Improved efficiency of indium-tin-oxide-free flexible organic light-emitting devices

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Abstract

An indium-tin-oxide (ITO)-free flexible organic light-emitting device (OLED) with improved efficiency has been demonstrated by employing a template stripping process to create an ultrasmooth PEDOT: PSS anode on a photopolymer substrate. The device performance has been improved owing to lowered surface roughness of the PEDOT: PSS anode. A 38% enhancement in efficiency has been obtained. The ITO-free OLEDs on the polymer substrate have shown flexibility, and the device is free of cracks and dark spots under small bending radius. Moreover, the elimination of the H₂SO₄ residues on the surface of the H₂SO₄-treated PEDOT: PSS by the template stripping has demonstrated its beneficial effect on the device stability.

1. Introduction

The rapid development of organic light-emitting devices (OLEDs) in recent years makes them increasingly competitive in flat-panel display and solid-state lighting applications [1–9]. In particular, the flexibility of the OLEDs becomes a very attractive feature and has potential applications in flexible devices due to the sufficient ductibility of the organic materials. Indium tin oxide (ITO) is currently dominant transparent anode in OLEDs, due to its high optical transparency in most of the visible range, high electrical conductivity and high work function. However, ITO presents several key drawbacks, such as its high cost due to the scarcity of indium, its relatively high refractive index (n_{ITO} ~ 2.0), which induce power lost to the total internal reflection at the ITO/glass and ITO/organic interfaces [10] and its poor mechanical robust, which is unsuitable for applications in flexible devices [11]. There are several emerging materials that have shown promise for the replacement of ITO films, for example, metal grid [12], conducting polymer [12–17], carbon nanotube [18], graphene [19], and metal nanowire [20]. Among them, conducting polymer, particularly, poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate) (PEDOT: PSS) has been attracted much attention for organic optoelectronic devices, because it enables cost-effective flexible devices as well as roll-to-roll mass production [21]. Several methods have been reported to enhance the conductivity of PEDOT: PSS [11–16]. The treatment method of dropping H₂SO₄ solutions on the dried PEDOT: PSS films had been employed to obtain high conductivity [15]. Unfortunately, the dropped H₂SO₄ will increase the surface roughness of the spin-coated PEDOT: PSS, and as well as results in a residue of the H₂SO₄ on the PEDOT: PSS surface, which is adverse to the device performance.

In this letter, we have demonstrated a flexible ITO-free OLED with ultrasmooth PEDOT: PSS anode by template
2. Experimental details

2.1. Fabrication of PEDOT: PSS film on a flexible substrate

PEDOT: PSS aqueous solution (Clevios PH 1000) was purchased from Heraeus Clevios GmbH. The PEDOT: PSS films were prepared by spin coating the PEDOT: PSS aqueous solution on glass substrates at 2000 rpm for 30 s. The glass substrates were pre-cleaned with acetone, alcohol, and deionized water. The PEDOT: PSS films were dried at 120 °C on a hot plate for 15 min. The H2SO4 treatment was performed by dropping 100 μL H2SO4 (1 mol/L) solution on a PEDOT: PSS film on a hot plate at 160 °C. The films dried after about 5 min. They were cooled down to room temperature, and then were rinsed with deionized water. Finally, the polymer films were dried at 160 °C for about 5 min again. The thickness of PEDOT: PSS is decreased from 105.3 nm to 60.4 nm after the H2SO4 treatment. Then, the template-stripped PEDOT: PSS anodes on the polymer substrate have shown excellent flexibility, the devices are free of cracks and dark spots under a very small bending radius. In addition, the template stripping technique exhibits its effect on eliminating the H2SO4 residues on the anode surface, which is beneficial to the device stability.

2.2. Fabrication and characterization of OLEDs

The OLEDs with the as-deposited PEDOT: PSS anode on glass substrates and ultrasmooth template-stripped PEDOT: PSS anode on polymer substrates were both fabricated. After the fabrication of the PEDOT: PSS anode, the glass and polymer substrate were put into thermal evaporation chamber. Then the organic layers and top contact were deposited layer by layer at a rate of 1 Å s⁻¹ and at a base pressure of 5 × 10⁻⁴ Pa. 4,4',4″-tris (3-methylphenyl-phe-nylamino) triphenylamine (m-MTDATA) and N,N'-di-phenyl-N,N'-bis (1,1'-biphenyl)-4, 4'-diamine (NPB) were used as hole-injecting and transporting layers respectively. Tris-(8-hydroxyquinoline) aluminum (Alq3) was used as emitting and electron-transporting layer. A 100-nm thick Al film was used as top cathode. LiF was inserted into the cathode and organic layers to enhance the electron injection. The detailed structure of OLED is PEDOT: PSS/m-MTDATA (30 nm)/NPB (20 nm)/Alq3 (50 nm)/LiF (1 nm)/Al (100 nm) and shown in Fig. 1 (b). A hole-only device with the structure of PEDOT: PSS/m-MTDATA (30 nm)/NPB (70 nm)/Al (100 nm) was also fabricated to investigate the effect of the ultrasmooth template-stripped PEDOT: PSS anode on the hole injection. Here, the active area of the device is 2 × 2 mm². The voltage–luminance and voltage–current density characteristics of the devices were measured by Keithley 2400 programmable voltage–current source and photo research PR-655 spectrophotometer. All of the measurements were conducted in air at room temperature.

