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Combined AFM, XPS, and contact angle studies on treated indium–tin-oxide films for organic light-emitting devices

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Abstract

In the present work, surface modifications were performed on the indium–tin-oxide (ITO) substrates and the treated ITO surface properties were investigated by different characterization techniques. AFM and XPS methods were applied to measure surface roughness and chemical composition, respectively. Standard goniometry was used to determine contact angle and to calculate surface energy. Experimental results show that the ITO surface properties are subjected to the treatment methods which lead the surface to a certain degree of changes. Wettability of the modified surfaces was then monitored as a function of time elapsed after treatment and quantified. Furthermore, the polymer light-emitting electrochemical cells (LECs) with the differently treated ITO substrates as device electrodes were fabricated and characterized. We observe that the electrical and optical performances of the polymer LECs are affected by the treatment methods on the ITO surface which result in the modification of interface formation and electrical contact of the ITO substrate with the polymer blend in the polymer LECs.
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1. Introduction

Indium–tin-oxide (ITO) has attracted intensive interest in recent years because of its unique characteristics of good electrical conductivity, high optical transmittance over the visible wavelength region, excellent adhesion to the substrates, stable chemical property and easy patterning ability. The thin films of ITO as transparent electrodes have already been widely applied in many optoelectronic devices for instance polymer light-emitting electrochemical cells (LECs) [1–4], organic electroluminescent diodes [5–10], solar cells [11–13] and flat panel displays [14,15]. As a new type of organic light-emitting devices, polymer LECs have attracted increasing scientific and industrial interest due to their high electroluminescence efficiency, low operating voltage and ease of fabrication since its discovery by Pei et al. [1] in 1995. In general, a polymer LEC consists of a light-emitting active blend layer of conjugated luminescent polymer and solid electrolyte with supporting salt sandwiched between an ITO electrode and a metal electrode [1–4]. When a sufficiently high bias is applied onto the electrodes, electrochemical doping takes place accompanied by the redistribution of the ions in the polymer blend film. As a result, the contact at the polymer electrode interface is ohmic, and the conjugated polymer is doped p-type near the anode and n-type near the cathode respectively, and a dynamic p–i–n junction is created in situ. Hence, light is emitted from the intrinsic region near the center. Since the polymer blend layer is in direct contact with the ITO electrode, the surface characteristics of ITO and the interfacial properties between the polymer blend layer and the ITO electrode play an important role in the operation of polymer LECs.

In the present work the effects of different surface modifications upon the surface properties of ITO substrates and its aging were investigated by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), contact angle and surface energy. Also, we studied the influence of surface modifications of the ITO substrates on the performance of polymer LECs with respect to the electrical and optical characteristics of the devices.

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2. Experimental section

2.1. Materials

Commercial ITO-coated glasses with film thickness of 150 nm and sheet resistance of 30 Ω/sq were produced by CSG Holding Co. Ltd. and cut into 3.0×3.0 cm^2 plates. The solvents used for cleaning ITO substrates were acetone (99.7%, from Shanghai Chem. Reagent Co.), and alcohol (99.9%, from Bejing Chem. Co.), respectively. For contact angle measurement, distilled water (H_2O) and methylene iodide (CH_2I_2) were chosen as the test liquids [16–19]. Both of them were reagent grade, and their surface tension and surface tension components are listed in Table 1. The organic materials of poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), poly(ethylene oxide) (PEO) and lithium trifluoromethanesulfonate ($LiCF_3SO_3$) were purchased from Sigma-Aldrich Chemical Company to fabricate the polymer LECs and used as received.

2.2. Surface modifications

Two different sets of processing techniques, wet and dry cleanings were used to modify the surface of ITO substrates. They are:

Ultrasonic degreasing (S1) — The substrates were successively washed in an ultrasonic bath of acetone and alcohol each for 15 min, then rinsed in deionized water, and dried with nitrogen.

Hydrochloric acid treatment (S2) — The substrates were dipped into 10% hydrochloric acid solution for 15 min at room temperature, and then rinsed in deionized water and finally dried in a flow of nitrogen.

