

Electropolymerization of Highly Hydrophobic Polythiophene Films with High Adhesion Force

Weili Yu, Tongjie Yao, Xiao Li, Tieqiang Wang, Hainan Gao, Junhu Zhang, Bai Yang

State Key Lab for Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, People's Republic of China

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ABSTRACT: Electrochemical cyclic voltammetry (C-V) method was reported to prepare highly hydrophobic polythiophene (PTh) films with high adhesion force. Using this technique, the morphology and surface roughness of PTh film can be controlled by adjusting cycle number, monomer concentration, and applied voltage. After fluorination, the PTh film with hierarchical morphology showed high hydro-

phobicity as well as a strong adhesion force. This method provides a simple solution for the preparation of highly hydrophobic polymer film with high adhesion force. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1052–1059, 2011

Key words: polythiophene; electropolymerization; adhesion; hydrophobic

INTRODUCTION

The wettability of solid surfaces by a liquid is a very important aspect of surface chemistry.^{1–3} Superhydrophobic surfaces usually refer to those which are similar to that of the lotus leaf exhibiting a water contact angle (CA) larger than 150° and a water slide angle (SA) smaller than 5°. Superhydrophobic surface may have a variety of practical applications, such as self-cleaning surfaces, anticorrosion, and microfluidic devices.^{4–7}

Recently, inspired by the gecko lizard's feet, highly hydrophobic surfaces with high adhesion forces have received much attention due to their potential values in fundamental researches and promising applications. It promoted the design of open microfluidic devices for increasing needs for controlled transport of small liquids in biochemical separation, targeted drug delivery, immunoassay, etc.^{8–10} Several techniques have been established to mimic the gecko-feet structure, such as the template method, soft-lithography, the reactive ion etching method and the layer-by-layer method.^{10–14} For example, Jiang and coworkers made polystyrene nanotube arrays using porous alumina membrane template;^{10,13} Wang and coworkers prepared sticky

carbon nanotube arrays by photolithographic pattern process,¹⁴ etc. In these works, both aligned polystyrene nanotube arrays and carbon nanotube arrays had seta-like morphology and were observed to enhance the adhesion forces of highly hydrophobic surfaces. At the same time, it is worth mentioning that to obtain such particular surface structure, the fabrication process is usually complex and time-consuming. Besides that, the area of resulting materials is usually unsatisfied for practical applications. Thus a simple and time-efficient method to prepare large area highly hydrophobic surface with high adhesion force is urgent.

To achieve this goal, the electrochemical method is particularly attractive due to its several advantages including low toxicity, the low cost of electrochemical workstation and fast preparation process. By this method, various materials can be used to fabricate films, including metals, metal oxides or conducting polymers.^{15–18} Polythiophene (PTh) is a representative class of conducting polymer, which is widely used in photo-electronic devices, sensors, anticorrosion, etc.^{19–21} The combination of highly hydrophobic characteristic and the conducting property of PTh film will lead to the development of the material from both scientific and industrial viewpoints. As most of the properties of PTh films and the efficiency of the PTh devices are sensitive to oxygen and moisture, it is expected that such hydrophobic conducting films enhance their environmental stability, and provide that their intrinsic electronic and optical properties be conserved.²² Shi and coworkers have fabricated PTh films with highly hydrophobicity or high adhesion force by electropolymerization method.^{23,24} However, to the best of

Correspondence to: J. Zhang (zjh@jlu.edu.cn).

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our knowledge, fabrication of PTh film combining both high hydrophobicity and high adhesion force without templates by the electrochemical method has not been reported yet.

In this research, we present a simple approach to prepare high-adhesive and highly hydrophobic conducting PTh film by electrochemical method. By adjusting the electrical chemical parameters, such as cycle numbers, monomer concentration, and applied voltage, the morphology of PTh could be easily controlled to a certain extent,²⁵ then a fluorination process was applied to realized highly hydrophobic and high adhesion force. As the electrochemical method combines synthesis and deposition of PTh into one step, we demonstrate this method presents a template-free, time saving and low cost way of processing highly hydrophobic films with high adhesion force.

