Polymer Films

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Reversible Conversion of Conducting Polymer Films from Superhydrophobic to Superhydrophilic**

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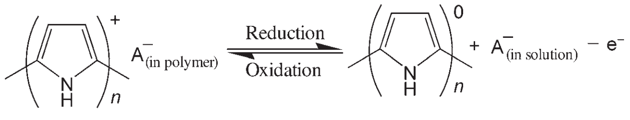
Controlling the wettability of a solid surface is important for myriad applications, ranging from self-cleaning surfaces to microfluidics to biomedicine.[1–3] Recently, a variety of smart surfaces with reversibly switchable wettability have been developed. The reversible switching is realized through the adjustment of electrical potential,[4–6] temperature,[7,8] and light illumination,[9–13] adsorption of biopolymer,[14] and treatment of selective solvents.[15,16] Among these approaches, the switch of the electrical potential receives special attention because it is simple and conveniently controlled by electricity. Moreover, the switching is readily individually addressable when an array of small surfaces is involved. Lahann et al.[4] constructed a reversibly switching surface by depositing a low-density carboxylate-terminated self-assembled monolayer on a gold surface. Electrical potential was used to trigger the conformational transition of the monolayer, resulting in switching of the surface wettability. However, the change in surface wettability is small (20 to 30° water contact angle), which is likely to limit its practical applications. It is reported that ZnO films[11,12] and poly(*N*-isopropylacrylamide)-modified patterned surfaces[7] can undergo reversible wettability switching between two extremes, superhydrophobicity (water contact angle $>150°$) and superhydrophilicity (water contact angle $<5°$) through the use of ultraviolet light and a temperature change, respectively. The photoswitching requires several days to achieve the hydrophilic-to-hydrophobic conversion, and both the photoswitching and thermal switching are difficult to implement to individually address an array of small surfaces. Herein we report a simple electrochemical process to fabricate superhydrophobic conducting polypyrrole (PPy) films and demonstrate that their properties can be switched conveniently from superhydrophobic to superhydrophilic by changing the electrical potential.

Conducting polymers (also called conjugated polymers or synthetic metals) such as polypyrrole (PPy) have been studied in great detail because their unique optical, electrical, and mechanical properties offer many new possibilities for device fabrication.[17,18] Interest has recently developed in their surface properties such as wettability because of potential applications in corrosion protection,[19] conductive textiles,[20] and antistatic coatings,[21] and in the immobilization of biopolymers[22] and growth control of living cells.[23] Usually the conducting polymers contain a positively charged conjugated backbone and negatively charged counterions (dopants). The wettability of conducting polymers depends greatly on the types of dopants used.[22] For example, a PPy film containing a perfluorinated dopant exhibited hydrophobicity (water contact angle $>90°$), while ClO_4^--doped PPy was hydrophilic.[21] Furthermore, the doping level can be controlled by changing the electrical potential, resulting in reversibly switchable surface wettability.[23,24] Scheme 1 shows the reversible switching process between the doped (oxidized) state and dedoped (neutral) state of PPy. To achieve a large variation in wettability (water contact angle difference $\geq 80°$) between the doped and neutral states of conjugated polymers, researchers have focused on fabricating hydrophilic conducting polythiophene and then converting it into hydrophobic neutral polythiophene.[25,26] This study



Scheme 1. A^- = anion.

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describes the first synthesis of superhydrophobic conducting polymers and the reversible control of the wettability of conducting polymer films between superhydrophobicity and superhydrophilicity.

Superhydrophobic PPy films were synthesized on a conducting surface such as Au-coated glass by electrochemical polymerization. The electroplating solution contained 0.1M pyrrole, 0.05M tetraethylammonium perfluorooctanesulfonate (TEAPFOS, $Et_4N^+CF_3(CF_2)_7SO_3^-$), and 2.0×10^{-4}M $FeCl_3$ in acetonitrile. The electropolymerization was carried out galvanostatically. Figure 1a is a typical top view obtained by scanning electron microscopy (SEM) of the as-deposited perfluorooctanesulfonate (PFOS)-doped PPy film. The image reveals an extended porous structure of the PPy film. The pore size ranges from 10 to 50 µm. A magnified image of a single pore shows that the pore wall is also highly porous (Figure 1b). Figure 1c reveals the structure of the pore wall. The smaller pores (compared with the pores in Figure 1a) are on the order of 1–4 µm. The particle assemblies surrounding the smaller pores are composed of submicron PPy particles with diameters of 0.5–1 µm. As will be discussed later, this porous structure with roughness on both coarse and fine scales is most effective in achieving superhydrophobicity and superhydrophilicity.

