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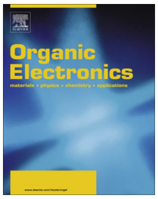

Improved efficiency of indium-tin-oxide-free organic light-emitting devices using PEDOT:PSS/graphene oxide composite anode

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ABSTRACT

We have demonstrated an indium-tin-oxide free organic light-emitting device (OLED) with improved efficiency by doping poly (3,4-ethylene dioxythiophene):poly (styrene sulfonate) (PEDOT:PSS) with graphene oxide (GO) as a composite anode. In comparison with a pure PEDOT:PSS anode, 55% enhancement in efficiency has been obtained for the OLEDs based on the PEDOT:PSS/GO composite anode at an optimal condition. The PEDOT:PSS/GO composite anode shows a lower hole-injection barrier, which contributes to the improved device efficiency. Moreover, both high transmittance and good surface morphology similar to that of the pure PEDOT:PSS film also contribute to the enhanced efficiency. It is obvious that composite anode will generally be applicable in organic optoelectronic devices which require smooth and transparent anode.

1. Introduction

Organic light-emitting devices (OLEDs) have attracted significant interest, because of their light-weight, high-brightness and low-cost, as well as flexibility for display and light applications [1–5]. Indium tin oxide (ITO) is currently transparent anode in OLEDs, due to its high optical transparency, electrical conductivity and work function. However, ITO presents several key drawbacks, such as its high cost due to the scarcity of indium, its relatively high refractive index, which induce power lost to the total internal reflection at the ITO/glass and ITO/organic interfaces [6], and its poor mechanical robustness, which is unsuitable for applications in flexible devices [7]. A number of candidate materials have been examined to replace ITO as transparent electrodes including conducting polymers [8–10], carbon nanotubes [11,12], graphene [13,14], and metallic nanowires [15–18]. However, poor uniform dispersion in most solvents of carbon nanotubes, inconvenient synthesis method and lower work function of graphene and high surface roughness of metallic nanowires are major challenges in employing these electrodes. Conducting polymers, particularly poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), have attracted much attention for organic optoelectronic devices because they can enable cost-effective flexible devices as well as roll-to-roll mass production. Both efficiency and stability of optoelectronic devices based on the PEDOT:PSS anodes have been improved significantly [8–10]. In our primary work, we also have demonstrated an improved OLEDs with PEDOT:PSS by employing a template stripping process to regulate surface morphology of PEDOT:PSS[19], while further improvement is still required for their commercial application.

It has been demonstrated reducing the injection barrier plays a crucial role in improving the performances of the OLEDs. For this purpose, a thin film of graphene oxide (GO) was recently reported as an efficient hole transport layer for high-performance OLEDs and organic photovoltaic devices (OPVs) [20,21]. However, the cell performance is highly sensitive to the film thickness of the GO due to its insulating property. A precise control of the thickness is required, which limits the repeatability of the device performance. As a result, composite anodes have attracted much attention due to the potential creation of synergistic effects on their properties. The composites of PEDOT:PSS with GO, rGO and Graphene have been reported[22–24]. Particularly, Wu et al. [24] reported a PEDOT:PSS with GO hybrid film as an anode for OLEDs and obtained improved performances of OLEDs, where a surfactant sodium dodecyl benzene sulfonate (SDBS) was needed to improve the dispersion of graphene in PEDOT:PSS solution. It will intercalate into GO and may affect the interaction between PEDOT:PSS and GO.

In this letter, we report a solution-processable composite anode of simply mixing of PEDOT:PSS and GO to demonstrate an enhanced efficiency of OLEDs. It is convenient to control the doping

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ratio of the PEDOT:PSS/GO composite anode exactly, so that a high repeatability of the device performance can be obtained. Compared to the pure PEDOT:PSS anode, the PEDOT:PSS/GO composite anode exhibits a higher work function, which contributes to enhanced hole-injection from the anode into the organic layer. The maximum current efficiency of the OLEDs based on the composite anode is 5.71 cd/A, which corresponds to a 55% enhancement in the efficiency compared to that of the pure PEDOT:PSS anode-based OLEDs. In addition, the PEDOT:PSS/GO composite anode has similar root-mean-square (RMS) roughness of 1.52 nm with that of the pure PEDOT:PSS film (1.28 nm), whereas the pure GO film showed a rough surface morphology with a large RMS roughness value of 3.50 nm. Therefore, the PEDOT:PSS/GO composite anode will generally be applicable in organic optoelectronic devices which require smooth and transparent anode.

2. Experimental details

2.1. Preparation of GO

GO is prepared by a modified Hummers method from natural graphite (Aldrich, <150 μm) [25,26]. Natural graphite powder (2 g) was mixed with $NaNO_3$ (2 g) and H_2SO_4 (96 mL) under stirring in an ice-bath. Then $KMnO_4$ (12 g) was added slowly into the mixed solution under stirring, and the temperature of the system was controlled at 0 °C. After 90 min the ice-bath was removed and the system was heated at 35 °C for 30 min. Distilled water (80 mL) was slowly added into the system, and it was stirred for another 15 min. Then distilled water (200 mL) and a 3% H_2O_2 aqueous solution were added to reduce the residual $KMnO_4$ until the bubbling disappeared. Finally, the system was centrifuged at 12,000 rpm for 30 min, and the residue was washed with distilled water until the upper layer of the suspension reached a pH of ~7. The obtained sediment was redispersed into water and was treated by mild ultrasound for 15 min. A homogeneous suspension was collected after removing the trace black residues by centrifugation at 3000 rpm for 3 min. GO powder was obtained after freezing and drying of the suspension. The GO powder was redispersed into water again, and the concentration of the GO solution was controlled at 4 mg/mL.

