



# A feasible electrochemical method for tuning coatings wettability from superhydrophilicity to superhydrophobicity



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## ABSTRACT

A feasible electrochemical method for controlling arbitrarily the surface wettability between superhydrophilicity and superhydrophobicity was presented in details. A series of composited polythiophene films (PL-PEDOT) with wettability from superhydrophilicity to superhydrophobicity were readily fabricated by tuning precisely the electrodeposition charge (EC) of overlying hydrophobic poly(2,2'-bithiophene) (PLTH) moieties on the underlying poly(3,4-ethylenedioxythiophene) (PEDOT) moieties. The various wettability of the resulting PL-PEDOT film could be attributed to the combination of the conducting and porous nanostructure of PEDOT films and the flexible electrodeposition strategy. The wettability change of PL-PEDOT films is also accompanied by the changes in their spectral colors. This electrochemical method could present a feasible technique for the preparation of various wettability surfaces in practical applications.

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## 1. Introduction

Controlling the wettability of a variety of surfaces between superhydrophilicity and superhydrophobicity has recently received the special attention. The superhydrophobic surfaces with water contact angle (WCA) of  $>150^\circ$  have been intensively developed due to their potential applications in self-cleaning and anti-sticking coatings [1–5], micro-fluid control systems [6], and even bio-interfacial materials [7–11]. Similarly, the superhydrophilic surfaces with  $WCA < 10^\circ$  have also many important applications, such as enhanced boiling heat transfer and antifogging coatings [12–15]. In general, the wettability of the solid surfaces was governed by their chemical composition and geometric micro/nano-structure [16–19]. Many studies have revealed that the increase in roughness on the hydrophobic or hydrophilic surfaces could cause the increase or decrease in WCA values [20–23]. For the fabrication of the superhydrophobic or superhydrophilic surfaces, many investigations have focused on exploiting the physical and chemical methods to enhance the surface roughness, such as lithography techniques, phase separations, layer-by-layer methods, sol-gel technique and so on [3,21]. For example, Lu et al., created the robust superhydrophobic self-cleaning coatings by

using the commercial adhesives to bond perfluorosilane-coated titanium dioxide nanoparticles onto hard or soft rough materials surfaces [24]. Recently, although some stimuli-responsive surfaces with reversible wettability switching between superhydrophilicity and superhydrophobicity have been successfully realized, it is not easy for such a stimuli-responsive surface to create a special WCA values under external stimuli [25–28]. Rafiee et al. developed a facile technique to control WCA values of graphene films over a wide range from superhydrophobicity to superhydrophilicity by using water, acetone, or a combination of water and acetone as a solvent [12]. However, changing arbitrarily wettability properties of coatings between superhydrophobicity and superhydrophilicity by tuning the surface chemical have not been studied in detail [29,30].

Among wetting/anti-wetting materials, the  $\pi$ -conjugated polymer films have received widely interest due to their facile electrochemical preparation and their excellent photoelectric properties [31]. So far, the investigation of the wettability of the electrodeposited  $\pi$ -conjugated polymer film ranges from the superhydrophilic/superhydrophobic surfaces to the reversible wetting-switching surfaces, and even multi-functional surfaces [32,33]. Several studies have revealed that the electrodeposited  $\pi$ -conjugated polymer films present not only controllable rough structure but also tunable chemical composition, which is favorable to controlling simply and rapidly the wettability of a surface [34–37]. Thus, generating  $\pi$ -conjugated polymer films with various

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wetting properties between superhydrophilicity and superhydrophobicity by using the electrodeposited method might be a feasible strategy.

In the earlier studies, several self-cleaning and superhydrophobic polythiophene films have been successfully prepared by using a double-layered electrodeposition method reported by prof. Lu and his coworkers [37,38]. Those surfaces were investigated in detail about their electro-responsive wetting transformation between superhydrophobicity to superhydrophilicity, and water-droplet adhesion switching between pinned and sliding superhydrophobic states. Although the wetting surface with different WCA values can be realized by applying a suitable doping potential, the neutral surfaces with various WCA could not be investigated in details.

In this work, we reported a series of composited polythiophene films (PL-PEDOT) with wettability over a wide range from superhydrophilicity to superhydrophobicity. These films were prepared by tuning the electrodeposition charge (EC) of the overlying hydrophobic poly(2,2'-bithiophene) (PLTH) moieties on the underlying superhydrophilic poly(3,4-ethylenedioxythiophene) (PEDOT) film. With the EC increase of overlying PLTH moieties, the WCA values of the resulting film can increase gradually from  $\sim 0^\circ$  to  $>150^\circ$ . More interestingly, the wettability of the resulting PL-PEDOT film can be tuned between superhydrophilicity and superhydrophobicity by electrodepositing PLTH or PEDOT moieties onto the film, or by doping the film under the potential in electrolyte solution. Such polythiophene films with arbitrarily tunable wetting may be favorable to the investigation in some special wetting coatings.

## 2. Experimental section

### 2.1. Materials

HPLC grade acetonitrile (ACN) was provided by Shanghai Lingfeng Chemical Reagent Company and was used without further purification. 3,4-Ethylenedioxythiophene (EDOT, Adamas, 99%), 2,2'-bithiophene (LTH, J&K, 98%), thiophene (TH, J&K, 99%), 3-dodecylthiophene (DTH, J&K, 98%) and anhydrous lithium perchlorate ( $\text{LiClO}_4$ , J&K, 99%) were used directly without further purification.