3. Results and discussion

The surface morphology and conductivity of electrode plays a fundamental role in the behavior of OLEDs. The surface morphology of the bottom electrode will affect its contact area with the deposited organic layer as shown in Fig. 1 (c) and (d). Generally, organic molecules are in form of large clusters when they deposited on an electrode by thermal evaporation, and they can not fill the depression of the rough electrode surface. Therefore, the contact...
area between the electrode and the organic layer will decrease with the increased surface roughness of the bottom electrode. The contact area between PEDOT: PSS film and organic layer must be greatly increased with the increasing of the surface smoothness, so that the charge injection from PEDOT: PSS into the organic layer can be enhanced. The AFM images of the surface morphology for both as-deposited and template-stripped PEDOT: PSS films have been shown in Fig. 2(a) and (b). Their root mean square (rms) roughness is 1.15 nm and 0.456 nm respectively, which demonstrates a much enhanced surface smoothness for the template-stripped PEDOT: PSS. The H2SO4-treated method has been employed to further enhance the conductivity of the PEDOT: PSS anode. The sheet resistance of the as-deposited PEDOT: PSS can be increased from over 20000 Ω/□ for the untreated PEDOT: PSS to 70.36 Ω/□ for the H2SO4 treated PEDOT: PSS. For the as-deposited PEDOT: PSS, the surface morphology after the H2SO4 treatment were examined by AFM and shown in Fig. 2(c). The rms roughness is 1.86 nm, which is higher than that before the H2SO4 treatment (1.15 nm). Therefore, the H2SO4-treated process will enlarge the rms roughness of the PEDOT: PSS surface. While, in case of the template-stripped PEDOT: PSS, the surface morphology of the opposite side for the peeled-off PEDOT: PSS would not be influenced by the H2SO4 treatment, so that the rms roughness of 0.468 nm (Fig. 2(d)) is comparable to that of the untreated surface (0.456 nm). Besides the improved surface smoothness, the template-stripped PEDOT: PSS films also exhibit enhancement in the conductivity. Its sheet resistance is improved from 70.36 Ω/□ for the as-deposited PEDOT: PSS to 54.39 Ω/□. This enhancement is also originated from the improved surface morphology, because lower roughness is in favor of transport of carriers. Generally, charge transport in organic film is determined by scattering of conduction electrons at defects, grain boundaries, and surfaces. The charge transport within a single grain is easier and faster than that through the grain boundaries. In case of improved surface morphology, charge transport will be improved distinctly because of fewer grain boundaries for the films with smooth surface [27–30].

Fig. 3(a) presents the transmittance spectra in the visible range of PEDOT: PSS films without and with H2SO4 treatment on both glass and photopolymer substrate. The results indicate that the transmission of PEDOT: PSS before and after H2SO4 treatment are almost identical. Therefore, the H2SO4 treatment did not affect the transparency of the PEDOT: PSS film. Moreover, the transmittance of the PEDOT: PSS either on glass substrate or on photopolymer substrate is higher than 90% in the wavelength below 500 nm, and decreases a little but still higher than 80% at the wavelength above 500 nm. The current density–voltage characteristics of hole-only devices with the template-stripped and as-deposited PEDOT: PSS are compared and shown in Fig. 3(b). The current density of the hole-only devices with the template-stripped anode is obviously higher than that of the devices with the as-deposited anode. Both the improved conductivity induced by the improved surface smoothness and the increased carrier injection induced by the improved contact between the ultra-smooth electrode and organic film contribute to the enhanced current density.

The EL performance of the OLEDs with the ultrasmooth template-stripped and as-deposited PEDOT: PSS anode were investigated and summarized in Fig. 4. They exhibit identical EL spectra as can been seen in Fig. 4(a). Both current density and efficiency of the OLEDs with the ultrasmooth PEDOT: PSS anodes are obviously improved. Its maximum current efficiency is 6.21 ± 0.43 cd/A, while it is 4.71 ± 0.44 cd/A for that with the as-deposited PEDOT: PSS anode on glass substrate, which corresponds to 38% enhancement. These improvements arise from the enhancement in both conductivity and hole-injection as a result of the lowered surface roughness for the template-stripped PEDOT: PSS anode. Moreover, the efficiency of the template-stripped OLEDs is even higher than that of the devices based on ITO anode with the same device structure [31]. On the other hand, the template-stripped OLEDs based on the photopolymer substrates exhibit high flexibility. The photographs of the operating OLEDs before and after bending were shown in the inset of Fig. 4(b). There are no cracks and dark spots on OLEDs even at an almost completely folded bending.

