A Low-Voltage Droplet Manipulation via Tunable Wetting on a Polypyrrole(DBS) Surface

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ABSTRACT

The electrowetting on dielectric (EWOD) technique has been used to manipulate microliter-sized individual droplets for microfluidic applications. However, EWOD-based techniques typically require relatively high actuation voltages (12-80V), which is undesirable for biomedical applications or applications including on-site operation. In this work, we studied a new mechanism of liquid droplet manipulation at low voltages (< 1.5 V) by utilizing tunable wetting on a dodecylbenzenesulfonate doped polypyrrole (PPy(DBS)) surface. In particular, manipulations of a liquid droplet on both a PPy(DBS) coated plate and in a microchannel configuration were studied. A quasi-lateral transport of the droplet in a slightly tilted microchannel has also been demonstrated.

Keywords: droplet manipulation, tunable wetting, polypyrrole, microfluidics

1 INTRODUCTION

Digital microfluidic systems, which manipulate individual droplets, have been developed in the past decade for biological and chemical applications [1]. The electrowetting on dielectric (EWOD) technique has been demonstrated for various manipulations of individual droplets, including transportation, mixing and separation [2]. However, an EWOD-based electrostatic actuation scheme typically requires high voltages (12-80V). The use of such high voltages potentially hampers the biological application and the portability for on-site operation. Although there are efforts to lower the voltages required for the electrowetting effect, the voltages are still in the range of tens of volts. Therefore, an alternative technique to realize a low-voltage droplet manipulation would be extremely beneficial.

Conjugated polymers have been considered as an alternative scheme to realize low-voltage droplet manipulation in digital microfluidic systems due to the tunable surface wetting. For example, dodecylbenzenesulfonate doped polypyrrole (PPy(DBS)) can change the surface wetting property upon reduction or oxidation when a low voltage is applied because of the re-orientation of the surfactant dopant molecules (DBS) in PPy. The surface state of PPy(DBS) can be switched from hydrophilic on reduced PPy(DBS) to hydrophobic on oxidized PPy(DBS) (Fig. 1) [3].

In this work, we studied the tunable wetting properties of a PPy(DBS) surface for the manipulation of liquid droplets including both on a plate and in a microchannel configuration. A controlled quasi-lateral transport of liquid droplet has also been demonstrated in a slightly tilted microchannel.

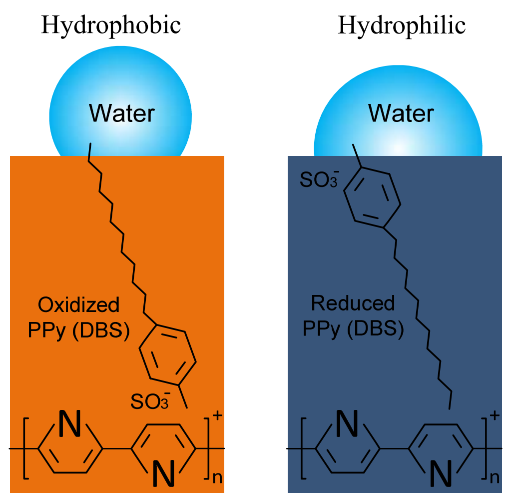

Figure 1: Wetting property of PPy(DBS) surface switches between hydrophobic and hydrophilic when applied a low voltage (< 1.5 V) due to the re-orientation of the surfactant dopant molecules in PPy(DBS) in redox process. Oxidized PPy(DBS) is hydrophobic and reduced PPy(DBS) is hydrophilic.

2 EXPERIMENTAL METHODS

The PPy(DBS) films were fabricated using an electropolymerization method. Specifically, a polished silicon/silicon dioxide wafer was first coated with Cr (10 nm) and Au (30 nm) by using e-beam evaporation (PVD 75, Kurt Lesker). The Cr/Au coated Si substrate was then submerged in an aqueous pyrrole solution consisting of 0.1 M pyrrole (Aldrich) and 0.1 M sodium dodecylbenzenesulfonate (NaDBS) (Aldrich) as a working electrode. A saturated calomel electrode (SCE) (Fisher Scientific Inc.) and a platinum mesh were also submerged in the solution as reference and counter electrodes. The deposition of PPy(DBS) on the Au surface was operated at 0.52 V versus SCE by using a potentiostat (263A, Princeton Applied Research, Oak Ridge, TN) [4].