2.2. Fabrication and characterization of PEDOT:PSS/GO composite anode

PEDOT:PSS aqueous solution (Clevios PH 1000) was purchased from Heraeus Clevios GmbH. The PEDOT:PSS solution was directly mixed with a prepared GO solution because they are both well dispersed in water. The PEDOT:PSS/GO composite films were prepared by spin coating solution on glass substrates at 2000 rpm for 30 s. The glass substrates were pre-cleaned with acetone, alcohol, and deionized water. The adhesive tapes were adhered onto glass substrate setting aside a strip with a width of 5 mm. After spin-coating PEDOT:PSS, the tape will be peeled off and a PEDOT:PSS strip with 5 mm width will be obtained and used as anode. Then composite films were dried at 120 °C on a hot plate for 15 min. The H_2SO_4 treatment was performed by dropping 100 μL H_2SO_4 (1 mol/L) solution on composite 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. This method has been demonstrated to enhance the conductivity of PEDOT:PSS [10,19]. Finally, the polymer films were dried at 160 °C for about 5 min again. The sheet resistance, surface morphology and the transmittance spectra of GO, PEDOT:PSS and composite film were measured by a 4-point probe (RTS-5, 4probes Tech.), atomic force microscopy (AFM, iCON, Veeko) and UV–Vis spectrophotometer (UV-2550, SHIMADZU Co., Inc., Japan) respectively.

2.3. Fabrication and characterization of OLEDs

The OLEDs with pure PEDOT:PSS and PEDOT:PSS/GO composite anode were both fabricated. After the fabrication of anodes, the substrates 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} at a base pressure of 5×10^{-4} Pa. N,N′-diphenyl-N, N′-bis (1,1′-biphenyl)-4,4′-diamine (NPB) was used as transport layers. Tris-(8-hydroxyquinoline) aluminum (Alq_3) was used as emitting and electron-transport layer. A 100-nm thick Al film was used as top cathode. LiF was inserted into the cathode and organic layers to enhance electron injection. The detailed structure is anode/NPB (52 nm)/Alq_3 (48 nm)/LiF (1 nm)/Al (100 nm), as shown in Fig. 1(a). Al cathode area was determined by shadow mask of 2 mm width. The devices area (2×2 mm^2) is overlapping part between anode and cathode. 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 chemical structures of PEDOT:PSS and GO are shown in Fig. 1(b). GO contains chemical functional groups such as carboxyl, hydroxyl, and epoxy groups. The functional groups, in this case the epoxy and hydroxyl groups, disrupt the sp^2 conjugation of the hexagonal graphene lattice in the basal plane. Thus, GO behaves as an insulator with a large band gap of around 3.6 eV [20,21,26,27]. This implies that the ratio of GO in PEDOT:PSS-GO composite anode should not be heavy, for avoiding excessive GO leading to low conductivity of the anode.

The transmittances of the anodes play a fundamental role in the behavior of bottom-emitting OLEDs because the light emission is from this direction. Fig. 2(a) presents the transmittance spectra in the visible range of PEDOT:PSS, GO and composite films in different ratio. Although the transmittance of the GO films is lower than that of the PEDOT:PSS, a small amount of GO has little impact on the transmittance of PEDOT:PSS/GO films. The transmittance of the PEDOT:PSS/GO composite films in different ratio are almost higher than 85% in the wavelength below 550 nm, and decreases a little but still close to 80% at the wavelength above 600 nm. We also have measured thickness of composite anode with and without H_2SO_4 treatment as shown in Table 1. The averaged results from three sets of samples indicate that the thickness of PEDOT:PSS is decreased after the H_2SO_4 treatment due to the removal of some PSSH chains from the PEDOT:PSS film. While, the thickness of the PEDOT:PSS has no obvious change after doping GO. The device averaged characterizations of three sets of OLEDs with PEDOT:PSS, and PEDOT:PSS/GO anodes with different doping ratio are presented in Figs. 2(b)–(d). The device performance is increased with the GO increased to the optimum volume ratio of 15:1. Then it is decreased when the doping ratio is further increased. The use of an excessive volume ratio of GO in PEDOT:PSS decreased the device efficiency, because the conductivity of the composite anode is deteriorated after the adding of an excessive amount of the GO insulator into the anode. The averaged results from three sets of samples of sheet resistance for the composite anode with different doping ratio as shown in Table 1 can approve this analysis. A small amount of GO has little impact on sheet resistance, but excessive GO leads to much increase of the sheet resistance. At the optimal doping ratio of 15:1, the maximum