

PIV Measurement for Electroosmotic Flow in SiO₂PDMS Surface Modified Microchannel

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Abstract

Electroosmotic is a flow created under the application of electric field on the fluid. Recently, PDMS exhibits great potential in microfluidic device for many applications. The less ability to support electroosmotic flow and flow instability with time are the phenomena associated with the fluid flow in PDMS microchannel. To improve fluid flow in PDMS, microchannel surface modified with SiO₂, different thicknesses, by PECVD was employed. Surface characterizations were carried out using atomic force microscope (AFM) and scanning electron microscopy (SEM). Whereby; UV-visible spectrometer and X-ray diffraction (XRD) were employed to identify optical properties and structural phase of the modified PDMS respectively. Particle image velocimetry (PIV) was used to track particles in PDMS microchannel, native and modified. We demonstrated that PDMS surface modified with SiO₂ slowing down fluid flow comparing to native PDMS allowing reaction and/or measurements taken place in microchannel. Fluid stability in PDMS, native and surface modified, were monitored via electrical resistance – time measurements with the aid of Cd²⁺ aqueous solution mixed with AuNP colloidal. SiO₂PDMS surface modified microchannel achieved stable time- fluid flow.

Keywords: PDMS surface modification, microfluidic, and Electrophoresis flow.

I. Introduction

Recently, Microfluidic devices have received considerable attention due to their wide applications in chemical and biochemical sensing. These devices offer many advantages such as reducing the sample size, reagent consumption, analysis time, and high-sensitivity [1].

Several materials were used to fabricate them as; silicon wafers (Si), glasses, and polymers. Polydimethylsiloxane (PDMS) has several advantages, such as elastomeric, biocompatibility, gas permeability, optical transparency, molding in submicrometer features, ease of bonding, relatively chemical inertness, and low cost those make it the most polymers used for microfluidic device [1]. Microfluidic devices were redesigned to allow bulk fluids and molecular species transportation in microchip electrokinetically (including both electro-osmosis and electrophoresis) upon the application of the electric field [2]. These electrokinetically driven microsystems can be easily integrated with a variety of separation and sample detection techniques [1]. Enhancing fluid spreading and staying over surfaces for a while to let reactions, mixing or the measurement taken place are one of the major microfluidic material requirements [3]. PDMS improvement was the main goal for several research groups. PDMS surface oxidizing using different methods as UV and plasma treatments [4]. Treatments will create weak bonds between oxidized PDMS surface and water molecules allowing fluids spreading over the surface. However, diffusion of low molecular weight chains from the bulk to surface results in PDMS originally hydrophobicity regains [5]. Shanker et

al referred this regains in PDMS surface oxygen plasma treatment to Si-

O group creation that has the ability to change to Si-OH group within three hours at ambient air [2]. Other groups have worked on PDMS surface modifications via thin film deposition, gold [6], titanium dioxide (TiO₂) [7], and SiO₂ layer [8,9]. To enhance the sustainability of PDMS surface hydrophobicity Dogheetal had deposited SiO₂ layer by atmospheric pressure plasma enhanced chemical vapor deposition. First, hydrocarbon layer was coated on PDMS surface using C₄H₈ as the reactant gas then a hydrophilic SiO_x layer was deposited using tetraethyl orthosilicate and oxygen (TEOS-O₂) [8]. SiO₂ layer was deposited also by another group via in-situ sol-gel modification to increase and stabilize electroosmotic flow in microchannel [9].

Recently, attention has been focused on studying and optimizing fluid's transportation in microchannel rather than just improving its surface hydrophobicity [10]. The studies focused on electro-osmosis flow (EOF) and its variables with time and measurement condition.

Different techniques have been used to study electro-osmosis flow (EOF) in microchannel. Current monitoring technique is an average velocity measurement of electroosmotic flow (EOF) by monitoring the electric current change with time [11]. Kahsal measured fluid flow in microchannel, fabricated with self-assembly hydrophilic particles, using optical imaging in

measuring marker's displacement between two buffers solutions [12]. Particle image transport was used to measure the large particles or cells' velocities through the rectification of the (AC) electro-osmotic flows in open microchannels [13].

