the inner wall of the channel. Bello et al.[40] proposed that the EOF velocity could be progressively suppressed by the coated polymer layer onto the channel wall. Hjerten[41] stated that the electroosmotic flow could be eliminated in channels by coating a layer of neutral polymer. Paumier et al.[42] measured the EOF velocity in channels grafted with neutrally charged polymers and reported that the thickness of the coated layer could control the development of EOF. When the polymer layer is thicker than the EDL, the EOF can be effectively prohibited

even the channel surface with nonzero zeta potential. On the contrary, if the thickness of the coated polymer layer is smaller than that of EDL, the EOF could still occur unimpeded. Raafatnia[43] et al. further investigated the mobility of polyelectrolyte-grafted colloids in monovalent salt solutions. They presented that the mobility is dominated by the polyelectrolyte brush regime at high ionic concentration. In Manning's theory, the neutralization of DNA charges only determined by the valence of counterions in the solvent and independent of its type and concentration[44]. Guo et al. studied the effects on this issue and reported that the DNA charge neutralization is also dependent on the pH value of solutions or the concentration of hydrogen ions[35]. Moreover, the molecular structure of DNAs can be influenced by ultraviolet(UV) irradiation, thus changing the charges carried by DNAs[45–47]. Therefore, UV illumination can be an elegant way to modulate EOF in the DNA coated channels without any additives.

As reviewed above, although many experimental studies have been conducted to understand effects of the EOF modulation by using the surface coating method, the complicated interactions between DNA and mobile counterions in the solution result in new questions about EOF in these DNA modified channels. More researches are required to further examine the fundamental characteristics of EOF influenced by the interactions between electrolyte solutions and the coated surface. At present, the experimental results of EOF velocity in PDMS nanochannels grafted with DNA brushes are still very limited. In order to provide improved understandings of electrokinetic transport in nanochannels grafted with DNA brushes, in this work, EOF velocities are measured by using the current monitoring method in the microchannels, large nanochannels as well as very small nanochannels with overlapped EDL [48]. The effects of the incubation time, the type of the coated layer, pH and ionic concentration of electrolyte solutions on the performance of surface modification and EOF are studied in h-PDMS channels. The EOF velocities with UV illumination are also measured in DNA grafted channels. For comparison, corresponding measurements of EOF velocity in the pristine channels with UV illumination are also presented in this paper.

2. Materials and methods

2.1 Chemicals and Oligonucleotides

The chemicals employed in this study include electrolytes of KCl (≥ 99%, Fisher Scientific), pure water (18.2 MΩ Mini Q, Direct-Q3) which is used to prepare all the electrolyte solutions, KOH (≥ 85%, Fisher Scientific) and HCl solution (37%, Sigma-Aldrich) which are used to regulate the pH of KCl electrolyte solutions. Regular PDMS (Sylgard 184, Dow Corning) and hard PDMS (h-PDMS) are utilized to fabricated EOF measurement chips[49]. 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC; ≥ 98%, Millipore corporation, American) and N-hydroxy succinimide (NHS; 97%, Alfa Aesar) are used to treat the channel surface in the first step of the surface modification; 15 base single-stranded DNA (ssDNA), 15-mer poly-T and poly-A (abbreviated as 15T and 15A, respectively), are grafted on the channel surface in the second step of the surface modification.

2.2 Fluidic chip fabrication

In this study, the nanochannel molds were fabricated by using the solvent-induced cracking method[49]. The nanochannel chips were produced by casting a bilayer of h-PDMS and regular PDMS on the nanochannel molds. The h-PDMS can precisely replicate the molds' feature and minimize the deformation and collapsed effects on channel size. The regular PDMS is relatively soft and used to support the fragile h-PDMS layer[50]. Firstly, the h-PDMS was spin-coated onto a nanochannel mold and then placed in an oven at 80°C for 10 minutes. Afterward, the regular PDMS was cast onto the h-PDMS layer and heated with the same temperature for 2 hours. In order to easily deliver the testing liquid in a nanochannel, the nanochannel chip was connected to a microchannel which was replicated from a SU8 photoresist microchannel mold fabricated on a silicon wafer with the standard photolithography method. This PDMS microchannel chip was also produced with the bilayer of h-PDMS and regular PDMS so that the zeta potential value was constant on all surface of the system. The microchannel network was bonded with the nanochannel chip by Plasma

treatment (Harrick plasma, PDC-32G). Figure 1 shows an example of the fluidic chip for EOF velocity measurement, where the nanochannel bridges the two "U" shape microchannels with a depth of 30μm and a width of 150μm.

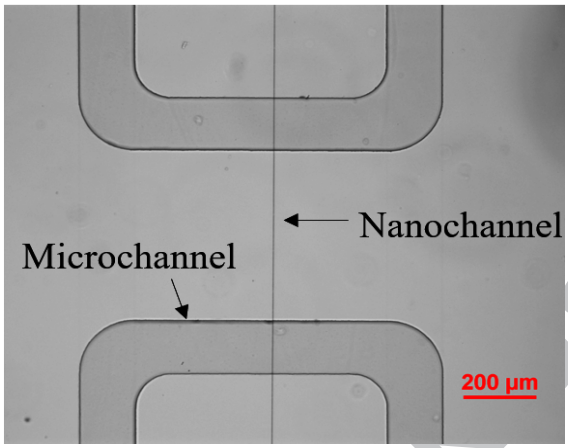

Figure 1. A picture of an h-PDMS nanofluidic chip for EOF velocity measurement captured by an optical microscope.

