Organic Electronics 31 (2016) 247–252

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Ultrasmooth, highly conductive and transparent PEDOT:PSS/silver nanowire composite electrode for flexible organic light-emitting devices

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ARTICLE INFO

Article history:
Received 5 December 2015
Received in revised form
5 January 2016
Accepted 9 January 2016
Available online xxx

Keywords:
Ultrasmooth and transparent composite electrode
Template stripping method
Silver nanowire
Flexible OLEDs

ABSTRACT

The next generation of optoelectronic devices requires transparent conductive electrodes to be flexible, inexpensive and compatible with large scale manufacturing processes. We report an ultrasmooth, highly conductive and transparent composite electrode on a flexible photopolymer substrate by employing a template stripping method. A random silver nanowire (AgNW) network buried in poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) film constituted the composite electrode. Besides the effectively decreased surface roughness, its sheet resistance and transmittance are comparable to those of conventional PEDOT:PSS electrode. As a result, the efficiency of the OLEDs based on the composite electrode exhibited 25% enhancement compared to the OLEDs with conventional PEDOT:PSS electrode. Moreover, the performance of the flexible OLEDs remains stable after over one hundred bending cycles.

1. Introduction

Organic light-emitting devices (OLEDs) experienced a rapid development, making them increasingly competitive in flat-panel display and solid-state lighting applications [1–6]. Indium tin oxide (ITO) is currently dominant transparent anode in OLEDs due to its excellent properties in transparency, electrical conductivity and work function. However, with some key drawbacks of ITO such as rising cost of indium resources and the demand of deformable electrodes, an increasing number of efforts are being made to search for substitute of ITO as flexible transparent electrodes such as carbon nanotubes [7], graphene [8,9], conducting polymers [10–12], and metal nanowires [13–17], which have been proved valid. Among them, silver nanowires (AgNWs) are attractive for its high electrical conductivity and flexibility, which is suitable for flexible OLEDs. Nevertheless, there are still some limitations for the single-material of AgNWs as the transparent electrodes [18]. High surface roughness of the AgNWs film results in its poor contact with the carrier-transport layer in OLEDs, which is disadvantage to the carrier injection and long-term stability of the OLEDs. Usually, a surface modification is necessary to improve the contact. On the other hand, high transparency and high conductivity of the electrode are both needed for the high efficiency of the OLEDs, while they have a contrary requirement on the density of the AgNWs in the electrode film. The tradeoff between the transmittance and conductivity remains a challenge for the application of the AgNWs as the transparent electrode of the OLEDs.

In this work, we develop a poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/AgNW composite electrode to take advantage of both the short-range conductivity of PEDOT:PSS and the long-range conductivity of AgNWs to simultaneously improve the transmittance and sheet resistance. Moreover, the composite electrode exhibits a ultrasmooth surface morphology with sub-nanometer surface roughness by employing a template stripping method [19]. The maximum current efficiency of the OLEDs based on the composite electrodes has been improved by 25% compared to that of the OLEDs with traditional modified PEDOT:PSS electrodes. The OLEDs based on the ultrasmooth and transparent composite electrodes exhibit excellent flexibility and mechanical robustness.

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http://dx.doi.org/10.1016/j.orgel.2016.01.014
1566-1199/

