Electrochemical Assembling of Functionalized PEDOT Thin Films with Excellent Electroactivity and Superhydrophobicity

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Abstract. We synthesized dodecyloxymethyl functionalized EDOT monomers and fabricated homogeneous thin films via cycle voltammetry electrochemical deposition method on platinum and ITO substrates. The PEDOT-C12 thin films showed good electrochemical activity. Meanwhile, by increasing the cyclic voltage-scan number during electrochemical deposition process, the surface roughness was also enhanced. The large surface roughness and occurrence of micro-nano surface morphologies would lead to higher water contact angles for the PEDOT-C12 thin films. The water contact angle for the PEDOT-C12 thin films with 10 deposition cyclic voltage-scans was 160° and showed superhydrophobicity. The achieved superhydrophobic PEDOT-C12 thin films would have potential applications in corrosion protecting for metal electrodes in aqueous environment.

1. Introduction

Conducting polymers, which possess similar conductivity to metal, have gained great development since the first discovery in 1977.[1-4] Among them, poly(3,4-ethylenedioxythiophene) (PEDOT) materials have been commonly used in the fields of chemical and biological sensing, energy storage, bioelectronics due to the low oxidant voltage and good aqueous stability.[5-9] However, further applications would not only demand excellent electric conductive, but also extra functional properties based on various requirements. Introducing proper functional groups into PEDOT chain would expand the potential application fields for PEDOT materials. For instance, carboxylic acid functionalized EDOT thin films would specific bind with target cells via antibody-antigen interaction;[10] phosphorylcholine functionalized PEDOT thin films displays high resistance to nonspecific enzyme/cell binding.[11]

Besides, superhydrophobic thin films have gained great interests from researchers, which possess water contact angle higher than 150° and sliding angle smaller than 10°.[12-15] Superhydrophobic thin films show excellent repellence to water and would prevent it from penetrate into the materials. Combination superhydrophobicity with conducting polymer thin films would be effective method for fabricating electroactive corrosion protecting thin films based on current researches.[16, 17] Two main factors influence the hydrophobicity of conducting polymer thin films. First is the surface energy of the materials. Low surface energy is necessary for fabricating superhydrophobic thin films. Meanwhile, proper nano morphologies on the surface would also determine the hydrophobicity of thin films, in
which micro-nano surface morphologies have been proved to be the key point for superhydrophobic surface. Therefore, synthesizing functional EDOT monomer with low surface energy and realizing controllable nano assembly of the functionalized PEDOT are necessary for fabricating superhydrophobic PEDOT thin films.

Herein, we synthesized EDOT monomer with dodecyloxymethyl groups into the EDOT chain (PEDOT-C12). Cyclic voltammetry Electrochemical deposition method was used to realize the homogeneous assembling of PEDOT-C12 both on platinum and ITO conductive substrates. The achieved PEDOT-C12 thin films showed good charge exchange property based on cyclic voltammetry measurement. Meanwhile, the PEDOT-C12 thin films showed high surface roughness by increasing the deposition scans. The high surface roughness would lead to enhancing of water contact angles, and the PEDOT-C12 thin films with 10 deposition scans showed superhydrophobicity. The achieved PEDOT-C12 thin films possessed both electroactivity and superhydrophobicity, which would have potential application in corrosion protecting of electrodes in aqueous environment.

2. Results and discussion
To achieve the superhydrophobic PEDOT thin films, it is necessary to synthesize functional EDOT monomer with low surface energy. Starting from the hydroxyl modified EDOT (EDOT-OH), dodecyloxymethyl functionalized EDOT (EDOT-C12) could be synthesized by a simple chemistry pathway. The long alkyl chain would provide relatively low surface energy for the achieved EDOT-C12 monomer.