2.3 Surface modification

In this work, the surface modification process is achieved by the chemical reaction between the channel inner surface and the functional molecular groups to form covalent bonds[39,51,52]. As shown in Figure 2, the nanochannel chip and microchannel chip were pretreated by oxygen plasma for 180s, and then they were irreversibly bonded together. After leaving the chip standing for 30 minutes at room temperature of about 23 ^{o}C, the inner surface modification can be achieved by a two-step chemical reaction and an incubation process. Firstly, 2μl EDC solution (20mM) and 2μl NHS solution (20mM) were filled into the chip to couple carboxylic groups to amines on the channel surface. After that , 10μl DNA 15T solution (10μM) was added to the channel and bonded to the inner surface. Finally, the chip was fulfilled with 100mM MES buffer solution and incubated at the temperature of 4^{o}C for a certain period before using. For the duplex DNAs modified nanochannels, 10μl DNA 15A solution (1μM) was filled into the chip after the incubation process. By one extra

hour incubation at the room temperature, the DNAs of 15A could hybridize with the grafted DNA 15T and form dual-stranded structure[36,53].

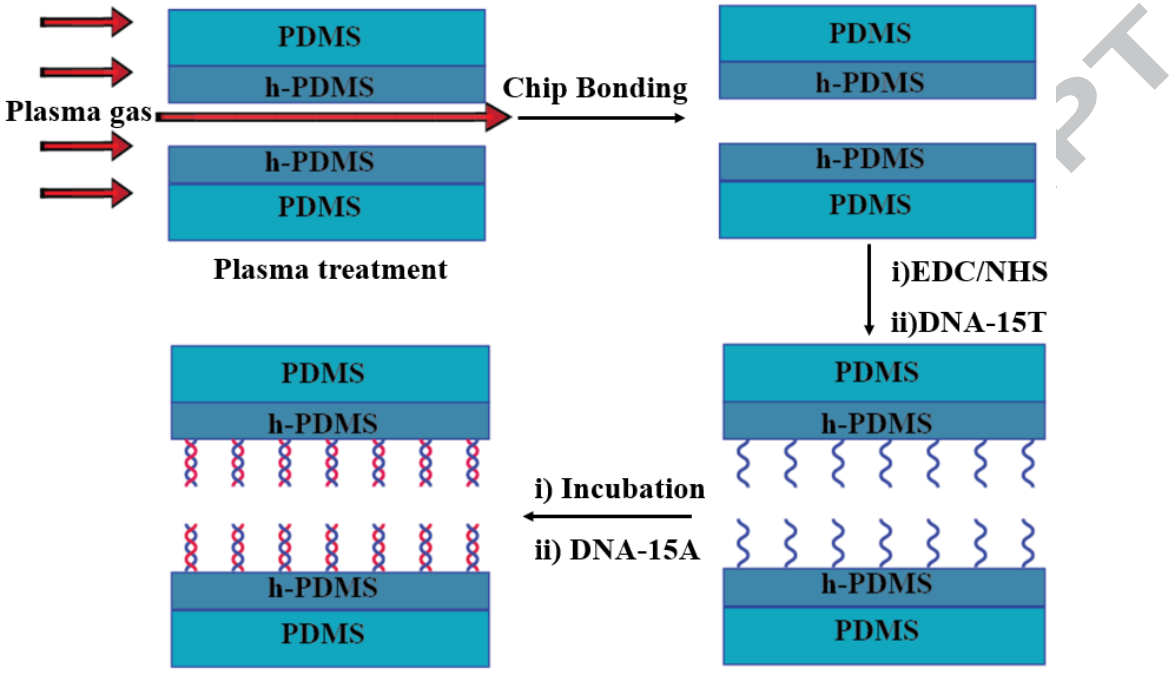

Figure 2. Schematic representation of the formation of the grafted DNA layer on h-PDMS channel inner surfaces.

2.4 Measurement of EOF velocity

Electric current monitoring method is a widely used technique that can evaluate the EOF velocity in microchannels[54]. As the conductivities of electrolyte solutions are related to their ionic concentrations, the EOF velocity can be measured by monitoring the electric current change in the displacement process between two electrolyte solutions with slightly different ionic concentrations. The time of a higher concentrated electrolyte solution displaced by a lower concentrated electrolyte solution can be recorded, and the EOF velocity can be calculated by knowing the channel length and the replacement time. However, it is difficult to ascertain the exact starting time and the ending time of the displacement process in an experiment. To improve the measurement method and minimize the experimental error, Ren et. al[48] proposed to calculate the EOF velocity by using the slope of the current-time curve instead of the time period of the complete displacement process. Pend and Li[55] also

measured the EOF velocity in nanochannels by using the current slope method. In this work, all channels initially were filled with an electrolyte solution of a high concentration and then the same electrolyte solution of a slightly lower concentration was filled into the channels to displace the original solution by EOF. For each working condition, in this paper, the measurement of the current slope was repeated for at least 5 times in 5 independent chips. All the experiments are conducted at the room temperature of around 23°C. Because the electrical resistance of the microchannel is much smaller than that of the nanochannel, the voltage drop in the microchannels is negligible compared with that in the nanochannel. According to the current slope method, the EOF velocity can be calculated by the following the equation.

$$\mathrm{V}_{EOF} = \frac{k_{slope}\, L}{I_2 - I_1} \qquad (1)$$

where V_{EOF} is the velocity of the electroosmotic flow; I_1 and I_2 are the initial electric current value and the final electric current value in the nanochannel, respectively; k_{slope} is the slope of the liner part of the current-time curve; L is the length of the nanochannel.

The EOF measurement system, as shown in Figure 3, consists of a multifunctional electrometer (Keithley, Model 6517A) used to supply DC voltage and transfer the electric current signal to a computer by a LabVIEW program (National Instrument Corp.), platinum electrodes (Sigma-Aldrich), an electric switch, an UV controller, and a nanofluidic chip. The UV ray turns on only in the experiments of testing UV effects.