The manipulation of droplets on the fabricated PPy(DBS) surface was first studied on a PPy(DBS) coated

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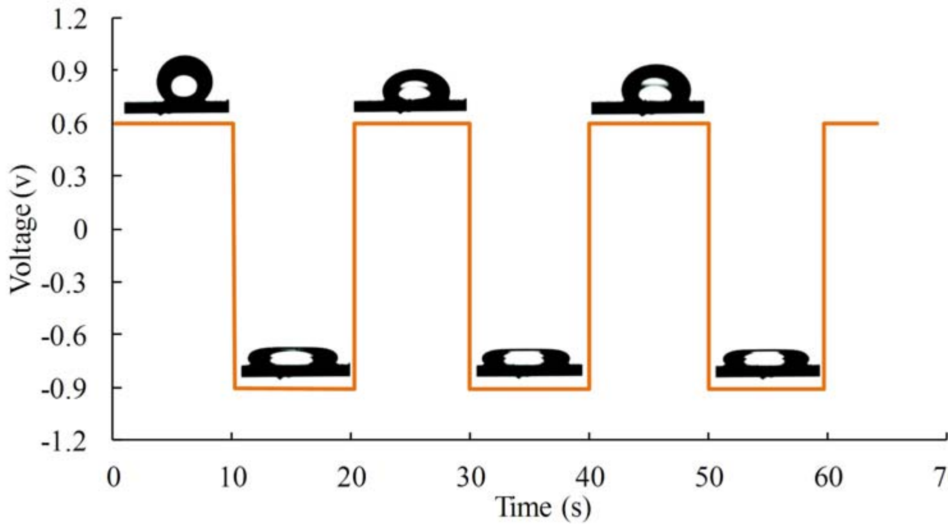

Figure 2: A dichloromethane (DCM) droplet dispersed on a PPy(DBS) substrate in 0.1M $NaNO_3$ aqueous solution. Square pulse potential (-0.9 to 0.6 V) was applied to the substrate for PPy(DBS) redox (Pulse length: 10 s). The DCM droplet was flattened to a disk-like shape while the PPy(DBS) was reduced, and changed back to a spherical shape while the PPy(DBS) returned to oxidized state.

plate upon continuous reduction and oxidation. A droplet of dichloromethane (DCM) was placed on a ~200 nm thick PPy(DBS) film-coated substrate in a 0.1 M $NaNO_3$ aqueous solution. The PPy(DBS) coated substrate was used as the working electrode. An SCE and a platinum mesh were connected as reference and counter electrodes, respectively. A square pulse potential was applied to the PPy(DBS) substrate to study the droplet actuation upon continuous reduction (-0.9 V vs SCE) and oxidation (+0.6 V vs SCE) reactions. The pulse length is 10 s. The manipulation of the droplet on the PPy(DBS) film was observed with a goniometer (Model 500, Rame-hart, Netcong, NJ) [4].

The manipulation of droplets in a microchannel configuration was then investigated. A PPy(DBS) coated substrate was used as the bottom plate and another Au coated silicon/silicon dioxide chip was used as the top plate. After the microchannel was immersed in a DCM environment, a 0.1 M $NaNO_3$ aqueous droplet (2~3 mL) was dispensed between the two plates. The applied potential was between -1.5 V and +0.6 V. The manipulation of droplets in the microchannel was first studied with a leveled stage, and then on a slightly tilted stage (4°) for quasi-lateral transportation of a droplet [5]. The same setup was used for the manipulation of droplets in the microchannel.

3 RESULTS AND DISCUSSION

3.1 Droplet Manipulation on Plate

Droplet manipulation on a plate was investigated in a continuous reduction and oxidization process. The PPy(DBS) was oxidized initially (+0.6 V vs SCE). When a reductive potential (-0.9 V vs SCE) was applied to the oxidized PPy(DBS) film, the spherical DCM droplet on the PPy(DBS) surface was flattened with a decrease of 65% in the height, as shown in Fig. 2. The contact diameter of the droplet with the substrate increased during the flattening. Upon the application of oxidative potentials, the droplet returned to a spherical shape. The dichloromethane (DCM) droplet on PPy(DBS) substrate continuously converted the profile between a spherical shape when PPy(DBS) was oxidized and a disk-like shape when PPy(DBS) was reduced in an aqueous electrolyte environment (0.1M $NaNO_3$).