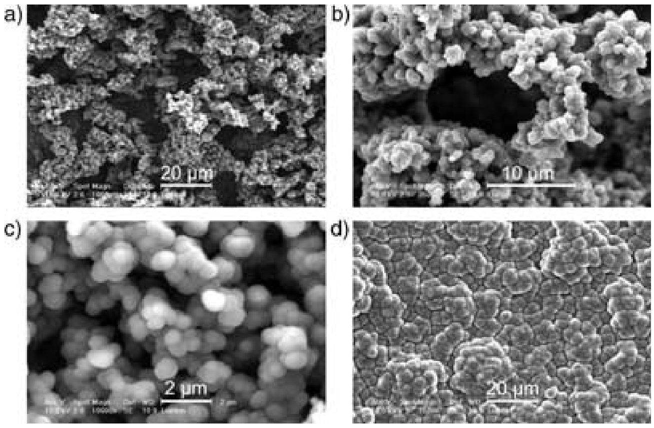
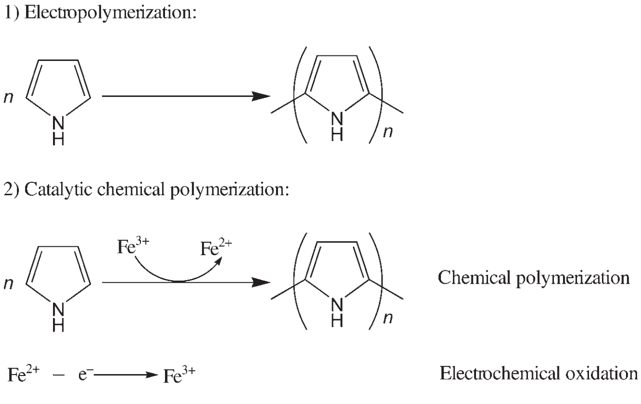


Figure 1. SEM images of PPy films. a) Top view of a large area of the porous film. The pore size ranges from 10–50 µm. b) Top view of a single pore and the surrounding PPy particle assemblies. c) Structure of the pore wall of the porous PPy. The small pores are on the order of 1–4 µm; the diameters of the PPy particles range from 0.5–1 µm. d) Top view of the compact PPy film.

The tiny amount of Fe in the plating solution plays a key role in the formation of this highly porous structure. When no Fe was in the solution, a compact structure (Figure 1d) was obtained. Fe^{3+} and Fe^{2+} salts have been used as catalysts for the chemical polymerization of conducting polymers such as PPy and polyaniline (PAni), while oxygen, ozone, or H_2O_2 were used as the oxidizing reagent.[27–29] In our system, the formation of the porous PPy film may be attributed to the coexistence of electropolymerization and chemical polymerization processes. Without Fe in the plating solution, the PPy was produced by only electropolymerization and had a compact structure. When Fe^{3+} was included in the solution, besides the electropolymerization, Fe^{3+}-catalyzed bulk chemical polymerization may also occur (Scheme 2). For the Fe^{3+}-catalyzed polymerization, the tiny amount of Fe^{3+} first oxidizes the pyrrole monomer to give PPy and the Fe^{3+} ions are reduced to Fe^{2+} ions. Then the Fe^{2+} ions are oxidized into Fe^{3+} by the positive potential and used again to chemically synthesize PPy. Thus, Fe^{3+} acts as a catalyst in the synthesis of PPy. The need to regenerate Fe^{3+} by the electrode is believed to confine the chemical polymerization to the vicinity of the electrode surface, leading to closely coupled electropolymerization and chemical polymerization. And this combined polymerization process promotes the growth of porous and rough PPy film.



Scheme 2.

Other types of iron salts, such as $FeCl_2$, $Fe(ClO_4)_3$, $Fe(ClO_4)_2$, and $FeSO_4$, can also be used to produce similar PPy structures. To control the rate of chemical polymerization and the import of excess amounts of codopants such as Cl^-, ClO_4^-, and SO_4^{2-}, the concentration of the iron salts is usually kept very low ($< 10^{-3}$M).