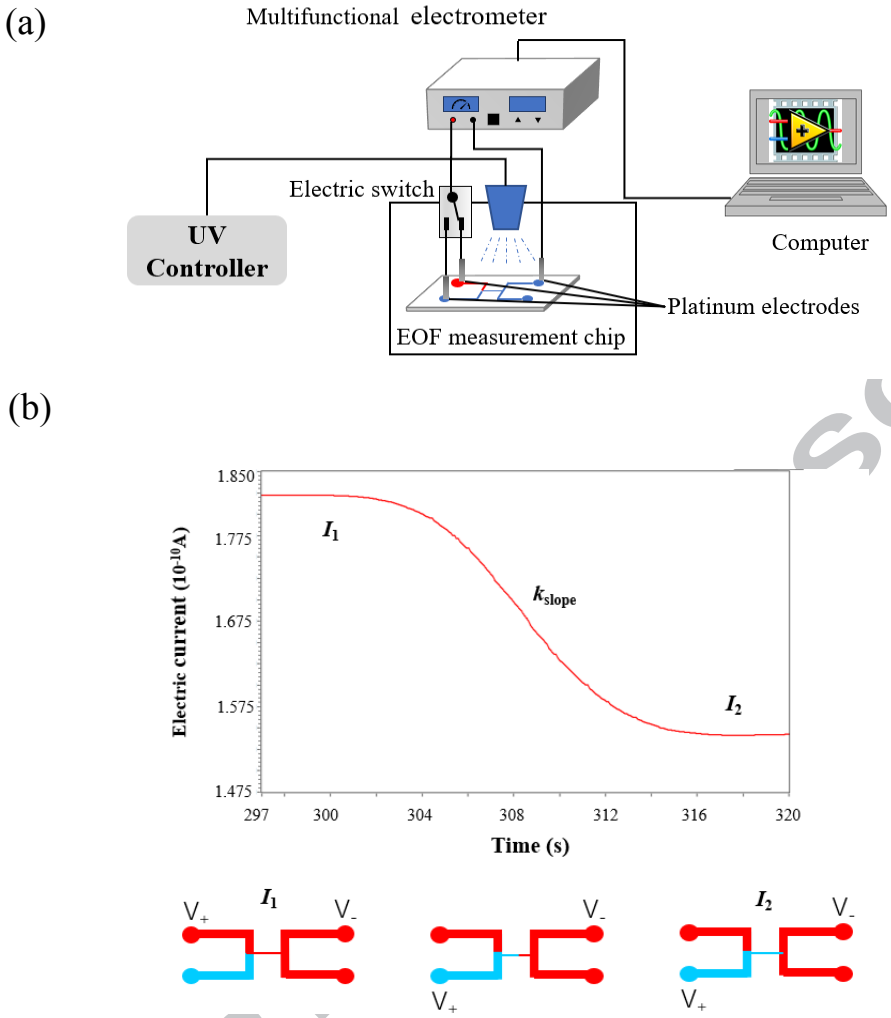

Figure 3. (a) Schematic diagram of the EOF velocity measurement system and (b) an example of the measured current curve by this system.

3. Results and discussion

3.1 Surface modification characterization by atomic force microscope (AFM)

The quality of the modified h-PDMS surface and the grafting density of DNA attached on the surface were characterized by an AFM (Multiode^{TM} SPM, Digital Instruments). All images were captured in the conventional tapping mode. The DNA 15T modified h-PDMS chips were firstly treated with the surface modification process as described previously and then incubated at the temperature of 4^{o}C for 3h and 24h, respectively. The unmodified h-PDMS surface was used as a reference. The AFM height images of these surfaces modified with

different conditions are shown in Figure 4. The surface profiles were measured correspondingly to the directions of the white lines on the AFM height images. The surface profile can indicate the surface structure and the grafting density of DNAs. As shown in the figure, the unmodified h-PDMS surface was very smooth. At the incubation of 3h, the surface roughness increases, indicating DNA chains was grafted on the surface. Furthermore, the magnitudes of the peaks in the surface profile line are around 0.5 nm. At the incubation time of 24 h, the distance between the peaks of the surface profile is much smaller and the magnitudes of the peaks are larger than that at the incubation time of 3h. These results illustrate that the grafting density of DNAs on the PDMS surfaces is proportional to the incubation time, and the high grating density will force the DNA chains transfer from folded to extended state, thus having a relatively long length.