Microparticle's image velocimetry (PIV) was also employed together with a current monitoring technique, to track particles and obtain electrokinetically bulk fluid flow velocity [1, 14]. Xueqin demonstrated that in low ionic strength solutions near neutral pH, oxidized PDMS had four-fold greater EOF mobility compared to native PDMS [2].

The aim of this work is to modify PDMS surface by deposition hydrophilic SiO₂ layer, deposited by plasma enhances chemical vapor deposition (PECVD) and studying its effect on electro-osmosis flow (EOF) in microchannel, species adsorption prevention, and elimination of PDMS surface hydrophobicity recovery. Amorphous Si interlayer was used to create a direct and stable bond with free Si-O- group that creates on DPMS surface by oxygen plasma treatment. The modified PDMS properties were evaluated by surface morphology, optical properties, and water contact angle measurement. The effect of PDMS surface modification on electrophoresis mobility was studied by particle's image velocimetry. The effect of inert SiO₂ layer on the absorption of Cd²⁺ in aqueous solution mixed with AuNP colloidal was demonstrated through electric resistance measurement's stability in microchannel.

II. Experimental work

2.1 PDMS Fabrication and surface modification by SiO₂

Sylgard® 184 oligomer and curing agent were thoroughly mixed at 10:1 mass ratio degassed for 30 min and poured over cleaned flat and patterned Si wafer. For electrophoresis measurements, photolithography was used to get Si wafer mold contain single straight micro-channel, 300 μm in width, 50 μm in depth and 4 cm in length. The poured PDMS was cured at 65°C for 180 min. Then master was kept overnight inside an oven maintained at 60°C. The cured PDMS layers were carefully peeled off from the wafers, flat PDMS were cut into the required dimensions. Flat and slabs with microchannel features PDMS were cleaned ultrasonically for 10 min with deionized water; ethanol and deionized water subsequently then dried using air flow.

PDMS, flat and patterned, were oxygen plasma treated using 124 watts RF power for 3 minutes. Within 30 minutes, treated PDMS were loaded in BMR, low temperature plasma enhance chemical vapor deposition machine (PECVD) to deposit 2 and 4 nm thickness amorphous silicon layers by applying 1000 watts RF power and using

H₂ and SiH₄ gases with flow rates of 50 and 25 sccm (Standard Cubic Centimeters per Minute) respectively. Hydrophilic SiO₂ thin films with 10, 20, and 30 nm thickness were deposited next step using 25, 10, and 7 sccm gas flow rates for O₂, Ar, and SiH₄ respectively maintaining the chamber pressure at 10 m Torr (milliTorr) and RF power at 1000 watt.

2.2 PDMS microchip's fabrication for electrophoretic and electric resistance measurements

For electrophoretic measurements, PDMS layer with microchannel, native or modified, and thin flat PDMS were sealed together to form PDMS microchip by clamping them between two PMMA sheets. To indicate species absorption via electric resistance stability a simple microchip was designed and fabricated as shown in Fig.1. That formed from two inlet reservoirs for Cd aqueous solution and AuNP (gold nanoparticles) colloidal, 10 cm length mixing microchannel perpendicular to 3 cm length measurement microchannel. Two reservoirs were used for Cu measurement electrodes. PDMS with microchannel features and thin flat PDMS, native or modified, were sealed together between two PMMA sheets. Cd²⁺ aqueous solution prepared from dissolution of cadmium acetate in distilled water, and AuNP colloidal were inlets into micro-channels under negative pressure driven at room temperature.

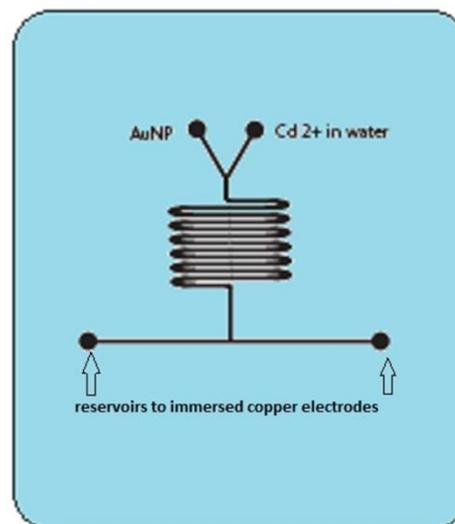


Figure 1. Sketch design for Microfluidic used to detect Cd²⁺ in water via electric resistance measurement.

