Light outcoupling enhanced flexible organic light-emitting diodes

Qing-Dong Ou,1,2,3 Lu-Hai Xu,1,3 Wen-Yue Zhang,1 Yan-Qing Li,1 Yi-Bo Zhang,1 Xin-Dong Zhao,1 Jing-De Chen,1 and Jian-Xin Tang1,*

1Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou 215123, China
2Department of Materials Science and Engineering, Monash University, Clayton, Victoria 3800, Australia
3These authors contributed equally to this work
*jxtang@suda.edu.cn

Abstract: Flexible organic light-emitting diodes (OLEDs) are emerging as a leading technology for rollable and foldable display applications. For the development of high-performance flexible OLEDs on plastic substrate, we report a transparent nanocomposite electrode with superior mechanical, electrical, and optical properties, which is realized by integrating the nanoimprinted quasi-random photonic structures into the ultrathin metal/dielectric stack to collectively optimize the electrical conduction and light outcoupling capabilities. The resulting flexible OLEDs with green emission yield the enhanced device efficiency, reaching the maximum external quantum efficiency of 43.7% and luminous efficiency of 154.9 cd/A, respectively.

©2016 Optical Society of America

OCIS codes: (230.0250) Optoelectronics; (230.3670) Light-emitting diodes; (250.3680) Light-emitting polymers; (310.1210) Antireflection coatings; (310.7005) Transparent conductive coatings; (350.4238) Nanophotonics and photonic crystals.

References and links

1. H. Kang, S. Jung, S. Jeong, G. Kim, and K. Lee, “Polymer-metal hybrid transparent electrodes for flexible electronics,” Nat. Commun. 6, 6503 (2015).
2. A. Sandström, H. F. Dam, F. C. Krebs, and L. Edman, “Ambient fabrication of flexible and large-area organic light-emitting devices using slot-die coating,” Nat. Commun. 3, 1002 (2012).
3. N. Aizawa, Y. J. Pu, M. Watanabe, T. Chiba, K. Ideta, N. Toyota, M. Igarashi, Y. Suzuri, H. Sasabe, and J. Kido, “Solution-processed multilayer small-molecule light-emitting devices with high-efficiency white-light emission,” Nat. Commun. 5, 5756 (2014).
4. Q.-D. Ou, L. Zhou, Y.-Q. Li, S. Shen, J.-D. Chen, C. Li, Q.-K. Wang, S.-T. Lee, and J.-X. Tang, “Extremely efficient white organic light-emitting diodes for general lighting,” Adv. Funct. Mater. 24(46), 7249–7256 (2014).
5. Z. B. Wang, M. G. Helander, J. Qiu, D. P. Puzzo, M. T. Greiner, Z. M. Hudson, S. Wang, Z. W. Liu, and Z. H. Lu, “Unlocking the full potential of organic light-emitting diodes on flexible plastic,” Nat. Photonics 5(12), 753–757 (2011).
6. T.-H. Han, Y. Lee, M.-R. Choi, S.-H. Woo, S.-H. Bae, B. H. Hong, J.-H. Ahn, and T.-W. Lee, “Extremely efficient flexible organic light-emitting diodes with modified graphene anode,” Nat. Photonics 6(2), 105–110 (2012).
7. N. Li, S. Oida, G. S. Tulevski, S. J. Han, J. B. Hannon, D. K. Sadana, and T. C. Chen, “Efficient and bright organic light-emitting diodes on single-layer graphene electrodes,” Nat. Commun. 4, 2294 (2013).
8. K. Ellmer, “Past achievements and future challenges in the development of optically transparent electrodes,” Nat. Photonics 6(12), 809–817 (2012).
9. M. Cai, Z. Ye, T. Xiao, R. Liu, Y. Chen, R. W. Mayer, R. Biswas, K. M. Ho, R. Shinar, and J. Shinar, “Extremely efficient indium-tin-oxide-free green phosphorescent organic light-emitting diodes,” Adv. Mater. 24(31), 4337–4342 (2012).
10. H.-Z. Geng, K. K. Kim, K. P. So, Y. S. Lee, Y. Chang, and Y. H. Lee, “Effect of acid treatment on carbon nanotube-based flexible transparent conducting films,” J. Am. Chem. Soc. 129(25), 7758–7759 (2007).
11. D. S. Hecht, L. Hu, and G. Irwin, “Emerging transparent electrodes based on thin films of carbon nanotubes, graphene, and metallic nanostructures,” Adv. Mater. 23(13), 1482–1513 (2011).
12. Y. Xia, K. Sun, and J. Ouyang, “Solution-processed metallic conducting polymer films as transparent electrode of optoelectronic devices,” Adv. Mater. 24(18), 2436–2440 (2012).
13. W. Gaynor, S. Hofmann, M. G. Christoforo, C. Sachse, S. Mehr, A. Salleo, M. D. McGeehe, M. C. Gather, B. Lüssem, L. Müller-Meskamp, P. Peumans, and K. Leo, “Color in the corners: ITO-free white OLEDs with angular color stability,” Adv. Mater. 25(29), 4006–4013 (2013).