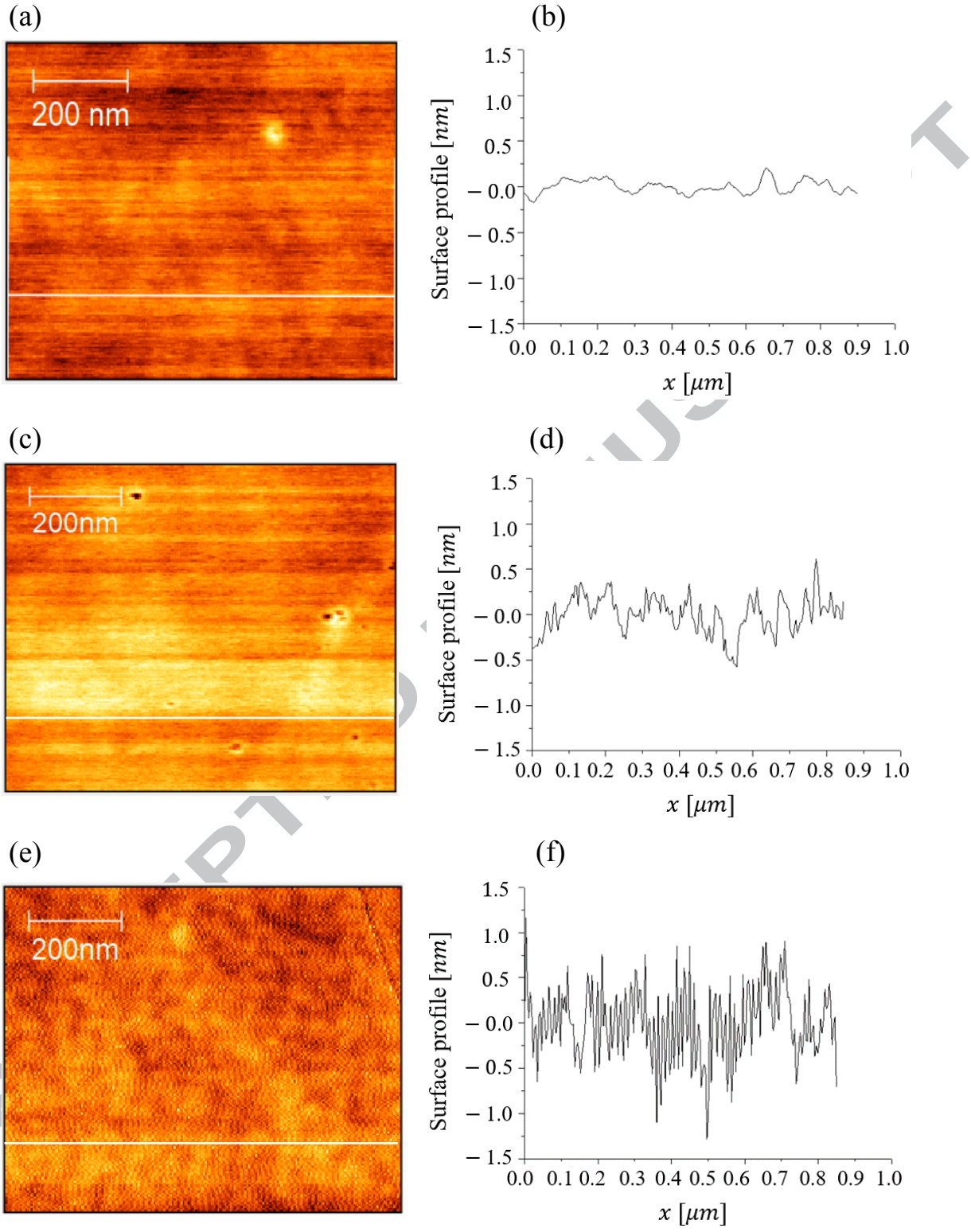

Figure 4. AFM images and surface profile of h-PDMS surfaces. (a) and (b) are the height image and surface profile of the unmodified h-PDMS surface, respectively; (c) and (d) are the height image and surface profile of DNA 15T modified h-PDMS surface with the incubation time of 3h, respectively; (e) and (f) are the height image and surface profile of DNA 15T modified h-PDMS surface with the incubation time of 24h, respectively.

3.2 Effects of incubation time

In general, the process that DNA molecules move from the bulk solution to the channel surface and the grafting density of DNA chains on the channel surface is related to the incubation time. In this work, the nanochannels modified with ssDNA 15T and incubated for 1h, 3h, 6h, and 24h were prepared, respectively. The electrolyte solution of 10^{-3} M KCl at pH 7 was utilized to investigate the effects of incubation time on EOF velocity in these nanochannels. It should be pointed out that most of the nanochannels used in this study have a much larger width than the depth, and the EDL may only overlap in the depth direction of the nanochannels. Consequently, the EOF velocity is mainly dominated by the interaction between the modified channel surface and the bulk solution in the depth direction. Therefore, the depth is regarded as the effective size of the nanochannels. Theoretically, the EOF velocity should be independent to the channel size in large nanochannels without overlapped EDL and reduced to a relatively small value in small nanochannels with overlapped EDL. However, as shown in Figure 5, the EOF velocity shows a decreasing tendency when the channel depth decreases from 2.5 μm to 650 nm which is still larger than the required size for EDL overlapping. This is because the relative space occupied by EDL increases in the nanochannel when the channel size becomes smaller although the size does not reach the critical value of overlapped EDL. For example, for the case of 10^{-3} M KCl solution, the calculated Debye length is approximately 9.6 nm, and the thickness of EDL may be approximately 30 ~ 50 nm. The maximum EOF velocity can only occur in a narrower center region in a small nanochannel compared with that in larger channels, even without overlapped EDL. As a result, the average velocity of EOF through the small nanochannel reduces.

For the effects of the incubation time on EOF velocity, as shown in Figure 5, the EOF velocity initially increases rapidly when the incubation period increases from 1h to 6h and then increases only slightly as the incubation time increases from 6h to 24h. This is because

more DNA chains will attach on the PDMS surface in a longer incubation process and this would generate a relatively higher surface charge density on the channels surface, thus increasing the EOF velocity. However, as the active surface groups that can be bonded with the DNA chains are limited on a fixed channel wall surface area, the increase of the number of DNA chains attached on the channel surface will reach a limit with the further increase of the incubation time. Consequently, it is expected that the EOF velocity finally reaches a maximum value and keep constant with the continuing increase of the incubation time.