2.3 Characterizations

Thin film crystalline structure, surface morphology, and roughness were identified by Rigaku Smart Lab X-ray Diffractometer, and PNI Nano-R AFM respectively. UV-Visible spectrometer from Shimadzu with wavelength range 190-850 nm

was employed to investigate changes in PDMS absorption spectrum.

It is well known hydrophilic changes determined through water contact angle (WCA), that can be measured by the angle formed between the solid and tangent to the drop surface. Average values from three measurements were considered for 10 μ l distilled water droplets volume. Water contact angles were analyzed using Lucia software.

2.4 Electroosmotic flow measurements

Initially, 20 μ m fluorescent polystyrene latex microspheres beads (from Polysciences Inc.) in distilled water were used to flow under driven pressure through fabricated PDMS microchips. DC potential values range (100-1000V) was applied on one reservoir while keeping another reservoir grounded. Particles velocities were measured with the aid of imaging using an optical microscope and fluorescence light. Electrophoresis mobility was calculated via beads migration through microchannel after 30 s of applying voltage. Fig. 2 illustrates beads tracking under applied potential.

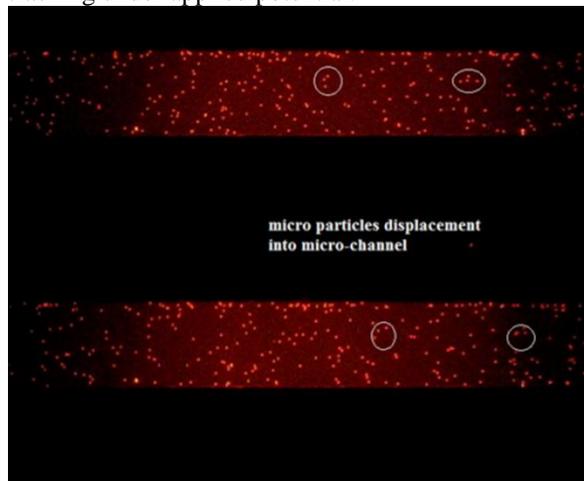


Figure 2: Image illustration for micro particles tracking into micro-channel

III. Results and discussions

3.1 Deposition layer appearance and Optical properties

PDMS with the SiO₂ deposition layers appeared glossier than native PDMS. SiO₂ deposited layer was flat and hard enough to resist scratching. Unless we hold PDMS samples on PMMA substrate during depositions and investigations, cracks were observed in SiO₂ surface layer under optical microscope Fig.3a, and under high resolution SEM, Fig. 3b. These cracks referred to; residual thermal stresses, which increases with film thickness, and to SiO₂ brittleness and its adhesion problems to PDMS. Niu referred brittle cracks in TiO₂ thin film coated

PDMS samples to flexibility and bending during handling [15], while Feng referred them to weak adhesion between gold as coating layer and PDMS surface [5].

The transmittance of the fabricated device is extremely crucial in monitoring fluid flow in micro-channels; hence the surface modification must not have a great impact on the device original transparency. The deposited SiO₂ thin films of different thickness had yellowish color. Fig. 4 shows native and coated PDMS transparence spectrums. PDMS is optically clear at a wide range of wavelengths, amorphous SiO₂ thin film absorb light in the visible region and reduce transparency.