2. Experimental details

2.1. Fabrication of the composite electrode

The AgNWs were purchased from Blue Nano Inc. as supplied with a concentration of 10 mg/ml in alcohol and used without other modification. PEDOT: PSS aqueous solution (Clevios PH 1000) was purchased from Heraeus Clevios GmbH. The process of fabricating the composite electrode is shown in Fig. 1: Firstly, precleaned Si substrate were treated in plasma cleaner for 10 min to improve the uniformity of polymer films in the coating process afterwards and patterned as a template with a strip uncovered in the middle. Following this, solutions of PEDOT:PSS and AgNW dispersions in alcohol were spin coated in sequence on the Si template at 2000 rpm for 60 s and 1000 rpm for 20 s, respectively. We choose this two-step method to make the composite films other than the one-step mixing of the PEDOT:PSS:AgNWs because AgNWs are easily aggregated in the mixing solution, leading to the solution of poor dispersion. The thickness of the two-layer film is about 110 nm. After thermal annealing the film at 120 °C for 30 min to increase the conductivity, a 500 μm-thick photopolymer (NOA63, Norland) was spin coated onto the film for 20 s at 1000 rpm and exposed to a UV light source with a power of 125 W for 5 min. Finally, the cured photopolymer film can be peeled off easily together with the PEDOT:PSS/AgNWs composite film from the Si substrate due to good adhesion between the PEDOT:PSS/AgNWs film and the cured photopolymer. The surface morphology of the electrodes on the photopolymer substrates were measured by atomic force microscopy (AFM, iCON, Veeko). The backing layer of NOA63 itself is flexible and can be used as the substrate to realize the flexible OLED combining with the flexible PEDOT:PSS/AgNW electrode.

2.2. Fabrication and characterization of OLEDs

The OLEDs with the as-prepared composite electrode on flexible substrates were fabricated in thermal evaporation chamber. The organic layers were deposited layer by layer at a rate of 1 Å s^{-1} and at a base pressure of 5×10^{-4} Pa. The device consists of layers of AgNWs/PEDOT:PSS as transparent anode, N, N′ diphenyl-N, N′-bis (1,1′-biphenyl)-4,4′-diamine (NPB, 40 nm) as hole transporting layer, tris(2-phenylpyridine)iridium(III) (Ir(ppy)3) doped N, N′-dicarbazolyl-3,5-benzene (mCP, 6%, 20 nm) as emitting layer, 1,3,5-tris(N-phenyl-benzimidazol-2-yl)benzene (TPBi, 35 nm) as electron transporting layer, and LiF (1 nm)/Al (80 nm) as cathode. The active area of the device is 2×2 mm^2. A device with conventional modified PEDOT:PSS (DMSO doped PEDOT:PSS) [20,21] as anode was also fabricated for comparison. The voltage–luminance and voltage–current density characteristics of the devices were measured by Keithley 2400 programmable voltage–current source

