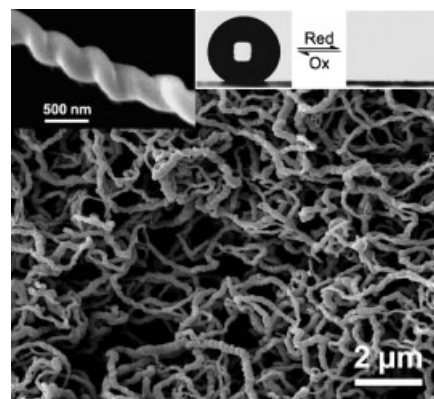


Electrochemical Synthesis of Perfluorinated Ion Doped Conducting Polyaniline Films Consisting of Helical Fibers and their Reversible Switching between Superhydrophobicity and Superhydrophilicity^a

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Superhydrophobic conducting polyaniline (PAni) films were electrochemically deposited in acetonitrile-H₂O electrolyte containing aniline monomer and perfluorooctanesulfonic (PFOS) acid. The films exhibited an extended network structure composed of helical PAni sub-micron fibers. The helical fibrous structure is thought to form through a supermolecular templating process. The surface of the PFOS-doped PAni films showed a water contact angle of 153°. Reducing the PFOS-doped PAni (in emeraldine salt form) by negative potential led to de-doped PAni films (in leucoemeraldine base form) which were superhydrophilic (water contact angle close to 0°). By controlling the electrical potential, PAni films were changed between the doped state and de-doped state, resulting in reversibly switchable superhydrophobic and superhydrophilic surfaces.



Introduction

Among conducting polymers, polyaniline (PAni) stands out because of its many outstanding properties, including remarkable processability, good environmental stability, wide and controllable conductivity and ease of synthesis.^[1] Micro- or nano-structured PAni fibers and tubes

have received great interest for potential uses in micro-electronic devices,^[2] sensors,^[3] fuel cell catalyst supports,^[4] etc. A number of techniques, such as template-directed synthesis,^[5] interfacial polymerization,^[6] dilute polymerization,^[7] “nanofiber seeding” synthesis,^[8] electrospinning^[9] and direct electrochemical synthesis^[2] are employed to fabricate polyaniline fibers and tubes. However, to date, the synthesis of PAni micro- or nanofibers with a helical morphology has seldom been reported. Chiral PANis have been extensively investigated for their promising applications in fields such as surface-modified electrodes, chiral separations and chemical and biological sensors.^[10–17] It has been suggested that the chirality of PAni arises from the preferential adoption of a one-sense helical screw by the developing PAni chains, depending on the chirality of the dopant anions used,^[10–12] but usually no obvious helical structure is directly observed in these

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chiral PANis by microscopic techniques such as transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Hatano et al. synthesized helical PANi nanofibers using synthetic lipid assemblies as templates,^[18] and Lu et al. obtained helical PANi micro-wires through poly(acrylic acid)-guided synthesis,^[19] but, for both methods, the bulk synthesis of helical fibers or wires is not yet available. In this work, we produced bulk polyaniline microfibers with a helical morphology in the presence of achiral perfluorinated acid.

Low surface energy perfluorinated molecules are widely used in modifying or constructing rough structures to produce highly hydrophobic and even superhydrophobic (water contact angle $>150^\circ$) surfaces.^[20,21] Recently, using perfluorinated dopants, we have successfully fabricated superhydrophobic polypyrrole (PPy) films with both coarse-scale and fine-scale roughness (i.e., double roughness), by combining electrochemical polymerization and chemical oxidation in a single step synthesis.^[22] Also, controlling the wettability of a solid surface is important for numerous applications, ranging from self-cleaning surfaces to microfluidics to biomedicine.^[23–26] Diverse smart surfaces with reversibly switchable wettability have been developed and the reversible switching is realized through the adjustment of electrical potential,^[27–30] temperature,^[31,32] light illumination,^[33–36] pH^[37] and elastic force.^[38] Among these approaches, the electrical potential switch receives special attention for its simple control by electricity and convenience to implement to individually address an array of small surfaces. We have demonstrated that perfluorooctanesulfonate-doped PPy films with double roughness structure exhibit reversible wettability and can be switched between two extremes of superhydrophobicity and superhydrophilicity (water contact angle $<5^\circ$) by applying a weak electrical potential.^[22] Previous work by other researchers also showed that PANi had electrically switchable wettability, but the contact angle change (around 30°) was rather small.^[39,40] For practical applications, a large change in surface wettability is desirable. Herein, we report a simple electrochemical process to fabricate superhydrophobic conducting PANi fiber films and demonstrate their convenient electrical potential controllable switching from superhydrophobic to superhydrophilic.

