

Droplet Actuation in PPy Redox Process

Yao-Tsan Tsai, Chang-Hwan Choi and Eui-Hyeok Yang

Department of Mechanical Engineering, Stevens Institute of Technology

Castle Point on Hudson, Hoboken, NJ 07030

ytsai@stevens.edu; ph: +1-201-216-8213; fx: +1-201-216-8315

ABSTRACT

This paper presents a reversible manipulation of a dichloromethane (DCM) droplet at low voltages. The mechanism is governed by the reduction-oxidation reaction (redox) of dodecylbenzenesulfonate-doped polypyrrole (PPy) film. The voltages ranging from -0.9V to 0.6V (vs. Ag/AgCl reference) was applied to PPy film to change its reduction and oxidation states to control the shape of DCM droplet. The redox reaction was performed *in-situ*, and the manipulation of a DCM droplet was monitored using a goniometer. The experimental result in this work shows that the DCM droplet spreads out without an observable change of contact angle, which disagrees with the typical wetting behavior of a liquid droplet,

Keywords: polypyrrole, wettability, redox

1 INTRODUCTION

Fluid transportation is a basic operation within microfluidic devices [1, 2]. Several techniques have been reported to manipulate fluids, including capillary force, pressure, electro-osmosis, dielectrophoresis, and electrowetting on dielectric (EWOD) [3-6]. Among those techniques, EWOD is uniquely based on the operation of discrete droplets, allowing digital-microfluidics. EWOD typically requires 40-80V to manipulate liquid droplets [7-12]. While enormous effort has been devoted to investigating and lowering the driving voltage required for EWOD [13-16], it is still in the range of tens of volts, which is not practical for portable devices requiring standard batteries (e.g., 1.5V lithium AA). Here, we report on the preliminary results on a tunable wetting of conjugated polymers as a novel interlayer material at low voltages (-0.9V to 0.6V).

Conjugated polymers experience a change in their mechanical and electrical properties when “doped” (i.e., undergo a reduction and oxidization process) [17-19]. PPy exhibits a shift in surface energy under reduction or oxidation, whereby the surface state can be switched from hydrophilic to hydrophobic due to re-orientation of its surfactant dopant molecules, dodecylbenzenesulfonate (DBS) [20-22]. The surface wettability of a PPy layer is changed under electrochemical reduction and oxidation at -1~1V. Halldorsson et al. have recently demonstrated that droplet transport of an organic fluid can be realized by the

redox of a PPy coated on Pt mesh [23]. In this paper, we demonstrate the manipulation of a DCM droplet on the PPy fabricated on a silicon substrate, since it can leverage the tenability of the PPy surfaces to integrate into the silicon-based micro-electro-mechanical systems (MEMS), such as for lab-on-a-chip applications.

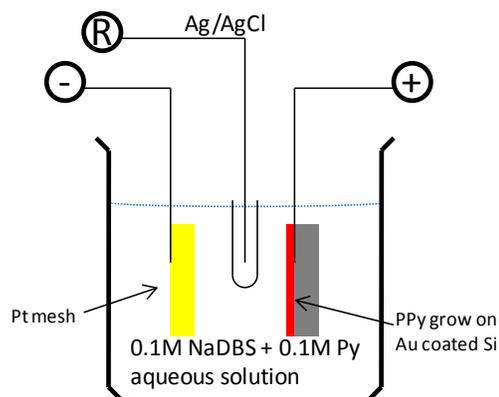


Figure 1: Electrochemical cell setup for polymerization of polypyrrole (PPy) in an aqueous solution.

2 FABRICATION AND CHARACTERIZATION

Polypyrrole was electropolymerized from aqueous monomer pyrrole solution. An Au/Cr coated Si wafer was submerged in a freshly prepared pyrrole aqueous solution consisting of 0.1M pyrrole and 0.1M sodium dodecylbenzenesulfonate (NaDBS). The substrate was set as a working electrode (Figure 1). A calomel reference electrode (Fisher Scientific Inc.) and a platinum mesh were configured as reference and counter electrodes, respectively. A 263A potentiostat (Princeton Applied Research, Oak Ridge, TN) was used to potentiostatically deposit PPy at 0.52V. Thickness of PPy film was precisely controlled by adjusting the amount of applied charge, which was confirmed using a profilometer. In general, a 1C/cm² surface charge can produce a 3 μm thick PPy film. After polymerization, the PPy coated substrate was rinsed with de-ionized (DI) water and dried with nitrogen.