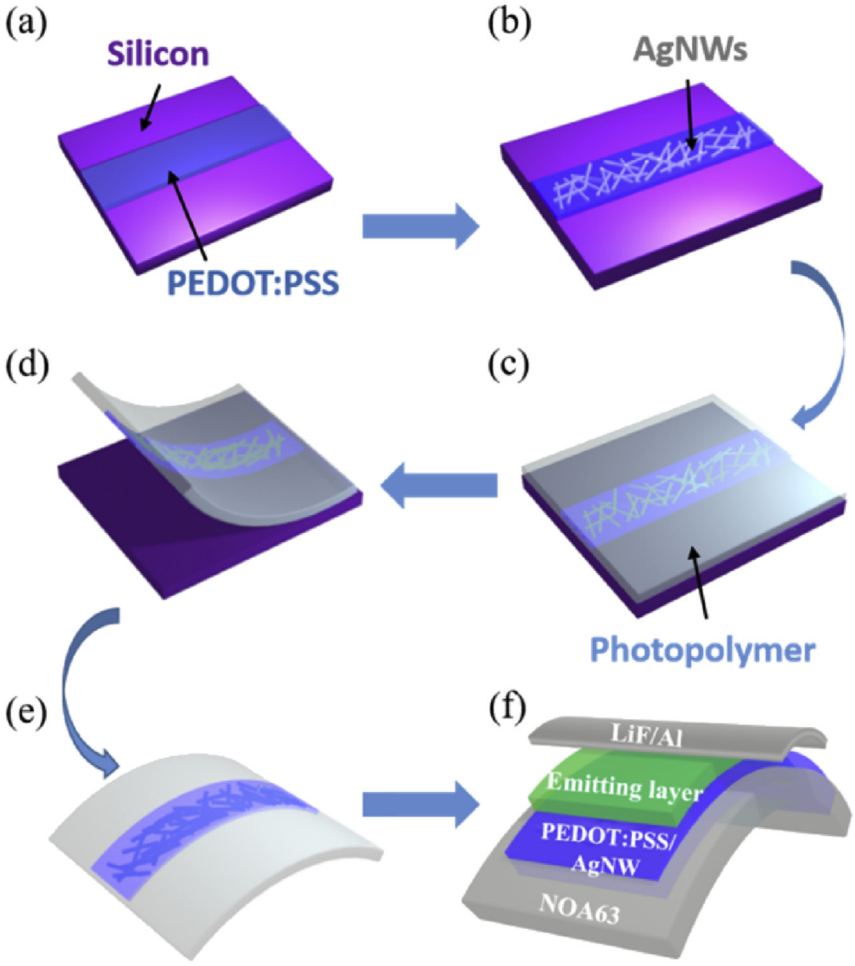

Fig. 1. Schematic illustration of the composite anode-based OLEDs based on the template stripping process. (a) Spin coating PEDOT:PSS onto the silicon slice. (b) Spin coating of AgNWs onto the PEDOT:PSS followed by thermal annealing. (c) Spin coating photopolymer of NOA63 onto the composite layer followed by UV curing. (d) Stripping off the photopolymer film together with the composite layer from the silicon slice. (e) Rolling over the polymer film as the flexible substrate and the composite film above it as the flexible anode. (f) Fabrication of the composite film-based OLEDs on the flexible substrate.

and photo research PR-655 spectrophotometer. All of the measurements were conducted in the air at room temperature.

3. Results and discussion

The surface morphology plays a key role in the performance of OLEDs. As can be seen in Fig. 2, the concentration of AgNWs is 0.5 mg/ml and the stripped-off composite electrode film on the photopolymer substrates is extremely smooth with a root mean square (RMS) roughness of 0.372 nm, which is much lower than that coated on the Si substrates (RMS = 27.2 nm). These obvious improvements originate from the stripped-off process which rolls

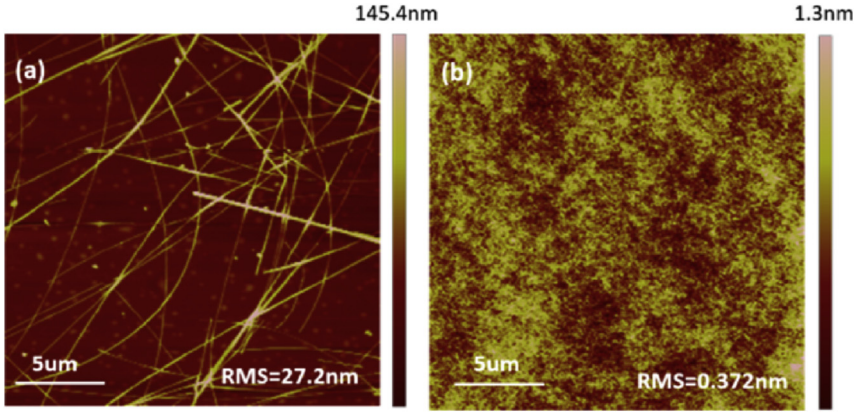

Fig. 2. AFM images of surface morphology of spin-coated composite film on Si substrate (a) and stripped-off composite film on photopolymer substrate (b).