Electrochemical deposition was carried out to polymerize the EDOT-C12 monomer. Acetonitrile with 100mM Tetrabutylammonium Hexafluorophosphate (TBAPF6) was chosen to be the electrochemical solution. 5mM EDOT-C12 monomer was dissolved into the electrochemical solution. Platinum and ITO conductive substrates were used as working electrode and platinum net was used as counter electrode. Typical cycle voltammetry electrochemical deposition method was chosen by applying cyclic potentials from -0.6-1.45 V (vs Ag/Ag+). Figure 1 illustrate the deposition curve for the PEDOT-C12 thin films on ITO and platinum substrates. Obviously, the current become large with high deposition scans, indicating more EDOT-C12 monomers were deposited both on ITO and platinum substrates.

The achieved PEDOT-C12 possessed excellent electrochemical properties. Cycle voltammetry measurement was used to testify the electrochemical properties for the PEDOT-C12 thin films in acetonitrile solution with 100mM TBAPF6. Figure 2 showed the CV curve for the PEDOT-C12 thin films with various scanning rate. PEDOT-C12 thin films showed good electrochemical properties on ITO and platinum substrates. Meanwhile, the oxidant current in the cycle voltammetry measurement was increased linearly with higher scan rate, indicating that the cycle voltammetry measurement was activated on the PEDOT-C12 thin films, rather than in the electrolyte.

![Figure 1](image1.png)

**Figure 1** Cycle voltammetry electrochemical deposition curves for EDOT-C12 on ITO (a) and platinum (b) conductive substrates. The conductive of the thin films increased with high scanning numbers.
Figure 2. Cycle voltammetry measurement curves for PEDOT-C12 thin films on ITO (a) and platinum (c) conductive substrates. The scanning rate was 10, 20, 50, 100, 200, 300 and 400 mV, respectively. The relationship between current and scan rate for the PEDOT-C12 thin films on ITO (b) and platinum (d) conductive substrates in the cycle voltammetry measurement.

Besides of the electrochemical activity, the increasing of deposition scan number would also affect the surface roughness of the PEDOT-C12 thin films due to the nano assembling of monomers during the electrochemical deposition process. Atomic force microscopy (AFM) was used to measure the surface morphologies and surface roughness for the PEDOT-C12 thin films. As shown in Figure 3, the surface was quite smooth for the PEDOT-C12 thin films with 1 and 2 deposition cyclic voltage-scans from -0.6 to 1.45 V. The surface roughness was 6.7 and 15.1 nm, respectively. Keep increasing the scan number, micro-nano surface morphologies were occurred on the PEDOT-C12 thin films. The surface roughness was increased to 226.3 and 497.7 nm for PEDOT-C12 thin films with 5 and 10 scan numbers.

Figure 3. Roughness (as calculated on AFM measurements) for EDOT-C12 deposited on ITO plates within a) 1, b) 2, c) 5 and d) 10 deposition cyclic voltage-scans from -0.6 to 1.45 V.

The increasing of surface roughness and the occurrence of micro-nano surface morphologies would contribute to the superhydrophobicity, as the micro-nano surface morphologies could preserve small air chamber and suit for Cassie-Baxter model. Figure 4 showed the wettability of the achieved PEDOT-C12 thin films. Obviously, with the increasing of surface roughness, the water contact angles were also enhanced. The PEDOT-C12 thin films with 10 deposition cyclic voltage-scans possess the largest surface roughness and the water contact angle of the thin film was 160°, which showed excellent superhydrophobicity.
3. Conclusion
In this work, we designed dodecylxoyxmethyl functionalized EDOT monomers and fabricated homogeneous thin films via cycle voltammetry electrochemical deposition method on platinum and ITO substrates. The PEDOT-C12 thin films showed good electrochemical activity. Meanwhile, by increasing the cyclic voltage-scan number during electrochemical deposition process, the surface roughness was also enhanced. The large surface roughness and occurrence of micro-nano surface morphologies would lead to higher water contact angles for the PEDOT-C12 thin films. The water contact angle for the PEDOT-C12 thin films with 10 deposition cyclic voltage-scans was 160° and showed superhydrophobicity. The achieved PEDOT-C12 thin films possessed both superhydrophobicity and excellent electrochemical activity, which would have potential applications in corrosion protecting for metal electrodes in aqueous environment.