EXPERIMENTAL

Materials

Tetrabutylammonium hexafluorophosphate (TBAPF₆), 1H, 1H, 2H, 2H-perfluorooctyl trichlorosilane (POTS) and thiophene monomer were obtained from Sigma-Aldrich. Acetonitrile was analytical grade and used as received. In all preparations, absolute ethanol, and deionized water were used.

Electrochemical polymerization of PTh film

Electropolymerization of thiophene monomer was performed in a typical three-electrode cell by cyclic voltammetry (C-V) method. The ITO glass (20 Ω/square) was used as a working electrode with a platinum wire as a counter electrode and an Ag/Ag⁺ electrode as a reference electrode. The ITO glass was cleaned with water, acetone, and ethanol in turn before use. In our electrochemical process, the typical electrolyte was an acetonitrile solution consisting of 0.1 M thiophene monomer and 0.1 M TBAPF₆. After electrochemical polymerization, the film was rinsed with acetonitrile to remove the remaining TBAPF₆, and then dried in N₂ flow.

Preparation of highly hydrophobic PTh film

First, the electropolymerized PTh film was treated with oxygen plasma cleaner for 5 min. Then, the film was exposed to the fluorine gas mixtures of the POTS and air. In detail, the as-prepared PTh film was placed in a sealed vessel (2 L), on the bottom of which was dispensed 0.5 mL of POTS which vaporized resulting in a POTS ambience. There was no direct contact between the substrate and the drops. The vessel was placed in an oven at 120°C for 2.5 h

to enable the vapor of POTS to react with the hydroxyl groups on the PTh film surface. Finally, the substrate was taken out from the vessel and placed in an oven at 150°C for another 1.5 h to volatilize the unreacted POTS molecules on the substrate.

Characterization

The oxygen plasma cleaner was obtained from Harrick Plasma. Scanning electron microscopy (SEM) measurements were performed on a JEOL JSM-6700F SEM instrument. X-ray photoelectron energy spectroscopic (XPS) examinations were performed by the use of an ESCALAB 250 spectrometer (VG, Thermo Scientific). The surface topology and root-mean-square (RMS) roughness were recorded by atomic force microscopy (AFM) images in a tapping mode with a nanoscope IIIa scanning probe microscope from digital instruments under ambient conditions. The static CA was measured on a shape analysis system (DSA 10 MK2, KRÜSS) at ambient temperature. Three microliter of deionized water was dropped onto the samples each time and the average of at least three measurements was taken at different positions on each sample. The conductivity of PTh film was measured by four-point probe method.

RESULTS AND DISCUSSION

Surface morphology by SEM

As we know, the C-V method could exhibit the oxidation and reduction information, it was easy to control the oxidative charge and the amount of polymerized thiophene monomer. In this case, the C-V method was applied and a proper condition with a voltage of -1.0 to 1.8 V and monomer concentration of 4 mg/mL was chosen to investigate the effect of cycle numbers on the morphology of PTh film. The typical C-V curve of electropolymerization of thiophene monomer is shown in Figure 1. It can be seen that the oxidation current keeps on improving with the increase of the cyclic numbers. This indicated that the PTh was electropolymerized and deposited on the ITO glass continuously. Figure 2 presents the SEM images of PTh film after sweeping different number of cycles. After the first C-V cycle, the surface of the ITO glass was covered with scattered PTh nanoparticles [Fig. 2(a)]. These particles were generated from the nonuniformity of the active sites on the ITO glass where the thiophene monomer polymerized first. Moreover, it grew much faster on active sites than the surrounding places.²⁶ When the second cycle finished, all PTh nanoparticles accumulated into submicrospheres and they connected with

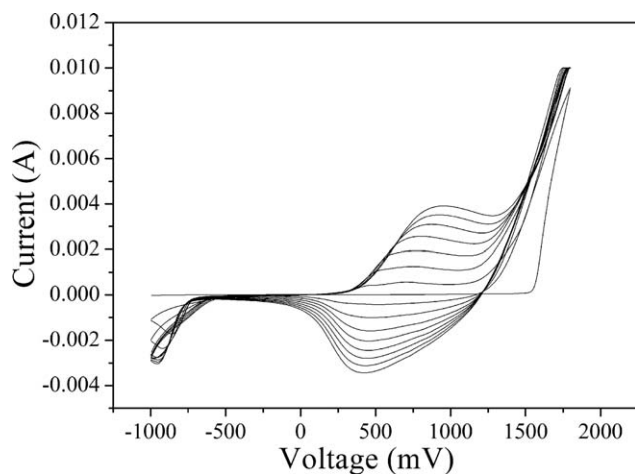


Figure 1 Cyclic voltammograms of electropolymerizing PTh in the range of -1 to 1.8 V versus Ag/Ag^+ recorded in acetonitrile solution containing 0.1 M TBAPF_6 at a scan rate of 100 mV/s with monomer concentration of 4 mg/mL.

