Organic Electronics 26 (2015) 81–85

Contents lists available at ScienceDirect

Organic Electronics

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

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

Yue-Feng Liu, Jing Feng *, Yi-Fan Zhang, Hai-Feng Cui, Da Yin, Yan-Gang Bi, Jun-Feng Song, Qi-Dai Chen, Hong-Bo Sun *

State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, 2699 Qianjin Street, Changchun 130012, People's Republic of China

ARTICLE INFO

Article history:
Received 6 January 2015
Received in revised form 19 June 2015
Accepted 22 June 2015
Available online 14 July 2015

Keywords:
Organic light-emitting devices
Graphene oxide
PEDOT:PSS
Composite anode

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

* Corresponding authors.
E-mail addresses: jingfeng@jlu.edu.cn (J. Feng), hbsun@jlu.edu.cn (H.-B. Sun).

http://dx.doi.org/10.1016/j.orgel.2015.06.031
1566-1199/

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

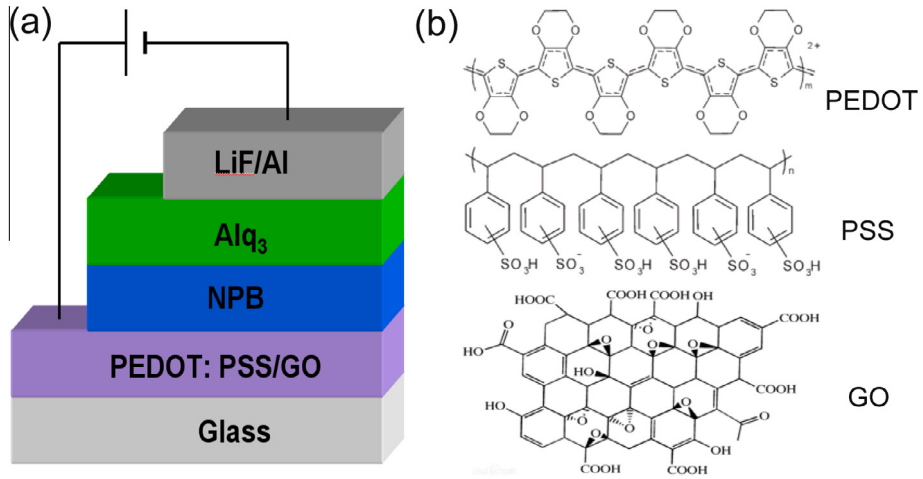

Fig. 1. (a) Schematic structure of OLEDs based on the PEDOT:PSS/GO composite anode. (b) The chemical structures of the PEDOT:PSS and GO.