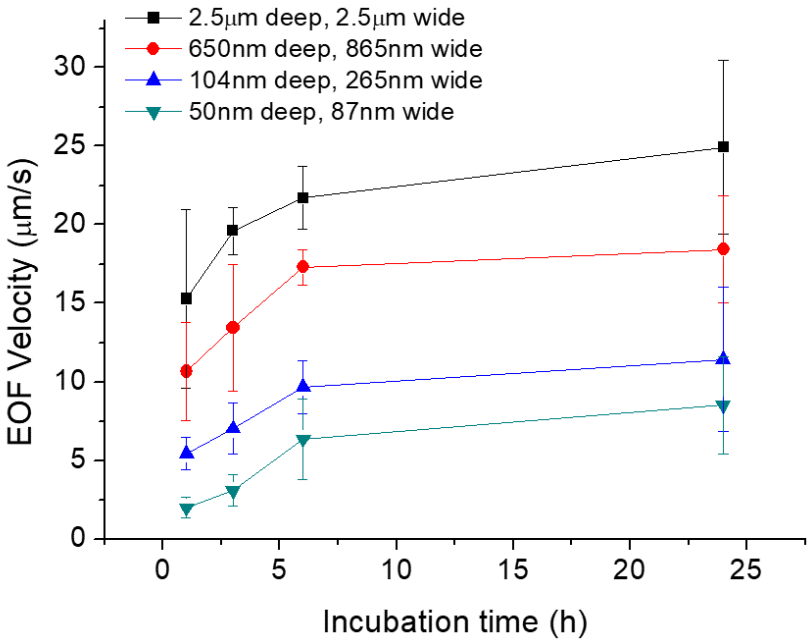

Figure 5. Measured EOF velocity as a function of the incubation time in ssDNA 15T modified nanochannels with size ranging from 50nm to 2.5μm. The applied electric field strength is 20V/cm. The solution used in the measurement is 10^{-3} M KCl at pH7.

3.3 Effects of the surface coating types

The properties of the grafted DNA layer on channel surface, such as surface charge, grafting density, and the thickness of the coated DNA layer, can critically affect the ion distribution in the EDL, thus influencing the distribution of EOF velocity in the modified channels[29]. In this work, the coated layer of DNAs is very thin (around 5nm), and the calculated thickness of EDL is 30~50nm for 10^{-3}M KCl solution used in this measurement[56,57]. Therefore, the EDL extends far beyond the coated layer, and the EOF depends mostly on the electric

properties of EDL[42]. However, these negative charges carried by DNA chains can increase the surface charge of the channel, thus resulting in large zeta potential and increasing the EOF velocity. To confirm the effects of surface modification with DNAs of 15T and 15A on EOF velocity, the nanochannels with depth ranging from 50nm to 2.5μm were modified by only the first chemical reaction step (EDC+NHS), two-step chemical reactions (EDC+NHS+15T), and duplex DNAs (EDC+NHS+15T+15A), respectively, by using the surface modification method described above. For comparison, the pristine channels are also prepared. All these channels were incubated with MES buffer solution at 4°C for 24h before using.

Figure 6 shows the experimentally measured EOF velocity of KCl solution with the ionic concentration of 10^{-3} M in modified nanochannels of different sizes. In comparison with the electroosmotic flow in pristine channels, the EOF velocity becomes smaller in all channels when the channel is modified only by the first chemical reaction step (EDC+NHS modification). In the 15T modified nanochannels, the EOF velocity shows a dramatic increase compared with that in the EDC+NHS modified nanochannels. Because the molecular groups carried by DNAs are negatively charged in solutions, and they will increase the surface charge when they are attached on the channel surface, thus increasing the zeta potential and leading to a larger EOF velocity. The largest EOF velocity occurs in the duplex ssDNA modified nanochannels. The ssDNA 15A will hybridize with the immobilized ssDNA 15T on the channel surface and form the dual-stranded structure. As both ssDNA 15T and ssDNA 15A are negatively charged in pH 7 KCl electrolyte solution, the channel surface charge will be further increased after the hybridization, thus increasing the zeta potential and EOF velocity[53].

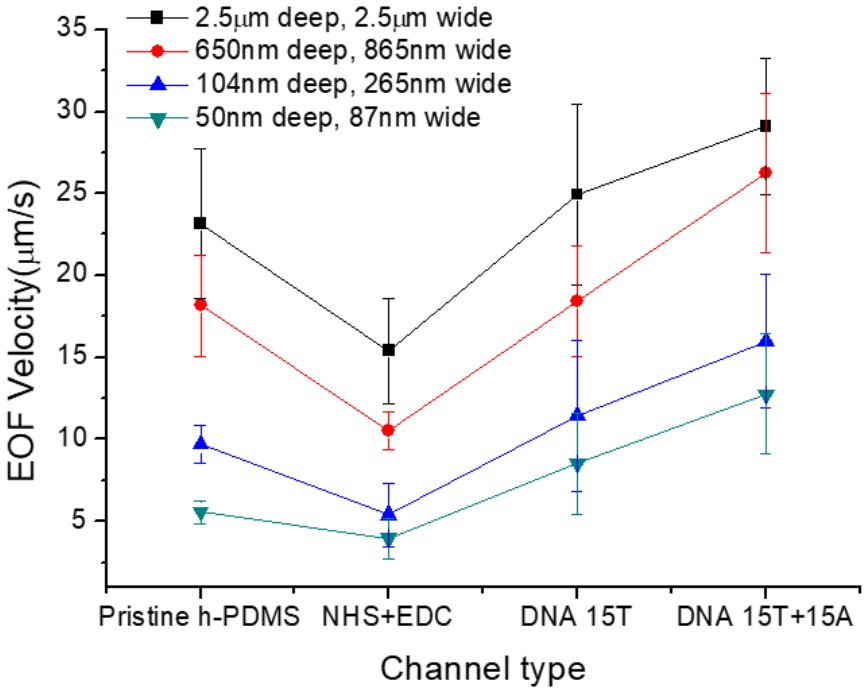

Figure 6. Experimental results of EOF velocity in nanochannels with different end-grafted layers. The applied electric field strength is 20V/cm. The solution used in the measurement is 10^{-3} M KCl solution at pH=7.

