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Characterization and Control of the Wettability of Conducting Polymer Thin Films

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ABSTRACT

The wettability of electrochemically deposited conducting polymer films is highly dependent on several parameters including the deposition conditions, the dopant, and the roughness of the working electrode. To produce superhydrophobic surfaces, one must be able to control the micro and nanostructure of the film. In this study, a template-free method of producing superhydrophobic (water contact angle of 154°) polypyrrole films was demonstrated. The polypyrrole was doped with the low surface-energy heptadecafluorooctanesulfonic acid and had microstructures with nanometer-scale roughness. The microstructures served to increase the roughness of the film and amplify the hydrophobicity of the surface. It is also of interest to be able to dynamically adjust the wettability of a polypyrrole surface after deposition. Applications of this functionality include microfluidics, self-cleaning surfaces, liquid lenses, and smart textiles. By oxidizing or reducing a polypyrrole film, one can change the surface morphology as well as the chemical composition, and control the wettability of the surface. This study characterizes the electrochemically-induced changes in surface energy of polypyrrole. The relationship between applied voltage, charge transferred, surface roughness, and water contact angle was investigated. Upon reduction, the polypyrrole film was switched to a superhydrophilic state and the maximum change in contact angle was observed to be 154°. Surface wettability was found to be not fully reversible, with some hysteresis occurring after the first electrochemical cycle.

INTRODUCTION

Conducting polymers are an interesting class of organic materials that have the ability to conduct electricity. The defining feature of conducting polymers is the conjugated backbone, which allows for electron delocalization, therefore making the polymers conductive [1]. Conducting polymers are typically doped to improve specific material properties. For example, doping with a large counterion has been shown to produce films with large active strains, while smaller counterions improve the film's conductivity [2].

Polypyrrole (PPy) has been studied extensively because of its stability in ambient conditions, relative ease of fabrication, and its ability to be biocompatible (depending on the dopant used) [2-4]. PPy is typically grown electrochemically, and different deposition conditions (current density, temperature of deposition environment, deposition solution recipe, working electrode substrate) will yield polymers with different properties [2].

Of particular interest is to tune the deposition conditions to produce superhydrophobic PPy films. The most common strategy for creating superhydrophobic PPy films is to dope the film with a low-surface energy sulfonic acid while at the same time creating a micro- and nano-

structured surface [5]. It is well known that a rough surface will amplify the inherent hydrophobicity or hydrophilicity of a surface by increasing the surface area with which a droplet interacts [6]. It is important to note that the surface must have surface roughness on two length-scales to mimic the “Lotus Effect,” which is the ability of the lotus leaf to have a superhydrophobic surface [7]. It has been shown that oxidation and reduction of polypyrrole can affect the wettability by driving ions in or out of the film, altering the chemical composition of the surface [8-9]. Specifically, since doping PPy with perfluorooctanesulfonate (PFOS) ions causes the film to be hydrophobic, reduction drives the PFOS ions out of the film switching the film to a hydrophilic state. Conversely, oxidation drives PFOS ions back into the film switching it back to a hydrophobic state.

PPy films that can reversibly switch from a superhydrophobic to a superhydrophilic state, have applications in microfluidics, self-cleaning surfaces, liquid lenses, and smart textiles. While there are several groups who have produced superhydrophobic conducting polymer films by creating micro- and nano-structured surfaces using hard-template methods [9-12] these methods have several disadvantages, the main one being the complexity of the fabrication process. Although there has been a group that has succeeded in creating PPy films with reversible wettability using template-free methods, the electrochemical switch is relatively slow, as each oxidation or reduction step is 20 minutes [13]. Since we ultimately seek to dynamically tune PPy wettability, we need a fast electrochemical switch. In this study, we seek to develop a template-free deposition protocol that produces robust PPy films that can be quickly and reversibly switched between superhydrophobic and superhydrophilic states. We also seek to characterize the electrochemical mechanism that produces the change in surface energy.

EXPERIMENTAL METHOD

Reagents and Materials

Pyrrole (Sigma-Aldrich 99%) was distilled and stored at -20°C. Potassium perfluorooctanesulfonate (KPFOS) (Sigma-Aldrich), ferric chloride hexahydrate (FeCl_3) (Sigma-Aldrich), acetonitrile (anhydrous, 99%) (Sigma-Aldrich) were of analytical grade and used as received.