Oxygen plasma treatment (S3) — The substrates were exposed to the oxygen plasma in a radio frequency (RF) plasma generator for 5 min at room temperature under pressure 20 Pa, plasma power 30 W and gas flow rate 20 sccm.

Prior to surface modifications, all the ITO substrates were cleaned first by rubbing with detergent, then in ultrasonic bath for 10 min in deionized water, and finally dried in a flow of nitrogen. In this paper, the untreated ITO is referred to as S0.

2.3. Characterization techniques

The ITO surfaces were structurally characterized by AFM with a Seiko Instruments SPA-400 in the contact mode. Measurements were achieved at room temperature in the air, using the same pyramidal Si_3N_4 tip. The surface roughness of the ITO samples was calculated with the AFM software.

Table 1
Test liquids and their surface tension components

Surface tension (mN/m)	γ_L^p	γ_L^d	γ_L
Distilled water (H_2O)	51.0	21.8	72.8
Methylene iodide (CH_2I_2)	2.3	48.5	50.8

The XPS measurements of the ITO substrates were carried out in a VG ESCALAB MK II spectrometer, using a monochromatic Al Kα 1486.60 eV as X-ray source. The vacuum in the analysis chamber was maintained at approximately 10^{-8} Pa or lower. All binding energies were referenced to the binding energy of the carbon C 1s peak at 285.0 eV. For the calculation of the atomic concentrations, a linear background correction was done, the peak areas were corrected with empirical sensitivity factors, the instruments transmission function and the specific mean free path lengths [20].

The contact angles were measured by the sessile drop technique [16] using a JY-82 type contact angle goniometry at 20 °C in an environmental chamber. The reported values of contact angles are the mean of five measurements, and the typical error is less than ±2°. H_2O and CH_2I_2 were used as the test liquids in our present experiment.

The surface energy (γ_S) was calculated from the measured contact angles (θ) using the geometric-mean expression [16]:

$$\gamma_L \cdot (1+\cos\theta) = 2(\gamma_S^p \cdot \gamma_L^p)^{1/2} + 2(\gamma_S^d \cdot \gamma_L^d)^{1/2} \quad (1)$$

where $\gamma_L=\gamma_L^p+\gamma_L^d$, $\gamma_S=\gamma_S^p+\gamma_S^d$, γ_L is the surface tension of the test liquid, γ_S is the surface energy of the solid, superscripts p and d refer to the polar and dispersion components of the surface tension of the test liquid and/or the surface energy of the solid, respectively.

2.4. Devices fabrication

Polymer LECs were fabricated using the polymer blend of MEH-PPV and PEO complexed with $LiCF_3SO_3$ as the active light-emitting layer, and the differently treated ITO substrates as device electrodes. The weight ratio of the MEH-PPV:PEO:$LiCF_3SO_3$ in the solution was 12:5:2. The polymer blend film of thickness of about 200 nm was prepared by spin-coating cyclohexanone solution onto the ITO substrate. The silver layer (150 nm) was then deposited on the top of the blend film by the vacuum sublimation technique (about 10^{-4} Pa) to form ITO/MEH-PPV+PEO($LiCF_3SO_3$)/Ag structure. The active area of each PLEC device was 0.6×0.6 cm^2. The polymer LECs fabricated with ITO substrates S0, S1, S2, and S3 were referred to as devices D0, D1, D2, and D3, respectively. The bias voltage was applied with the ITO electrode as anode and the Ag electrode as cathode. The current–voltage–luminance characteristics of the non-encapsulated devices were measured at a scan rate of 0.1 V/s with a KEITHLEY-4200 sourcemeter and a ST-86LA luminance meter. All measurements were performed in air at room temperature.

3. Results and discussion

3.1. The surface properties of treated ITO

Fig. 1 shows the AFM micrographs of the untreated and treated ITO substrates, in which the substrate S3 is observed to exhibit more smooth and homogeneous surface, compared with the other ITO substrates. Additionally, the values of root-mean-square roughness R_{rms} and average roughness R_a of all the ITO substrates are listed in

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