each other; therefore, the whole ITO glass surface was covered with PTh film [Fig. 2(b)]. A typical cross section of electropolymerized PTh film was acquired as shown in the inset of Figure 2(b). From the image, it can be observed that the PTh submicrospheres are hemispherical, which suggests that the PTh film originated from PTh particles. The surface of these submicrospheres was relatively smooth and no apparent protuberance could be observed. The SEM image of PTh film after four cycles is displayed

in Figure 2(c) which indicates that the growth of PTh submicrospheres continued. The size of the submicrospheres in Figure 2(b) was smaller than that in Figure 2(c). In addition, some nanoscale protuberances appeared on the surfaces of these submicrospheres, which revealed that hierarchical structures were formed. When the C-V cycle number was increased to eight, the average size of the PTh submicrospheres exceeded 500 nm and the size of the nanoscale protuberances on the submicrospheres was above 100 nm [Fig. 2(d)]. Figure 2 indicated that the growth of thiophene monomer on ITO glass proceeded from nanoparticles to the film and finally to a hierarchical structure. The growth mechanism was in accordance with previously reported three-dimensional (3D) nucleation and growth processes, and the reason was believed due to the separated electrically active sites on ITO surface.²⁷

The influence of C-V cycle numbers on the diameter distributing of PTh submicrospheres is shown in Figure 3. We investigated both the average diameter (D_a) and max diameter (D_{max}) of the PTh submicrospheres from the SEM and the AFM images. The result indicated that the size distribution of both D_a and D_{max} increased regularly with the increase of cycle number and there was a linear relationship between the diameters and the cycle numbers. From this figure, the slopes of two lines were calculated to be 67 nm per cycle and 80 nm per cycle for D_a and D_{max} , respectively. This result suggested that the

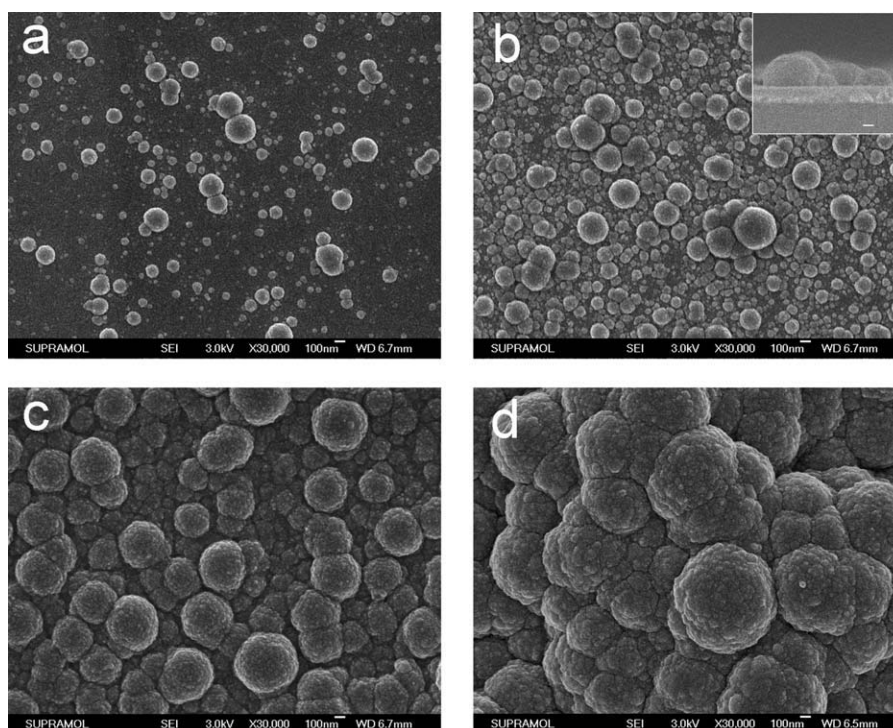


Figure 2 SEM of PTh film after sweeping different number of cycles. Cycle numbers: (a) 1, (b) 2, (c) 4, (d) 8 cycles. Monomer Concentration: 4 mg/mL; C-V (-1 to 1.8 V). Inset: the cross section of PTh in figure (b).