Experimental Part

Materials

Aniline (Aldrich), perfluorooctanesulfonic acid (TCI America), tetraethylammonium perfluorooctanesulfonate (Aldrich), $\text{NH}_3 \cdot \text{H}_2\text{O}$ (Aldrich) and acetonitrile (EMD) were all of reagent quality and were used as received.

Synthesis

Polyaniline (PANi) films were synthesized by the electrochemical oxidation of aniline monomer on conducting substrates (e.g., Au coated and indium tin oxide (ITO) coated glass slides). The electrochemical cell, which consisted of a 3 cm diameter glass tube terminating in a 1.6 cm² “O” ring seal, was placed on top of the conducting substrate and held in place with a clamp. The electroplating solution, which typically contained 0.1 M aniline and 0.12 M perfluorooctanesulfonic (PFOS) acid ($\text{CF}_3(\text{CF}_2)_7\text{SO}_3\text{H}$) in acetonitrile- H_2O (H_2O concentration about 5% (v/v)) was then added to the cell, and conducting PANi was deposited at a constant current of $\sim 0.2 \text{ mA} \cdot \text{cm}^{-2}$ in an argon atmosphere using a Solartron 1287A potentiostat/galvanostat. Pt wire and Ag/AgCl (4.0 M KCl) were used as the counter and reference electrode, respectively. The time for polymerization was usually 1 h. After polymerization, PANi films were washed in acetonitrile- H_2O (H_2O concentration about 5% (v/v)) and acetonitrile, and then dried under flowing argon. De-doped PANi fibers were obtained by dispersing the PANi film in 2 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ by ultrasonication, stirring in 2 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ overnight, and then removing the $\text{NH}_3 \cdot \text{H}_2\text{O}$ by centrifugation. After this, the de-doped PANi fibers were washed with water and acetonitrile, and then dried under flowing argon.

Switching Experiments

The device for switching experiments was the same as that used for PANi film synthesis. The solution for switching contained either 0.1 M tetraethylammonium perfluorooctanesulfonate ($\text{TEAPFOS} \cdot \text{Et}_4\text{N}^+\text{CF}_3(\text{CF}_2)_7\text{SO}_3^-$) in acetonitrile or 0.1 M PFOS acid in acetonitrile. For the switching in 0.1 M TEAPFOS solution, by holding the superhydrophobic PANi films in the solution at a potential of -0.1 V (vs. Ag/AgCl reference electrode) for 10 min, the emeraldine salt PANi was converted to the fully reduced leucoemeraldine base PANi. Leucoemeraldine base PANi films were then washed in acetonitrile and dried under flowing argon. By holding the fully reduced PANi films in the solution at a positive potential (0.6 V vs. Ag/AgCl reference electrode) for 10 min, the PANi was converted to PFOS-doped emeraldine salt PANi again. The emeraldine salt PANi films were then washed in acetonitrile and dried under flowing argon. The switching experiments can be repeated for many cycles. For the switching in 0.1 M PFOS acid solution, the potentials were -0.1 V (emeraldine to leucoemeraldine conversion) and 0.9 V (leucoemeraldine to emeraldine conversion), respectively.

