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Multilayered graphene anode for blue phosphorescent organic light emitting diodes

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In this work, we report on blue organic light emitting devices (OLEDs), which have multilayered graphene as its anode. Our graphene films have been grown catalytically and transferred to the support. The fabricated blue OLEDs with graphene anode showed outstanding external quantum efficiency of 15.6% and power efficiency of 24.1 lm/W at 1000 cd/m². Weak oxygen plasma treatments on graphene film surfaces improved the injection property between the anode and hole injection layer. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3697639>]

So far, in conventional organic light emitting devices (OLEDs), due to its optical and electrical characteristics and scalability, indium tin oxide (ITO) has dominated the anode material. However, highly brittle ITO is not an appropriate candidate for anode in flexible OLEDs.^{1–4} As a substitute for ITO, graphene offers three important merits, which are indispensable in realizing flexible OLEDs: high electrical conductivity, optical transparency and mechanical compliance. Recent progress in graphene has shown the possibility of producing p-doped large area graphene sheet of 30-in with sheet resistance of $\sim 30 \Omega/\square$ and transmittance of $\sim 90\%$ at $\lambda = 550 \text{ nm}$.⁵ Such values are comparable to those of ITO ($10\text{--}30 \Omega/\square$, $\sim 90\%$ at $\lambda = 550 \text{ nm}$).^{6–8} Also, the work function of graphene is $\sim 4.6 \text{ eV}$, which closely matches the value of ITO ($\sim 4.8 \text{ eV}$). Such features suggest graphene suitability for large area flexible OLEDs.^{6,7} Also, a few atoms' thick graphene is mechanically compliant enough to be employed as an electrode for flexible OLED applications.^{9,10} However, only few research groups have reported graphene OLEDs, of which power efficiencies ($< 1 \text{ lm/W}$) are considerably low and emitting areas are small.^{2,6} In this paper, we report the OLEDs that have graphene anodes. Our graphene is multilayered, which has been grown catalytically and transferred to the OLED substrate. We demonstrate that outstanding OLEDs characteristics, which are comparable to those of ITO anode OLEDs, can be obtained using graphene anodes.

Multilayered graphene films were synthesized by using a thermal chemical vapor deposition method. For the uniform growth of graphene films, we used a catalytic Ni film of 300 nm thickness, sputtered on SiO₂/Si substrates. Before forming graphene thin films on the Ni/SiO₂/Si, the substrates were pretreated in a gas mixture atmosphere of H₂ (50 sccm) and Ar (200 sccm) for 6 min at 1000 °C to remove the native oxides from the Ni surface. After being subjected to reaction gases of CH₄:H₂:Ar (50:50:200 sccm) for 5 s, the sample was

rapidly cooled to room temperature at a rate of $\sim 10^\circ \text{C s}^{-1}$ using flowing Ar. The catalytic Ni films were etched-off in an aqueous FeCl₃ (1 M) solution to isolate graphene films from the support. Graphene films were transferred to the substrates for OLED fabrications.⁵ In this work, we have used ITO (70 nm)/glass substrates. The ITO film was patterned to apply graphene film, as shown in Fig. 1(a). Using an infrared laser (wavelength: $\lambda = 1064 \text{ nm}$) patterning facility, the transferred graphene films were directly patterned to define pixels, separate anode and cathode. In this way, our graphene anode equipped OLED substrates were prepared. The active light emitting area was $2 \times 2 \text{ mm}^2$. All organic layers were deposited in a high vacuum chamber below $6.67 \times 10^{-5} \text{ Pa}$ and thin films of LiF and Al were deposited as a cathode electrode as shown in Fig. 1(a). The device structure of the sky-blue phosphorescent OLED (PhOLED) consists of graphene (2–3 nm)/1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC) (30 nm)/1,4,5,8,9,11-hexaazatriphenylene hexacarbonitrile (HAT-CN) (10 nm)/TAPC(30 nm)/HAT-CN(10 nm)/TAPC(30 nm)/4,4',4''-tri(*N*-carbazolyl) triphenylamine:iridium(III)bis[(4,6-difluorophenyl)-pyridinato-*N,C2'*]picolate (TCTA:FIrpic) (5 nm)/2,6-bis[3'-(*N*-carbazole)phenyl]pyridine:iridium(III) bis[(4,6-difluorophenyl)-pyridinato-*N,C2'*]picolate (DCzPPy:FIrpic) (5 nm)/1,3-bis(3,5-dipyrid-3-yl-phenyl)benzene (BmPyPB) (40 nm)/lithium fluoride (LiF) (1 nm)/aluminum (Al) (100 nm), as shown in Fig. 1(b). The total thickness of the hole-transport layer was determined via optical simulations to maximize the efficiency. The optical simulations were performed using commercially available OLED simulation software SimOLED, made by Sim4Tec. The electrical effect on OLED is not considered herein, but only the optical effects. The device structure used in this simulation is same as the device structure used in experiments. The electroluminescence (EL) spectra were measured using a spectroradiometer (Minolta CS-2000). The current density–voltage (*J*–*V*) and luminescence–voltage (*L*–*V*) characteristics were measured with a current/voltage source/measure unit (Keithley 238) and the aforementioned spectroradiometer.