3.4 pH effects

Hydrogen ion plays an important role in determining the adsorption of metal cations on the channel surface, and its concentration influences the surface charge density and zeta potential on channel surfaces, thus influencing the electrokinetic transport in the channels[11,14]. In KCl solutions, the hydrogen ion is correlated to the pH value of the solution. In order to examine how pH value influences the EOF in 15T DNA modified nanochannels, the EOF velocity of 10^{-3} M KCl solution with pH value ranging from 4 to 10 were experimentally measured. In this work, all EOF measurement chips are incubated with MES buffer solution at 4°C for 24h before using. As a reference, the EOF velocity is also measured in a pristine h-PDMS channel which is also incubated with MES solution at 4°C for 24h before ready to use.

The measured EOF velocities of 10^{-3} M KCl solutions are shown in Figure 7. As can be seen from Figure 7 (a), the EOF velocity of 10^{-3} M KCl solution increases monotonously in the

unmodified h-PDMS channel when the pH increases from 4 to 10. However, in all ssDNA 15T modified channels, the EOF velocity of 10^{-3} M KCl solution only increases slightly when the pH rises from 5 to 10. The obvious change in EOF velocity can be observed only when the pH decreases from 5 to 4. These results indicate that the ssDNA 15T coated channels have a relatively stable surface charge when the pH of KCl electrolyte solution changes. For the pristine h-PDMS channels, the carboxyl groups and silanol groups will deprotonate when the concentration of hydrogen ions decreases, thus leading to a more negatively charged channel surface and larger EOF velocity. For the ssDNA 15T coated channels, the EOF velocity is also controlled by the DNA charge density when the coated DNA layer is engulfed by a thick EDL[35,58]. In the Manning theory, the fraction of the neutralized DNA charge is determined only by the valence of the counterions [35,59]. Consequently, for the 10^{-3} M KCl solution, pH effects on EOF velocity become less prominent in the ssDNA 15T modified channels.

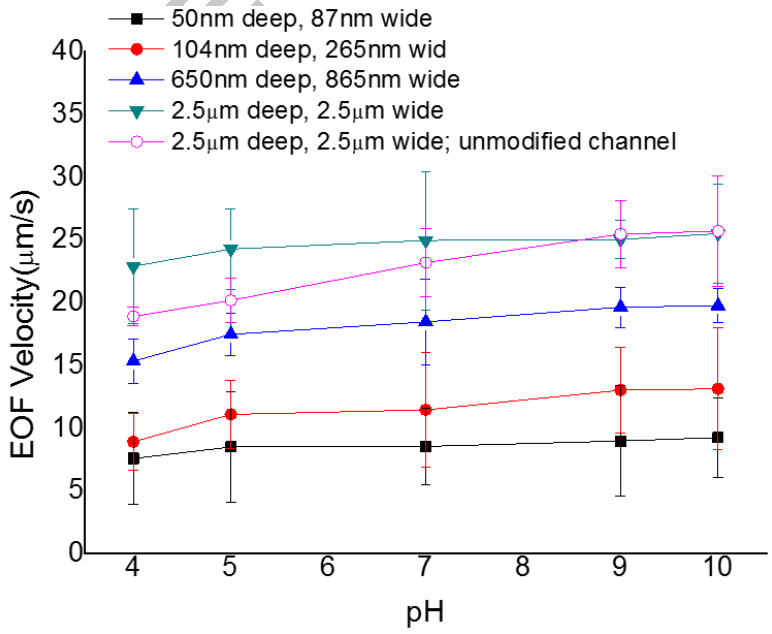

Figure 7. Measured EOF velocity as a function of the pH of 10^{-3} M KCl solution in DNA modified nanochannels with size ranging from 50nm to 2.5μm and an unmodified microchannel. The applied electric field strength is 20V/cm.

3.5 UV illumination effects

The UV illumination could induce more negative charges on DNAs and affect the zeta potential of the DNA coated channel surface[47,53]. Moreover, the change in zeta potential caused by UV illumination is reversible that the zeta potential will turn back to the original value after the irradiation with visible light. To investigate the UV light effects on EOF velocity in DNA modified channels, the EOF velocity of KCl solution is measured in the channels with UV illumination. As a reference, the EOF velocity is also measured in the pristine h-PDMS channels with UV light illumination. The concentration of KCl electrolyte used in the experimental is 10^{-3} M, and the calculated thickness of EDL is significantly larger than the coated DNA layer. Therefore, the EOF velocity mainly depends on the surface charge density. All measurement chips are incubated with MES buffer solution at 4°C for 24h before ready to use. The wavelength of UV light used in this experiment is 350nm.

Figure 8 shows the EOF velocities response to UV illumination. To simplify the figure, only the depth of the channels is plotted as the x-axis in the figure. For h-PDMS channels, exposing channels to UV light could produce carboxyl groups on the surface and influence the surface charge density and EOF velocity[60]. However, all channels used in this experiment have been pretreated with a plasma device in the process of chips bonding. Most charged molecular groups of the channel surface have been activated by the plasma treatment. According to Figure 8, the EOF velocity only increases slightly with the UV illumination compared that with visible light radiation in all pristine h-PDMS channels. These observations indicate the effects of UV illumination on EOF in the h-PDMS channels are inconspicuous. After ssDNA 15T coating, the negatively charged DNA brushes are grafted on the channel surface, and the surface charge density relates the negative charges carried by the DNAs. As UV illumination can affect the component and the surface charge of DNA, the EOF velocity should respond to the UV illumination in DNA modified channels as well. From Figure 8, in comparison with the case of pristine h-PDMS channels, it can be seen that the EOF velocity is increased significantly in the ssDNA 15T modified channels with UV illumination compared that with visible light radiation, and the increment of the EOF velocity

is larger than 20% in all size channels. The results show that the UV illumination could increase the surface charge of the ssDNA 15T and consequently increase the EOF velocity in the DNA modified channels.