Characterization

Scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) spectra were obtained on an XL30 FEG scanning electron microscope. Transmission electron microscopy (TEM) was carried out on a FEI-PHILIPS CM300 transmission electron microscope operating at 200 keV. Contact angle measurements were performed using a VCA Optima contact angle equipment at ambient temperature. The water droplet size used for measurements was 2.0 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-visible absorption spectra of PPy films were obtained on a Varian Cary 50 UV-Vis spectrophotometer.

Results and Discussion

PAni fiber films were synthesized on a conducting surface like Au-coated glass by electrochemical polymerization. A typical electroplating solution contained 0.1 M aniline and 0.12 M perfluorooctanesulfonic (PFOS) acid ($\text{CF}_3(\text{CF}_2)_7\text{SO}_3\text{H}$) in acetonitrile- H_2O (H_2O concentration about 5% (v/v)). The electropolymerization was carried out galvanostatically. Figure 1(a) and 1(b) show typical SEM images of the as-prepared dark green PAni films. The PAni films are composed of sub-micron fibers with helical structures. Both left handed and right handed helices can be found. The typical length of the fibers is about 10–20 μm and the diameter ranges from 200–800 nm, but most are around 400 nm. A high magnification SEM image of a section of a PAni fiber with right handed helicity is shown in Figure 1(c). The inset shows a fiber with helicity reversal (the arrow points at the reversal point between left handed and right handed helices). Figure 1(d) is a tilted view of the cross-section of a broken PAni film. The PAni film consists

of submicron fibers extending from the bottom to the top surface. The PAni fibers are tangled together forming an interconnected network structure with good mechanical integrity and stability. The helical structure of PAni fibers can also be observed in the TEM images. Figure 2 is the TEM image of an assembly of a few helical PAni fibers. The inset shows the high magnification TEM image of a small section of a PAni fiber.

A small amount of water (about 2–5% (v/v)) in the electrolyte is important in the synthesis of PAni fibers. If no water is used, the aniline salts of PFOS acid cannot dissolve in acetonitrile well and polymerization cannot be effectively carried out. However, if too much water (larger than 10% (v/v)) is used, no good polymer film deposits on the conducting substrate. The concentration of PFOS acid in electrolyte is usually slightly higher than that of aniline to ensure a slightly acidic environment for PAni synthesis. The formation of the helical PAni fibrous superstructure can be well reproduced.

It is known that linear perfluorinated chains adopt a helical structure in the crystalline state,^[41] and it has also been reported that the helical configuration of perfluorinated chains exists in solution.^[42,43] Recently, Cui et al. obtained a helical superstructure from 1H,1H,2H,2H-perfluorooctyltriethoxysilane ($\text{C}_6\text{F}_{13}(\text{CH}_2)_2\text{Si}(\text{OEt})_3$) through surface and solution self-assembly processes.^[44] Usually, chirality and amphiphilicity are presented in the mole-