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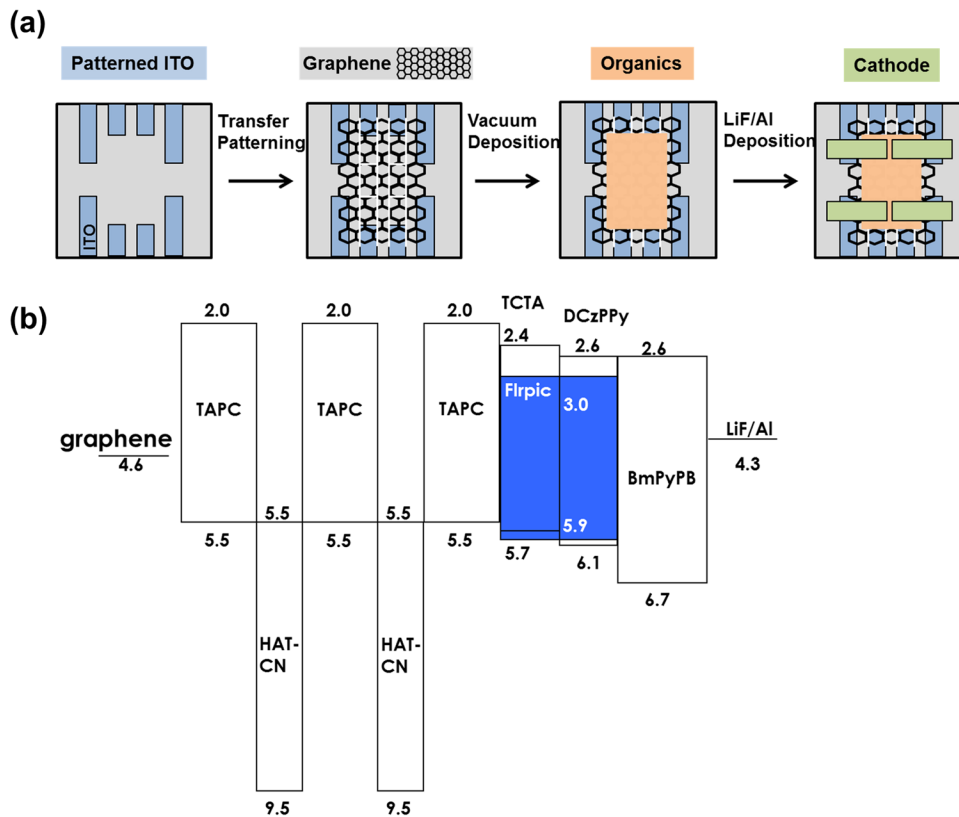


FIG. 1. (a) The preparation of substrates and graphene anodes. (b) The energy level diagram of sky-blue phosphorescent OLEDs.

