



Short communication

The electrochemical manipulation of apolar solvent drops in aqueous electrolytes by altering the surface polarity of polypyrrole architectures



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ABSTRACT

We demonstrate an electrochemically assisted three-dimensional robotic system for the pickup, transport and release of dichloromethane drops in electrolytes using polypyrrole-coated O-rings. Changing the oxidation state of the polymer by means of cyclic voltammetry, pickup, transport and release of drops is demonstrated. Also, the drop manipulation is evaluated as a function of different doping agents in the polypyrrole coatings. Moreover, other polypyrrole-coated architectures such as chips and meshes are utilized to manipulate dichloromethane drops to successfully trap and release them on demand in moving electrolytes. These architectures are envisioned for use as microfluidic tools such as microreactors or microseparators.

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1. Introduction

Controlled manipulation of fluids at the drop level offers a wide range of opportunities in many fields of research such as electrochemistry, biotechnology, micro- and nanorobotics, microfluidics or process engineering. The manipulation of small fluid volumes can be performed using several approaches based on different physical principles [1]. These methods include the use of acoustic radiation pressure, optical forces, capillarity and magnetic or electric fields [2–7]. Recently, electrically driven drop manipulation approaches have received significant attention due to their high versatility. These methods can be used to perform many different operations such as drop generation with control over their size, fusion, sort or isolation [7–11], and they include electroosmosis, dielectrophoresis and electrowetting on a dielectric. A promising strategy consists of using electrochemical actuation (EA) for drop manipulation [12–15]. This approach is also very useful to measure interfacial forces as demonstrated in ref. [16]. EA is based on the change of the surface polarity of a material by subjecting it to reduction–oxidation reactions. Conducting polymers (CP) incorporating appropriate doping agents (DA) enable EA of drops by applying relatively low potentials (below or around 1 V) [12,17]. The application of a potential

produces changes in the chemical composition of the CP, which in turn affects its solvophilic character. Yang and co-workers have recently demonstrated the manipulation of a dichloromethane (DCM) droplet by electrochemically tuning the surface energy of the CP polypyrrole (Ppy) doped with dodecylbenzenesulfonate (DBS) anions [18]. The authors suggested that transformations in the surface state of Ppy(DBS) are due to exchange of sodium ions between the solution and the CP and to changes in the orientation of DBS molecules inside the CP. In this work, we exploit the capabilities of EA with Ppy architectures for picking up and placing DCM drops in aqueous solutions. In addition, we show a strategy to trap and release the drops on demand with Ppy-coated grid electrodes.

2. Experimental procedure

Electrochemical deposition of Ppy was performed in a one-compartment three-electrode cell. A double junction Ag|AgCl reference electrode was used with a 3 M KCl inner solution. The outer solution was selected as a function of the electrolyte. A Pt spiral served as the counter electrode. Ppy was electrodeposited from an electrolyte containing 0.1 M pyrrole (py) and 0.1 M NaDBS. Py was vacuum distilled and stored at 4 °C under an inert atmosphere of nitrogen. In all cases, Ppy films were deposited galvanostatically at a current density of +1.2 mA cm⁻² and a deposition time of 60 s. The electrodeposition of Ppy was performed on the following: (i) Au/Ti-coated silicon chips, (ii) stainless steel wires with a diameter of 500 μm wound into a ring