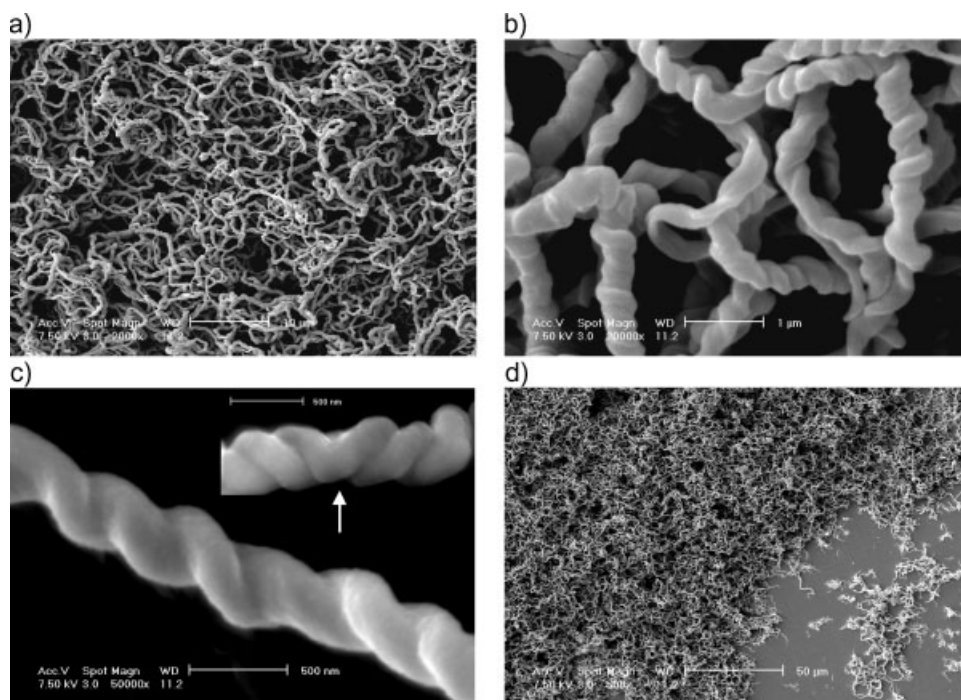


Figure 1. SEM images of perfluorooctanesulfonate-doped polyaniline film on Au coated glass surface. (a) Top view at low magnification. (b) Top view at high magnification. (c) Top view at high magnification of a section of a helical polyaniline fiber; inset: a helical fiber with chirality reversal. (d) Tilted view of a broken polyaniline film. Scale bars: (a) 10 μm , (b) 1 μm , (c) 500 nm (inset: 500 nm), (d) 50 μm .

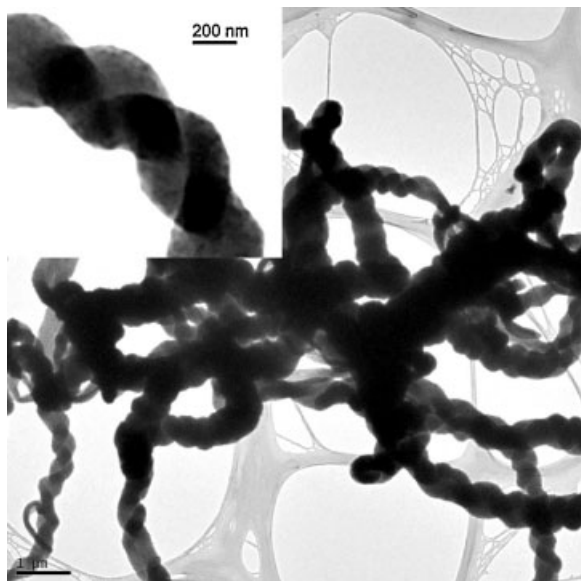


Figure 2. TEM image of an assembly of a few perfluorooctane-sulfonate-doped helical polyaniline, inset: high-magnification of a small section of a polyaniline fiber. Scale bar: 1 μm (inset: 200 nm).

cules for their self-assembly into fibers with helical or twisted morphologies.^[45,46] We suppose that the PFOS ions used in this study adopt a helical conformation (molecular chirality) and self-assemble into helical chains (supermolecular chirality), which are driven and maintained by the strong hydrophobic and lipophobic interactions between the long fluorocarbon chains^[47] and the strong electrostatic and hydrogen bonding interactions between the sulfonate and protonated aniline.^[12,19] The helical PFOS ion chains then act as supermolecular templates and also PFOS ions act as dopants in the growth of helical PANi fibers. Since PFOS ions are achiral (both left handed and right handed conformations may exist), racemic products are obtained in our synthesis, as is suggested by the SEM and TEM images (Figure 1 and 2). Even though the formation mechanism of helical PANi fibers is not yet clearly understood, the proposed supermolecular templating appears to be consistent with the microscopic observations.

