On-Demand Capture and Release of Organic Droplets Using Surfactant-Doped Polypyrrole Surfaces

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Supporting Information

**ABSTRACT:** In this paper, we demonstrate the controlled capture and release of dichloromethane (DCM) droplets on dodecylbenzenesulfonate-doped polypyrrole (PPy(DBS)) surfaces in an aqueous environment. The droplets captured on oxidized PPy(DBS) surfaces were released on-demand via a reduction process at −0.9 V, with controlled release time and droplet morphology. The release time of an entire droplet (2 ± 1 μL) was proportional to the thickness of the PPy(DBS) coating, increasing from 11.5 to 26.3 s for thicknesses ranging from 0.6 to 5.1 μm. The droplet-release time was also affected by the redox voltages, and among the tested redox voltages, the fastest release was achieved at −0.9/0.1 V. The PPy(DBS) surfaces with larger thicknesses were more durable for the droplet capture and release. The droplets were more rapidly released from PPy(DBS) surfaces with increased surface roughness ratios, such as 6.0 s on a micropillared surface and 10.3 s on a meshed surface, as compared to 14.6 s on the 1.8 μm thick PPy(DBS) surfaces coated on frosted-glass substrates (i.e., with random microstructures). The release of a single droplet was achieved by increasing the underwater oleophobicity of PPy(DBS) surface via O2 plasma treatment.

**KEYWORDS:** droplets, polypyrrole, adhesion, surfactants, microstructures

**INTRODUCTION**

The control of adhesion of liquid droplets on solid substrates has broad implications in surface cleaning, water treatment, microfluidics, biochemistry, and lab-on-a-chip devices. By the changing of the surface chemistry and morphology, various surfaces have been developed for controlled liquid adhesion from adhesive to repellant for applications including coating, printing, droplet manipulation, and water repellency. Further developments of smart surfaces have also resulted in on-demand adhesion control of liquid droplets on solid substrates using external stimuli such as light, heat, electrical potentials, magnetic fields, or mechanical stress. Besides these methods, which are mainly based on the tunable wetting property of solid substrates, the on-demand control of liquid adhesion has recently been explored through the change of the surface property of liquid droplets (e.g., surface tension or surface polarity) using polypyrrole (PPy)-coated surfaces. Polypyrrole as a conjugated polymer has gained great attention in several applications, including actuators, supercapacitors, biosensors, and microfluidics, due to its good stability, biocompatibility, high conductivity, and mechanical property. Recently, there has been a growing interest in the study of the roles of experimental parameters.

Here, we demonstrate on-demand capture and release of dichloromethane (DCM) droplets on PPy(DBS) surfaces with controlled release time and droplet morphology via the redox process electrochemically manipulated upon low-voltage actuations. We elucidate the mechanism and study the effects of PPy(DBS) coating thickness and redox voltage on the droplet capture and release behaviors, including the release time, durability, and the number of droplets released. We further investigate the effects of surface morphology and wettability on

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the droplet capture and release process, demonstrating controllable droplet capture and release for tailored applications.

■ RESULTS AND DISCUSSION

Droplet Capture and Release. Figure 1a illustrates the mechanism of on-demand capture and release of organic droplets on PPy(DBS) surfaces in an aqueous electrolyte environment via an electrochemical redox process, requiring relatively low voltage (<1 V) for the actuation. The PPy(DBS) surface turns into an oxidized state upon application of an oxidative voltage (e.g., 0.1 V), in which doped DBS− molecules bond to the PPy chains via polar sulfonic acid groups, while dodecyl chains protrude out from the polymer chains, constituting the surface layer (Figure 1a-i).30 Because the dodecyl groups are hydrophobic (or oleophilic), the oxidized PPy(DBS) surface exhibits a state of underwater oleophilicity and high adhesion to organic droplets. Consequently, the organic droplets can be captured by the oxidized PPy(DBS) surface, even when the sample is placed upside down (Figure 1a-ii).