The droplet deformation is related with the Marangoni stress. Specifically, when a reductive potential was applied to the PPy(DBS) surface, only the PPy(DBS) surface exposed to $NaNO_3$ aqueous solution was reduced while the PPy(DBS) surface underneath the DCM droplet remained oxidized. This is because the sodium ions, which are necessary for reduction of PPy(DBS), only existed in the $NaNO_3$ aqueous solution. Since the reduced PPy(DBS) surface has a higher surface tension than the oxidized PPy(DBS), the surface tension gradient across the droplet boundary induced Marangoni stress. The Marangoni stress caused the movement of liquid droplet from the region of low surface tension (oxidized PPy(DBS)) to the region of high surface tension (reduced PPy(DBS)), which was exhibited by the flattening of DCM droplet to a disk-like shape [4].

3.2 Droplet Manipulation in Microchannel

We also studied the low-voltage manipulation of an aqueous droplet in a microchannel via tunable wetting on PPy(DBS). The microchannel was configured with a PPy(DBS) coated bottom plate and an Au coated top plate, which was immersed in a DCM environment. A 0.1 M

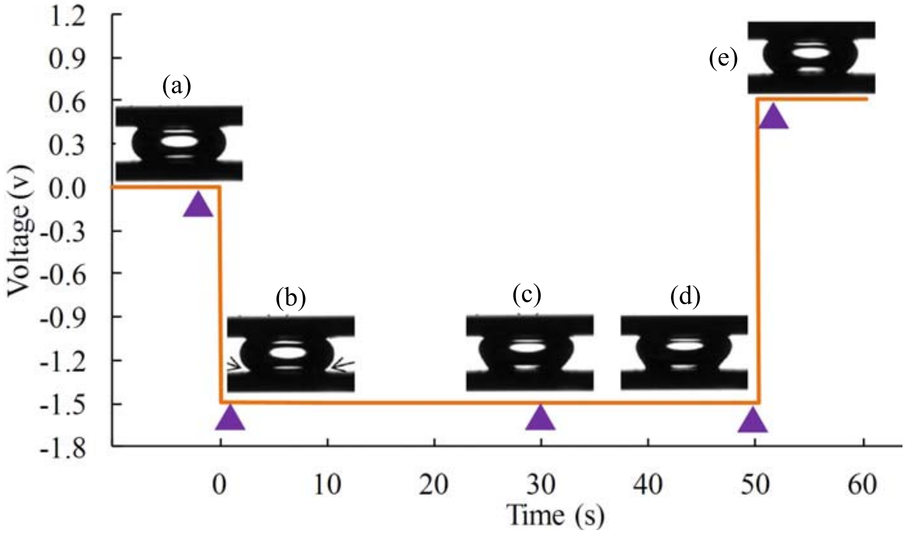

Figure 3: An aqueous droplet (0.1 M $NaNO_3$) in a microchannel within a DCM environment upon the application of a reductive potential (-1.5 V). (a) The aqueous droplet was initially in a symmetric shape in the microchannel. (b) When a reductive potential was applied, the droplet receded with a slight increase in contact angle. (c–d) The droplet was further deformed to a ''funnel'' shape upon the reductive potential. (e) The droplet reverted to its initial symmetric shape when an oxidative potential (+0.6 V) was applied.

$NaNO_3$ aqueous droplet, which was dispensed between the two plates, initially exhibited a symmetric disk-like shape, as shown in Fig. 3a. When a reductive potential (-1.5 V) was applied to the PPy(DBS) coated bottom plate, the aqueous droplet slightly receded immediately with an increase in contact angle (Fig. 3b). With the prolonged application of the reductive potential, the droplet further deformed to a "funnel" shape with a pinned contact line and a decrease of contact angle (Fig. 3c and d). The droplet reverted to its initial shape when an oxidative potential (+0.6 V) was applied again (Fig. 3e).

The initial droplet deformation in which the contact line receded with an increase of contact angle is also related with the Marangoni stress induced by the surface tension gradient between reduced and oxidized PPy(DBS) surface, as explained in the previous section. With the continuous application of reductive potential, sodium ions in the reduced PPy(DBS) surface underneath the $NaNO_3$ aqueous droplet diffused through the PPy(DBS) layer to the outside of the contact boundary of the droplet. As a result, the PPy(DBS) film in the region near the contact boundary of the droplet was reduced upon the reductive potential. Therefore, the contact angle of the aqueous droplet in DCM decreased during the prolonged reduction. Meanwhile, due to a strong pinning effect of the reduced PPy(DBS) surface on the aqueous droplet, the droplet was pushed up and formed a funnel shape [5].