© 2016 Optical Society of America

Received 15 Jan 2016; revised 22 Feb 2016; accepted 25 Feb 2016; published 17 Mar 2016

© 2016 OSA
Flexible organic light-emitting diodes (OLEDs) have attracted considerable research interest as a leading technology for applications of rollable or foldable displays and wearable intelligent electronics due to their intriguing merits in mechanical flexibility, light weight, and color gamut, and the possibility of roll-to-roll processing [1–7]. For high-performance flexible OLEDs, one challenging issue is to replace the conventional indium-tin-oxide (ITO) electrode because of its brittle nature, material scarcity, and the high-temperature fabrication [6–9]. Besides the poor flexibility and high manufacturing cost, the use of ITO in OLEDs inevitably limits the outcoupling efficiency due to the severe waveguide trapping of internally emitted light in ITO/organic layers [6–8].

An amount of techniques have been reported for the design of alternative transparent and flexible electrodes, such as graphene [6,7], carbon nanotube [10,11], conductive polymers [12], metallic nanowires [13,14], metal mesh [15,16], metal/dielectric composite stacks [5,17], or some hybrid nanostructures [18,19]. Among these proposed materials and structures, the metal/dielectric composite stack that consists of an optical coupling layer (e.g., Ta2O5, TeO2, ZnO), a sandwiched semitransparent metal film (e.g., Au, Ag) and an electrical modulating layer (e.g., LiF, MoO3) [5,17,20,21], is one of the most promising electrode materials for flexible devices because of its excellent electrical conductivity, low optical loss, and superior mechanical flexibility. However, a trade-off is present for constructing such a composite stack between the optical transparency and metallic film formation. The layer
thickness of the sandwiched metal films in a metal/dielectric composite stack should be as thin as possible for maximum optical transmission, whereas it is rather difficult to form an ultrathin metal film with homogeneous morphology due to the dewetting problem. For example, the deposited Ag film (≤10 nm) tends to form discrete three-dimensional (3D) islands in the Volmer-Weber growth style with an isolated granular morphology, which adversely degrades the optical transmittance and electrical conduction due to particle plasmon absorption and film disconnection [22,23].

In this work, we present an efficient nanostructured composite electrode (denoted as NCE) on plastic substrate, which is composed of a nanostructured calcium:silver (Ca:Ag) alloy film sandwiched between two molybdenum trioxide (MoO₃) dielectric layers (that is, nanostructured MoO₃/Ca:Ag alloy/MoO₃). Compared to a planar MoO₃/Ca:Ag alloy/MoO₃ composite electrode (denoted as CE), the key feature of this NCE stack is that an ultrathin Ca:Ag alloy film with homogeneous morphology is formed to allow low electrical resistance, while the integration of nanoimprinted quasi-random photonic structures enables the outcoupling enhancement of the waveguided light with minimized optical loss. Flexible OLEDs using a NCE stack yield the enhanced device efficiency, which is over 2.7 times that in a standard ITO-substrate emitting architecture. The luminous efficiency (ηLE) and external quantum efficiency (ηEQE) for green emission reach the maximum values of 154.9 cd/A and 43.7%, respectively, which remain as high as 132.2 cd/A and 37.4%, at a high brightness of 10,000 cd/m².