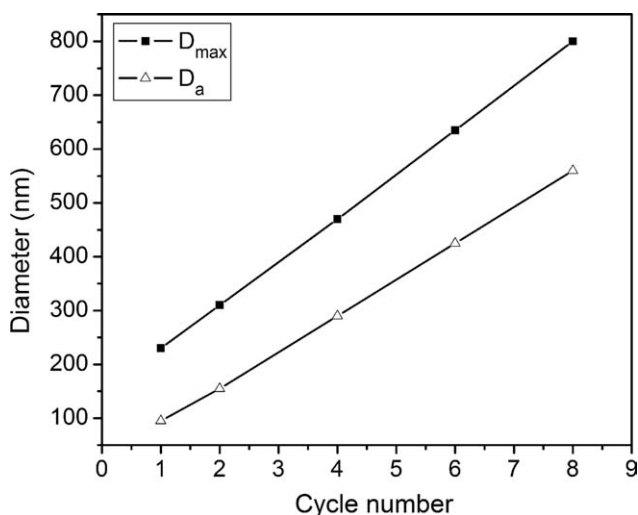


Figure 3 The influence of C-V cycle numbers on the average diameter (D_a) and max diameter (D_{max}) of PTh submicrospheres. Monomer Concentration: 4 mg/mL; C-V (-1 to 1.8 V).

size of PTh submicrospheres could be monitored and the surface morphology could be controlled via the cycle number. When D_a reached 120 nm, the PTh submicrospheres connected and a continuous film formed [Fig. 2(b)]. When D_a was above 277 nm, the PTh submicrospheres overlapped, and PTh film with hierarchical structures was observed [Fig. 2(c)]. Keeping on increasing the cycle number, the hierarchical structures continued to exist [Fig. 2(d)].

Besides the cycle numbers, it was worth mentioning that monomer concentration and applied voltage also played key roles in determining the electropolymerization process and the surface morphology of resulting PTh film. Increasing either monomer concentration or applied voltage, the surface morphology of PTh film showed regular changes similar to that of PTh film prepared by increasing cycle numbers. In detail, when the voltage and cycle number were constant, the PTh film generated and grew with monomer concentration increasing from 1 mg/mL to 8 mg/mL when PTh film with hierarchical structures was achieved (Fig. 4). When monomer concentration and cycle numbers were constant, the PTh film showed the oxidation voltage dependence similarly (Fig. 5). The effect of monomer concentration, voltage and cycle numbers on PTh film morphology was due to that increasing each of the parameters led to the increase of total charge, which suggested more PTh was electropolymerized. By changing each parameter, it was observed that an electropolymerization charge density above 400 mC/cm² was necessary to achieve a PTh film with hierarchical morphology.

Surface composition by XPS

After electropolymerization, the PTh film on ITO glass was fluorinated to improve its hydrophobicity.^{28,29} First, the electropolymerized PTh film was