There would remain H2SO4 residues after the H2SO4 treatment for the PEDOT: PSS surface, which may results in the damage to the organic molecules by the strong acid.  

Fig. 2. Surface morphologies of the as-deposited (a) and template-stripped (b) PEDOT: PSS films without the H2SO4 treatment, and as-deposited (c) and template-stripped (d) PEDOT: PSS films with the H2SO4 treatment.
The organic molecules will contact with the opposite side of the PEDOT: PSS film in case of the template-stripped PEDOT: PSS, and the H$_2$SO$_4$ residues would be eliminated at this interface. The as-deposited and template-stripped PEDOT: PSS films before and after the H$_2$SO$_4$ treatment was characterized by X-ray photoelectron spectroscopy (XPS) to investigate the H$_2$SO$_4$ residues, and shown in Fig. 5(a)–(d). The two XPS peaks at 167.75 and 168.85 eV are the S$_{2p}$ band of the sulfur atoms in PSS, whereas the two XPS peaks at 163.8 and 164.85 eV are that in PEDOT. In case of the H$_2$SO$_4$, the peak at 169.2 eV is the S$_{2p}$ band of the sulfur atoms in the H$_2$SO$_4$ (Fig. 5(e)). The S$_{2p}$ XPS intensity ratio of PEDOT to PSS saliently increases after the H$_2$SO$_4$ treatment, which indicates the removal of some PSSH chains from the PEDOT: PSS film. It is beneficial to the conductivity of PEDOT: PSS owing to the conduction of...
PEDOT and the insulation of PSS. It can be seen in Fig. 5(a) that the peak at 168.85 eV was increased and higher than that at 167.75 eV, compared to that of the PEDOT: PSS film without the H$_2$SO$_4$ treatment (Fig. 5(b) and (d)). We can deduce that it may retain amount of H$_2$SO$_4$ after the H$_2$SO$_4$ treatment, because the peak at 168.85 eV is very close to that at 169.2 eV in the XPS spectra of H$_2$SO$_4$ (Fig. 5(e)). However, in case of the template-stripped PEDOT: PSS with the H$_2$SO$_4$ treatment (Fig. 5(c)), its XPS spectra is similar to that of the untreated films (Fig. 5(b) and (d)), which demonstrates that no H$_2$SO$_4$ residues on the opposite side of the PEDOT: PSS films. In addition, the XPS spectra indicate that the C/S molar ratio is 18.9% in as-deposited films and 18.3% in template-stripped films after the H$_2$SO$_4$ treatment, which identifies an identical removal of PSSH chains from the PEDOT: PSS film after the H$_2$SO$_4$ treatment. The above data demonstrates that the template stripping process can eliminate the residues of the H$_2$SO$_4$ on the PEDOT: PSS surface, and maintain its good conductivity.

To clarify the advantage of eliminating the H$_2$SO$_4$ residues on the device performance, the devices with residual H$_2$SO$_4$ have been fabricated as control. In this case, H$_2$SO$_4$ (0.5 mol/L) was doped into the PEDOT: PSS with ratio of 1:8, so that there remain the residues of the H$_2$SO$_4$ on the PEDOT: PSS surface after the template stripping. Photographs of the operating devices without encapsulation were shown in Fig. 6. The devices operate in a highly humid atmosphere up to 75% RH at room temperature to accelerate its degradation. The driving voltage for the operating devices is 8 V. It is obvious that the devices with the residual H$_2$SO$_4$ exhibit more dark spots and both size and number of the dark spots increase quickly. The devices decay completely after 60 min operation. While in case of the devices without the residual H$_2$SO$_4$ less dark spots and more homogeneous luminescence can be observed even after 60 min. Therefore the template stripping provides an avenue to persist the advantage of the conductivity improvement of the H$_2$SO$_4$ treatment on the PEDOT: PSS film, and avoid the disadvantage of the H$_2$SO$_4$ residues, which is very important for the application of this treatment.

4. Conclusions

In conclusion, an efficient ITO-free flexible OLED with ultrasmooth PEDOT: PSS anode has been demonstrated by template stripping process combined with the treatment method of dropping H$_2$SO$_4$. Compared to as deposited PEDOT: PSS film on glass substrate, the PEDOT: PSS film on polymer substrate fabricated by employing the template stripping process has shown superiority on both conductivity and surface morphology. The OLEDs based on the template-stripped PEDOT: PSS anode on the polymer substrate therefore exhibit improved efficiency and high flexibility. Moreover, the H$_2$SO$_4$ residues on the surface of the PEDOT: PSS induced from the H$_2$SO$_4$ treatment has been eliminated by the template stripping method, which demonstrates its beneficial effect on the OLED stability. From this research, we have confirmed that template stripping is an efficient and simple method to realize large area fabrication of conductive polymer, which are promising for cheaper flexible organic devices in manufacturing industries.

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References