As-prepared highly porous PPy films have interesting surface properties. As can be seen from the SEM images (Figure 1a–c), the porous PPy films exhibit both coarse-scale and fine-scale roughness (so-called double-roughness structure), which is a favorable structure for mimicking the lotus-leaf effect for repelling water.[30] When low-surface-energy perfluorooctanesulfonate (PFOS) was used as a dopant in the polymerization, the PPy films showed superhydrophobicity with a static water contact angle as high as 152 ± 2° (Figure 2a left), while the water contact angle of the compact smooth PPy film was about 105 ± 2° (Figure 2b left). It is well-known that surface roughness amplifies hydrophobicity.[31–33] The common way to obtain superhydrophobicity is to modify a rough surface with low-surface-energy materials such as perfluorinated materials, or to produce a rough structure on a hydrophobic surface. The advancing (θ_A) and receding (θ_R) contact angles of the superhydrophobic surface were measured to be 155 ± 2° and 147 ± 2°, respectively. The low contact angle hysteresis (~8°) of water on the PPy surface confirms the lotus effect which results from the double-roughness structure of the porous PPy films. Our method offers a simple, one-step process to fabricate conducting

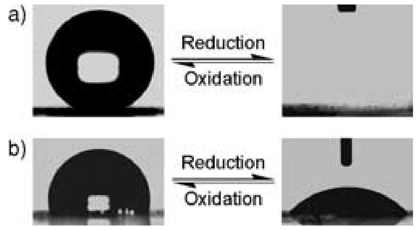


Figure 2. Electrical-potential-induced wettability conversion between PFOS-doped (oxidized) PPy films and dedoped (neutral) PPy films. Under negative potential (−0.6 V vs. Ag/AgCl), the oxidized PPy films were reduced to neutral PPy films, and under positive potential (1.0 V vs. Ag/AgCl), the neutral PPy films were again oxidized to oxidized PPy films. The conversion is reversible. a) The profile of a water drop on a highly porous PPy film. Oxidized PPy film shows superhydrophobicity with a water contact angle of 152 ± 2° (left); neutral PPy film shows superhydrophilicity with a water contact angle of ≈ 0° (right). b) The profile of a water drop on a compact PPy film. Oxidized PPy film is hydrophobic with a water contact angle of 105 ± 2° (left); neutral PPy film is hydrophilic with a water contact angle of 48 ± 2° (right).

polymers with superhydrophobicity. The superhydrophobic PPy films can be deposited on common conducting substrates such as metals and indium tin oxide (ITO)-coated glasses. Our experiments revealed that the superhydrophobic PPy films adhered well to the Au-coated glass surface, and they can be easily peeled off for convenient transfer to other substrates.

Conducting polymers like PPy can be reduced and oxidized reversibly by controlling the electrochemical potential. It is expected that the oxidized (doped) PPy and neutral (dedoped) PPy show different wettability. Neutral PPy, which contains pyrrole moieties, is usually slightly hydrophilic. Surface roughness enhances both the hydrophilicity of hydrophilic surfaces and the hydrophobicity of hydrophobic ones. When we held the PFOS-doped PPy in a 0.05 M solution of TEAPFOS in acetonitrile at a negative potential (−0.6 V vs. Ag/AgCl reference electrode) for 20 minutes, the superhydrophobic PPy film was converted to neutral PPy film, which exhibits a water contact angle of about 0°, indicating that a superhydrophilic PPy surface was achieved (Figure 2a). The superhydrophilicity results from the imbibition of water into the texture of neutral PPy films with high roughness and a hydrophilic nature (see Supporting Information). Under similar switching conditions, the compact PPy film changed to a neutral one having a contact angle of 48 ± 2° (Figure 2b). When we held the superhydrophilic (neutral PPy) film in a 0.05 M solution of TEAPFOS in acetonitrile at a positive potential (1.0 V vs. Ag/AgCl reference electrode) for 20 minutes, the superhydrophobic (oxidized PPy) surface was regenerated. Through controlling the electrochemical potential, PPy films were changed between the oxidized state and neutral state repeatedly, resulting in a reversibly switchable superhydrophobic and superhydrophilic surface (Figure 3).

The neutral and oxidized PPy films are different not only in their surface properties but also in their chemical composition, electronic structure, color, conductivity, and volume. Energy dispersive X-ray (EDX) spectra reveal that little PFOS dopant exists in the neutral PPy films but significant amounts are found in the oxidized ones. Neutral PPy films are brown, while the PFOS-doped PPy films are black. The major UV/Vis absorption band of the PPy film is blue-shifted from 460 nm (2.7 eV in energy) for the PFOS-doped PPy film to 395 nm (3.1 eV in energy) for the neutral one. The conductivities of the PFOS-doped PPy film and the neutral film are around 50 $\mathrm{S\,cm^{-1}}$ and 0.02 $\mathrm{S\,cm^{-1}}$, respectively. (A trace amount of the PFOS dopant still exists in the neutral film.) The volume (the pores and submicron PPy particles) of the PPy film retracted after the oxidized PPy was reduced to neutral PPy.