Prior to the fabrication of OLED with graphene anode, we examined basic properties of graphene films. The transmission electron microscopy (TEM) image shows that our graphene film consists of 5–8 sheets with total thickness of 2–3 nm (Fig. 2(a)). In Fig. 2(b), atomic force microscopy (AFM) images on the pristine graphene and O_2 plasma treated graphene surfaces are shown. The root-mean-squares roughness and sheet resistances of pristine graphene are 1.6 nm and $289 \Omega/\square$, respectively, and those of O_2 plasma

treated graphene are 2.8 nm, and $552 \Omega/\square$. The sheet resistance of pristine graphene used in this experiment is approximately 10 times larger than that of ITO, even though its roughness is acceptable to be applied as an anode. We have concluded that O_2 plasma treatment damaged and peeled off graphene layer from the surface, which led to the increased roughness as well as increased sheet resistance. The pristine graphene and O_2 plasma treated graphene will be applied in OLED as anodes and O_2 plasma treatment effect on device

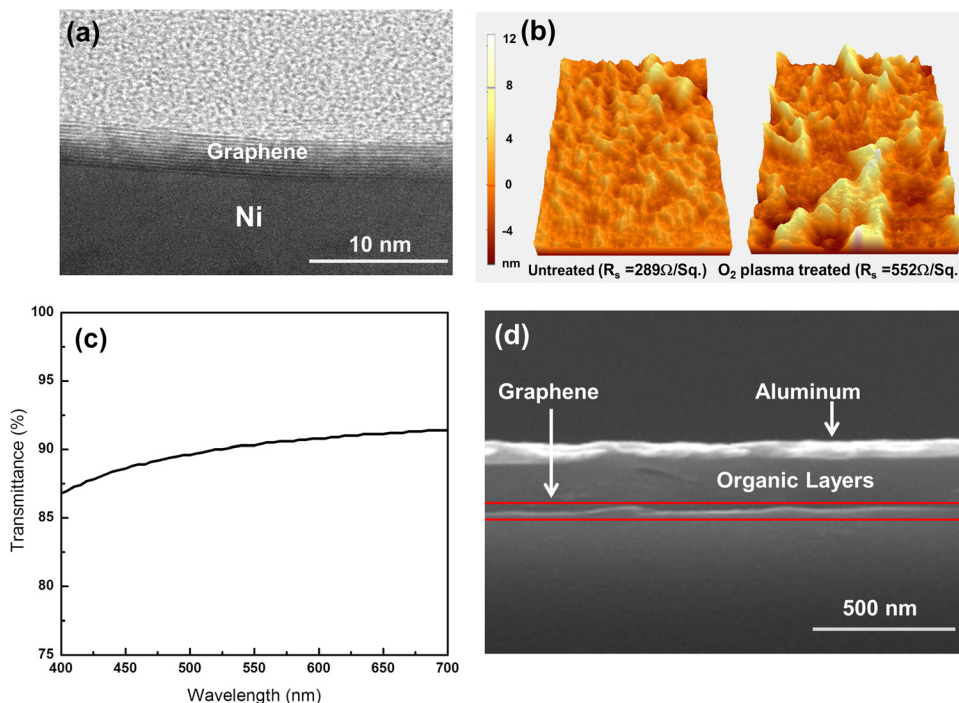


FIG. 2. (a) The high resolution TEM image of as-grown graphene films on Ni/SiO₂/Si substrate. (b) The AFM images of pristine graphene film and O_2 plasma treated graphene film on SiO₂/Si substrate. (c) Transmittance versus wavelength of graphene layers. (d) The cross-sectional SEM image of graphene anode on OLED.