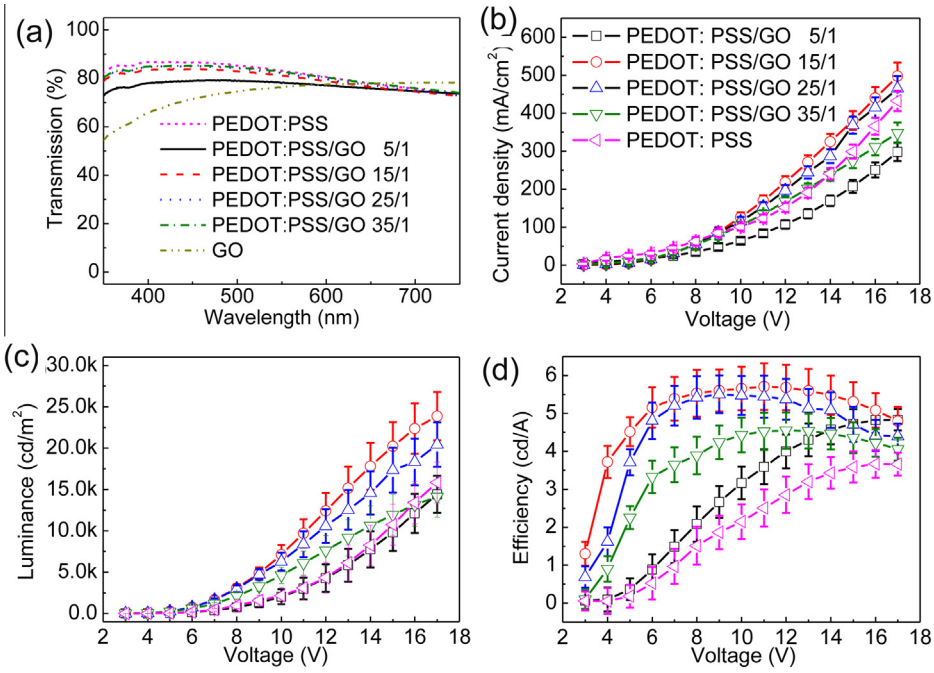

Fig. 2. (a) Transmittance spectra of the pure PEDOT:PSS film and PEDOT:PSS/GO composite films with different doping ratio. (b) Current density–voltage, (c) luminance–voltage and (d) efficiency–voltage characteristics of the OLEDs with composite anodes in different doping ratio.

Table 1
The average sheet resistance and thickness of the pure PEDOT:PSS and composite anode with different doping ratio.

PEDOT:PSS/GO (volume ratio)	5:1	15:1	25:1	35:1	Pure PEDOT:PSS
Average sheet resistance (Ω/□)	136.4	82.3	74.7	73.4	69.2
Average thickness without H_2SO_4 treatment (nm)	107.3	103.3	105.9	106.2	106.5
Average thickness with H_2SO_4 treatment (nm)	57.5	57.1	58.9	58.2	61.3

current efficiency of the device is 5.71 cd/A, while it is 3.67 cd/A for that with pure PEDOT:PSS anode, which corresponds to 55% enhancement.

To clarify the advantages of PEDOT:PSS/GO composite anode, hole-only devices have been fabricated and characterized. The detailed structure is anode/NPB (100 nm)/Al (100 nm). As shown in Fig. 3(a), the current density of the hole-only devices with PEDOT:PSS/GO composite anode in condition of optimum volume ratio is obviously higher than that of the devices with pure PEDOT:PSS. This improvement indicates that the composite anode is beneficial to the hole injection from the anode to the hole-transporting layer. GO sheet is composed of unoxidized graphitic patches and heavily oxidized domains functionalized by hydroxyl and epoxide groups. Therefore, it can be viewed as a two dimensional, random diblock copolymer with distributed nanosize graphitic patches and highly oxidized domains, thus capable of guiding the assembly of other materials through both π–π stacking and hydrogen bonding [28]. Adding the GO into the PEDOT:PSS can effectively make the interaction between GO and PEDOT but not PSS because of the electronegativity of GO. Therefore, it should be the interaction between GO and PEDOT that is responsible for the enhancement of the hole injection.

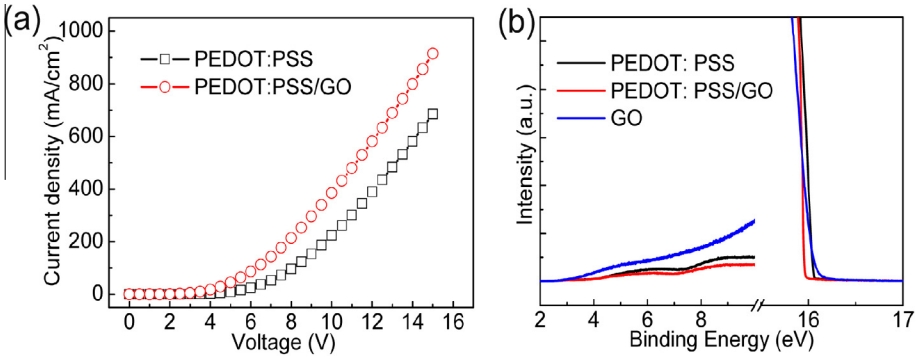

Fig. 3. (a) Current density–voltage characteristics of hole-only devices with PEDOT:PSS anode and PEDOT:PSS/GO (15:1) composite anode. (b) UPS spectra of PEDOT:PSS, PEDOT:PSS/GO (15:1) and GO films.