The PPy(DBS) surface turns into a reduced state upon application of a reductive voltage (e.g., −0.9 V). The DBS− molecules reorient within the reduced PPy(DBS), exposing the hydrophilic (or oleophobic) sulfonic acid groups at the outermost surface. This change reduces the interfacial tension between the PPy(DBS) surface and aqueous medium, causing the reduced polymer surface to be more underwater oleophobic. Furthermore, a minute amount of DBS− molecules is desorbed from the PPy(DBS) matrix during reduction, and therefore, a portion of desorbed DBS− molecules, which are near the droplet boundary, accumulate at the interface between the organic droplet and the aqueous electrolyte (Figure 1a-iii).20 The accumulated DBS− molecules, acting as surfactants, result in a decrease of interfacial tension between the organic droplet and aqueous electrolyte. Once the decreased interfacial tension can no longer balance external forces (e.g., gravity), the droplet elongates, thinning in its middle section (Figure 1a-iv), and a portion of the droplet falls downward (Figure 1a-v).35,36 Subsequently, the portion of the droplet remaining on the PPy(DBS) surface often falls in a similar manner, forming additional drops (Figure 1a-vi). After the release of the entire droplet, the area of PPy(DBS) surface, which was initially in contact with the droplet, is then exposed to the electrolyte and likewise reduced by the reductive voltage. The reduced PPy(DBS) surface can then be switched back to a high-adhesion state upon application of oxidized voltages.

Figure 1b shows a demonstration of the on-demand capture and release of a dichloromethane (DCM) organic droplet on a PPy(DBS) surface immersed in an aqueous environment (0.1 M NaNO3). The PPy(DBS) surfaces were prepared by coating the polymer on Au/Cr-coated frosted glass via the electrodeposition process.
process (Figure 1c) (fabrication details are described in the Experimental section). The random microstructures on the frosted glass surface can effectively improve the adhesion between the PPy(DBS) film and the substrate, preventing the coated PPy(DBS) film from being peeled off during redox. The surface roughness ratio (i.e., the ratio of actual area of the solid surface to the projected area) of the PPy(DBS) surface coated on frosted glass is 1.09 (the measurement method of surface roughness ratio is explained in the Experimental section). During the droplet capture-and-release process (the configuration of the experimental setup is shown in Figure S1), a DCM droplet was first dispensed on an O₂-plasma-treated glass slide submerged in aqueous electrolyte, showing a high contact angle of ∼160° (Figure 1b-i). The O₂ plasma treatment increased the surface hydrophilicity and underwater oleophobicity of the glass slide, thereby increasing the contact angle. The PPy(DBS) surface oxidized at 0.1 V was then lowered to contact the DCM droplet on the glass slide (Figure 1b-ii). Following contact, the PPy(DBS) surface was raised, and the droplet was captured by the oxidized PPy(DBS) surface due to strong adhesion (Figure 1b-iii). The captured droplet was transported to the oxidized PPy(DBS) surface to a new location without falling. A reductive voltage of −0.9 V was then applied to the PPy(DBS) surface (Figure 1b-iv), causing the captured droplet to gradually elongate, developing a thin cylindrical neck with a decreased contact area with the PPy(DBS) surface (Figure 1b-v–vii) due to the decrease of interfacial tension between the organic droplet and aqueous electrolyte against gravity (Density of DCM: 1.33 g/cm³). The decrease of the PPy(DBS)-droplet contact area (as a result of reduced interfacial tension between the PPy(DBS) surface and aqueous medium) also contributed to the droplet elongation due to mass conservation. The droplet fully segregated into two portions in ∼3 s (Figure 1b-viii). The lower portion of the droplet was released from the PPy(DBS) surface under gravity, forming the primary falling drop (i.e., the first falling drop), while the upper portion remained on the PPy(DBS) surface. The droplet was usually broken in the middle section, not from the interface between PPy(DBS) surface and droplet. This behavior indicates that the balance of the interfacial tension (i.e., between the organic droplet and the aqueous electrolyte) and the external forces (e.g., gravity) dominates the mechanics for the release of droplet. After the release of the primary drop, the remaining portion of the droplet on the PPy(DBS) surface repeated deformation and released several satellite drops in a similar manner until there was virtually no organic liquid remaining on the PPy(DBS) surface (Figure 1b-ix–xv). After a few seconds (∼4.2 s for this specific example), the captured DCM droplet was fully released from the PPy(DBS) surface, forming multiple drops on top of the glass slide. In this work, we have tested DCM droplets with volumes ranging from 0.7 to 7.3 µL (∼10× difference in volume) for the on-demand capture and release of droplets (Figure S2).