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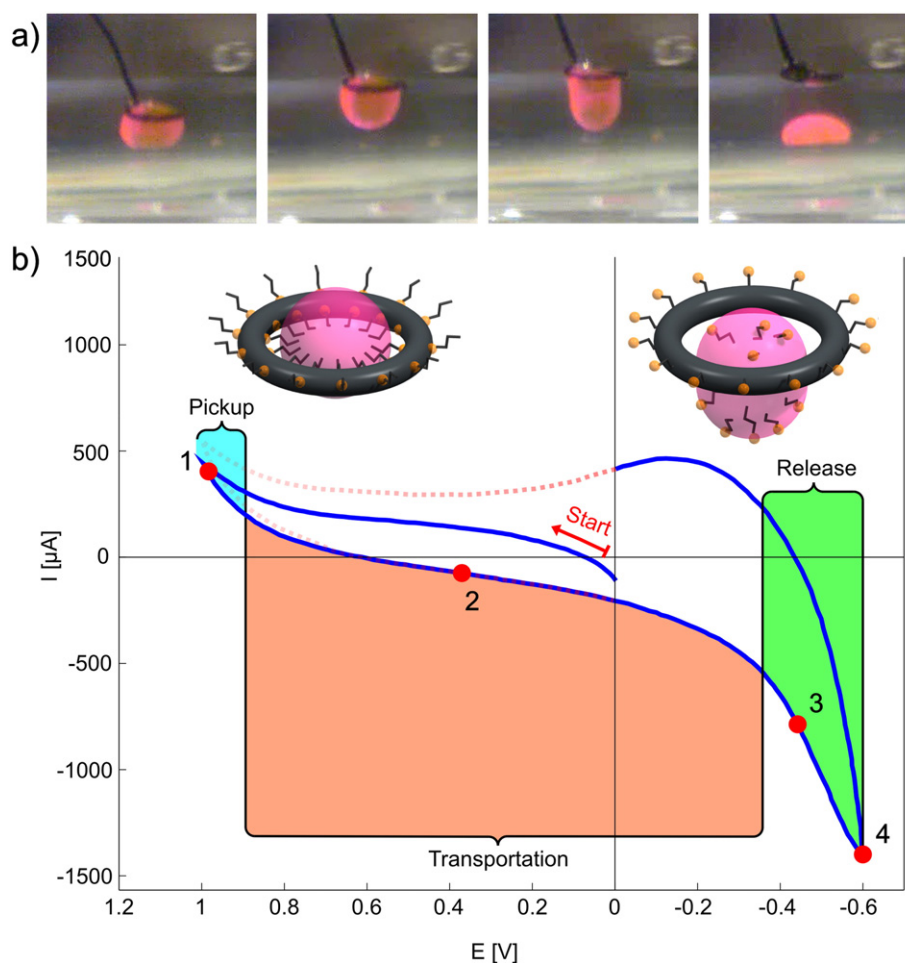


Fig. 1. (a) Image sequence showing the pickup and release of a DCM drop. (b) Cyclic voltammetry plot of the pickup probe. The numbers on the curve in panel b show locations of the events shown in the image sequence (a).

2 mm in diameter and (iii) stainless steel meshes with nominal aperture of 1.5 mm. In our experimental setup, the three electrodes were connected to a potentiostat/galvanostat (Gamry Reference 3000, Gamry Instruments, USA) that was controlled by the Gamry Framework software. The electrochemical manipulation of drops was performed with the Ppy-coated architectures, which acted as working electrodes. A Pt spiral acted as a counter electrode. A double junction reference electrode Ag|AgCl with an inner solution and an outer solution containing 3 M KCl and 1 M NaNO₃, respectively, was employed. The drops were generated with a micropipette and were carefully placed on glass slides immersed in a solution containing 1 M NaNO₃. The glass slides were previously treated with a mixture of 3:1 H₂SO₄ and H₂O₂ to render the glass surface hydrophilic. DCM was colored with rhodamine B (Rh-B) or Solvent Green 3 (SG-3) in order to facilitate drop tracking by computer vision techniques.

3. Results and discussion

3.1. Pickup and release of drops using stainless steel O-rings

Fig. 1a displays a sequence in which a DCM drop is picked up and released by a ring coated by DBS-doped Ppy. The ring was polarized by means of cyclic voltammetry (CV) (Fig. 1b) with a scanning speed of 50 mV s⁻¹. As the probes were cycled from 0 to +1 V, the drop was picked up at a potential interval of +[0.8–1] V and then moved with a micro-manipulator. The transport could be performed either while the potential scanning was progressing, or by pausing the CV. We found out that it is not the positive charge imparted to the ring during polarization what actually picks the drop up, but the fact that the Ppy is in a more oxidized state. The release of the DCM drop was observed at the reducing potential interval of –[0.4–0.6] V. The changes in wettability of Ppy surfaces that

Table 1

Pickup and release behavior of dichloromethane (DCM) drops with O-rings coated with Ppy electrodeposited using different DA: DBS, sodium dodecylbenzenesulfonate; KPPOS, potassium perfluorooctanesulfonate; GLY, glycolic acid ethoxylate lauryl ether; KPEGNSE, poly(ethylene glycol) 4-nonylphenyl 3-sulfopropyl ether potassium.

Bath	Pickup	Release
0.1 M py + 0.1 M NaDBS	Complete pickup of drops was observed	Sometimes, drop was released in the form of smaller droplets
0.1 M py + 0.015 M KPPOS + 0.0008 M FeCl ₃ in acetonitrile	Complete pickup of drops was always observed	Release was not always observed
0.1 M py + 0.1 M GLY	Only parts of an entire drop could be picked up	Release of complete drops
0.1 M py + 0.1 M KPEGNSE	Only parts of an entire drop could be picked up	The release of drops was not observed

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