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Work function engineering of electrodes via electropolymerization of ethylenedioxythiophenes and its derivatives

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ABSTRACT

The work functions of two commonly used electrodes, Au and indium-tin-oxide (ITO), can be modified by surface-electropolymerization of ethylenedioxythiophenes (EDOT) or its derivatives. The resulting work function is tunable continually by varying the electropolymerization condition. The value of work function of ITO (or Au) electrodes can be adjusted to decrease by 0.6 eV (or increase by 0.4 eV) when the deposited EDOT film is thin (<40 nm). By contrast, when the EDOT film deposited with thickness greater than 40 nm, the work function is controlled by the intrinsic property of the polymers regardless of the electrode materials. A diode devices with EDOT-COOH modified on ITO surface demonstrates the possibility of improving contact property in organic electronics using the proposed method.

Keywords: Work function; PEDOT; Electropolymerization

1. Introduction

Considerable progress has been made in the development of organic electronic devices to be commercially competitive with traditional silicon technology [1–4]. Among these devices, organic light emitting diode is one of the most successful cases [5]. In addition, organic transistors, sensors, solar cells and other devices have also been demonstrated recently [6–9]. One remaining issue in organic electronics is improvement of the device performance and current density *via* efficient carrier injection through better contact property between electrodes and organic materials layer [10]. The current density in organic electronic devices is strongly affected by the surface condition and band energy alignment between semiconductors and electrodes. However, the HOMO energy level of semiconductors do not normally match well with the Fermi energy of commonly used electrode materials. Therefore, fine-tuning the work function of the electrode is critical to enhance the carrier injection across semiconductor–electrode contact, improving the performance of devices.

One strategy to adjust the work function of material is modifying the electrostatic charges at the surface [11]. Self-assembled monolayers (SAM) have been utilized to control the work function of Au electrode [12–16]. Therefore, reduction of energy barrier at the electrode interface is achieved by grafting a Au-thiol SAM that possesses permanent dipole moment with various organic thiols. However, SAM from particular thiolated molecules in principle allows only certain work function modification. Therefore, fine tuning of work function is not feasible by using only one thiolated molecule. Besides, the formation of SAM is time-consuming (normally several hours) and the choice of electrode materials is limited by the available chemical bonding between electrodes and grafted molecules, i.e. Au and thiolated molecules. As a result, it is not a generic method for all electrodes. Furthermore, the precise environmental control (i.e. cleanness of the electrode surface) is crucial for SAM formation and the reproducibility has always been a concern for large-scale fabrication.

Poly(3,4-ethylenedioxythiophene) (PEDOT) displays extraordinary electrical properties and is currently applied in various electronic products such as antistatic coatings for cathode ray tubes, hole transport layers for light-emitting diodes,

photovoltaic devices, organic thin film transistors, and sensors [17–20]. Here, we show that the work functions of two commonly used electrodes, Au and indium-tin-oxide (ITO), are modified by surface-electropolymerization using ethylenedioxythiophenes (EDOT) or its derivatives (EDOT–OH and EDOT–COOH as shown in Fig. 1a). The EDOT monomers with various functional side-chains were tested to understand the effect of functional groups to the work function tuning. The resulting work function is tunable by varying the electropolymerization condition and polymer side-chain functional groups. Most importantly, the process is applicable for a wide range of electrodes, not only limited to Au and ITO. Interestingly, the value of work function of ITO (or Au) electrodes can be adjusted to decrease by 0.6 eV (or increase by 0.4 eV) when the deposited film is thinner than 40 nm. When the deposited film is thin, the surface dipole is dominantly resulted from the interaction between electrodes and PEDOT and irrelevant to the side chain of the EDOT monomers. In contrast, when the film deposited with thickness greater than 40 nm, the work function is controlled by the intrinsic property of the functionalized polymers regardless of the electrode materials.