The gradual deformation of the droplet during the release process indicates the decrease of interfacial tension between the organic droplet and the aqueous electrolyte due to the accumulation of the surfactants at the interface. As shown in Figure 2, the change of the interfacial tension was measured by analysis of the profile of the deformed pendant droplet; the interfacial tension was only measured after the droplet exhibited an apparent deformation within measurement accuracy of a goniometer. The initial interfacial tension between the DCM droplet and the aqueous electrolyte (γow) was 27.8 mN·m⁻¹, measured using a pendant-droplet method. After 0.5 s of reductive voltage (−0.9 V) application, the interfacial tension was significantly decreased to 5.2 mN·m⁻¹ and continued to decrease to 1.9 mN·m⁻¹ before the release of the droplet. This result confirms the decrease of the interfacial tension between the organic droplet and the aqueous electrolyte, induced by the gradual accumulation of the surfactants desorbed from PPy(DBS) on the droplet surface, as explained in Figure 1a. Due to the decrease of interfacial tension, the droplet cannot be held as before by interfacial tension against the gravitational force, which results in the release of the droplet. The portion of the droplet remaining on the PPy(DBS) surface was subsequently released in a similar manner. The effect of DBS molecules on the change of interfacial tension was further confirmed by the PPy surface that was not doped with DBS molecules. The DCM droplet on an “undoped” PPy surface did not show any change in shape during a redox process.

Figure 3a shows an example of the capture and release of DCM droplets on a PPy(DBS) surface coated on a frosted glass substrate during the cyclic redox process (surface charge density for PPy(DBS) electrodeposition: 300 mC/cm²). Droplets of 2 ± 1 µL were used in the cyclic capture and release process for consistency. The release time of the primary falling drop (i.e., the time taken for the first portion of droplet to be released from the substrate) during each cycle was mainly between 2.2 and 11.0 s, whereas at some rare and random cycles, the release time was shorter than 1 s or longer than 20 s (Figure 3b). The average release time of the primary drop was 7.3 s, and the total release time for the entire droplet (the time that the entire droplet is released) was 11.5 s on average (Figure 3b inset) for this example. The contact angles of captured DCM droplets on the oxidized PPy(DBS) surface gradually increased with addition of redox cycles; as shown in Figure 3c, the contact angle increased from 67° to 120° after 16 redox cycles, which indicates that the PPy(DBS) surface in an oxidized state gradually changed toward higher underwater oleophobicity. There are several factors that we consider for this change of the wetting property of PPy(DBS) surfaces during the cyclic redox process. First of all, as is well known, PPy(DBS) undergoes volume changes during redox. Liu et al. reported the increase of surface roughness of the PPy(DBS) in a reduced state as a result of volume change. The increase of surface roughness could cause the change of wetting property of a PPy(DBS) surface by the formation of a Wenzel or Cassie–Baxter state. In addition, the influx of water from the aqueous electrolyte into the polymer and the accumulation of

![Figure 2. Decrease of interfacial tension of a pendant DCM droplet (in 0.1 M NaNO₃) captured on a PPy(DBS) substrate upon the application of a reductive voltage of −0.9 V.](Image)
surfactant dopants desorbed from the polymer onto the polymer surface during the redox process could also increase the underwater oleophobicity of a PPy(DBS) surface. Meanwhile, we observed that the contact radii of the droplets on the oxidized PPy(DBS) surface were reduced (Figure 3c), and the number of falling drops formed during the release decreased from approximately 5 to 2 after 16 redox cycles (Figure 3d). The number of drops formed during the release is related to the change of contact radii of droplets on the substrate. According to Harkins and Brown, the actual volume percentage of a drop falling from a capillary is correlated with the capillary radius. As shown in Figure 1, the falling of droplets from the PPy(DBS) surface is similar to the situation in which the droplet falls from a capillary, and the droplet contact radius on the PPy(DBS) surface is analogous to the capillary radius. In this example, the droplet contact radius, normalized by the cube root of volume, decreased from approximately 0.54 to 0.26 after 16 redox cycles (Figure 3c), and as a result, the volume percentage of the primary falling drop to the entire droplet increased from \(\sim 60\) to \(\sim 90\%\) (Figure 3d), which agrees with Harkins and Brown’s study. The number of falling drops formed during the release process consequently decreased with the increase of volume percentage of falling drops to the entire droplet.