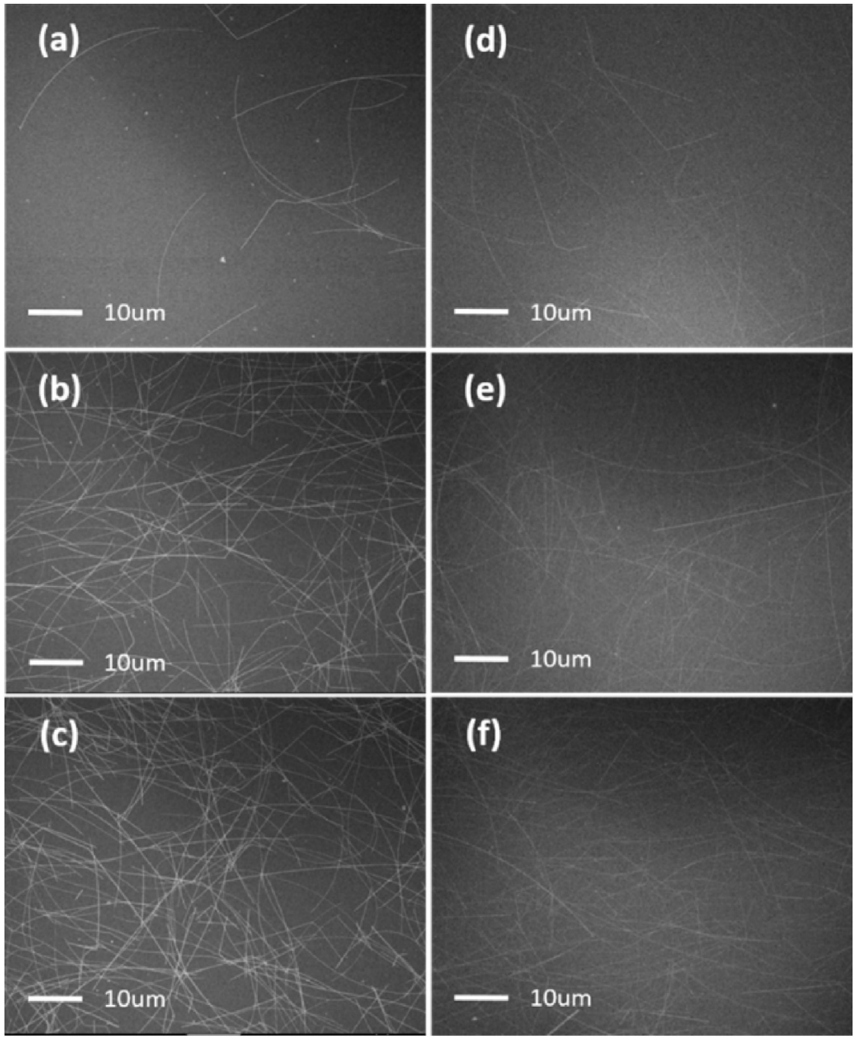

Fig. 3. SEM images of the surfaces of spin-coated composite films on Si substrates with various concentration of 0.1 mg/ml (a), 0.5 mg/ml (b) and 1.5 mg/ml (c); and stripped-off composite films on photopolymer substrates with various concentration of 0.1 mg/ml (d), 0.5 mg/ml (e) and 1.5 mg/ml (f).

over the bottom surface facing the Si substrate to be the top surface, duplicating the ultrasmooth morphology of the Si slice. Furthermore, as shown in Fig. 2(b), the AgNWs are embedded in the film of PEDOT:PSS, which improve the conductivity of the polymer effectively. To investigate the concentration dependence of the optical and electrical performances of the composite films, we have prepared a series of films with various AgNW concentrations from 0.1 mg/ml to 1.5 mg/ml. The AgNWs employed have an average diameter of ~10 nm and a length of ~20 to 50um. Fig. 3 shows the SEM images of the composite films on Si substrate and on the polymer substrate after transferring process with different AgNW densities of 0.1 mg/ml, 0.5 mg/ml and 1.5 mg/ml, respectively. It can be seen from the SEM images that the AgNW networks become more compact when the concentration increases. Besides, the network structure remain almost intact after stripping, indicating that this method will not damage the films and the AgNWs do not break or buckle. Therefore, the stripping off process did not change the inner structure of the composite films, thus the whole process would not influence the transparency of the composite films.