2. Results and discussion

Fig. 1b shows the values of the measured work function (relative to a reference Au) for sputtered Au and ITO electrodes electropolymerized with EDOT, EDOT–OH and EDOT–COOH as a function of electropolymerization time from 0 to 160 s. In our previous studies, we concluded that the materials deposited on the surface of the electrode are proportional to the electropolymerization time [21,22]. The original work function of ITO is ~4.55 eV and the work function of the electrode is raised up to 5.05 eV when the EDOT monomer is electropolymerized for 5 s. Similar changes in work function are also observed for EDOT–OH and EDOT–COOH, proving that the method is feasible for work function engineering on electrodes. We observed that the initial change in work function for three monomers are almost identical, indicating that the surface dipoles are formed on ITO electrodes and they are not strongly related to the side chains when the polymer film is thin (thickness < 40 nm). Therefore it is likely that the formation of the surface dipole is due to the interaction between ITO and PEDOTs (polymer main chain of the polymerized

films). For the Au electrodes, the measured work function was also similar for three monomers when only thin films were deposited, where the work functions were decreased from 5.2–5.3 eV to 4.9–5.1 eV. When thicker films were deposited after electropolymerization for a longer period of time, the values of work function are determined by the composition of polymer films regardless the electrode materials underneath. The work function values measured on Au electrode when PEDOT films were deposited for 160 s were identical to those on ITO electrodes, which could be due to that the penetration depth of electric dipole is short. Besides, from the point of view of band bending, the Fermi level alignment between electrodes and PEDOT introduces a local exchange of charges, where the effect is pronounced when the PEDOT is very thin. However, when a thick film of PEDOT is formed, the intrinsic surface property of polymers will dominate the workfunction value [11,23]. Therefore, thick PEDOT films from three different monomers clearly showed different work functions.

The AFM images in Fig. 2 show the effect of polymerization time on the surface morphology for EDOT–COOH and EDOT–OH coated Au electrodes. With longer electropolymerization time, it was observed that the grain size was larger and the morphology became very different for both polymers. The combination of the differences in surface morphology and the polymer intrinsic properties could be the reason why the measured work function was different with deposited polymer film and deposition time.

ITO is widely used in the organic electronic devices due to its high conductivity and transparency. Normally, ITO serves as anode for hole-injection. Therefore increasing the work function of ITO is able to enhance the injection of carriers. We have fabricated the diodes with the structure of Au (thermal evaporated 100 nm)/pentacene (50 nm)/PEDOT–COOH/ITO (schematically shown in the inset of Fig. 3a) to demonstrate the effect of work function shift on the electrical performance of the diodes. Fig. 3b plots the current density of the diodes driven by different voltages as a function of electropolymerization time on ITO electrodes. The device containing PEDOT layer from electropolymerization of EDOT–COOH for 40 s displays the highest current density. This observation agrees with the experimental data in Fig. 1b that the work function of ITO after tuning (~5.2 eV) with

electropolymerization is close to the pentacene (literature value: 5.1–5.2 eV) [24,25]. The matching of work function resulted in a lower charge-injection barrier, thereby lowering contact resistance between ITO and pentacene [24]. Fig. 3b clearly shows that the evolution of current density of the diodes is consistent with our experimental work function data when the polymerized film is very thin, where the interface dipole between ITO and PEDOT is significantly contributing to the charge-injection process. Although Fig. 3b also demonstrates that the current density of the diodes modified with thicker PEDOT (>40 s electropolymerization) is consistent with the work function data, other contributing factors which may reduce the current density such as increasing thickness of the PEDOT or the interface dipole between PEDOT and pentacene, are necessary to be taken into consideration. The effects of these factors warrant further studies. In brief, the simple hole-injection barrier, simply estimated by the work function difference between the electrode and the pentacene, is able to explain the electrical characteristics for this diode.