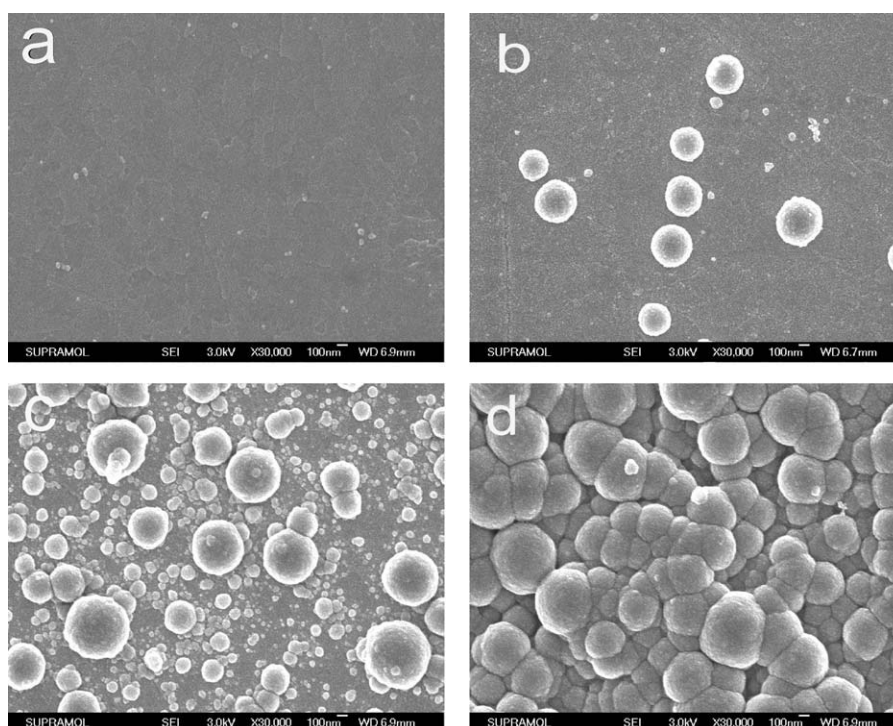


Figure 4 SEM images of electropolymerized PTh film with different monomer concentration. Monomer concentration: (a) 1 mg/mL, (b) 3 mg/mL, (c) 4 mg/mL, (d) 8 mg/mL. C-V (-1 to 1.8 V); two cycles.

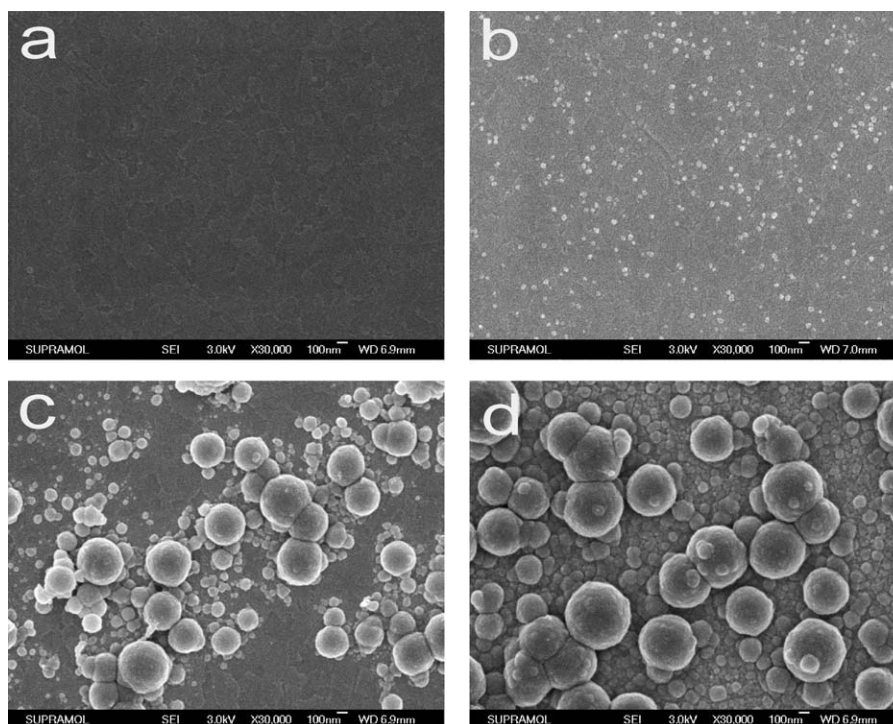


Figure 5 SEM images of electropolymerized PTh film by C-V method with different voltage. The potential cycling range was -1 to X V. X is (a) 1.4, (b) 1.5, (c) 2.0, (d) 3.0 V, respectively. Monomer concentration: 2 mg/mL; two cycles.