Ultraviolet photoelectron spectroscopy (UPS) measurements have been performed and presented in Fig. 3(b) to clarify the holes injection enhancement. The work function values of the anodes were calculated from the UPS results. The PEDOT:PSS and GO show work function of 5.13 eV and 5.00 eV, respectively, while PEDOT:PSS/GO composite films show value of 5.32 eV. The hole-injection barrier at the anode/NPB interface is reduced by 0.19 eV when the GO is in the presence, which contribute to the enhanced hole injection.

In addition, the surface morphology of bottom electrode plays an important role in the behavior of the OLEDs. Generally, organic molecules are in the form of large clusters when they are deposited on an electrode by thermal evaporation, and they cannot fill the depression of the rough electrode surface. The contact area between the electrode and the organic layer will decrease with the increased surface roughness of the bottom electrode [19,29,30]. Therefore, the charge injection increases with the decreased surface roughness of the bottom electrode. Moreover, lower surface roughness is also beneficial to eliminating tip discharge. The AFM images of the surface morphology for PEDOT:PSS, GO and PEDOT:PPS/GO composite films have been shown in Fig. 4. The root mean square (rms) roughness of the pure PEDOT:PSS and composite films were 1.28 nm and 1.52 nm, respectively. The doping of the GO into the PEDOT:PSS with the doping ratio of 15:1 has little impact on the surface roughness of the PEDOT:PSS. On the contrary, roughness of the pure GO film is much large (3.50 nm). These results indicate that composite anode will generally be applicable in organic optoelectronic devices which require smooth and transparent anode.

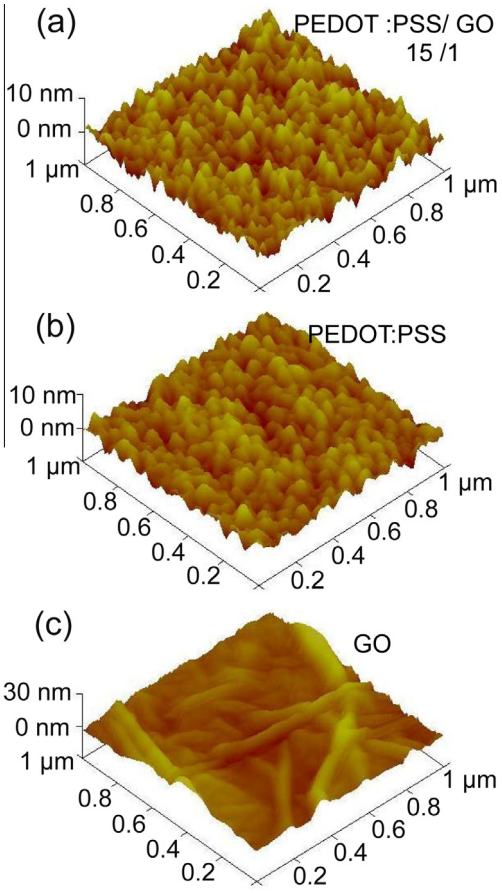

Fig. 4. Surface morphologies of the PEDOT:PSS/GO (15/1) films (a), PEDOT:PSS films (b) and GO films (c).

4. Conclusions

In conclusion, an ITO-free OLED with improved efficiency by using PEDOT:PSS/GO composite anode has been demonstrated. A 55% enhancement in efficiency has been obtained at an optimal condition which the volume ratio of PEDOT:PSS and GO is 15:1. The maximum current efficiency of device is 5.71 cd/A, while it is 3.67 cd/A for that with pure PEDOT:PSS anode. The improved efficiency has been proved that arose from the enhancement of hole-injection. The work function of the PEDOT:PSS-GO composite film is 0.19 eV higher than that of the PEDOT:PSS film, which contributes to a decreased hole-injection barrier. Moreover, both high transmittance and good surface morphology of the composite anode are also beneficial to the hole injection. From this research, we have confirmed that as an efficient and simple method to realize large area fabrication of anode, the solution-processable PEDOT:PSS/GO composite film is promising for organic optoelectronic devices in manufacturing industries.

Acknowledgements

The authors gratefully acknowledge support from the 973 Project (2013CBA01700) and NSFC (Grant Nos. 61322402, 91233123, 61177024 and 51373064).