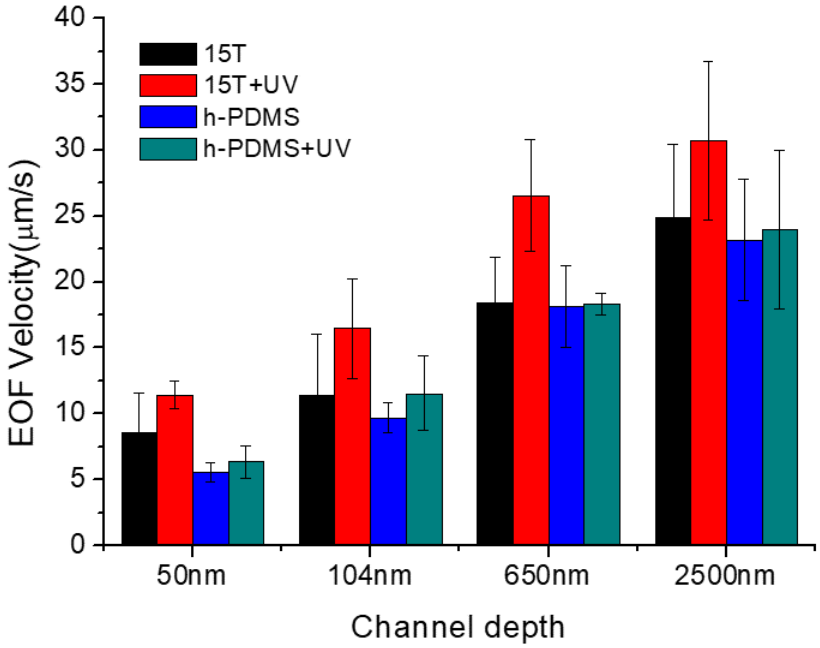

Figure 8. Measured EOF velocity response to UV illumination in pristine h-PDMS channels and ssDNA 15T modified h-PDMS channels. The applied electric field strength is 20V/cm. The solution used in the measurement is 10^{-3} M KCl solution at pH=7.

3.6 Concentration effects

Figure 9 shows the experimental results of ionic concentration effects on EOF velocity in the pristine h-PDMS channels and ssDNA 15T modified channels. The electrolyte solutions of KCl with concentrations ranging from 0.2 M to 10^{-3} M were used to study the concentration effects in these channels. For the case of the pristine h-PDMS channels, shown in Figure 9 (a), the EOF velocity decreases monotonically in the microchannel and the large nanochannel, because the zeta potential of the channel surface is inversely proportional to the ionic concentration [55]. In the small nanochannels with depth 104 nm and 50 nm, the EOF velocity increases initially while the ionic concentration increases from 10^{-3} M to 10^{-2} M, and then shows a decreasing trend as the ionic concentration increases further. This is because the

lower ionic concentration contributes to not only a higher zeta potential but also a larger thickness of EDL. For the 10^{-3} M KCl solution, the calculated EDL can reach 50nm. In the nanochannel with the depth of 104 nm, the EDL can extend almost to the whole channel. It is well-known that the electroosmotic flow field inside the electric double layer develops from zero velocity at the compact layer (immobile counter-ions adsorbed at the charged solid surface) to the maximum velocity at the outer boundary of the diffuse layer. For a channel with a relatively thick EDL, the maximum EOF velocity can occur only in a small portion of the space in the center of the channel. For such cases, the EOF velocity averaged over the channel cross section becomes much smaller although there is no overlapped EDL. When the EDL overlaps, the effective ionic concentration will be enhanced , contributing to a smaller zeta potential[12]. Therefore, in the 50nm channel, the EOF velocity is further reduced due to the effects of the strongly overlapped EDL. From the Figure 9 (a), the EOF velocities of the 0.1M and 0.2M solution are essentially same in all the channels, because the EDL is very thin at these high ionic concentrations, and the EDL effects on EOF velocity are negligible.

For the case of ssDNA 15T modified channels, the EOF velocity shows a similar trend to that in pristine h-PDMS channels at low ionic concentration. EOF velocity decreases in the large channels and increases in the small nanochannels when the ionic concentration increases from 10^{-3} M to 10^{-2} M. However, as the ionic concentration increases further, the EOF velocity increases firstly when the ionic concentration rises from 10^{-2} M to 0.1 M, and then decreases with the ionic concentration in all the channels. Similarly, the EOF velocities are essentially the same in all the channels when the ionic concentrations of KCl solution are larger than 0.1 M due to the EDL is very thin. Previous theoretical works showed that the impact of the charge density of the coated brush layer is weak at a low ionic concentration (thick EDL), whereas the EOF velocity is dominated by the brush regime at a high ionic concentration (thin EDL)[43,58,61]. The aggregation of counterions within the brush layer could affect their contribution to the overall EOF velocity. Furthermore, the length of ssDNA will dramatically decrease when the ionic concentration of the monovalent salt solution is

larger than 10^{-2} M [62]. This transformation in the structure of the coated DNA brushes could also influence the EOF velocity by changing the hydrodynamic screening of EOF[42].