### 2.2. Characterization

The surface chemical compositions of PL-PEDOT films were determined by X-ray photoelectron spectroscopy (XPS) on a Kratos Axis Ultra<sup>DLD</sup> spectrometer (Kratos Analytical-A, Shimadzu, Japan) with a monochromated Al-K $\alpha$  radiation source (1486.6 eV) and a take-off angle of  $90^\circ$ . Static water contact angle measurements were performed by the sessile drop method on a Contact Angle System OCA 20 (DataPhysics Instruments GmbH, Germany) in air. The contact angle reported herein is mean value measured by dropping several water droplets (4  $\mu\text{L}$ ) on five different positions of the sample. Water sliding angles (SA) were determined by slowly tilting the sample stage until a 4  $\mu\text{L}$  water drop started moving. Field-emission scanning electron microscopy (FE-SEM) was performed with a Nova NanoSEM instrument (FEI, USA). Atomic force microscopy (AFM) height images were taken in tapping mode by using a Digital Instrument NanoScope (USA) and the roughness of the films was checked with AFM. UV/vis spectra of the films on the ITO substrate were measured on a Perkin-Elmer Lambda 20 UV/vis spectrometer. Photographs and movies were taken with a camera. The adhesion force between the droplet and the sample was assessed by using a high-sensitivity micro-electromechanical balance system (DataPhysics DCAT11, Germany). The sample surface was drawn near and retracted from a 4  $\mu\text{L}$  water droplet suspended on a hydrophobic metal ring at

velocity of  $0.02 \text{ mm s}^{-1}$  under relative humidity of  $\sim 40\%$ . The maximum force value recorded in the force–distance curves was the adhesion force.

### 2.3. Electrochemical experiments and preparation

All electrochemical experiments were performed in an electrochemical cell ( $1 \text{ cm} \times 1 \text{ cm} \times 4.5 \text{ cm}$ , seeing its scheme in Fig. S1) with a three-electrode system by using a computer-controlled CHI 630E Electrochemical Analyzer. The working electrode was indium tin oxide (ITO) glass ( $<10 \Omega \text{ sq}^{-1}$ ,  $0.9 \text{ cm} \times 5 \text{ cm}$ ), which was washed successively under ultrasonication with deionized water and absolute ethanol and then dried with a stream of  $\text{N}_2$  before use. The counter electrode was a platinum wire (1 mm diameter), which was cleaned before each examination. An Ag/AgCl wire was used as a quasi-reference electrode. All electrochemical experiments were performed at room temperature and  $<40\%$  relative humidity. All polythiophene films were prepared and doped/dedoped in the ACN solution containing 0.2 M  $\text{LiClO}_4$  as the supporting electrolyte. Before characterization, the resulting films were twice rinsed with ACN ( $2 \times \text{ca. } 1 \text{ mL}$ ) and then dried under flowing  $\text{N}_2$  at room temperature.

For the preparation of the composited polythiophene films (PL-PEDOT or PD-PEDOT), PEDOT films, as underlying superhydrophilic substrates, were electrodeposited firstly on ITO electrodes by using cyclic voltammetry (CV, scan ratio of  $0.2 \text{ V s}^{-1}$ ) in monomer-containing electrolyte; After that, the overlying hydrophobic poly(2,2'-bithiophene) (PLTH) or poly(3-dodecylthiophene) (PDTH) moieties with various EC were electrodeposited on the as-prepared PEDOT films by using the constant potential (CP) in LTH/DTH electrolyte solution. The constant potential method was used to dope/dedope PEDOT, PL-PEDOT, PLTH and PD-PEDOT films in monomer-free electrolyte solution. Electrochemical parameters applied during the electrochemical preparations of PEDOT, PL-PEDOT, PLTH and PD-PEDOT films are shown in details in the following Table 1:

### 2.4. Electrochemical characterization of the films

The electrochemical properties of the PEDOT and PL-PEDOT films were characterized in electrolyte solution by sweeping potentials between  $-0.5$  and  $+1.0 \text{ V}$  at scan rates from 100 to  $300 \text{ mV s}^{-1}$ .

## 3. Results and discussion

### 3.1. PL-PEDOT films: surface chemical compositions and electrochemical properties

PEDOT film was firstly electrodeposited on ITO electrode by CV in 0.2 M  $\text{LiClO}_4/\text{ACN}$  solution containing 0.01 M EDOT monomer (Table 1, Fig. S2a). The resulting PEDOT film not only presents the highly porous network-like nanostructure (Fig. 1a), but also the excellent electrochemical redox activity (Fig. S3a and b), which means that other polythiophene moieties can be introduced easily on the nanostructure of PEDOT film [39]. In this work, for the investigation of the wettability of the composited polythiophene films (PL-PEDOT), the as-prepared PEDOT films with EC of  $18.5 \sim 23.5 \text{ mC cm}^{-2}$  were used as the porous conducting substrates. After electrodepositing the hydrophobic PLTH moieties with EC of  $0 \sim 27 \text{ mC cm}^{-2}$  onto PEDOT films, a series of PL-PEDOT films with various WCA values were expected to be generated (Table 1). Notably, the conducting and porous properties of the underlying film are important for the preparation of uniform and controllable composited films. Other porous conducting coatings, such as polypyrrole films and nano-silver coatings, as underly-

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