References

[1] S. Chen, L. Deng, J. Xie, L. Peng, L. Xie, Q. Fan, W. Huang, Recent developments in top-emitting organic light-emitting diodes, Adv. Mater. 22 (2010) 5227–5239.
[2] Q. Wang, Z. Deng, D. Ma, Realization of high efficiency microcavity top-emitting organic light-emitting diodes with highly saturated colors and negligible angular dependence, Appl. Phys. Lett. 94 (2009) 233306.

[3] S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lussem, K. Leo, White organic light-emitting diodes with fluorescent tube efficiency, Nature 459 (2009) 234–238.
[4] Y. Sun, N.C. Giebink, H. Kanno, B. Ma, M.E. Thompson, S.R. Forrest, Management of singlet and triplet excitons for efficient white organic light-emitting devices, Nature 440 (2006) 908–912.
[5] Y. Bai, J. Feng, Y.-F. Liu, J.-F. Song, J. Simonen, Y. Jin, Q.-D. Chen, J. Zi, H.-B. Sun, Outcoupling of trapped optical modes in organic light-emitting devices with one-step fabricated periodic corrugation by laser ablation, Org. Electron. 12 (2011) 1927–1935.
[6] K. Saxena, V.K. Jain, D.S. Mehta, A review on the light extraction techniques in organic electroluminescent devices, Opt. Mater. 32 (2009) 221–233.
[7] M. Cai, Z. Ye, T. Xiao, R. Liu, Y. Chen, R.W. Mayer, R. Biswas, K.-M. Ho, R. Shinar, J. Shinar, Extremely efficient indium–tin-oxide-free green phosphorescent organic light-emitting diodes, Adv. Mater. 24 (2012) 4337–4342.
[8] Y.H. Kim, C. Sachse, M.L. Machala, C. May, L. Müller-Meskamp, K. Leo, Highly conductive PEDOT: PSS electrode with optimized solvent and thermal post-treatment for ito-free organic solar cells, Adv. Funct. Mater. 21 (2011) 1076–1081.
[9] M. Vosgueritchian, D.J. Lipomi, Z. Bao, Highly conductive and transparent PEDOT:PSS films with a fluorosurfactant for stretchable and flexible transparent electrodes, Adv. Funct. Mater. 22 (2012) 421–428.
[10] Y. Xia, K. Sun, J. Ouyang, Solution-processed metallic conducting polymer films as transparent electrode of optoelectronic devices, Adv. Mater. 24 (2012) 2436–2440.
[11] M.W. Rowell, M.A. Topinka, M.D. McGehee, H.-J. Prall, G. Dennler, N.S. Sariciftci, L. Hu, G. Gruner, Organic solar cells with carbon nanotube network electrodes, Appl. Phys. Lett. 88 (2006) 233506.
[12] D.-J. Yun, S.-W. Rhee, Composite films of oxidized multiwall carbon nanotube and poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) as a contact electrode for transistor and inverter devices, ACS Appl. Mater. Interfaces 4 (2012) 982–989.
[13] L. Gomez De Arco, Y. Zhang, C.W. Schlenker, K. Ryu, M.E. Thompson, C. Zhou, Continuous, Highly Flexible, and Transparent Graphene Films by Chemical Vapor Deposition for Organic Photovoltaics, ACS Nano 4 (2010) 2865–2873.
[14] H. Meng, J. Luo, W. Wang, Z. Shi, Q. Niu, L. Dai, G. Qin, Top-emission organic light-emitting diode with a novel copper/graphene composite anode, Adv. Funct. Mater. 23 (2013) 3324–3328.
[15] J. Meiss, M.K. Riede, K. Leo, Towards efficient tin-doped indium oxide (ITO)-free inverted organic solar cells using metal cathodes, Appl. Phys. Lett. 94 (2009) 013303.