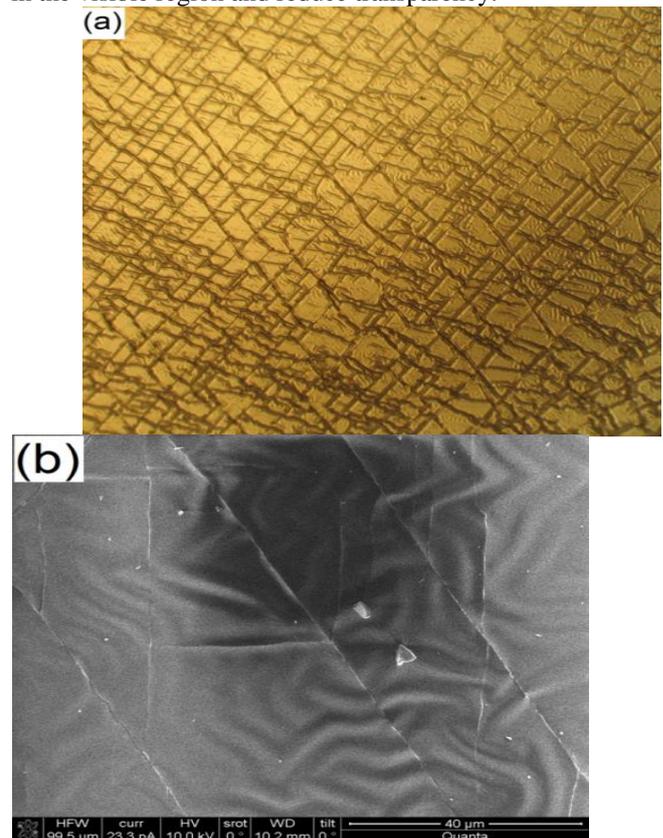


Figure 3: Modified PDMS surface images by a-optical microscope b- SEM

3.2 Surface morphology

Amorphous Si interlayer, via XRD results, affect surface morphology of the subsequent SiO₂ layer. In its early stage of nucleation amorphous Si formed islands that increased with thickness; these plays a very important role in determining the subsequent roughness evolution[16].Increasing Si interlayer thickness to 4 nm would increase the roots mean square (rms) roughness of SiO₂ surface (Table 1). Fig. 5 depicts the AFM images for surface morphology. We can indicate that SiO₂ surface morphology, with nano thickness, fellows amorphous Si under layer morphology.

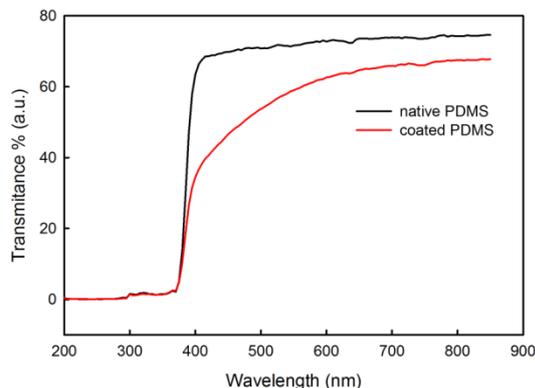
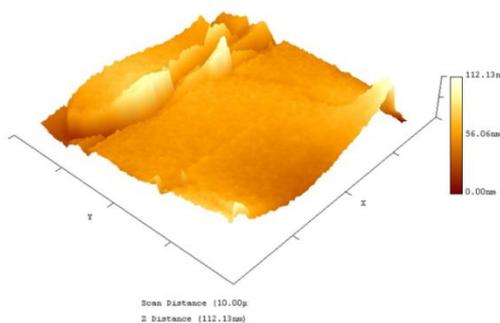


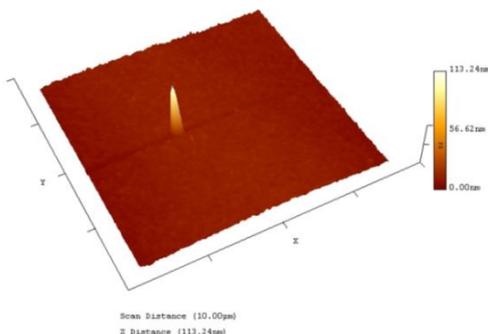
Figure 4: UV-Visible spectrum for native and modified PDMS

Table 1: Effect of the Si interlayer thickness on the roughness of SiO₂ modified PDMS surface.

