

# WATER DROPLET MANIPULATION BY TUNABLE WETTING ON SMART POLYMER AT ULTRA-LOW VOLTAGES

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## ABSTRACT

In this paper, we report experimental results and analyses on the controlled manipulation of liquid droplets using local reduction and oxidation (redox) processes of conjugated polymers of dodecylbenzenesulfonate doped polypyrrole (PPy(DBS)). The electrochemically tunable wetting property of PPy(DBS) permitted the manipulation of an organic droplet of dichloromethane (DCM) at very low voltages ( $<0.6\text{V}$ ). Our experimental results illustrate that, upon the reduction of PPy(DBS), the surface tension gradient across the droplet contact line induced Marangoni stress and caused the deformation of droplets even at low voltages. We envision that the electrochemical redox process on smart polymers demonstrated in this work can open a new door to a low voltage manipulation of liquid droplets for digital microfluidic applications.

## KEYWORDS

Digital microfluidics, Droplet actuation, Tunable wetting, Conjugated polymers, Marangoni stress, Microchannel

## INTRODUCTION

For micro-scale fluid transportation, the control of interfacial energies becomes an important issue. The electro-wetting on dielectric (EWOD) technique has been shown to manipulate individual droplets on dielectric surfaces [1]. EWOD requires relatively high actuation voltages (12-80V), which may hamper its compatibility with biomedical applications as well as device portability for direct field applications [2]. Therefore, investigation of an alternative mechanism operational with lower actuation voltages (e.g.,  $\sim 1.5\text{V}$  obtainable by a standard battery) would be extremely beneficial. Manipulation of an organic droplet at ultra-low voltages using a switchable wetting surface has been demonstrated and analyzed in the previous research[3]. To extend the capability of the proposed actuation mechanism for practical applications[4-6], investigations were performed to study the manipulation of an aqueous droplet upon reduction and oxidation reactions (redox) of conjugated polymers. Herein, we demonstrate a novel tunable wetting mechanism using a smart polymer – dodecylbenzenesulfonate-doped polypyrrole (PPy(DBS)) – for manipulating liquid droplets at ultra-low-voltages ( $<0.6\text{V}$ ) towards advanced digital microfluidics.

## EXPERIMENT

The PPy(DBS) substrate was prepared by the electrochemistry approach [3]. In this study, we tested the manipulation of a droplet of salt water surrounded by an immiscible organic fluid, bulk dichloromethane (DCM,  $\text{CH}_2\text{Cl}_2$ ), and successfully demonstrated movement of the droplet in a tilted PPy(DBS) microchannel configuration. The microchannel assembly was set in DCM solution for continuous redox processes (**Figure 1**). To manipulate an aqueous droplet, the PPy(DBS) substrate was set as a working electrode and the top Au electrode was assigned as a counter electrode. The 263A potentiostat was programmed with pulse potentials controlled by the PowerSuite software (Princeton Applied Research).

## RESULT AND DISCUSSION

The surface state of PPy(DBS) can be ‘tuned’ via re-orientation of its surfactant dopant molecules, dodecylbenzenesulfonate (DBS) [7], as shown in **Figure 2**, with applied voltages of  $-1.5\sim 0.6\text{V}$ . **Figure 3** illustrates the droplet behaviors on the leveled (non-tilted) stage. Initially, the PPy(DBS) surface remains oxidized (**Figure 3a**). For a complete reduction of PPy(DBS) film, sodium ions ( $\text{Na}^+$ ) in the liquid need to move into the PPy(DBS) for charge neutralization [8]. When a salt water droplet is dispensed on the PPy(DBS) surface, sodium ions would be available only on the area covered by the droplet. Therefore, the PPy(DBS) surface underneath the droplet would be fed by sodium ions from salt water when the reductive potential is applied. On the other hand, the PPy(DBS) surface exposed to DCM remains oxidized, since no such ions would be available on the area outside the salt water droplet. This selective supply of sodium ions creates dissimilar surface states across the droplet contact line as shown in **Figure 3b**. The surface tension gradient, i.e., the Marangoni stress causes the liquid to flow away from regions of low surface tension towards regions of high surface tension. Since oxidized PPy(DBS) possesses lower surface energy than reduced PPy(DBS) [3], the induced Marangoni stress drives the contact line inward (i.e. from oxidized PPy(DBS) to reduced PPy(DBS) surface). The contact angle of the droplet is increased from  $\theta_{wo}$  to  $\theta_{wo}'$  due to mass conservation. Controlling the contact angle via the Marangoni effect is the basis of our droplet manipulation concept, and has not been employed or engineered elsewhere for digital microfluidics.