3. Experimental

Unfunctionalized EDOT was purchased from Sigma–Aldrich and the EDOT functionalized with carboxylic acid group (EDOT–COOH) were synthesized from the known hydroxymethyl-EDOT (EDOT–OH) [26] incorporating an ester linkage [27]. (Fig. 1a). Electropolymerization of all monomers were performed in acidic aqueous microemulsion solution containing 10 mM of the respective monomer and 0.1 M lithium perchlorate (LiClO_4), 0.01 M HCl, and 0.05 M sodium dodecyl sulfonate (SDS) as supporting electrolyte. The electropolymerization on electrode surface was carried out when the electrolysis potential was kept at 0.9 V (vs. Ag/AgCl) on Au electrodes and 1.0 V on ITO electrodes. The work function before and after electrolysis was measured by Kelvin probe method (SKP system) [23], conducted in air with a 3 mm diameter of stainless head coated with Au as a reference electrode. The contact potential difference (CPD) was taken as the averaged value over 30 repeated measurements at one position. The standard deviation of the experiment was 10 mV. The work function was calculated relative to a reference Au (5.0 eV). For the fabrication of diode device, the pentacene was thermally evaporated onto the ITO electrodes with or without electropolymerized films.

4. Conclusion

In summary, we demonstrate that the work function of Au and ITO can be tuned continually by electropolymerization using EDOT, EDOT-COOH and EDOT-OH. This method is controllable and suitable for wide-range selections of electrodes. A thin layer of polymer (~40 nm) results in a most pronounced effect on work function change. Furthermore, the diode devices with EDOT-COOH modified on ITO surface demonstrate the possibility of improving contact property in organic electronics. It requires more studies to reveal details of the mechanism of short-range dipole formation and the study of the work function tuning method to other types of organic devices are currently underway.

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List of Figures

- Fig. 1 (a) Chemical structures of EDOT, EDOT - OH and EDOT - COOH. (b) Measured work function for sputtered Au and ITO electrodes electropolymerized with EDOT, EDOT - OH and EDOT - COOH as a function of electropolymerization time.
- Fig. 2. AFM images for (a) plain Au, and those electropolymerized with (b) 5 s (c) 10 s and (d) 40 s of EDOT - COOH monomer. AFM images for those electropolymerized with (e) 5 s (f) 10 s and (g) 40 s of EDOT - OH monomer.
- Fig. 3 (a) Current density of the diodes with the structure of Au (thermal evaporated 100 nm)/Pentacene(50 nm)/PEDOT-COOH/ITO. Inset shows the schematic illustration for the device. (b) The current density of the diodes driven by different voltages as a function of electropolymerization time on ITO electrodes.