Using the standard four probe method, the conductivities of the PFOS doped PANi films were measured to be in the range of 1–2 $\text{S}\cdot\text{cm}^{-1}$, comparable to the values of nanostructured PANi doped with inorganic acids, such as HCl, H_2SO_4 , HBF_4 and H_3PO_4 .^[48] The UV-vis spectra of PFOS-doped PANi and de-doped PANi fibers are shown in Figure 3. The doped form of PANi exhibits a peak maximum at 450 nm and a broad band at around 950 nm assigned to polaron band transitions,^[49] indicating that the as-prepared PANi is in conducting emeraldine salt form. The de-doped form of PANi fibers has absorbance

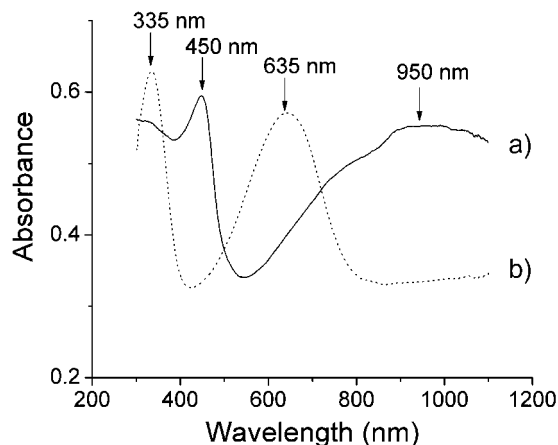


Figure 3. UV-vis spectra of sub-micron polyaniline fibers dispersed in acetonitrile: a) PFOS-doped polyaniline (solid line); b) de-doped polyaniline (dotted line).

peak maxima at 335 and 635 nm, which agrees well with those of the emeraldine base form of PANi.^[50]

A unique characteristic of a conducting polymer (such as polyaniline, polypyrrole and polythiophene) is that the charged backbone can be balanced with many different negatively charged counter ions (dopants). The wettability of the conducting polymer surfaces can thus be manipulated by varying the dopant used.^[51] When a low surface energy ion is employed, a hydrophobic surface can be obtained. The hydrophobicity can be further enhanced by surface roughness.^[22,52–54] As-prepared PANi films doped with low surface energy PFOS have an extended porous structure composed of interconnected helical PANi fibers (Figure 1). Such a highly rough surface showed superhydrophobicity with a static water contact angle of $153^\circ \pm 2^\circ$ (Figure 4(a) left). The advancing (θ_A) and receding (θ_R) contact angles were measured to be $155^\circ \pm 2^\circ$ and $143^\circ \pm 2^\circ$, respectively. The contact angle hysteresis ($\approx 12^\circ$) is a little higher than that of the superhydrophobic PPy (contact angle hysteresis $\approx 8^\circ$) with double roughness structure we obtained before.^[22] The static contact angle is comparable to those of recently reported superhydrophobic conducting polymer surfaces obtained by electrodeposition, such as films (contact angles all slightly higher than 150°) of PFOS-doped PPy,^[22] poly(alkylpyrrole),^[52] and poly(fluorinated thiophene),^[53] but a little lower than that of superhydrophobic PANi/polystyrene films (contact angle $\approx 166.5^\circ$) fabricated by electrospinning,^[54] and superhydrophobic rambutan-like hollow spheres of polyaniline (contact angle $\approx 164.5^\circ$) through a self-assembly method.^[55]

Conducting PANi can be reduced and oxidized reversibly by controlling the electrical potential.^[56] It is expected that oxidized PANi and reduced PANi will show different wettability.^[39,40] Because of the degradation of fully