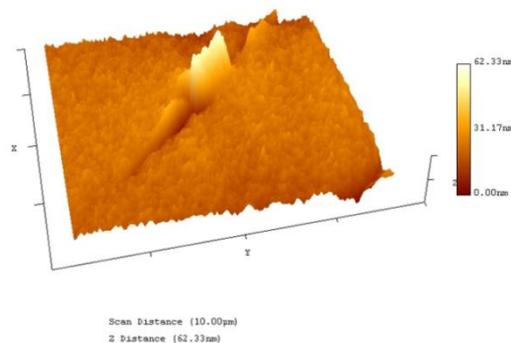
| Si thickness nm | SiO ₂ thickness nm | rms roughness nm |
|-----------------|-------------------------------|------------------|
| 2 | 10 | 1.511 |
| 2 | 20 | 1.610 |
| 2 | 30 | 1.544 |
| 4 | 10 | 3.129 |
| 4 | 20 | 3.702 |
| 4 | 30 | 4.37 |



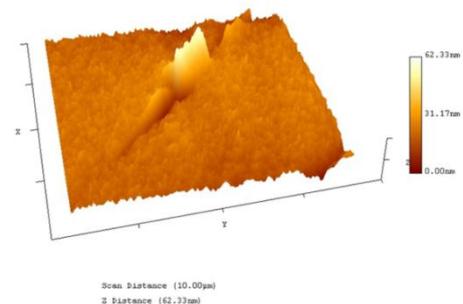
A



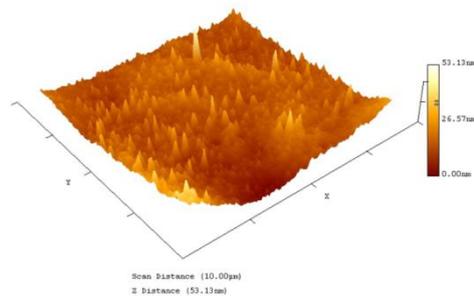
B



C



D



E

Figure 5: The AFM morphology images for the modified PDMS surface samples. (a) 2Si-10SiO₂ (b) 2Si-20SiO₂, (c) 4Si-10 SiO₂ (d) 4Si-20 SiO₂ (e) 4Si-30 SiO₂

3.3 Contact Angle and XRD

Surface wettability (or hydrophilic properties) has a great impact on fluid flow and bubbles formation in PDMS microchannels. Fig. 6 reveals WCA changes over the PDMS samples with time under atmospheric condition. The PDMS samples coated with SiO₂ films are more hydrophilic than the native one in contrary; they lost their hydrophobicity with time.

WCA of the native PDMS was 83° changed to 15-32° directly after SiO₂ deposition. After 3 hr. WCA began increasing to 50-67° within 7 hr and stayed stable for several days. Those results are in

good agreement with previous works. Maturos found that PDMS coated with titanium dioxide thin film before oxygen plasma treatment lost its hydrophobicity within 3 hr. [7]. PDMS hydrophobic recovery refers to the migration of uncured and highly mobile oligomers from the bulk to the surface changing Si-O- bond on the surface to Si-OH at room temperature [2]. No crystalline peaks were detected by XRD technique from SiO₂ deposited layers.