treated with oxygen plasma cleaner for 10 min, during which the surface C-H bond of PTh was transformed into hydroxyl or carboxyl. Then, the PTh film covered ITO glasses were fluorinated after placing in POTS atmosphere. The PTh surfaces before and after fluorination were characterized by XPS and the spectra were depicted in Figure 6. Before fluorination, the surface of PTh contains F, C, S, O elements with atomic ratios of 0.42 : 7.51 : 1.00 : 0.51. The small amount of fluorine atoms is due to the electrolyte TBAPF₆. The small amount of oxygen

atoms is possibly due to the oxidation of neutral polythiophene by the oxygen in air. After fluorination, the surface of fluorinated PTh contains F, Si, C, S, O elements with atomic ratios of 20.78 : 7.42 : 8.30 : 1.00 : 13.10. The enhanced oxygen atoms are believed due to the hydroxyl or carboxyl caused by oxygen plasma. The high content of fluorine and silicon elements is believed coming from the POTS molecules. The XPS spectra indicated that during fluorination, the POTS reacted with the PTh film, and this resulted in the formation of a thin, partially

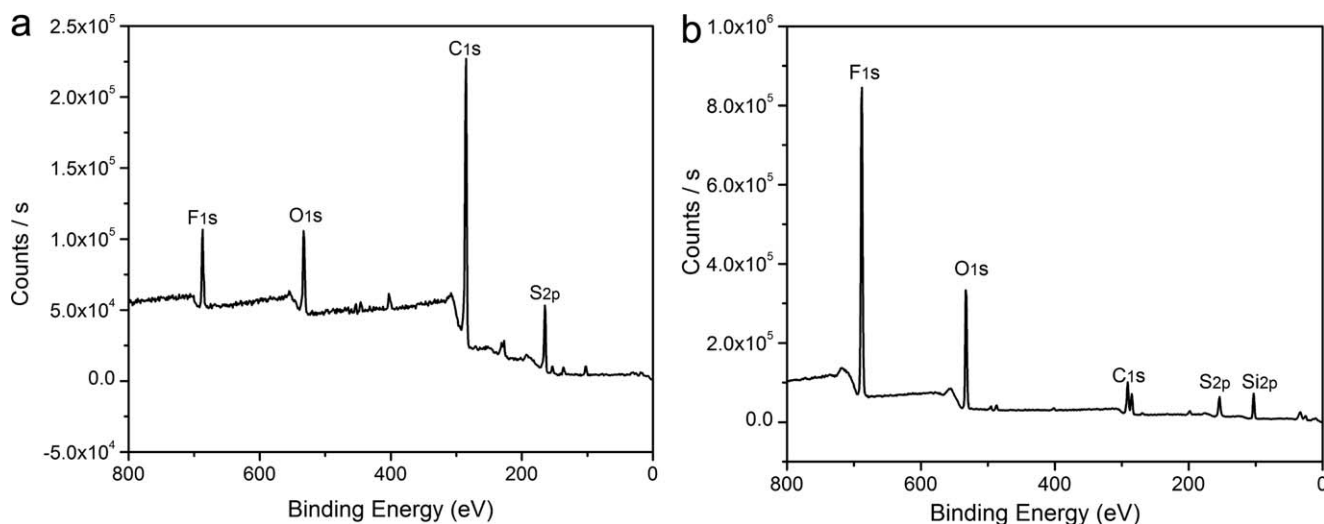


Figure 6 XPS spectra of electropolymerized PTh before (a) and after (b) fluorination.