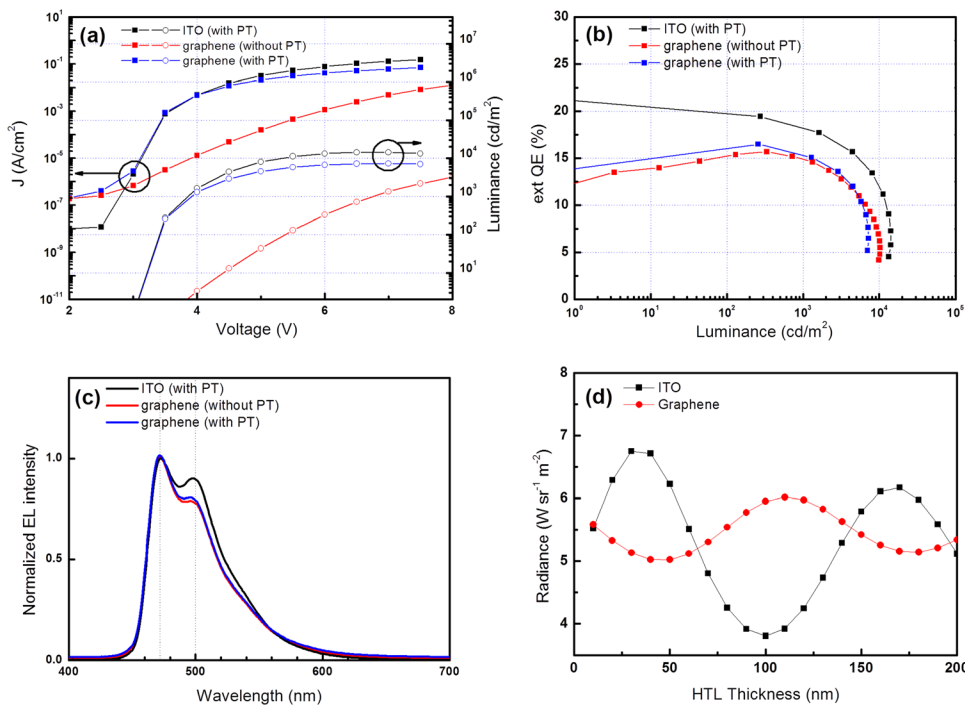


FIG. 3. (a) The JVL characteristics without and with O₂ plasma treated sky-blue phosphorescent OLEDs. (b) External quantum efficiency. (c) Electroluminescent spectra of sky-blue phosphorescent OLEDs (PT refers to plasma treatment). (d) The optical simulation results on radiance and HTL thicknesses on ITO and graphene anodes.

performance will be discussed later. The optical transmittance of the graphene as shown in Fig. 2(c) was approximately 90% at 550 nm in ambient condition, which is almost comparable to the transmittance of ITO. The cross-sectional scanning electron microscopy image in Fig. 2(d) shows the uniformity of the transferred graphene films on the substrate. Various physical and electrical properties meet the requirements for anode in OLED applications.

The current density-voltage-luminescence (JVL) characteristics of sky-blue PhOLED are shown in Fig. 3(a). For reference, the JVL characteristics of OLEDs with ITO anodes are also plotted. As a mean to improve the hole-injection property, we have treated the graphene surface with mild O₂ plasma. Along with O₃ treatment or CF_x plasma, O₂ plasma has been widely used to improve the ITO/hole-injection layer (HIL) interface and enhance the hole-injection property.¹¹ The surface defects form localized energy levels and trap electrons, resulting in low charge transport.¹² However, strong O₂ plasma treatment can be used to remove graphene layers completely.⁶ Bearing this fact in mind, our samples were treated with O₂ plasma in mild condition, i.e., 1 min with 3 sccm of O₂ flow rate, to prevent total removal of graphene layers. This condition is fairly low compared to reported oxygen dry etching condition of graphene, i.e., 5 min with 20 sccm O₂ flow, 300 W RF power, in other report.¹³ From the lower voltage range (2–4 V) in JVL curves, significantly lower hole-injection is taking place between the graphene anode and the hole-injection layer compared to the ITO anode case. O₂ plasma treatments on the graphene surface significantly improve the hole-injection property close to the level of hole-injection in ITO anode, as shown in Fig. 3(a). Similar to the ITO's case, this phenomenon can be attributed to the modified work function through O₂ plasma. Since the work-function of graphene is lower than that of ITO, i.e., 4.6 eV and 4.8 eV relatively, it is possible that the graphene's work-function can be dragged near

the ITO's work-function by the mechanism above and thus approach equivalent hole-injection to ITO.¹⁴