**Effects of Coating Thickness and Redox Voltage.** We furthermore studied the droplet-release time and durability of PPy(DBS) surfaces (i.e., capability of maintaining the droplet capture and release functionalities), along with the effects of PPy(DBS) coating thickness and redox voltages during multiple redox cycles. Within each redox cycle, the PPy(DBS) surface was first oxidized for the droplet capture and then reduced for the droplet release as illustrated in Figure 1. The thickness of the PPy(DBS) coating was controlled by the surface charge density during the electrodeposition process. As shown in Figure 4a, by using three different surface charge densities of 100, 300, and 1000 mC/cm\(^2\), the PPy(DBS) surfaces were coated with an average thickness of approximately 0.6, 1.8, and 5.1 \(\mu\)m, respectively. The average release time of the primary drop and the total release time increased with the coating thickness (i.e., 6.3, and 11.5 s on the 0.6 \(\mu\)m thick samples; 10.6 and 14.6 s on the 1.8 \(\mu\)m samples; and 20.9 and 26.3 s on the 5.1 \(\mu\)m samples) (Figure 4b). We attribute this change in release time to slower desorption of DBS\(^{-}\)molecules from thicker PPy(DBS) surfaces, which has been reported elsewhere through an EDS study to the content change of DBS\(^{-}\)molecules in PPy(DBS) during multiple redox cycles. However, the PPy(DBS) surfaces with thicker coating showed better durability. For example, the droplets were captured and released for an average of 39 cycles on the 5.1 \(\mu\)m thick samples, compared to 2 cycles on the 0.6 \(\mu\)m thick samples and 14 cycles on the 1.8 \(\mu\)m thick samples. After these redox cycles, the captured droplet would not be released from the PPy(DBS) surface, even it elongated under reduction (Figure S3). The better durability of thicker PPy(DBS) coatings is attributed to the abundance of DBS\(^{-}\)molecules within the volume of the PPy(DBS) film, wherein DBS\(^{-}\)molecules may be desorbed during prolonged redox cycles.

According to the cyclic voltammetry (CV) of the electropolymerized PPy(DBS) surface (Figure 4c), the reduction was completed at \(-0.9\) V, while the oxidation was completed at 0.1 V.
The increase of the current with the oxidative voltage higher than 0.6 V indicates the occurrence of side reactions such as cross-linking, overoxidation, and the reaction of monomers with water to form amide groups.\textsuperscript{30,48} To this end, we compared three different combinations of reduction and oxidation voltages (i.e., $-0.9/0.1$, $-0.9/0.6$, and $-0.6/0.1$ V) to investigate the effect of redox voltages on the droplet capture and release behaviors (Figure 4d). The average release times of the primary drop and the total release time on the samples operated at $-0.9/0.1$ V were 10.6 and 14.6 s, respectively (surface charge density for electrodeposition: 300 mC/cm$^2$). When the oxidative voltage was increased to 0.6 V, the release time of the primary drop and the total release time increased to 17.4 and 24.5 s, respectively. However, when the reductive voltage was lowered from $-0.9$ to $-0.6$ V, the release time of the primary drop and the total release time were also increased to 18.2 and 25.5 s, respectively. We attribute this to a stronger repulsive force that $-0.9$ V applied on the negatively charged DBS$^-$ molecules than $-0.6$ V, facilitating the desorption of DBS$^-$ molecules from PPy(DBS). According to this result, a relatively higher reductive voltage ($-0.9$ V) and a lower oxidative voltage (0.1 V) would cause a shorter release time. The durability was similar (i.e., 12 to 14 cycles) on those samples operated at different redox voltages, confirming that the thickness should be the primary factor determining the durability of PPy(DBS) surfaces.