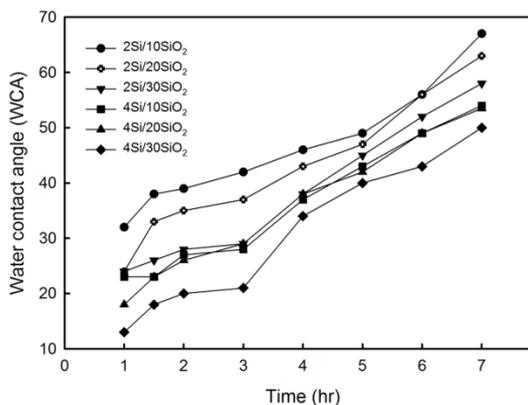


Figure 6 : WCA for modified PDMS surface

3.4 Electrophoreses flow in native PDMS microchannel

Introducing aqueous solution was difficult and bubble formation appeared during negative pressure driven flow in native PDMS microchannels. While electro osmotic flow (EOF) had non uniform beads velocities. This is due to poor surface charge and nonpolar hydrophobic species absorption in the surface [17]. Native PDMS composes of repeating group Si-CH₃, which does not expect to have a net surface charge [2]. Negative charged SiO⁻ groups create at PDMS-liquid interface when PDMS be in contact with moderate pH aqueous solution for a while [1]. These charged silanol groups attract cationic species from bulk liquid, repel anions and forming electrical double layer (EDL). The potential drop occurred across diffuse portion of EDL is defined as the zeta potential. When an external electric field applied parallel to EDL wall near zeta potential portion, it will exert force on the diffuse ions and moves them toward the cathode. While the uncharged bulk liquid, during electroosmotic flow, pumped by viscous interactions between EDL ions and the liquid [1] as illustrated in Fig.7. These would explain particles non uniform velocities in native PDMS microchannel with applied potential strength. Fig.8 shows particles velocities (in micron/sec) increasing with applied potential in native PDMS microchannel. Increasing applied potential subsequently will increased external electric field applied parallel to EDL wall near zeta potential

portion, that exert large force on the diffuse ions and increase their velocities toward the cathode.

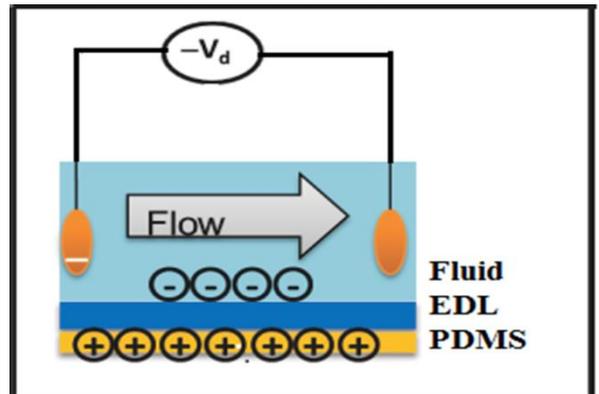


Figure7: Sketch illustrates EOF driving force into PDMS.

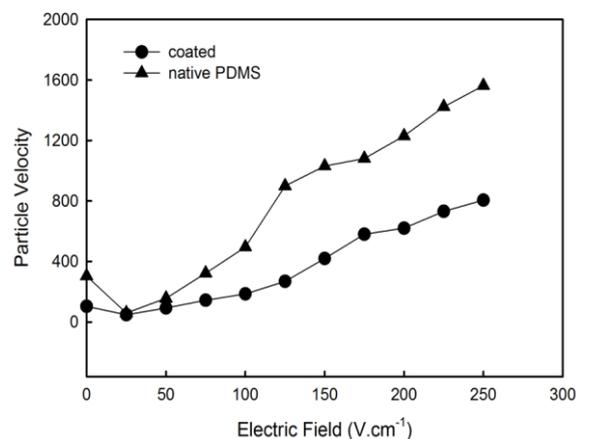


Figure8: PIV for native and modified PDMS surface microchannel

3.5 Electrophoresis flow in modified PDMS microchannel

Pressure driven flow in modified PDMS microchannel was without difficulties faced introducing aqueous solution, limitation in bubbles formation, stable fluid flow, and uniform beads velocities across microchannel.

The effect of PDMS surface modification on electrophoresis mobility was studied by particle's image velocimetry. As shown in Fig.9 microchannel constructed from PDMS modified with SiO₂ had lower beads velocities than native PDMS microchannel under different applied potentials strength and with various SiO₂ thicknesses used. It could be noticed also, beads velocities decreased with SiO₂ thicknesses. As well-known SiO₂ is inert and non-charged layer, so it presents a barrier prevents species absorption, eliminates EDL and zeta potential formation, and enhances stable EOF with uniform beads velocities across microchannel. Thus,

eliminates EDL and zeta potential formation would increase forces needed to move fluid ions and beads in it. That does explain particles slowing down velocities under the same applied potential condition into modified PDMS microchannel compared to native PDMS microchannel. In addition to that and as explained before SiO_2 on PDMS roughened microchannel surface, that is a common cause of premature breakdown and slowing down fluid stream over materials surface [18]. Moreover, SiO_2 surface film had cracks, observed clearly via optical microscope. These grooves in film surface exert as specious capturing regions, which slowing down them and elongate their staying time [19].