Close observations on the higher voltage (4–8 V) regions of OLEDs with graphene anodes in Fig. 3(a) reveal that, in addition to improved interface characteristics between graphene and HIL, the plasma treatment brings forth decrease of current density, which might be attributed to increase in the sheet resistance of graphene anodes. Recalling our plasma conditions, AFM and sheet resistance data, it is clear that O₂ plasma treatment has peeled off graphene sheets from the graphene film, which results in increased sheet resistance.^{6,15,16} However, although the JVL curve is easily saturated due to the increased sheet resistance, adequate surface treatment on graphene surface comes up as a requisite for attainment of high luminance in graphene anode OLEDs. In order to fully utilize graphene as an OLED anode material, in depth study on the graphene/HIL interface must be pursued. Also, the chemical changes of graphene under the influence of O₂ plasma must be investigated.

The external quantum efficiency (EQE) of sky-blue Phosphorescent OLEDs using graphene and OLED is shown in Fig. 3(b). At 1000 cd/m², the EQEs of O₂ plasma treated and untreated graphene OLEDs differ marginally with values of 15.1% and 15.6%, respectively. The power efficiency of O₂ plasma treated graphene OLEDs is 24.1 lm/W. The untreated graphene OLED is 14.5 lm/W. Based on the interpretation and experimental results above, we attribute the huge improvement in power efficiency to O₂ plasma treatment, which has effects of enhancing the hole injection property and lowering the operating voltage. In high luminance region, the substantial roll-off effect was observed, which could be attributed to exciton-exciton interaction, exciton-charge carrier interaction and exciton dissociation. Especially, the exciton quenching in high voltage region tends to be dominated by electric-field assisted dissociation, rather than exciton charge carrier interaction.^{17,18} Fig. 3(c) shows

TABLE I. The key parameters of sky-blue Phosphorescent OLEDs with or without O₂ plasma treatment.

At 1000 cd/m ²	V (V)	J (mA/cm ²)	EQE (%)	P.E. (lm/W)	CIE
	Blue (ITO w/o O ₂ plasma)	4.2	2.8	16.6	28.8
Blue (Graphene w/o O ₂ plasma)	6.8	3.5	15.1	14.5	(0.17, 0.32)
Blue (ITO w/O ₂ plasma)	3.8	2.7	18.5	28.5	(0.15, 0.37)
Blue (Graphene w/O ₂ plasma)	3.9	4.0	15.6	24.1	(0.15, 0.34)

the spectra of our OLEDs, which all have their main peaks around 470 nm. The results show that graphene films are not causing any significant alteration in the spectrum distribution. In graphene anode cases, the spectrum is slightly skewed toward the 1st peak, indicating the presence of different internal optical effects in OLEDs with graphene and ITO anodes.

Fig. 3(d) shows the simulation results on the radiance dependency on the hole-transporting layer (HTL) thickness. In both graphene and ITO anodes, the radiance shows periodicity, strongly indicating the presence of interference effects. Graphene anode equipped OLED showed maximum radiance at HTL thickness of 110 nm. The phase shift is thought to have its origin in the dissimilar optical path.

Important OLED parameters are summarized in Table I. The EQEs and power efficiencies of graphene equipped OLEDs reached 90% of those of OLEDs with ITO anodes. Substituting graphene as an OLED anode in ITO optimized OLEDs will alter the anode/HIL injection property in a negative way. Our works show that the graphene/HIL interface can be improved by an appropriate surface treatment on graphene. However, the sheet resistance of graphene is still almost 10 times larger than that of ITO. In large area application, the high sheet resistance will cause emission non-uniformity across the panel. The sheet resistance problem may be resolved by doping the original graphene film to have high conductivity or by supplying auxiliary metal electrodes to compensate the current-voltage drop.