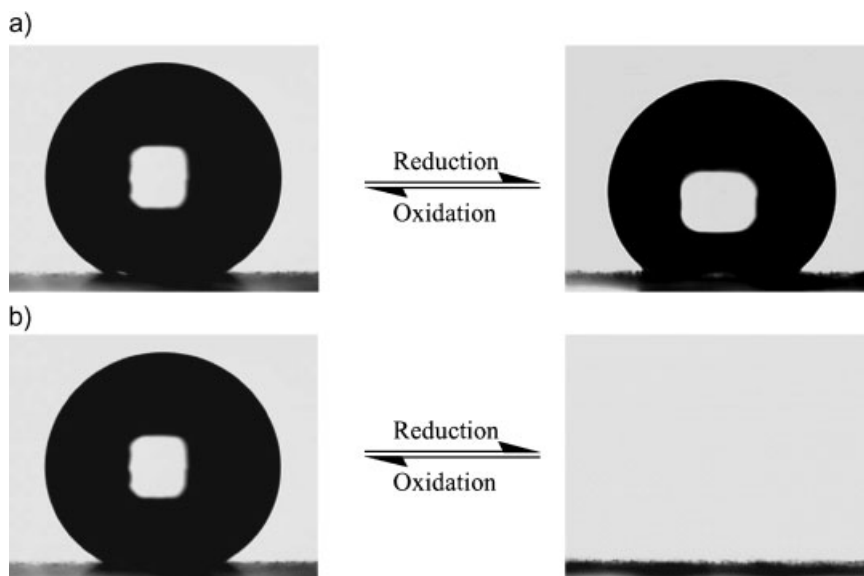


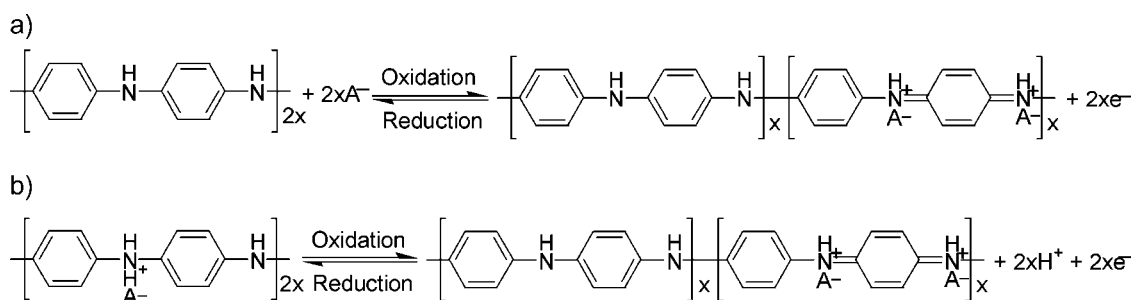
Figure 4. Electrical potential induced wettability conversion between oxidized PFOS-doped PANi (in emeraldine salt form) films and reduced PANi (in leucoemeraldine form) films. (a) The switching is conducted in 0.1 M PFOS acid solution. (b) The switching is conducted in 0.1 M TEAPFOS acetonitrile solution.

oxidized pernigraniline,^[56] we performed wettability switching over the potential range corresponding to the redox of half-oxidized emeraldine and fully reduced leucoemeraldine. Herein we demonstrate the wettability switching in two different electrolytes: 0.1 M PFOS acid acetonitrile solution and 0.1 M tetraethylammonium perfluorooctanesulfonate (TEAPFOS:Et₄N⁺CF₃(CF₂)₇SO₃⁻) acetonitrile solution respectively. For the switching in 0.1 M PFOS acid acetonitrile solution, after holding the PFOS-doped PANi at a potential of -0.1 V (vs. Ag/AgCl reference electrode) for 10 min, the superhydrophobic PANi (in emeraldine salt form) film was converted to leucoemeraldine PANi film having a contact angle of 140° ± 2° (Figure 4(a)). Interestingly, when we held the PFOS-doped PANi film in 0.1 M TEAPFOS acetonitrile solution at -0.1 V for 10 min, the superhydrophobic PANi was converted

to a leucoemeraldine PANi film exhibiting a water contact angle of 0° (Figure 4(b)), indicating that a superhydrophilic PANi surface was achieved. When the superhydrophilic reduced PANi film was kept in 0.1 M TEAPFOS solution at 0.6 V (vs. Ag/AgCl reference electrode) for 10 min, the superhydrophobic (contact angle: 150° ± 2°) PANi (PFOS-doped emeraldine salt form) surface was regenerated. Through controlling the electrical potential, PANi films were changed between the oxidized emeraldine salt form and reduced leucoemeraldine form repeatedly, resulting in a reversibly switchable superhydrophobic and superhydrophilic surface. The leucoemeraldine film obtained in 0.1 M PFOS acid solution can also be switched back to superhydrophobic PANi by keeping it in 0.1 M PFOS acid solution at 0.9 V for 10 min.