4. Experimental Section
4.1. Materials
Hydroxyl functionalized 3,4-dimethoxythiophene (99%+), NaH, 18-crown-6 ether and bromoethane were purchased from Alfa Aesar (China). Tetrabutylammonium Hexafluorophosphosphate (99%) and LiClO4 were purchased from Energy Chemical Reagent Co., Ltd (Shanghai, China). Sodium dodecyl sulfate (99%) was purchased from J&K Chemical Reagent Co., Ltd (Shanghai, China). Acetonitrile (99%), dichloromethane (99%) THF(99.5%+) were purchased from Ling Feng Chemical Reagent Co., Ltd (Shanghai, China) and used without further purification. ITO glass and platinum were purchased from Shenzhen Huanan Technology Company.

4.2. Fabricating of EDOT-C12 monomer
A mixture of NaH (3.48 g, 145 mmol) and 18-crown-6 ether (0.767 mg, 2.9 mmol) dissolved in anhydrous THF (70 mL) was stirred under nitrogen at 0 °C. 2,3-Dihydrothieno[3,4-b][1,4]dioxin-2-yl)methanol (EDOT-OH) (5 g, 29 mmol) in 30 mL of anhydrous THF was added. The mixture was stirred at room temperature for 1 h and then cooled down to 0 °C. Bromoethane (3.792 g, 34.8 mmol) was added droplet within10 min. After stirring at room temperature overnight, the mixture was diluted with 200 mL NH4Cl aqueous solution. The mixture was extracted with dichloromethane (200 mL) three times. The combined organic phases were washed with water, dried over MgSO4, and evaporated in vacuo. This yielded a colorless oil (8.19 g, 83%). 1 H NMR (500 MHz, CDCl3 , δ): 6.33-6.31 (m, 2H), 4.32-4.28 (m, 1H), 4.25 (dd, J = 11.5, 2.0 Hz, 1H), 4.06 (dd, J = 11.5, 7.5 Hz, 1H), 3.68 (dd, J = 10.0, 4.5 Hz, 1H), 3.59 (dd, J = 10.0, 6.0 Hz, 1H), 3.49 (t, J = 7.0 Hz, 2H), 1.60-1.55 (m, 2H), 1.35-1.22 (m, 18H), 0.88 (t, J = 7.0 Hz, 3H). 13 C NMR (500 MHz, CDCl3 , δ): 141.6, 141.5, 99.7, 99.5, 72.6, 72.1, 69.1, 66.3, 31.9, 29.7, 29.6, 29.6, 29.5, 29.4, 29.4, 26.0, 22.7, 14.1;

4.3. Electrochemical polymerization
Electrochemical polymerization of PEDOT-C12 thin films performed using Autolab PGSTAT128N potentiostat (Metrohm Autolab) and a three-electrode electrochemical cell, with a platinum net as the counter electrode, ITO glass and platinum conductive substrates as working electrode. Electrochemical solvents were prepared by dissolving EDOT-C12 (5mM) and Tetrabutylammonium Hexafluorophosphate (0.1 M) in acetonitrile. EDOT-OH (10mM) were dissolved in water containing 50mM SDS and 100mM LiClO₄. PEDOT-OH thin films were pre-coated on ITO glass by applying cycle voltammetry from -0.6 V to 1.13 V vs Ag/AgCl standard electrode. PEDOT-C12 thin films were prepared on pre-coated ITO glass and platinum conductive substrates by applying cycle voltammetry from -0.6 V to 1.45 V vs Ag/Ag⁺ standard electrode. Each measurement was calibrated using a standard ferrocene/ferroenium redox system.

4.4. Characteristic

The Cycle voltammetry test were measured by Autolab PGSTAT128N potentiostat (Metrohm Autolab) and a three-electrode electrochemical cell, in which Pt would act as counter electrode, PEDOT-C6 thin films as working electrode and Ag/Ag⁺ electrode as reference electrode. Acetonitrile with 100mM Tetrabutylammonium Hexafluorophosphate was used as electrolyte.

Surface morphologies of the thin films were measured by Atomic force microscope (Agilent5500). Water contact angles was measured by contact angle measurement system (Theta Lite 101, Attention).

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