Fig. 4 shows the transmittance spectra and the corresponding sheet resistance (Rs) before and after template-stripping process for the composite films with various AgNWs concentration and the sheet resistance of the composite film (0.5 mg/ml) after 150 times of bending. As expected, composite films with higher transparency typically showed higher Rs, thus it is significant to find a proper point that leads to a best photoelectrical performance. From Fig. 4(a) we can see that the transparency of the composite films decreased while the concentration of AgNWs increased, while it is notable that nearly all composite films have a decent transparency of over 80% in average. Especially, the composite films with the AgNWs concentration lower than 1 mg/ml shows even higher transmittance than that of the pure PEDOT:PSS films. It is clear to be seen from Fig. 4(b) that pure AgNW films have a very high resistance at various AgNW concentration and are even nonconductive at the concentration of lower than 0.5 mg/ml. On the other hand, the pure PEDOT:PSS also has a rather high resistance of over 20,000Ω/sq. Such low conductivity suggests that neither of the two materials is reasonable to be utilized in the electrodes separately. However, the conductivity of the composite film has been improved to a large extent compared to the single-component films. In particularly, the sheet resistance of the composite films has been further decreased after stripped off from the Si substrates as the polymer molecules could join together via the network of AgNWs. Furthermore, the ultrasmooth surface morphology may contribute to its improved conductivity because the surface defects of the polymer films were effectively reduced because of the forming of ultrasmooth surface, thus enhancing the surface free charge transport, leading to the decrease of resistance. It should be noted that the stripped-off composite films with the AgNW concentration of 0.5 mg/ml exhibit good performance in both transmittance and conductivity. Its transmittance is around 95% within the wavelength region from 400 to 800 nm, and the sheet resistance is 195 Ω/sq. Furthermore, the sheet resistance of the composite films gets little influenced after over 100 times of bending according to Fig. 4(c). Combining with its ultrasmooth surface morphology, the composite film indicates its potential as transparent bottom anode in OLEDs.