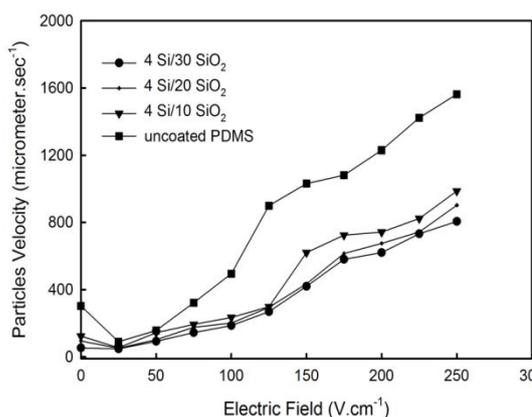


Figure9: The PIV for different SiO_2 thickness modified PDMS surface microchannel

3.6 Electric resistance of Cd+2 aqueous solutions mixed with AuNP colloidal in modified PDMS surface

Cadmium acetate aqueous solution classified as coordination polymer, featuring acetate ligands interconnecting cadmium centers. Its aqueous solution with AuNP colloidal mixture, prepared in our previous work [20], can exhibit water soluble conjugated conductive polyelectrolyte. Conductive polyelectrolyte phenomenon refers to carboxylate groups on AuNPs surface that bonded to Cd^{+2} owing to nanoparticles aggregating and networking [21]. This could be understood from the electric resistance measurements at modified PDMS microchannel that decreased with Cd ions in polyelectrolytes as shown in Fig.10 due to nanoparticles aggregating and networking increasing. Fig.11 shows polyelectrolytes electrical resistance with time in native and modified microchannel. Stable electric resistance observed at modified microchannel after 0.5 min compared to native microchannel. SiO_2 deposited layer gives evidence to prevent species absorption into PDMS surface and enhance getting stable fluid flow into microchannel fabricated from PDMS.

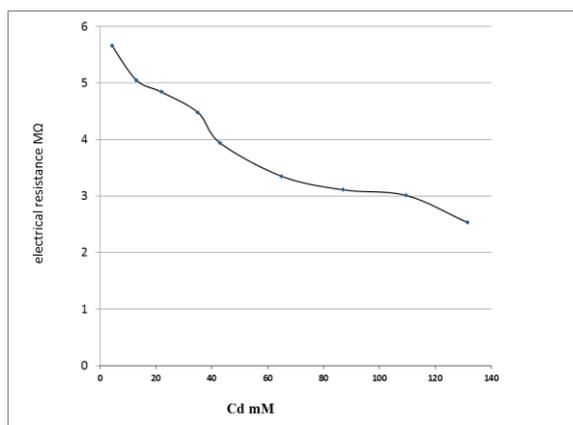


Figure10: The electric resistance for Cd aqueous solution and AuNP colloidal mixture at modified PDMS microchannel

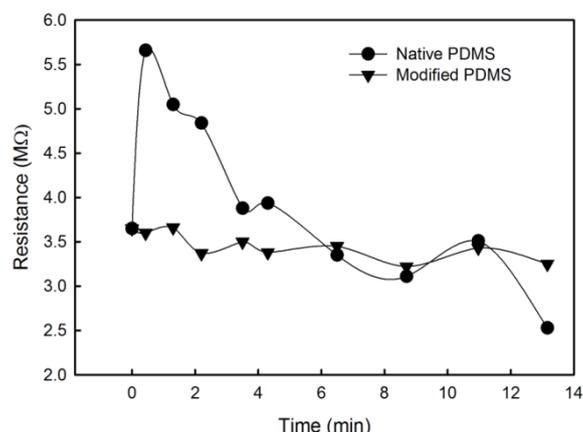


Figure11: The electric resistance stability with time at native and modified PDMS microchannel.

IV. Conclusions

In summary, we report in PDMS surface modification by deposition of SiO_2 in micro-channel. SiO_2 alters the PDMS optical and surface properties. PDMS new surface recovers part of its hydrophobicity after 7 hours and became stable for several days, increasing Si interlayer and SiO_2 thickness found to reduce surface lost hydrophobicity. Electrophoresis flow on modified and native PDMS were studied using the particles image velocimetry. Particles velocities in modified PDMS microchannels became more stable, slowing down to approximately its half value with SiO_2 thickness and electric field strength. SiO_2 deposition layer prevents species absorption into PDMS microchannel surface and enhance the solutions stabilities into microchannel.

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