An electrochemical deposition cell was fabricated out of Teflon. Gold-coated stainless steel foil was used as the counter-electrode and a 25 mm $\times$ 25 mm $\times$ 3 mm glassy carbon substrate was used as the working electrode. A VMP2 Multichannel Potentiostat (Princeton Applied Research) was used for the electrochemical depositions as well as the oxidation-reduction experiments.

Electrochemical Deposition of Polypyrrole

Polypyrrole doped with KPFOS was synthesized via galvanostatic polymerization with a current density of 1.5 A/m² at ambient temperature for two hours. The deposition solution contained 0.1 M pyrrole, 0.0008 M FeCl_3 , and 0.015 M KPFOS in acetonitrile.

Electrochemical Wettability Switch

The electrolyte solution used for the oxidation-reduction experiments contained 0.015 M KPFOS in acetonitrile. The KPFOS-doped PPy film was first reduced until the film was converted from a superhydrophobic to a superhydrophilic state. Each reduction step held the

film at -0.6 V (vs. a silver wire reference electrode) for 30 seconds. The reduced PPy film was then oxidized until the film was converted back to a superhydrophobic state. Each oxidation step held the film at $+0.6$ V (vs. a silver wire reference electrode) for 5 minutes. The contact angle as well as the open-circuit voltage and the charge transferred were measured after each reduction or oxidation step. The contact angle of a $5\text{ }\mu\text{L}$ droplet of distilled water was measured using a Canon 50D EOS digital camera and a custom-written Matlab script. Gold-coated stainless steel foil was used as the counter-electrode.

RESULTS AND DISCUSSION

The initial goal of this study was to find a deposition recipe that produced polypyrrole films that could reversibly switch between superhydrophobic and superhydrophilic states. PPy films grown under the conditions described in the previous section were found to be superhydrophobic, with an initial contact angle of up to 154° . SEM micrographs, shown in Figure 1a, of the films showed that the films had a network of secondary structures on top of a thin smooth layer that had a surface roughness on two length scales. The rough structures can be largely attributed to the ferric chloride in the deposition solution. Ferric chloride is typically used as an oxidizing agent for the chemical (electroless) polymerization of PPy, as it polymerizes the pyrrole monomer in solution without an electrical potential driving force [14]. The presence of Fe^{3+} ions oxidize a small amount of the pyrrole in solution creating clusters of PPy, while the driving current polymerizes the PPy clusters at the working electrode. This results in a network of rough microstructures on top of a smooth layer of PPy on the working electrode. PPy films grown under the same conditions as the superhydrophobic films except with ferric chloride omitted from the deposition solution were much smoother and did not have the secondary microstructures. The water contact angles of these films (up to 84°) were much lower than that of the films grown with ferric chloride. SEM micrographs, shown in Figure 1b, revealed a cauliflower structure that is typical of galvanostatically deposited PPy.

A KLA Tencor P-11 Surface Profiler with a $2\text{ }\mu\text{m}$ diameter stylus was used to measure the film thickness and surface roughness. It was found that the film grown with ferric chloride in the solution had an underlying film thickness of $0.4\text{ }\mu\text{m}$, with a $30\text{ }\mu\text{m}$ thick network of secondary microstructures. The average surface roughness, S_a , was $4.13\text{ }\mu\text{m}$. The film grown without ferric chloride was much smoother with $S_a = 0.432\text{ }\mu\text{m}$.

Figure 1. SEM micrographs of PPy film grown at a current density of 1.5 A/m^2 , (a) with ferric chloride (contact angle of 154°), and (b) without ferric chloride (contact angle of 84°).