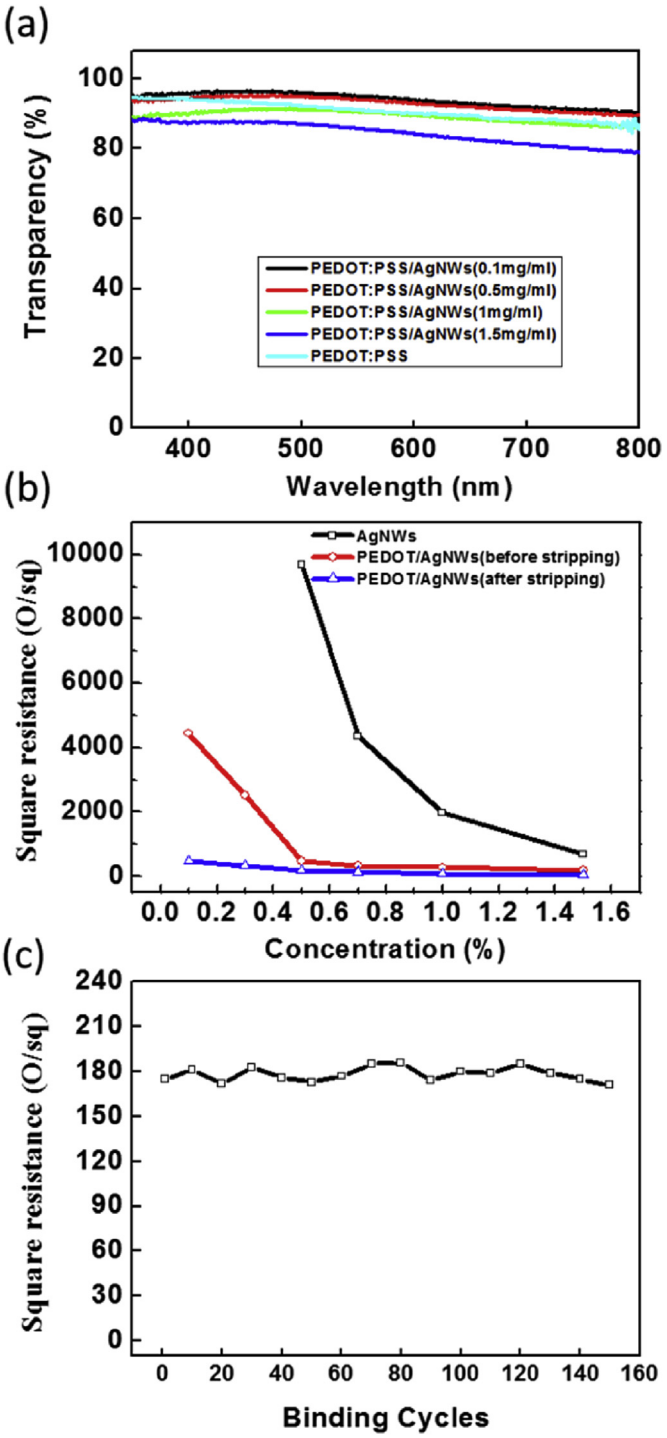

Fig. 4. (a) Transmittance spectra of composite films with different AgNW concentrations and pure PEDOT:PSS. (b) Sheet resistance of composite films with different AgNW concentrations on Si and photopolymer substrates. (c) Sheet resistance of the composite film (0.5 mg/ml) after 150 times of bending.

To evaluate the effect of the ultrasmooth composite film as the bottom anode on the EL performance of the OLEDs, the OLEDs based on the composite film with various AgNW concentrations are compared and summarized in Fig. 5. An OLED with the pure PEDOT:PSS (DMSO doped PEDOT:PSS) as the anode are fabricated for comparison. It can be seen obviously that the composite anode-based devices fabricated on the peeled-off photopolymer substrate with an AgNW concentration of 0.5 mg/ml exhibit the best performance, which show obvious enhancement in both luminance and efficiency compared to that of the device based on the pure PEDOT:PSS electrode (Fig. 5(a) and (b)). No obvious difference can be observed from the EL spectra of the OLEDs with the different anode (Fig. 5(c)). The maximum luminance is increased from 1792 cd/m^2 for the pure PEDOT:PSS-based OLEDs to 5380 cd/m^2 for the composite anode-based OLEDs. The maximum current efficiency is increased from 39.8 cd/A to 51.2 cd/A, which corresponds