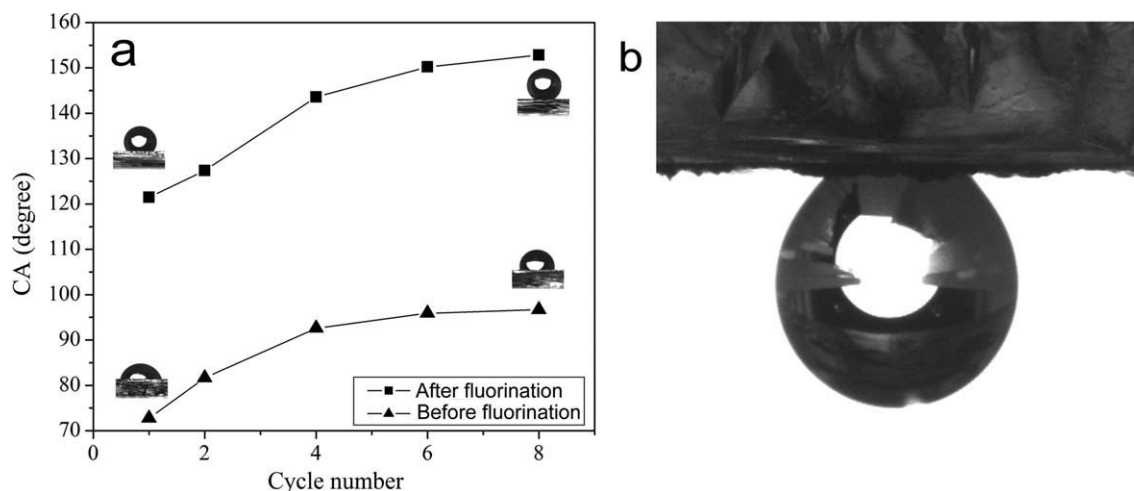


Figure 7 (a) Wetting ability of PTh films before and after fluorination with different cycle numbers; (b) Behavior of water droplet on PTh film with top side down (eight cycles).

fluorinated surface layer, which changed the wettability of PTh film dramatically.

The wettability and surface roughness of PTh film

Contact angle studies provide information about the outer 5–10 Å of a solid film.³⁰ During fluorination process, the thickness of fluorinated layer depends on reaction variables such as fluorine concentration, reaction time and reaction temperature.²⁹ In this case, the fluorine concentration and temperature were fixed at constant value and we have confirmed the fluorination time affected the water contact angle of fluorinated PTh film with hierarchical structure. The CA of the film reached 150° after 90 min and the value was stable after that.

The wettability of PTh film before and after fluorination under various cycle number is presented in Figure 7. Before fluorination, the CA of the PTh samples were between 73° (one cycle) and 97° (eight cycles). After fluorination, the static CA gradually increased from 122° (one cycle) to 153° (eight cycles), and high hydrophobicity was achieved. Further increasing the cycle number (e.g., 32 cycles), the high hydrophobicity of fluorinated PTh film remained stable with the CA remained at 153°. Comparing the surface morphology of PTh film under different C-V cycles, it was found that the high hydrophobicity could only be achieved when the hierarchical structures appeared [Fig. 2(c,d)]. This result is in accordance with previous report that surface structure plays a key role in determining the surface wettability.^{15,24}

It's worth mentioning that there is certain amount of F atoms which come from the doping of electrolyte in the PTh film before fluorination [Fig. 6(a)], and the doping level is closely connected with the

conductivity of electrodeposited PTh film. To further evaluate the relationship between conductivity (doping level) and hydrophobicity, we characterized the conductivity and wettability of PTh film. For doped PTh film as prepared, the conductivity was 0.52 S/cm, and the CAs were 97° before fluorination and 153° after fluorination, respectively. After dedoping at -0.2V, the conductivity of PTh film decreased to 2.3×10^{-3} S/cm, and the CA was 94° before fluorination and 153° after fluorination. The result indicates that the conductivity (doping level) of PTh film was not affected by the fluorination process apparently, and the PTh film can maintain high conductivity after fluorination.

To further investigate the roughness of various PTh films, RMS data in AFM images were obtained. The AFM images of electropolymerized PTh film after sweeping different number of cycles is depicted in Figure 8. The RMS of PTh film increases from 27.1 nm [Fig. 8(a)] to 224.8 nm [Fig. 8(d)]. If the C-V sweeping continues, the roughness of PTh film further increases. For example, when the cycle number reached 32, the surface RMS exceeded 1 μm. By analyzing the RMS data provided by the AFM images, it was found that the morphology and roughness of PTh film were linked together and the roughness of PTh could be controlled by the C-V cycle number. Considering the change of wettability [Fig. 7(a)], it could be concluded that the rougher the film was, the bigger the CA was. The Cassie-Baxter equation could be helpful to explain the high hydrophobicity of the as-prepared PTh film surface:

$$\cos \theta_r = f_1 \cos \theta - f_2 \quad (1)$$

where θ_r and θ are the CAs of a rough surface and a native flat surface, respectively; f_1 and f_2 (with $f_1 + f_2 = 1$) are the area fractions of a water droplet in