MacDiarmid et al. considered that for the redox switching of PANi in aqueous inorganic acid solution the proton transfer reaction is predominant at low pH, whilst the transfer of anions dominates at higher pH.^[56] We assume that the switching in our system follows a similar mechanism though it was conducted in acetonitrile solution (Scheme 1).

When PFOS-doped PANi was reduced in neutral TEAPFOS solution, the PFOS dopants were transferred out of the polymer and de-doped PANi in leucoemeraldine base form was obtained (Scheme 1(a)). EDX spectra (see Figure S1 in Supporting Information) reveal that little PFOS dopant exists in the as-obtained reduced PANi, confirming that it is in leucoemeraldine base form.^[56,57] Leucoemeraldine base, which contains N-H groups, is expected to be slightly hydrophilic. Surface roughness enhances both the hydrophilicity of hydrophilic surfaces and the hydrophobicity of



Scheme 1. Redox switching of PANi in a) 0.1 M TEAPFOS acetonitrile solution and b) 0.1 M PFOS acid acetonitrile solution.

hydrophobic ones, thus the highly rough leucoemeraldine base with a fibrous network structure exhibits a superhydrophilic characteristic.^[22,58] When the de-doped PANi was oxidized in TEAPFOS, the PFOS dopants were transferred into the polymer and superhydrophobic PANi in emeraldine salt form was regenerated.

In 0.1 M PFOS acid solution, the proton/electron transfer may play a major role in the redox switching (Scheme 1(b)). When PANi was reduced, protons were transferred into the polymer to neutralize the charge and the protons would bind to the amine groups in PANi to form protonated leucoemeraldine (also called leucoemeraldine salt).^[59] It is reported that, in aqueous electrolyte, the protonation is pH dependent, and it begins at about pH 2 and is completed at pH-1.^[60] Also, the protonation is dopant dependent.^[60] For example, in PANi doped with a low mobility big dopant such as PSS (poly(styrene sulfonate)), the proton transfer reaction controls the switching at about pH 1 in aqueous electrolyte,^[61,62] though generally for inorganic anion dopants the corresponding pH should be as low as 0.^[56] The solvent effect for the proton transfer reaction is not clear yet, but due to the protophobic nature of acetonitrile, it may be easier for the protons released by PFOS acid (a very strong acid) to bind to amine groups of PANi in acetonitrile solution, then protonation can take place in lower acidic concentration.^[63] As-obtained reduced PANi has similar EDX spectrum (see Figure S1 in Supporting Information) to that of the starting PFOS-doped PANi in emeraldine salt form, indicating that it would be primarily in the leucoemeraldine monoprotinated salt form. As the low surface energy PFOS dopants are still bound to the backbone of PANi, the protonated leucoemeraldine films show a very high contact angle close to that of the superhydrophobic PANi in emeraldine salt form. Since the backbone of protonated leucoemeraldine carries a positive charge, it is expected that the protonated leucoemeraldine would be oxidized at more positive potentials than the neutral leucoemeraldine base,^[56] as is confirmed by the cyclic voltammogram (CV) of the PFOS-doped polyaniline films in PFOS acid solution and TEAPFOS solution (see Figure S3 in Supporting Information).

Conclusion

In summary, we have demonstrated a facile electrochemical technique to fabricate PANi films with an extended network structure composed of helical fibers. These highly rough PANi films exhibit superhydrophobicity and can be reversibly switched between superhydrophobicity and superhydrophilicity by simply adjusting the electrical potential. These conducting polymers with switchable wettability have great potential for applications in drug

delivery, biochips, biosensors and microfluidic devices. Also, the unique helical structure of conducting PANi can be of both fundamental and practical interest. This study may provide a simple, inexpensive and fast way to produce novel conducting polymer superstructures.

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