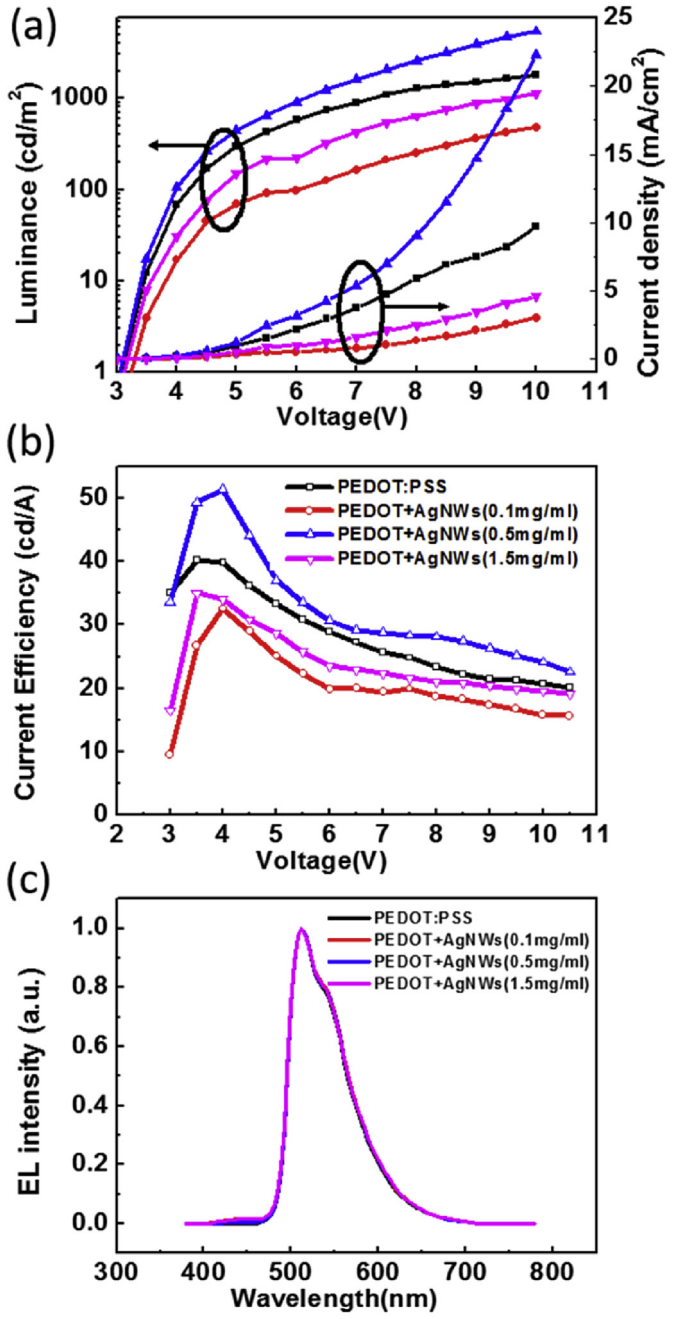

Fig. 5. EL performance of OLEDs with composite and pure PEDOT:PSS electrode. (a) Current density and luminance–voltage characteristics. (b) Efficiency–voltage characteristics. (c) EL spectra.

to an approximately 25% enhancement. The enhanced efficiency is attributed to the simultaneously improved conductivity and transparency for the composite film. On the other hand, the increased carrier injection due to the improved contact between the ultrasmooth anode and the organic film also contribute to the enhanced efficiency.

Finally, a bending test has been conducted to evaluate the flexibility and mechanical robustness of the OLEDs based on the composite electrode. We choose the composite electrode consisting of AgNWs with a concentration of 0.5 mg/ml which leads to the best performance. Fig. 6 shows the current efficiency performance of the flexible devices after repeated bending. The bending radius is around 1 cm. The efficiency of the OLEDs experienced a slight

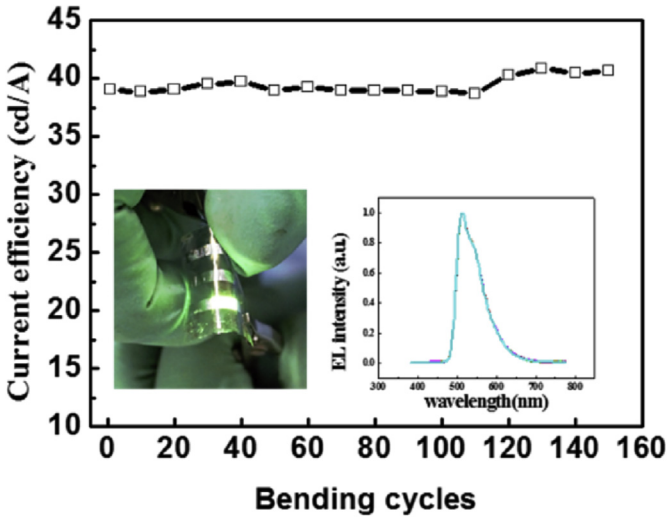

Fig. 6. Efficiency of the OLEDs at 8 V as a function of the number of bending cycles. Insets are photograph of the operating flexible OLEDs and its EL spectra under bending state.

fluctuation during the whole bending test without obvious deterioration, which indicates its excellent mechanical robustness. The photograph of the device operating at 8 V shown in the inset illustrates that the device is free of cracks and dark spots, and the EL intensity remains almost unchanged after the device being repeated bended to 150 cycles.

4. Conclusions

In conclusion, an ultrasmooth and transparent PEDOT:PSS/AgNW composite anode on flexible substrate has been fabricated for realizing highly flexible and efficient OLEDs. An ultrasmooth electrode surface with sub-nanometer surface roughness on the flexible substrate has been obtained by template stripping transferring process. Simultaneously improvements in the transmittance and sheet resistance have been realized for the composite electrode, which would much benefit the device performance. As a result, the OLEDs based on the composite anode exhibit a 25% enhancement in current efficiency compared to those of the devices utilizing conventional PEDOT:PSS electrode. Besides the improved EL performance, the satisfying flexibility characteristics of the OLEDs have been demonstrated by conducting the bending test. From this research, we have confirmed that the composite electrodes are a potential transparent electrode candidate, proving potential for realizing flexible optoelectronics applications in manufacturing industries.

Acknowledgments

The authors gratefully acknowledge support from the 973 Project (2013CBA01700) and NSFC (Grant Nos. 61322402, 91233123 and 61505065).

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