While the deformation of an aqueous droplet can be manipulated in a leveled microchannel via the low-voltage redox process of PPy(DBS), additional force, e.g. unidirectional buoyant force, is introduced to the droplet for lateral manipulation. **Figure 4** shows the case of a droplet ( $0.1\text{M NaNO}_3$ ) on a tilted stage, which settles the droplet at an “unbalanced” condition. The voltages of  $0.6\text{V}$  and  $-1.5\text{V}$  were chosen as oxidative and reductive potentials,

respectively. With a reductive potential, the droplet started moving to the right side (**Figure 4b, 4c**), while the droplet was in a stable state with an oxidative potential (**Figure 4d**). As explained in **Figure 3**, the application of a reductive potential increases the contact angle in the uphill side up to its advancing contact angle, which reduces surface friction, causing the droplet to move to the right by the upward buoyant force (**Figures 4b, 4c and 4e**). With an oxidative potential, the droplet is in a stable state, since the induced surface tension gradient has disappeared (**Figures 4a and 4d**).

Based on the results obtained in this work, we are currently working on demonstrating controlled manipulation (i.e. cut, transport, merge) of liquid droplets on the PPy(DBS) surface with underlying patterned electrode arrays (**Figure 5**).

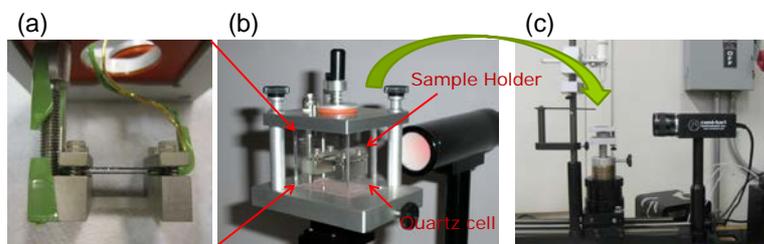


Figure 1: (a) Stage for the microchannel configuration. (b) Custom-designed sample holder for droplet manipulation. (c) Goniometer with video recording capability is equipped with an auto-dispensing system and a temperature/humidity control chamber.

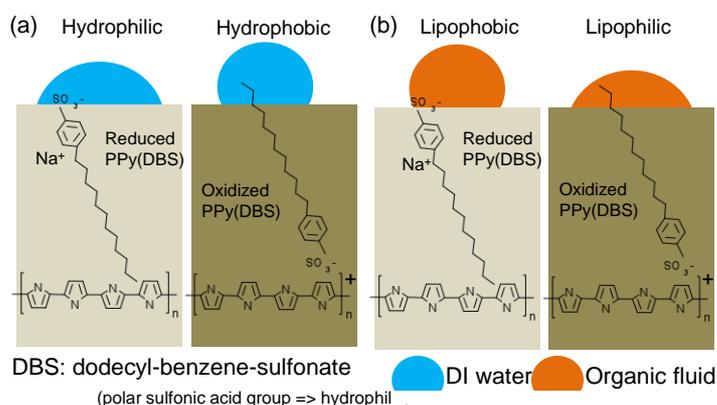


Figure 2: Surface state of PPy(DBS) switched between hydrophilic and hydrophobic (or between lipophobic and lipophilic). (a) Oxidation of the PPy(DBS) film increases the contact angle of a water droplet (hydrophobic). (b) The contact angle of an organic fluid droplet is decreased on oxidized PPy(DBS) surface (lipophobic). The key idea in this work is to utilize the tunable electrochemical reactions of PPy(DBS), whose surface wetting properties can be reversibly controlled in situ.