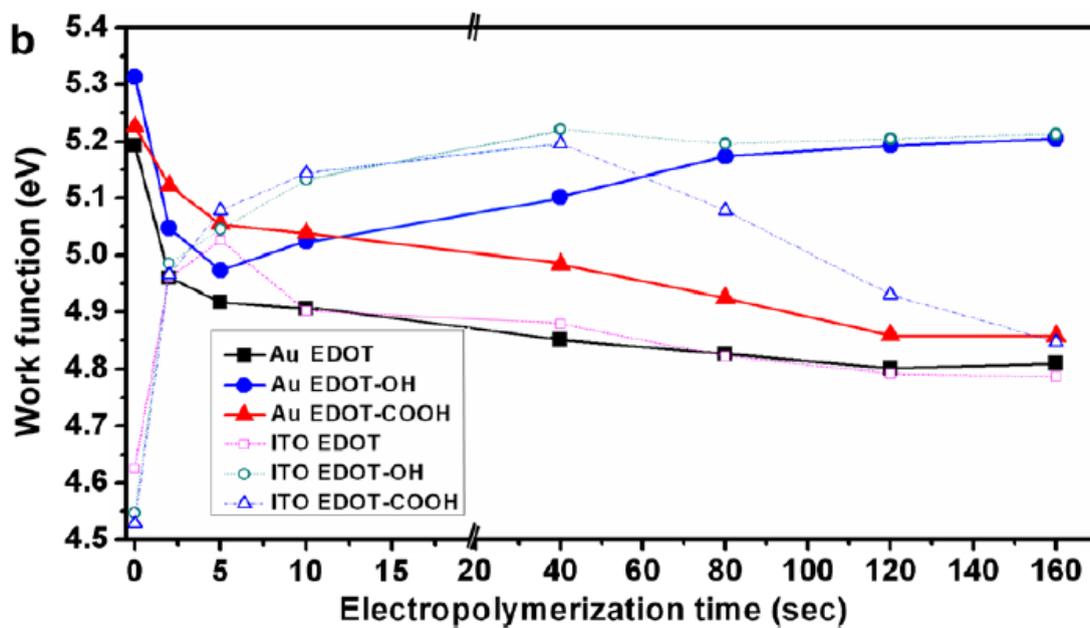
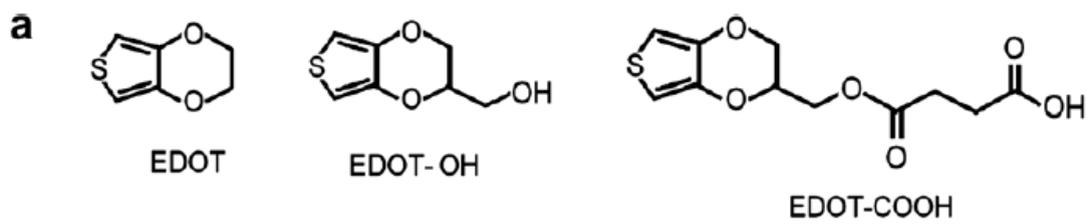