2. Experimental details

For the formation of quasi-random photonic structures, a UV-resin layer (D10, PhiChem) was firstly drop-casted uniformly on polyethylene terephthalate (PET) substrate and then patterned through multiple mold duplication processes with perfluoropolyether (PFPE) mold-assisted soft nanoimprint lithography technique, which was described in details in our previous reports [4,15]. The imprinted PET substrates were transferred into a high vacuum chamber (~2 × 10⁻⁶ Torr), where both the CE and NCE stacks were fabricated by the successive thermal evaporation of MoO₃/Ca:Ag alloy/MoO₃ film onto the flat and nanostructured PET substrates in the same batch. For comparison, ITO-coated PET substrates with a sheet resistance of ~35 Ω/sq were cleaned using a routine process and then deposited with a 5 nm-thick MoO₃ layer prior to the device fabrication. The OLEDs were fabricated by subsequently depositing the organic emitter and a LiF (0.5 nm)/Al (100 nm) bilayer cathode onto the substrates by thermal evaporation with shadow mask in the same chamber without breaking the vacuum. The deposition rate and film thickness were monitored by a quartz crystal oscillator. The green organic emitter consisted of a 4,4'-bis(carbazol-9-yl)biphenyl (CBP) hole transport layer (30 nm), a bis(2-phenylpyridine)(acetylacetonate)iridium(III) [Ir(ppy)₂(acac)] doped CBP emitting layer (8 wt%, 20 nm), and a 2,2',2"-(1,3,5-benzenetriyl)tris(1-phenyl-1H-benzimidazole) (TPBi) electron transport layer (60 nm). The effective device area was 10 mm². Each series of flexible OLEDs on ITO, CE, and NCE were simultaneously fabricated for the deposition of organic emitter and metal cathode to ensure the consistent results.

Optical transmittance spectra were recorded by a UV–vis/near-IR spectrophotometer (Perkin Elmer Lambda 750) with an integrating sphere. Surface morphologies were characterized by atomic force microscopy (AFM) (Veeco MultiMode V) in tapping mode and scanning electron microscopy (SEM) (FEI, Quanta 200FEG). The current density-voltage-luminance (J-V-L) characteristics and electroluminescent (EL) spectra of OLEDs were measured simultaneously under air ambience using a programmable source meter (Keithley 2400) and a luminance meter/spectrometer (PhotoResearch PR655).

Optical simulations of in-plane waveguide modes and near-field intensity distributions in OLEDs were performed based on the rigorous electromagnetic theory through finite difference time domain (FDTD) approach (Lumerical FDTD Solutions 8.7.3). For simplification, hexagonally packed nanocones with sinusoidal cross section profile with a periodicity of ~250 nm were constructed instead of randomly distributed geometry in the
device modeling. The refractive indices of related materials were experimentally determined from the measurements with the alpha-SE™ Spectroscopic Ellipsometer (J.A. Woolam Co., Inc.). Particularly, the complex refractive index of the Ca:Ag alloy film fits $n = 0.235 + 2.815i$ at the wavelength of 550 nm, which was used for simulation.

### 3. Results and discussion

Figure 1(a) illustrates the OLED structure, which was fabricated on NCE-coated plastic substrate. Figure 1(b) displays the AFM image and surface profile of a nanoimprinted UV-resin layer on PET substrate, which shows the 3D tapered morphology with a sub-wavelength periodicity of ~250 nm and a fill factor of ~0.6. It has been demonstrated that such a quasi-random nanostructures exhibit the broadband and quasi-omnidirectional light extraction capability [24].

To alleviate the film homogeneity problem for CE and NCE stacks, a sophisticated strategy for constructing ultrathin and smooth metallic films was performed by using a nucleation-inducing seed layer and the metal co-deposition effect [1,22,23]. Here, an 8 nm-thick Ca:Ag alloy film in the weight ratio of 1:1 was fabricated by thermal co-evaporation onto an 1 nm-thick aluminum (Al) seed layer, which was further coated with an additional 1 nm-thick pure Ag layer to optimize the film homogeneity of this Ca:Ag alloy ultrathin layer [25]. As shown in Fig. 2 of the SEM images, the use of Ca:Ag alloy can minimize the isolated metallic grains which are usually observed in the growth of pure Ag film. Therefore, it is expected that the degradation in optical transmittance and electrical conductance caused by the layer disconnection can be suppressed in the ultrathin Ca:Ag film. In addition, the four-point-probe measurement determined that the sheet resistance of an 8 nm-thick Ca:Ag alloy was about $27 \, \Omega/sq$, which is even superior to that of the ITO-coated PET ($35 \, \Omega/sq$).