Effects of Surface Morphology and Wettability. We further studied the effect of surface morphology on droplet capture and release behaviors. In addition to the PPy(DBS) samples coated on frosted glasses with random surface microstructures, we also tested PPy(DBS) samples with well-regulated micropillar and meshed structures (Figure 5). The PPy(DBS) micropillar structures were 7.8 $\mu$m in diameter and 6.0 $\mu$m in height, fabricated by electrodepositing PPy(DBS) on Au/Cr-coated silicon micropillar structures (Figure 5a-i). The PPy(DBS) mesh structures with square pores of $\sim$149 $\mu$m width were made by electrodepositing PPy(DBS) on Au/Cr-coated stainless steel meshes (Figure 5b-i). The surface charge density during electropolymerization was 300 mC/cm$^2$ for both samples; details of the fabrication process are explained in the Experimental section.

Figure 5a-ii shows the capture and release process of DCM droplets on PPy(DBS)-coated micropillar structures. The droplet showed a smaller contact angle of $\sim$52$^\circ$ in the oxidation state compared to that on the PPy(DBS) surface coated on frosted glass. This smaller contact angle indicates that the DCM filled gaps between micropillars and formed an underwater Wenzel state,\textsuperscript{42} as illustrated in Figure 5a-iii. Upon reduction, the release of the droplet started in 3.8 s and completed in an average of 6.0 s. We note that the droplet release time from the PPy(DBS) surface with micropillar structures was significantly shorter than that on the PPy(DBS)-coated frosted glass (average release time of the primary drop: 10.6 s; average total release time: 14.6 s) (Table 1). We attribute this difference to a larger surface roughness ratio (i.e., the ratio of actual area of the solid surface to the projected area) of the micropillar samples (2.47) compared to that of the frosted glass (1.09) (the measurement...
method of surface roughness ratio is described in the Experimental section). A larger effective surface area would facilitate greater desorption of DBS⁻ molecules near the droplet boundary, accumulating more DBS⁻ molecules on the interface between the organic droplet and aqueous electrolyte. The abundance of DBS⁻ molecules on the interface further lowers the interfacial tension, resulting in a faster release of the droplet. However, because the droplet was in an underwater Wenzel state on the oxidized micropillared PPy(DBS) surface with a decreased contact angle, the droplet had an increased contact radius with the PPy(DBS) substrate than that on the PPy(DBS) surface on the frosted glass (e.g., the contact radius normalized by the cube root of volume was 0.26 for the droplet shown in Figure 5a-ii). Therefore, a larger portion of a droplet remained on the substrate after the release of the primary droplet during the release process, as discussed in Figure 3. The average volume percentage of the primary falling drop to the initial entire droplet was ∼56% (Table 1), which was lower than that of the PPy(DBS) coated on frosted glass with random microstructures (∼78%). Because a larger volume of the droplet remained on the surface, there were more drops continually released while the reductive voltage was applied. For example, there were approximately five drops formed in average during the release process from the micropillared PPy(DBS) surface, while there were approximately three drops from the surface coated on the frosted glass with random roughness.

The capture and release process of DCM droplets on a PPy(DBS) mesh (Figure 5b-i) is shown in Figure 5b-ii. The droplet on PPy(DBS) mesh showed a higher contact angle of 122° with a smaller contact radius (the contact radius normalized by the cube root of volume was 0.26 for the droplet shown in Figure 5b-ii) than the micropillared surface. The droplet on the mesh showed a higher contact angle because the aqueous electrolyte filled the pores between the mesh structures, as illustrated in Figure 5b-iii, resulting in the formation of an underwater Cassie–Baxter state. The average release time of the primary drop on the PPy(DBS) mesh was 9.2 s, and the total release time was 10.3 s, which were also shorter than that of the PPy(DBS) coated on frosted glass. We attribute the reduced release time to the increased surface roughness ratio (2.67) of the PPy(DBS) mesh (both sides of the surface are counted in estimating surface roughness ratio) and, hence, a larger effective surface area for the desorption of the DBS⁻ molecules, as discussed for the case on the PPy(DBS) surface with micropillar structures. However, because the contact radius of the droplet with PPy(DBS) mesh decreased with the increase of contact angle, fewer DBS⁻ molecules would accumulate on the droplet surface compared to that on the micropillared PPy(DBS) surface. Therefore, the release time was longer on a PPy(DBS) mesh than that on the micropillared PPy(DBS) surface, even though the surface roughness ratios of the two samples were similar. In addition, because the contact radius became smaller, the droplet detached with a larger volume, compared to the case of the PPy(DBS) coated on frosted glass. The average volume percentage of the primary falling drop to the entire droplet on the PPy(DBS) mesh was 88% (Table 1).