Figure 2 depicts a cyclic voltammogram, showing the potentiodynamic deposition of PPy in 0.1M pyrrole and 0.1M NaDBS aqueous solution. PPy film was polymerized when the potential reached 0.52V (vs. Ag/AgCl).

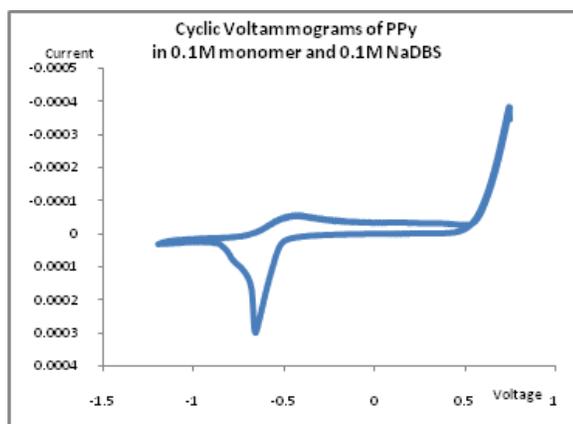


Figure 2: A cyclic voltammogram shows the potentiodynamic deposition of PPy in 0.1M pyrrole and 0.1M NaDBS aqueous solution. (Scan rate: 100 mVs⁻¹)

3 RESULTS AND DISCUSSION

A 200 nm planar PPy substrate was placed in a rectangular flask with 0.1M aqueous NaNO₃. A calomel reference electrode and a platinum mesh were connected as reference and counter electrode, respectively (Figure 3). A DCM droplet (~7 μL) was dispensed on the PPy film using a syringe. The potential between +0.6V to -0.9V was applied via the working electrode using a 263A potentiostat (pulse duration: 10 seconds).

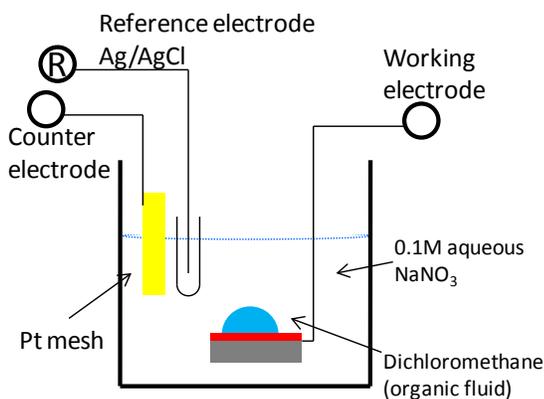


Figure 3: Electrochemical cell configuration for contact angle measurement.

The deformation and the contact angle change of the liquid droplet were observed using a goniometer (Ramehart Model 500) with video recording capability. Figure 4a shows a DCM droplet on the oxidized PPy surface, i.e. applied with +0.6V vs Ag/AgCl. The contact angle of DCM droplet on the oxidized state PPy film presents 120° within 0.1M NaNO₃ aqueous solution.