![Image](image.png)

Fig. 1. Device Structure and Morphology. (a) Schematic illustration of flexible OLED using a NCE anode on plastic substrate. (b) AFM image and surface profile of imprinted UV-resin layer with quasi-random nanostructures with a pseudo period of ~250 nm.

For both CE and NCE stacks, two MoO$_3$ dielectric layers were used to sandwich the Ca:Ag layer, which serve as a wetting layer and a hole injection layer, respectively. The layer thickness of both MoO$_3$ layers was optimized to synergistically enhance the optical properties. The thickness dependence of optical transmittance of a planar MoO$_3$/Ca:Ag (8 nm)/MoO$_3$ stack was simulated by FDTD method and shown in Fig. 3(a), where the optimum film thicknesses of the MoO$_3$ hole injection and wetting layers are 35 nm and 25 nm, respectively, for the green emission at a wavelength of 550 nm. The optical transmittance characteristics of PET substrates with various transparent electrodes were measured and displayed in Fig. 3(b). Note that all the transmittance spectra are not substrate corrected, and the use of a UV-resin layer has negligible influence on optical transmittance of the PET substrate. The transmittance of a planar CE is ~79.5% at 550 nm as shown in Fig. 3(c), which is in good agreement with the previous report [25]. It has been demonstrated that an ultrathin...
Ca:Ag alloy film can yield the unusually high transmittance as compared to a pure 8 nm-thick Ag film and even the successively deposited Ag/Ca bilayer [25]. Such a spectrally broad transmittance enhancement is related to the suppression of the strong particle plasmon absorption, which is induced by the formation of a favorable microstructure of the Ca:Ag alloy film based on an Al seed layer instead of the spontaneous formation of nuclei in the ultrathin pure Ag layers (Volmer-Weber growth mode) [26]. Compared to the ITO-coated PET substrate and a planar CE stack, the integration of quasi-random nanostructures in the NCE stack benefits the optical property with a comparatively uniform transmittance with an average value of ~86% in the entire visible wavelength range [27,28]. According to the optical simulation [28], the more efficient light transmission of a NCE stack is due to the change of the optical impedance from a planar structure to a nanostructured stack, leading to the reduced light loss. In addition to the high transmission characteristics, antireflective properties were also determined for the CE and NCE stacks in Fig. 3(d). Compared to the use of pure Ag films in the composite electrode, the planar CE and NCE stacks with a Ca:Ag alloy film show an average reflectance of ~15% and ~7% in the wavelength range from 400 to 750 nm, respectively. These reflectance levels for both CE and NCE stacks may guarantee the minimized microcavity effects [22].

Fig. 2. Film deposition and surface morphology. (a) Schematic of a Ca:Ag alloy deposited onto a MoO3 wetting layer cover with a metal seed layer, and the SEM image of 8 nm-thick Ca:Ag alloy film. (b) Schematic of pure Ag deposited onto a MoO3 wetting layer without the seed layer, and the SEM image of pure Ag film.

To test the charge injection and light extraction capabilities of the NCE stack, phosphorescent green OLEDs were fabricated with the identical organic emitter on various electrodes. The J-V characteristics in Fig. 4(a) show that the use of NCE and CE in flexible devices can remarkably reduce the driving voltage as compared to that on ITO. It indicates the lower electrode resistance of NCE and CE stacks and the reduced ohmic loss at the contact to the organic emitter. According to the in situ ultraviolet photoelectron spectroscopy measurement, the surface work function of the NCE stack was around 6.7 eV, which is effective at directly injecting holes into the CBP layer [5]. In addition, the luminance intensity
of flexible device on NCE is enhanced in comparison with its counterparts using ITO and CE [Fig. 4(a)]. However, the normalized EL spectra of three devices in Fig. 4(b) exhibit the identical spectral profiles, implying the minimized microcavity effect that is usually observed in OLEDs with metallic transparent electrodes [5]. Moreover, the angular emission spectra of flexible device on NCE is almost identical across the entire range of viewing angles. The suppression of optical microcavity effect when using NCE stack is due to the integration of quasi-random nanostructures, which destructively changes the resonance wavelength with irregular cavity lengths for light outcoupling.