We also investigated the effect of surface wettability on the capture and release of droplets on PPy(DBS) substrates. To avoid the influence of surface microstructures, the PPy(DBS) coatings deposited on flat Cr/Au-coated silicon substrates were used in this test (surface charge density for electrodeposition: 1000 mC/cm²; redox voltages: −0.9/0.1 V). The PPy(DBS) samples were treated with 25 W O₂ plasma for 2 min (the details are included in the Experimental section). Figure 6a shows the surface morphology of the PPy(DBS) surface before and after the treatment. Although there was no significant difference in microwe surface morphology, the PPy(DBS) surface after the treatment showed a change of nanoscale surface morphology with the formation of tiny nanodots. Due to the change of surface morphology and surface chemistry after the O₂ plasma treatment, the PPy(DBS) surface became underwater oleophobic with a contact angle of 142° (Figure 6b). With such a large contact angle and a small contact radius, the droplets were usually released as a single droplet (or two droplets, in which the volume percentage of the primary falling drop was over 99%). However, it should be noted that the total release time for the droplets on the plasma treated surface was ∼41 s, which was longer than that on untreated surfaces. This is due to the small contact radius of a droplet on the plasma-treated PPy(DBS) surface, resulting in a lower amount of surfactants desorbed from PPy(DBS) near the

Table 1. Capture and Release Behaviors of DCM Droplets on Various Microstructured PPy(DBS) Samples

<table>
<thead>
<tr>
<th>samples</th>
<th>roughness ratio</th>
<th>release time of primary drop (s)</th>
<th>total release time (s)</th>
<th>volume of primary drop (%)</th>
<th>number of falling drops</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPy(DBS) on frosted glass</td>
<td>1.09</td>
<td>10.6</td>
<td>14.6</td>
<td>78%</td>
<td>3.3</td>
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<td>(random microstructures)</td>
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<tr>
<td>PPy(DBS) micropillars</td>
<td>2.47</td>
<td>3.8</td>
<td>6.0</td>
<td>56%</td>
<td>5.3</td>
</tr>
<tr>
<td>PPy(DBS) mesh</td>
<td>2.67</td>
<td>9.2</td>
<td>10.3</td>
<td>88%</td>
<td>2.1</td>
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| aSurface charge density for PPy(DBS) electrodeposition is 300 mC/cm² and redox voltages are −0.9/0.1 V.

![Figure 5. On-demand capture and release of DCM droplets on (a) PPy(DBS) micropillars and (b) PPy(DBS) mesh in an aqueous electrolyte environment (0.1 M NaNO₃). (i) Surface morphology of PPy(DBS) substrates, (ii) the droplet-release process, and (iii) the schematics of the DCM droplet on PPy(DBS) substrates.](image)
a higher contact angle, enhance the efficacy of the droplet release by forming fewer drops during release. On the PPy(DBS) surfaces treated with O₂ plasma, the droplets can be released as a single droplet, compared to approximately three drops on the PPy(DBS) samples coated on frosted glass. The obtained knowledge on the mechanisms of the droplet capture and release would be applicable to droplet transportation and droplet-based microreactors.