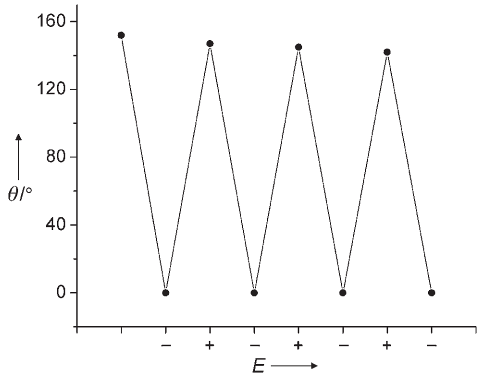


Figure 3. Reversible superhydrophobic-to-superhydrophilic conversion of the porous PPy films through applying alternative negative potential (−0.6 V vs. Ag/AgCl) and positive potential (1.0 V vs. Ag/AgCl). θ = contact angle.

In summary, we have demonstrated a simple facile electropolymerization of superhydrophobic PPy films and the reversible switching of the PPy films between superhydrophobicity and superhydrophilicity. The PPy films exhibit an extended porous structure. These highly porous conducting polymers may have unique surface properties. Though we used pyrrole monomer and PFOS dopant in our synthesis, it is expected that our method can be extended to prepare other types of conducting polymers such as polythiophene, polyaniline, and poly(*N*-methyl pyrrole), and polypyrrole with other types of dopants. The reversible superhydrophobic-to-superhydrophilic switching of the PPy films is achieved by simply adjusting the electrical potential. These smart films may find numerous applications, for example, in drug delivery, biochips, microfluidics (e.g., switches and pumps), and biosensors. In addition to the wettability switching, the volume, conductivity, and color of the PPy films also undergo reversible conversion, making it possible to construct multifunctional conducting polymer devices combining special mechanical, electrical, optical, and interfacial properties.

Experimental Section

Synthesis of superhydrophobic polypyrrole films: The electrochemical cell, which consisted of a glass tube 3 cm in diameter that terminated in a 1.6-$\mathrm{cm^2}$ "O" ring seal, was placed on top of the conducting substrate (such as Au-coated glass slides, steel foils, and ITO-coated glass slides) and held in place with a clamp. The electroplating solution, which contained 0.1 M pyrrole, 0.05 M tetraethylammonium perfluorooctanesulfonate (TEAPFOS), and 2.0×10^{-4} M $\mathrm{FeCl_3}$ in acetonitrile, was then added to the cell, and conducting polypyrrole (PPy) was plated at a constant current of ≈ 0.25 $\mathrm{mA\,cm^{-2}}$

in an argon atmosphere using a Solartron 1287 A potentiostat/galvanostat. Pt wire and Ag/AgCl electrode (sat. KCl) were used as the counter electrode and reference electrode, respectively. The time for the polymerization was usually 1 h. After polymerization, the PPy films were washed in acetonitrile and then dried under a flow of argon.

Switching experiments: The device for the switching experiments was the same as that used for the synthesis of the PPy films. The solution for switching contained 0.05 M TEAPFOS in acetonitrile. By holding the PFOS-doped (oxidized) PPy films in the solution at a negative potential (−0.6 V vs. Ag/AgCl reference electrode) for 20 min, the oxidized PPy was converted to neutral PPy. Neutral PPy films were then washed in acetonitrile and dried under a flow of argon. By holding the neutral PPy films in the solution at a positive potential (1.0 V vs. Ag/AgCl reference electrode) for 20 min, the neutral PPy was converted to oxidized (PFOS-doped) PPy. Oxidized PPy films were then washed in acetonitrile and dried under a flow of argon. The switching experiments can be conducted repeatedly on the same sample.

Characterization: SEM images and EDX spectra were obtained on an XL30 FEG scanning electron microscope. Contact angle measurements were performed using a VCA Optima contact angle instrument at ambient temperature (AST Products, Inc.). The water droplets used for measurements had a volume of 3.0 μL. Dynamic advancing (θ_A) and receding (θ_R) contact angles were recorded as water was added to and withdrawn from the water droplet, respectively. The conductivity of the samples in the plane direction was determined by a standard four-probe method. UV/Vis absorption spectra of PPy films were recorded on Varian Cary 50 UV/Vis spectrophotometers (190–1000 nm).

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