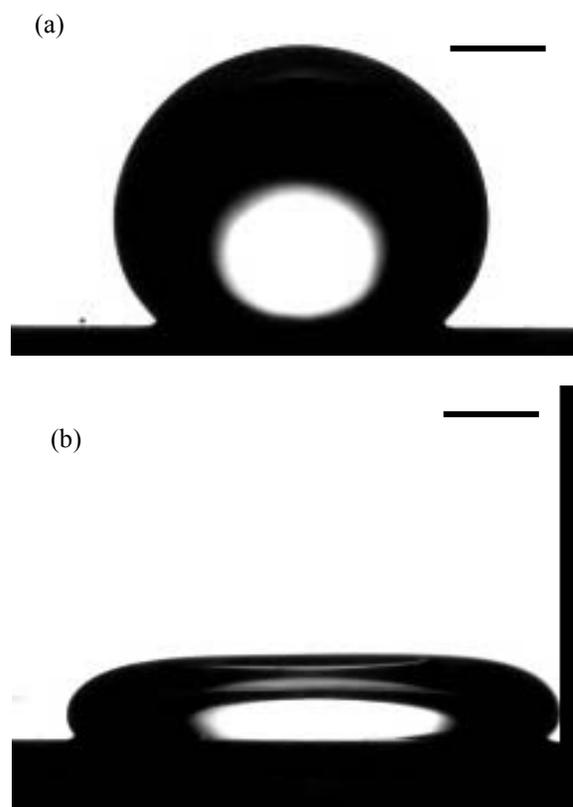


Figure 4: Deformation of a DCM droplet in PPy(DBS) redox processes in 0.1M NaSO₃ aqueous solution. (a) Oxidized state (+0.6V vs. Ag/AgCl); (b) Reduced state (-0.9V vs. Ag/AgCl). The scale bar in each image is 0.5 mm.

While -0.9V (vs. Ag/AgCl) was applied via the working electrode, PPy was switched to a reduced state. Sodium ions enter the polymer for charge neutrality, since the DBS⁻ molecules are immobile in the PPy [24]. The sulfonic acid in DBS⁻ group is oriented toward surface and reduced surface wettability for DCM [25]. Thus, the contact angle of an organic fluid (DCM) on the reduced PPy film is supposed to increase further when it is reduced. However, in our experiments, the DCM droplet did not show an observable amount of contact angle change (Figure 4b). On the contrary to the expectation that the droplet would build up with an increase of a contact angle due to the reduced wettability of the DCM on the reduced PPy state, it spread out with little change of the contact angle. Our speculation is in the following: The contact angle would initially increase at very short interval. However, due to the significant pinning effect at the contact line, the droplet could not recede. Meanwhile, to maintain the same volume of the droplet with the sudden increase of the contact angle, the droplet should be suppressed to be thinner. Then, the suppressed droplet would exert a compressive force for the droplet to spread out. Further work is underway to

investigate the detail mechanism of the droplet behavior and transport.

4 CONCLUSION

In this study, we demonstrated the manipulation of a DCM droplet on a PPy surface deposited on silicon substrates in 0.1M aqueous NaNO₃ at low voltages (from +0.6V to -0.9V). The cyclic actuation of the DCM droplet was successfully achieved at the low voltages. On the contrary to the conventional understanding of the droplet actuation due to the Laplace pressure induced by a large contact angle change, current experimental results suggest that the contact line pinning effects should play an important role and the droplet actuation would be caused by the compressive force induced by the droplet deformation according to the mass conservation law. Further detailed studies are necessary to verify the precise chemical and physical mechanism of the droplet actuation on the PPy surface in redox processes.

ACKNOWLEDGEMENTS

This research has been partially supported by the Air Force Office for Scientific Research (Award No. FA9550-08-1-0134). In addition, this research has been carried out in part at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