■ EXPERIMENTAL SECTION

Fabrication of PPy(DBS) Surfaces. PPy(DBS) thin films were coated via electropolymerization on various substrates, including Cr/Au-coated frosted glass (Micro Slides, VWR, Radnor, PA), flat silicon wafer (WRS Materials, San Jose, CA), micropatterned silicon wafer, and stainless steel mesh (Mesh 100 × 100, McMaster-Carr, Robbinsville, NJ). The Cr (10 nm) and Au (30 nm) coatings were deposited on different substrates by using an e-beam evaporator (Explorer 14, Denton Vacuum, Moorestown, NJ). The PPy(DBS) films were then electropolymerized on the Cr/Au-coated substrates. During the electropolymerization, the substrates were submerged in a solution consisting of 0.1 M pyrrole (reagent grade, 98%, Sigma-Aldrich, St. Louis, MO) and 0.1 M sodium dodecylbenzenesulfonate (NaDBS) (technical grade, Sigma-Aldrich, St. Louis, MO) as the working electrode. A saturated calomel electrode (SCE) (Fisher Scientific Inc., Pittsburgh, PA) and a Cr/Au-coated silicon wafer were also submerged in the solution as the reference electrode and the counter electrode, respectively. The deposition of PPy(DBS) was carried out at 0.7 V versus SCE using a potentiostat (263A, Princeton Applied Research, Oak Ridge, TN).30

The surface charge densities during coating were set to 100, 300, and 1000 mC·cm⁻² to coat PPy(DBS) films with different thicknesses to study the effect of the thickness of PPy(DBS) films on droplet capture and release behaviors. The substrates coated with PPy(DBS) were then rinsed with deionized (DI) water. The micropatterned structured silicon substrates used for PPy(DBS) coating were fabricated through photolithography and the deep reactive ion etching (DRIE) process.30

The surface morphology of the PPy(DBS) coatings was characterized via scanning electron microscope (Auriga Small Dual-Beam FIB-SEM, Carl Zeiss, Jena, Germany). The surface roughness ratios (i.e., the ratio of actual area of the solid surface to the projected area) of PPy(DBS) films on treated glass slide in a 0.1 M NaNO₃ ([NaNO₃]: 99.8%, Sigma-Aldrich) solution. O₂ plasma was used to treat the PPy(DBS) surfaces to change surface wettability. In this process, the silicon substrates with PPy(DBS) coating (surface charge densities during coating was 1000 mC·cm⁻²) were treated by using an inductively coupled plasma (ICP) etcher (HiEtch, BMR Technology Corp., Anaheim, CA) with 25 W O₂ plasma for 2 min. The O₂ flow rate was 30 sccm, and chamber pressure was 20 pa.

Droplet Capture and Release. The capture and release of organic droplets on different PPy(DBS) surfaces was studied in an aqueous electrolyte environment. In particular, a dichloromethane (≥99.8%, Sigma-Aldrich, St. Louis, MO) droplet was first placed on an O₂-plasma-treated glass slide in a 0.1 M NaNO₃ (≥99.0%, Sigma-Aldrich) solution. Droplets with volumes ranging from 0.7 to 7.3 μL have been tested. Droplets of 2 ± 1 μL were used for consistency during the cyclic droplet capture and release process. The PPy(DBS) sample submerged in the solution was oxidized by applying a positive voltage in a two-electrode configuration, in which the PPy(DBS) sample was used as the working electrode and a platinum mesh (13 mm × 35 mm) was connected as the counter electrode. The oxidized PPy(DBS) sample was then placed in contact with the DCM droplet and moved upward to capture it. After the droplet was captured, a negative voltage was applied to the PPy(DBS) surface to release the droplet. After the droplet was released, a new droplet was placed on the glass slide, and the PPy(DBS) sample was tested for another redox cycle until the droplet could not be captured or released any further. Three different combinations of reductive and oxidative voltages including −0.9/0.6, −0.9/0.1, and −0.6/0.1 V were tested to study the effect of redox voltages on the droplet capture and release behaviors. The entire capture-and-release process was monitored with a goniometer system (Model 250, Ramé-
Research Article

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b03787.

Figures showing a schematic illustration of the experimental setup, the release process of DCM droplets with different volumes, and the degradation of PPy(DBS) surfaces for droplet capture and release. (PDF)

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**Notes**

The authors declare no competing financial interest.

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