The efficiency characteristics of these flexible devices are summarized in Figs. 4(c) and 4(d) and Table 1. The $\eta_{\text{EQE}}$ of flexible OLED on ITO is below 20%, while the device on CE shows a higher $\eta_{\text{EQE}}$ close to 25%, which can be attributed to the reduction of optical loss induced by ITO waveguide mode. Moreover, the use of a NCE stack leads to further increase in efficiency, where the maximum values of $\eta_{\text{EQE}}$ and $\eta_{\text{LE}}$ reach 43.74% and 154.9 cd/A, respectively. Taking into account the identical organic emitter for three flexible OLEDs, the further efficiency enhancement with the use of a NCE stack is ascribed to the substantial outcoupling enhancement of internally emitted photons due to the integration of quasi-random nanostructures. Furthermore, it is noted that the devices on CE or NCE are featured by small efficiency roll-off at high luminance (see the details in Table 1). For instance, the device on NCE shows a striking $\eta_{\text{LE}}$ value of 132.2 cd/A at a luminance of 10,000 cd/m². This is due to the attenuation of charge trapping effect at the anode/organic interface and the elimination of strong microcavity effect.
Fig. 4. Performance characteristics of flexible OLEDs with green emission. (a) Current density and luminance as a function of driving voltage. (b) Normalized EL spectra. Inset: photograph of light emission from flexible OLED on NCE anode. (c) External quantum efficiency and (d) current efficiency as a function of luminance for flexible OLEDs with different electrodes.

Table 1. Comparison of $\eta_{\text{EQE}}$ and $\eta_{\text{LE}}$ for flexible OLEDs with different electrodes at the maximum values and at the luminance of 1,000 cd/m$^2$ and 10,000 cd/m$^2$. The values in parentheses represent the decreasing ratios when the luminance is increased from 1,000 cd/m$^2$ to 10,000 cd/m$^2$.

| Electrode | Maximum | 1,000 cd/m$^2$ | 10,000 cd/m$^2$ |
|-----------|---------|----------------|-----------------|
|           | $\eta_{\text{LE}}$ (cd/A) | $\eta_{\text{EQE}}$ (%) | $\eta_{\text{LE}}$ (cd/A) | $\eta_{\text{EQE}}$ (%) | $\eta_{\text{LE}}$ (cd/A) | $\eta_{\text{EQE}}$ (%) |
| ITO       | 67.9    | 18.1           | 58.6            | 15.7            | 45.4            | 12.1            |
|           | (22.5%) | (23.1%)        | (15.7%)         | (15.7%)         | (22.5%)         | (23.1%)         |
| CE        | 88.3    | 24.0           | 85.1            | 23.2            | 73.6            | 20.0            |
|           | (13.8%) | (13.8%)        | (13.5%)         | (13.5%)         | (13.5%)         | (13.8%)         |
| NCE       | 154.9   | 43.7           | 150.9           | 42.5            | 132.2           | 37.4            |
|           | (12.4%) | (12.1%)        | (12.4%)         | (12.4%)         | (12.4%)         | (12.1%)         |

4. Conclusion

In summary, we provide a new solution as flexible and transparent nanocomposite electrode on plastic for OLED applications with state-of-the-art performance. This nanocomposite electrode is obtained by integrating the nanoimprinted quasi-random photonic structures into the ultrathin metal/dielectric stack to collectively optimize the electrical conduction and light outcoupling capabilities. It allows the realization of high-efficiency ITO-free flexible devices. The resulting flexible OLEDs with green emission yield the enhanced device efficiency, leading to the maximum external quantum efficiency of 43.7% and luminous efficiency of...
154.9 cd/A, respectively. We anticipate that the nanocomposite electrode demonstrated here would be an effective and promising electrode for the fabrication of large-area flexible optoelectronic systems.

Acknowledgments

The authors acknowledge financial support from the National Basic Research Program of China (Grant No. 2014CB932600), the National Natural Science Foundation of China (Grant Nos. 91433116, 61520106012, 61522505, 11474214), Jiangsu Science and Technology Department (Grant No. BK20140053), Bureau of Science and Technology of Suzhou Municipality (Grant No. SYG201525, ZXG201422), Collaborative Innovation Center of Suzhou Nano Science and Technology, and the project of the Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institutions.