[16] L.-H. Chen, P. Lin, M.-C. Chen, P.-Y. Huang, C. Kim, J.-C. Ho, C.-C. Lee, Silver nanowire-polymer composite electrode for high performance solution-processed thin-film transistors, Org. Electron. 13 (2012) 1881–1886.
[17] K. Zilberberg, F. Gasse, R. Pagui, A. Polywka, A. Behrendt, S. Trost, R. Heiderhoff, P. Görrn, T. Riedl, Highly robust indium-free transparent conductive electrodes based on composites of silver nanowires and conductive metal oxides, Adv. Funct. Mater. 24 (2014) 1671–1678.
[18] Z. Yu, L. Li, Q. Zhang, W. Hu, Q. Pei, Silver nanowire-polymer composite electrodes for efficient polymer solar cells, Adv. Mater. 23 (2011) 4453–4457.
[19] Y.-F. Liu, J. Feng, Y.-F. Zhang, H.-F. Cui, D. Yin, Y.-G. Bi, J.-F. Song, Q.-D. Chen, H.-B. Sun, Improved efficiency of indium-tin-oxide-free flexible organic light-emitting devices, Org. Electron. 15 (2014) 478–483.
[20] B.R. Lee, J.-W. Kim, D. Kang, D.W. Lee, S.-J. Ko, H.J. Lee, C.-L. Lee, J.Y. Kim, H.S. Shin, M.H. Song, Highly efficient polymer light-emitting diodes using graphene oxide as a hole transport layer, ACS Nano 6 (2012) 2984–2991.
[21] S.-S. Li, K.-H. Tu, C.-C. Lin, C.-W. Chen, M. Chhowalla, Solution-processable graphene oxide as an efficient hole transport layer in polymer solar cells, ACS Nano 4 (2010) 3169–3174.
[22] H. Chang, G. Wang, A. Yang, X. Tao, X. Liu, Y. Shen, Z. Zheng, A. Transparent, Flexible, low-temperature, and solution-processible graphene composite electrode, Adv. Funct. Mater. 20 (2010) 2893–2902.
[23] X. Wu, F. Li, W. Wu, T. Guo, Flexible organic light emitting diodes based on double-layered graphene/PEDOT:PSS conductive film formed by spray-coating, Vacuum 101 (2014) 53–56.
[24] X. Wu, J. Liu, D. Wu, Y. Zhao, X. Shi, J. Wang, S. Huang, G. He, Highly conductive and uniform graphene oxide modified PEDOT:PSS electrodes for ITO-Free organic light emitting diodes, J. Mater. Chem. C 2 (2014) 4044–4050.
[25] F. Kim, J. Luo, R. Cruz-Silva, L.J. Cote, K. Sohn, J. Huang, Self-propagating domino-like reactions in oxidized graphite, Adv. Funct. Mater. 20 (2010) 2867–2873.
[26] Y.-G. Bi, J. Feng, Y.-F. Li, Y.-L. Zhang, Y.-S. Liu, L. Chen, Y.-F. Liu, L. Guo, S. Wei, H.-B. Sun, Arbitrary shape designable microscale organic light-emitting devices by using femtosecond laser reduced graphene oxide as a patterned electrode, ACS Photonics 1 (2014) 690–695.
[27] J.C. Yu, J.I. Jang, B.R. Lee, G.-W. Lee, J.T. Han, M.H. Song, Highly efficient polymer-based optoelectronic devices using PEDOT:PSS and a GO composite layer as a hole transport layer, ACS Appl. Mater. Interfaces 6 (2014) 2067–2073.
[28] V.C. Tung, J. Kim, L.J. Cote, J. Huang, Sticky interconnect for solution-processed tandem solar cells, J. Am. Chem. Soc. 133 (2011) 9262–9265.
[29] Y.F. Liu, J. Feng, D. Yin, Y.G. Bi, J.F. Song, Q.D. Chen, H.B. Sun, Highly flexible and efficient top-emitting organic light-emitting devices with ultrasmooth Ag anode, Opt. Lett. 37 (2012) 1796–1798.
[30] Y.-F. Liu, J. Feng, H.-F. Cui, Y.-F. Zhang, D. Yin, Y.-G. Bi, J.-F. Song, Q.-D. Chen, H.-B. Sun, Fabrication and characterization of Ag film with sub-nanometer surface roughness as a flexible cathode for inverted top-emitting organic light-emitting devices, Nanoscale 5 (2013) 10811–10815.