Effect of Current Density on Reversible Wettability

It was observed that the current density used during the galvanostatic deposition will affect the reversible wettability of the polypyrrole film. A film grown with a current density of 2.5 A/m^2 produces a film with remarkably different microstructures than a film grown with a current density of 1.5 A/m^2 , as shown in Figure 2. The films had a thicker underlying layer of PPy (measured to be $0.95 \text{ }\mu\text{m}$ thick), and a $25 \text{ }\mu\text{m}$ thick layer of secondary microstructures. In addition to the differences in the physical surface morphology of the films, the film grown with the higher current density underwent an irreversible wettability switch upon the first reduction reaction. SEM micrographs (Figure 2) of the film before and after reduction show that the grain size of the microstructures decreases significantly. The average surface roughness also decreased by 30%, from a value of $4.25 \text{ }\mu\text{m}$ to a value of $2.9 \text{ }\mu\text{m}$, indicating that reduction resulted in a volumetric change in the film in addition to the change in chemical composition. The film grown with the lower current density was able to be reversibly switched between superhydrophobic and superhydrophilic states, and was used for the switching experiments. SEM micrographs of the film before and after electrochemical cycling show that there was no significant change in the appearance of the microstructures. Surface roughness measurements also showed no significant change before and after cycling. Figure 3 shows the different wetting states of the polymer.

Figure 2. SEM micrograph of PPy film grown with a current density of 2.5 A/m^2 (a) before reduction, and (b) after reduction.

Figure 3. The PPy film grown with a 1.5 mA/cm^2 current density can be reversibly switched between superhydrophobic and superhydrophilic states via oxidation and reduction. The figures above show the different wetting states of the polymer. The water contact angles of the films above are as follows: (a) 22° , (b) 62° , (c) 90° , (d) 107° , (e) 150° .

Reversibility Experiments

The reversible wettability of the films was studied via the protocol described in Experimental Method. The total charge transferred from the first redox step to the current redox step (cumulative charge transferred) describes the state of the film. The contact angle measured after each oxidation or reduction step was plotted against the cumulative charge transferred. A typical plot is shown in Figure 4.

The film in the fully oxidized state was more conductive (with a conductivity of up to 1424 S/m) than in the fully reduced state (conductivity of 59 S/m). The switching experiments showed that there is a threshold of charge (approximately -0.5 Coulombs) that need to diffuse out of the film before the surface could be switched from a superhydrophobic to a superhydrophilic state. Once this threshold was reached, the film could be easily switched between a superhydrophobic and superhydrophilic state. The experiments also revealed that it was easier to reduce the film than it was to oxidize. Each reduction step was 30 seconds, while each oxidation step was 5 minutes. These times were determined to be the optimal durations for similar amount of charge transfer for oxidation and reduction. After reaching the charge threshold, the fastest switch from a superhydrophobic to a superhydrophilic state occurred in two reduction steps (total of 60 seconds), while the fastest switch from a superhydrophilic to a superhydrophobic state occurred in three oxidation steps (total of 15 minutes). The fast electrochemical switch may be due to the high surface area of the PPy film, which exposes more of the polymer to the electrolyte solution. Electrochemical cycling also showed that there was some hysteresis, as the maximum contact angle achieved after the first cycle (140 deg) was lower than the initial contact angle of the film (154 deg).

The open circuit voltage after each oxidation/reduction step was also measured and plotted against contact angle. A typical plot is shown in Figure 4 and it appears that the relationship between the contact angle and the open circuit voltage is linear, with an R^2 value of 0.862. As the open circuit voltage of the film increases, the surface energy of the film decreases, causing an increase in water contact angle.

Figure 4. (Left) Switching experiments showed that there is a threshold of ions that needs to diffuse out of the film before the surface is switched to a hydrophilic state. The oxidation/reduction steps were reversible, although the film exhibited slight hysteresis after the first cycle. (Right) The relationship between open circuit voltage and contact angle appears to be linear. The surface energy of the film decreases as the open circuit voltage increases.

CONCLUSIONS

This study presented a robust template-free protocol for electrochemically fabricating superhydrophobic polypyrrole. The polymer exhibited roughness on two length-scales, which served to amplify the inherent hydrophobicity and hydrophilicity of the film. The film was able to be reversibly switched between superhydrophobic and superhydrophilic states via oxidation and reduction.

Future work includes utilizing the reversible wettability properties of polypyrrole to induce fluid movement with a wettability gradient. This important property, combined with the biocompatibility of PPY, can be used to create low-cost microfluidic devices.

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