3.3 Droplet Transport in Tilted Micro-channel

While the manipulations of droplets with symmetric deformation along the droplet boundary were demonstrated, we also studied the asymmetric deformation of droplet in a slightly tilted (4°) microchannel for a quasi-lateral transport of a droplet. As shown in Fig. 4, a square pulse potential (+0.6 V to -1.5 V) was applied to a tilted microchannel submerged in a DCM environment. The aqueous droplet was initially pinned on the oxidized PPy(DBS) surface with an asymmetric deformation on the uphill and downhill side, since the tilted angle (4°) was much less than the critical angle that the droplet needs to be moved by the buoyant force. Upon the application of a reductive potential (-1.5 V) to PPy(DBS), the droplet was deformed further with a significant increase of contact angle on the uphill side (Fig. 4b). The increase of contact angle is similar with the situation mentioned in Section 3.2 due to the Marangoni stress, but under the effect of a unidirectional buoyant force, the change of contact angle mainly happens on the uphill side. When the contact angle reached the advancing angle, the droplet moved uphill (Fig. 4b). After the droplet moved uphill slightly, it pinned for a short time due to the loss of surface tension gradient (i.e., Marangoni stress) at the contact boundary (Fig. 4c) and then deformed and moved again (Fig. 4d). The droplet stopped moving once the oxidative potential was applied. Therefore, controlled low-voltage aqueous droplet transport has been achieved by utilizing a reductive potential as a moving mechanism and an oxidative potential as a stopping mechanism [5].

3.4 Droplet Transport on Patterned PPy(DBS)

In the slightly tilted microchannel, we have demonstrated the quasi-lateral transport of a droplet. Currently, we are working on the transport of a liquid

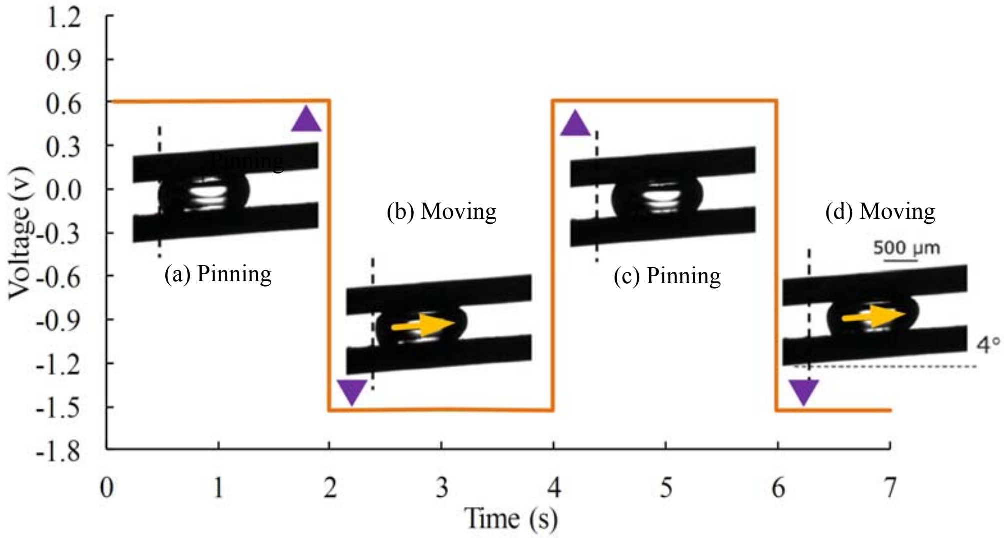

Figure 4: An aqueous droplet (0.1 M $NaNO_3$) in a tilted (4°) microchannel within a DCM environment upon the application of a square pulse potential (-1.5 V to 0.6 V, pulse: 2 s). The droplet moved uphill when a reductive potential (-1.5 V) was applied ((b) and (d)) and stopped when an oxidative potential (0.6 V) was applied ((a) and (c)).

droplet on patterned PPy(DBS) electrodes by individually controlling the surface wetting property of each PPy(DBS) electrode, towards digital microfluidics applications. For example, the patterned PPy(DBS) electrodes are initially set in the oxidized state by giving a positive potential. Upon application of a reductive potential to one electrode, the asymmetric surface wetting property between reduced and oxidized PPy(DBS) electrodes drives the liquid droplet to move following the electrode pattern, which will achieve a spatially controlled transportation of liquid droplets at a low voltage.

4 CONCLUSIONS

In summary, we have studied the tunable wetting on a PPy(DBS) surface and successfully demonstrated the applications for a low-voltage droplet manipulation and transportation. The reported mechanism will pave a new way for the development of future low-voltage digital microfluidics platform.

5 ACKNOWLEDGEMENT

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