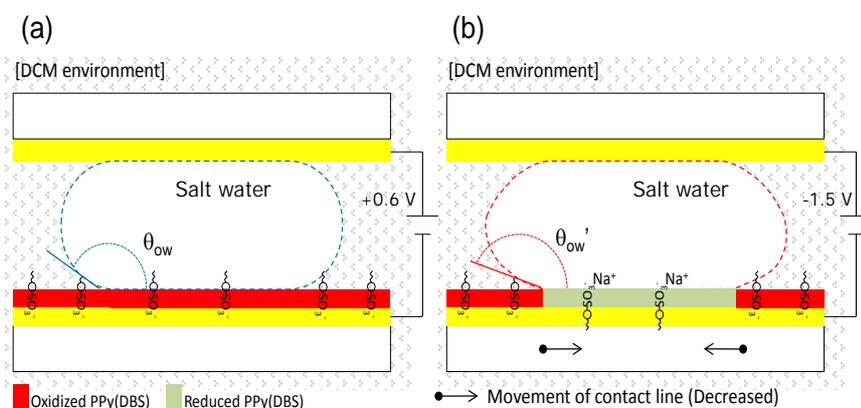


Figure 3: Droplet manipulation mechanism: (a) a 0.1 M  $\text{NaNO}_3$  aqueous droplet placed between the top electrode and PPy(DBS) (microchannel configuration); (b) When a reductive potential is applied on the PPy(DBS) substrate, the contact line moves inward due to induced Marangoni stress. The droplet contact angle is then increased as the contact radius is decreased.  $\theta_{ow}$  is the contact angles of a 0.1M  $\text{NaNO}_3$  droplet on the oxidized PPy(DBS) ( $\theta_{ow}'$  on the reduced PPy(DBS)).

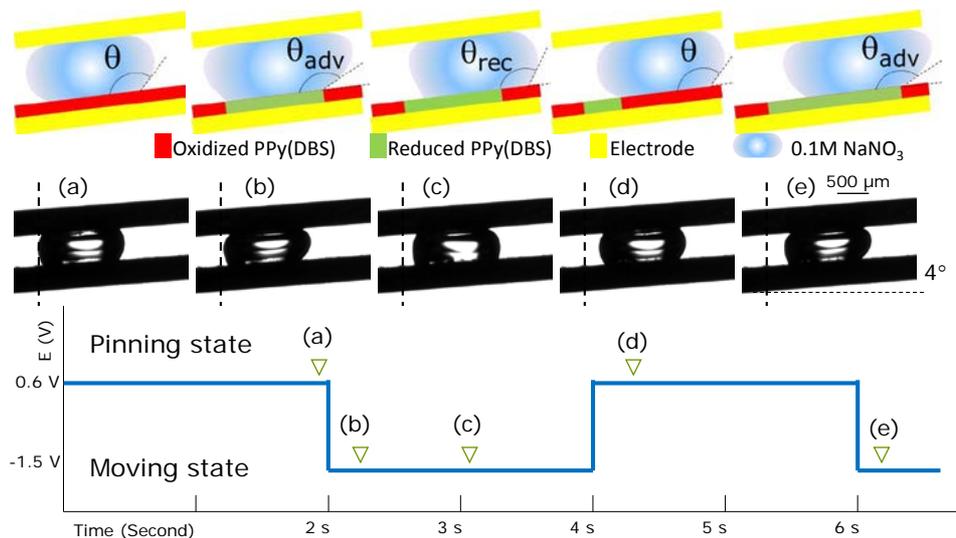


Figure 4: (Top) Lateral transportation of a salt water droplet on a tilted PPy(DBS) surface upon redox. ( $\theta$ : static contact angle;  $\theta_{adv}$ : advancing angle;  $\theta_{rec}$ : receding angle); (Center) Captured images of an aqueous droplet dispensed between parallel plates within DCM environment with a square pulse potential. The stage is tilted by 4°. This angle is much smaller than the angle required to moving the droplet solely by buoyant force (approximately 25°); (Bottom) Elapsed timeframe vs. square pulse potential.

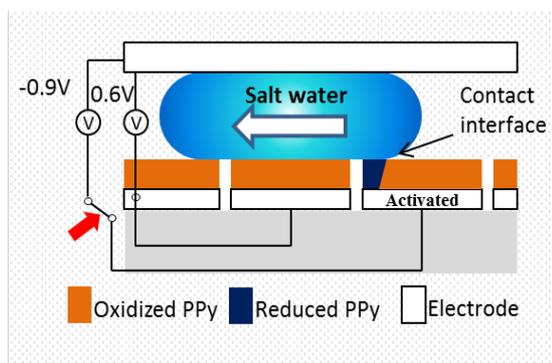


Figure 5: Conceptual schematic of a single operation unit (side view): Upon application of a reductive potential to an electrode, the induced Marangoni stress drives the contact line on the reduced PPy(DBS) surface to the left. The resulting asymmetric deformation of droplet establishes a pressure difference inside liquid, giving a rise to the droplet movement to the left (away from the activated electrode).

## CONTACT

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