Fig. 1

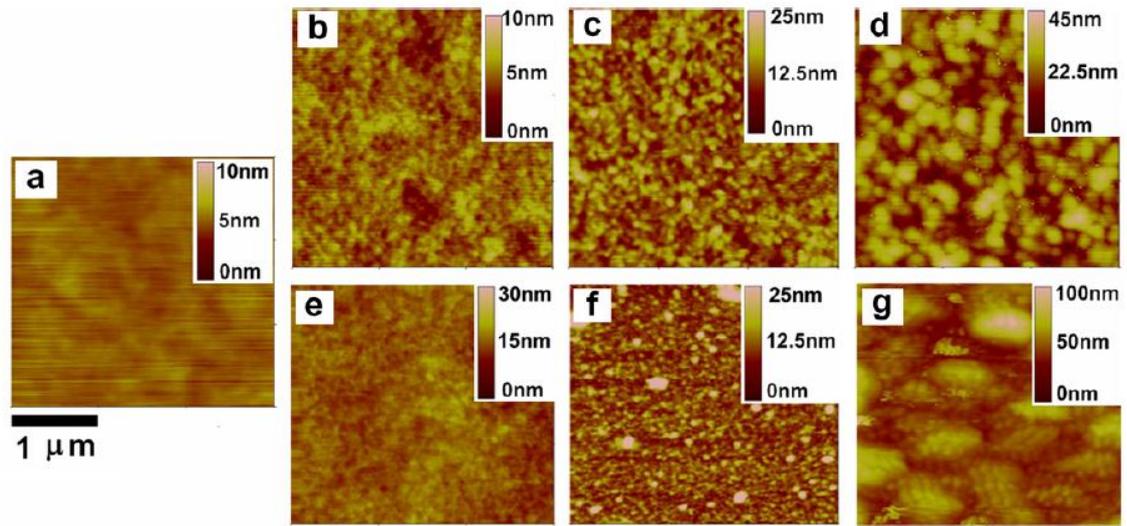


Fig. 2

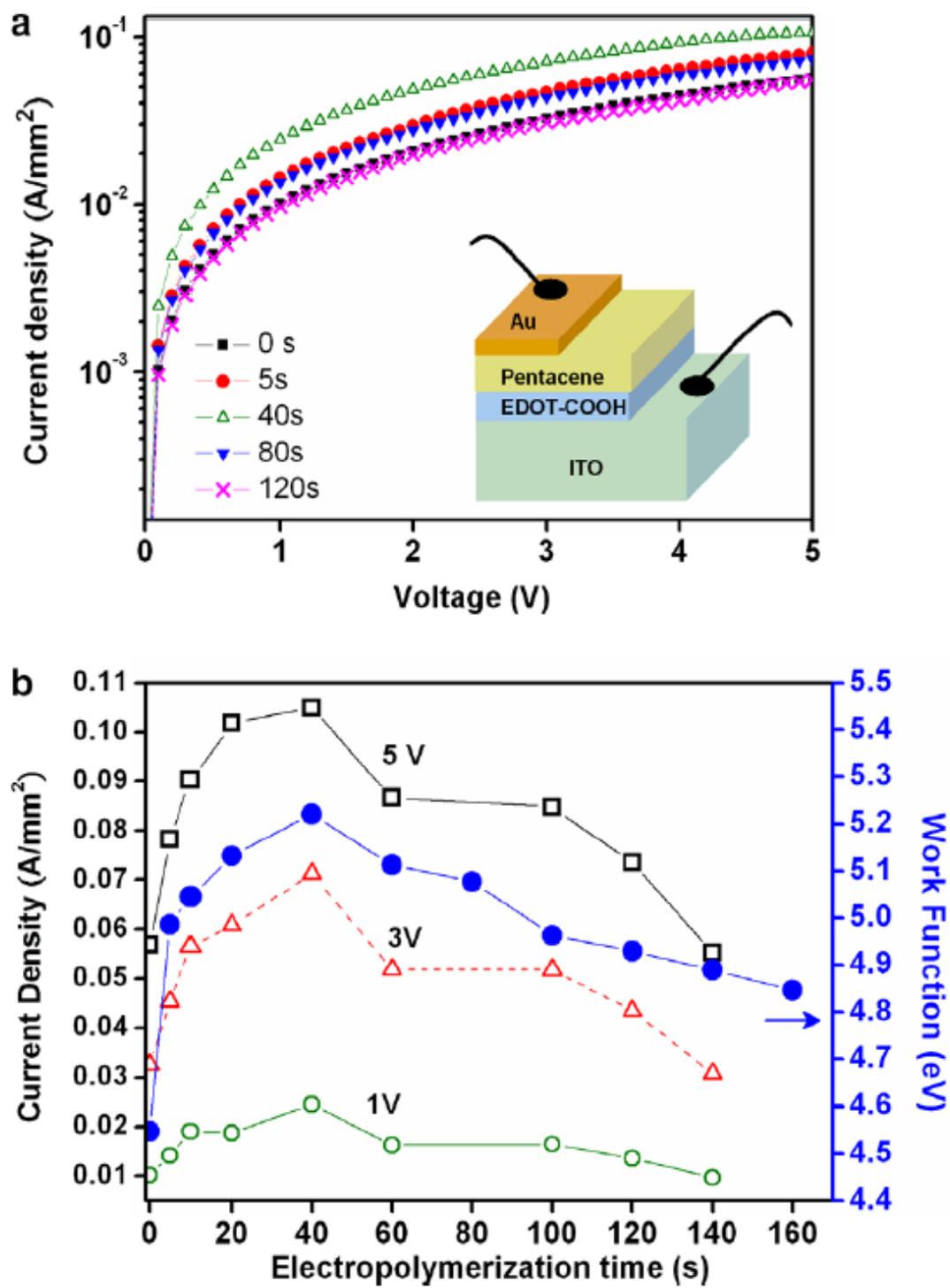


Fig. 3