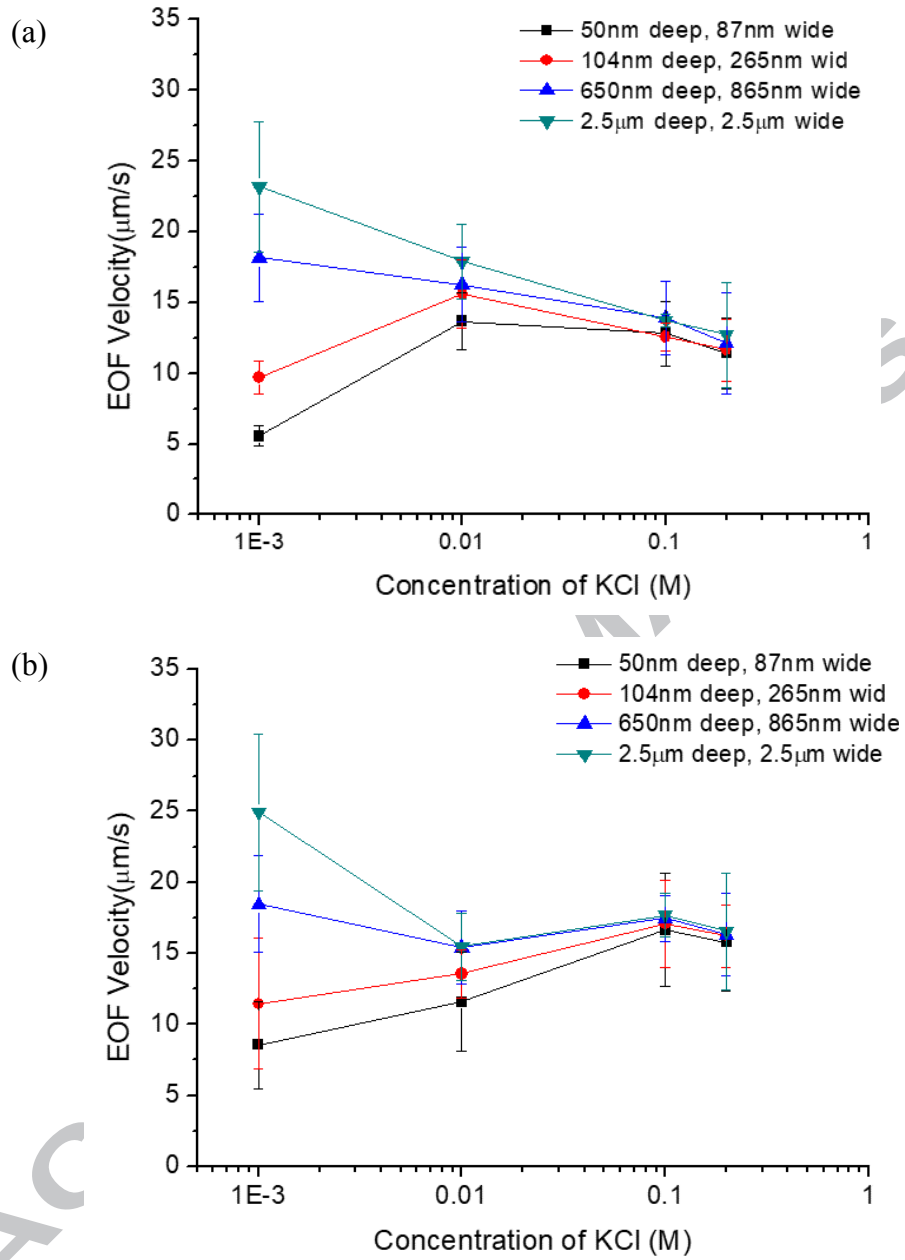

Figure 9. Measured EOF velocity as a function of the ionic concentration of KCl solution. (a) Measured EOF velocity in the unmodified h-PDMS channels. (b) Measured EOF velocity in ssDNA 15T modified h-PDMS channels. The applied electric field strength is 20V/cm.

4. Conclusions

This paper studies electroosmotic flow (EOF) in DNA modified channels with size ranging from 50nm to 2.5μm by using the current slope method. The influences of incubation time and type of DNAs on EOF velocity are investigated in the experiments. The EOF velocity of KCl electrolyte with various pH values and ionic concentrations are experimentally measured in the ssDNA 15T modified channels. The effect of UV illumination on EOF velocity are also tested in the DNAs modified channels and the pristine h-PMDS channels. In addition to the previous studies of EOF in PDMS nanochannels[11,14,55,63], this paper demonstrates different behaviors of EOF according to the changes in the environment of electrolyte solutions in DNA modified PDMS nanochannels. The surface coating with negatively charged DNAs can enhance the EOF in h-PDMS channels, and the EOF velocity is positively related to the grafting density of the coated DNAs. The pH effects on EOF velocity are less prominent in DNA modified channels compared with that in pristine PDMS channels. In contrast, the EOF velocity increases significantly in DNA modified channels with UV illumination whereas EOF velocity is essentially constant in normal channels. Ionic concentration influences EOF velocity in the DNA modified channels as well as the pristine channels. The EOF velocity is relatively smaller in small nanochannels than that in large channels at a low ionic concentration, and independent of the channel size at a high ionic concentration. However, different from the pristine channels, the EOF velocity becomes larger at the high ionic concentration of 0.1M that the thickness of EDL is similar to the length of coated DNA brushes. The experimental results presented in this paper offer improved understandings of the electrokinetic transport and provide a possible approach to effectively modulate EOF. Further, the functional groups can be anisotropically grafted on the channel surfaces, and the effects of the interactions between the grafted and pristine surfaces on EOF can be studied.

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Graphical abstract