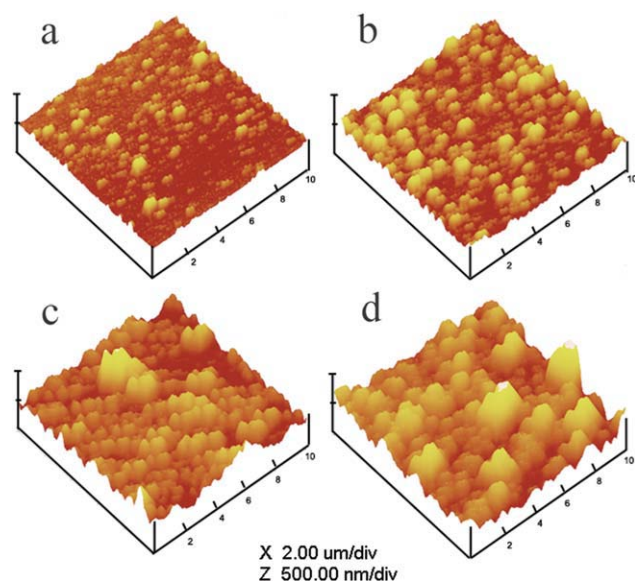


Figure 8 AFM of electropolymerized PTh film. Cycle numbers: (a) 1, (b) 2, (c) 4, (d) 8 cycles. Monomer concentration: 4 mg/mL; C-V (−1 to 1.8 V). [Color figure can be viewed in the online version of this article, which is available at wileyonlinelibrary.com.]

contact with the surface and with air on the surface, respectively.¹⁷ The equation assumes that the water droplet does not completely wet the rough substrate and the air is trapped in the interstices of the rough surface. The droplet interacts with the PTh surface that consists of the solid material and air pockets. According to the above eq. (1), the CA increases with the increase in the surface coverage and roughness, accompanied by the increasing f_2 value. It has been proved that both binary hierarchical structures can effectively increase the roughness of the surface; therefore, these structures facilitate the achievement of high hydrophobicity. The highly hydrophobic film shows hierarchical structures, which is believed to decrease the contact area between the solid PTh film and the water droplets at their interfaces and causing a high water CA.

Adhesion force

Besides high hydrophobicity, another property of the PTh film was that the water droplet on PTh film did not roll off even when the PTh film was inverted 180° [Fig. 5(b)]. This indicates strong adhesion forces exist between water and the PTh film. By dividing the gravity with contact area, the adhesion force was calculated to be 56.78 N/m² which was much higher than that of unfluorinated PTh film (13.47 N/m²) and close to the data provided by polystyrene nanotubes.^{10,13} This result proves that high adhesion force not only exists in natural gecko's feet and regularly aligned artificial polymer structures, but also in hier-

archical structures composed of submicrospheres and nanoscale protuberance. The hydrophobicity and adhesive force of electropolymerized PTh are much higher than that of the PTh film synthesized by chemical method according to reference.³¹

In this study, the high adhesion force was believed to be caused by the following reasons: first, the adhesion is mainly caused by the van der Waals' force between water and the PTh film.^{13,25} As the PTh film was composed of submicrospherical structures, which were covered by densely packed nanoscale PTh protuberances [Fig. 2(d)], this hierarchical structure was believed to create a large interface between the PTh film and water spheres, which greatly enhanced the van der Waals' forces between the PTh film and water. Second, there are numerous vacancies on the PTh film surface. When the droplet dipped onto it, the water penetrated into these vacancies, which led to the air in vacancies extruding out. Therefore, when the sliding angle becomes larger and larger, even the substrate is inverted 180°, the water droplet would not fall off due to the air pressure.¹³

CONCLUSIONS

In summary, we fabricated highly hydrophobic PTh film with high adhesion force by the traditional C-V method. The effect of cycle number, monomer concentration, and applied voltage on the morphology and wettability of the resulting films were investigated. After a simple fluorination process, a highly hydrophobic surface was obtained for PTh film with hierarchical morphology. These highly hydrophobic films have stronger adhesion force and the water drop on them would not drop off even if the film was inverted 180°. This work provides a very simple method for fabricating highly adhesive and highly hydrophobic film without affecting its conductivity, thus opens a solution for many technological applications.

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