REFERENCES

- [1] A. Mohamed, and R. W. Aaron, "The Digital Revolution: A New Paradigm for Microfluidics," *Advanced Materials*, 21(8), 920-925 (2009).
- [2] H. Stefan, and Z. Roland, "Microfluidic platforms for lab-on-a-chip applications," *Lab on a Chip - Miniaturisation for Chemistry and Biology*, 7(9), 1094-1110 (2007).
- [3] H. A. Stone, A. D. Stroock, and A. Ajdari, [Engineering flows in small devices: Microfluidics toward a lab-on-a-chip], (2004).
- [4] R. Daw, and J. Finkelstein, "Lab on a chip," *Nature*, 442(7101), 367-367 (2006).
- [5] T. M. Squires, and S. R. Quake, "Microfluidics: Fluid physics at the nanoliter scale," *Reviews of Modern Physics*, 77(3), 977-1026 (2005).
- [6] G. M. Whitesides, "The origins and the future of microfluidics," *Nature*, 442(7101), 368-373 (2006).
- [7] S. Y. Teh, R. Lin, L. H. Hung *et al.*, "Droplet microfluidics," *Lab Chip*, 8(2), 198 (2008).
- [8] C. Quilliet, and B. Berge, "Electrowetting: A recent outbreak," *Current Opinion in Colloid and Interface Science*, 6(1), 34-39 (2001).
- [9] F. Mugele, and J. C. Baret, "Electrowetting: From basics to applications," *Journal of Physics Condensed Matter*, 17(28), R705-R774 (2005).
- [10] J. Lienemann, A. Greiner, and J. G. Korvink, "Modeling, simulation, and optimization of electrowetting," *IEEE Transactions on Computer-Aided Design of Integrated Circuits and Systems*, 25(2), 234-247 (2006).
- [11] J. S. Gaurav, T. O. Aaron, P. Y. C. Eric *et al.*, "EWOD-driven droplet microfluidic device integrated with optoelectronic tweezers as an automated platform for cellular isolation and analysis," *Lab on a Chip - Miniaturisation for Chemistry and Biology*, 9(12), 1732-1739 (2009).
- [12] A. A. Darhuber, and S. M. Troian, [Principles of microfluidic actuation by modulation of surface stresses], (2005).
- [13] J. Berthier, P. Dubois, P. Clementz *et al.*, "Actuation potentials and capillary forces in electrowetting based microsystems," *Sensors and Actuators A: Physical*, 134(2), 471-479 (2007).
- [14] H. Moon, S. K. Cho, R. L. Garrell *et al.*, "Low voltage electrowetting-on-dielectric," *Journal of Applied Physics*, 92(7), 4080 (2002).
- [15] K. S. Yun, and C. J. Kim, "Low-voltage electrostatic actuation of droplet on thin superhydrophobic nanoturf," 20th IEEE International Conference on Micro Electro Mechanical Systems, MEMS 2007. 139-142.
- [16] R. He, and C. J. Kim, "A low temperature vacuum package utilizing porous alumina thin film encapsulation," 19th IEEE International Conference on Micro Electro Mechanical Systems. 2006, 126-129.
- [17] Gordon G. Wallace, Geoffrey M. Spinks, Leon A. P. Kane-Maguire *et al.*, [Conductive Electroactive Polymers: Intelligent Polymer Systems] CRC Press, Boca Raton, 270 (2008).
- [18] J. Tietje-Girault, C. Ponce de Leon, and F. C. Walsh, "Electrochemically deposited polypyrrole films and their characterization," *Surface and Coatings Technology*, 201(12), 6025-6034 (2007).
- [19] E. Smela, and N. Gadegaard, "Volume change in polypyrrole studied by atomic force microscopy," *Journal of Physical Chemistry B*, 105(39), 9395-9405 (2001).
- [20] X. Lianbin, C. Wilfred, M. Ashok *et al.*, "Reversible Conversion of Conducting Polymer Films from Superhydrophobic to Superhydrophilic," *Angewandte Chemie International Edition*, 44(37), 6009-6012 (2005).
- [21] K. S. Teh, Y. Takahashi, Z. Yao *et al.*, "Influence of redox-induced restructuring of polypyrrole on its surface morphology and wettability," *Sensors and Actuators A: Physical*, 155(1), 113-119 (2009).

- [22] Y. Takahashi, K. S. Teh, and Y. W. Lul, "Wettability switching technique of a biocompatible polymer." 459-462.
- [23] J. A. Halldorsson, S. J. Little, D. Diamond *et al.*, "Controlled transport of droplets using conducting polymers," *Langmuir*, 25(18), 11137-11141 (2009).
- [24] X. Wang, and E. Smela, "Color and Volume Change in PPy(DBS)," *The Journal of Physical Chemistry C*, 113(1), 359-368 (2008).
- [25] J. Isaksson, C. Tengstedt, M. Fahlman *et al.*, "A Solid-State Organic Electronic Wettability Switch," *Advanced Materials*, 16(4), 316-320 (2004).