In conclusion, we have fabricated blue OLEDs with multilayered graphene films as the anode. We have obtained 15.6% of external quantum efficiencies in blue phosphorescent OLEDs, which is the highest value of all among OLEDs with graphene anodes. It reached almost 90% of the efficiencies of ITO anode, which is a hopeful result for realizing flexible OLEDs with high efficiency. Weak O₂ plasma treatment brought forth significantly enhanced injection property

and lowered operating voltage, which led to almost doubled power efficiency. Further research is needed to analyze the properties of plasma treated graphene and also to fabricate large area OLEDs with graphene anode.¹⁹ So far, the properties of graphene sheets are very dependent on the fabrication methods. To fully implement graphene as OLED anode materials, there is a strong need to establish a standardized processing scheme to ensure the reliability in the electrical properties of graphene. Having resolved such obstacles, we are optimistic to see graphene films as a flexible and transparent anode in flexible OLEDs.

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- ¹J. M. Englert, C. Dotzer, G. Yang, M. Schmid, C. Papp, J. M. Gottfried, H. P. Steinruck, E. Spiecker, F. Hauke, and A. Hirsch, *Nature Chem.* **3**(4), 279 (2011).
- ²G. Eda, G. Fanchini, and M. Chhowalla, *Nature Nanotechnol.* **3**(5), 270 (2008).
- ³J. Lee, J.-I. Lee, J.-W. Lee, J.-Y. Lee, D.-M. Kang, W. Yuan, S.-K. Kwon, and H. Y. Chu, *J. Inform. Display* **10**(2), 92 (2009).
- ⁴J. Lee, J.-I. Lee, J. W. Lee, and H. Y. Chu, *ETRI J.* **33**(1), 32 (2011).
- ⁵S. Bae, H. Kim, Y. Lee, X. Xu, J. S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, and Y. I. Song, *Nature Nanotechnol.* **5**(8), 574 (2010).
- ⁶D. C. Kim, D. Y. Jeon, H. J. Chung, Y. S. Woo, J. K. Shin, and S. Seo, *Nanotechnology* **20**, 375703 (2009).
- ⁷H. Chang, G. Wang, A. Yang, X. Tao, X. Liu, Y. Shen, and Z. Zheng, *Adv. Funct. Mater.* **20**(17), 2893 (2010).
- ⁸K. K. Kim, A. Reina, Y. Shi, H. Park, L. J. Li, Y. H. Lee, and J. Kong, *Nanotechnology* **21**, 285205 (2010).
- ⁹D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. Dommett, G. Evmenenko, S. B. T. Nguyen, and R. S. Ruoff, *Nature (London)* **448**(7152), 457 (2007).
- ¹⁰Y. Xu, H. Bai, G. Lu, C. Li, and G. Shi, *J. Am. Chem. Soc.* **130**(18), 5856 (2008).
- ¹¹I. Chan, *Thin Solid Films* **444**(1–2), 254 (2003).
- ¹²H. Y. Yu, X. D. Feng, D. Grozea, Z. H. Lu, R. N. S. Sodhi, A. M. Hor, and H. Aziz, *Appl. Phys. Lett.* **78**(17), 2595 (2001).
- ¹³S. Pang, H. N. Tsao, X. Feng, and K. Mullen, *Adv. Mater.* **21**(34), 3488 (2009).
- ¹⁴J. T. Robinson, F. K. Perkins, E. S. Snow, Z. Wei, and P. E. Sheehan, *Nano Lett.* **8**(10), 3137 (2008).
- ¹⁵T. O. Wehling, K. S. Novoselov, S. V. Morozov, E. E. Vdovin, M. I. Katsnelson, A. K. Geim, and A. I. Lichtenstein, *Nano Lett.* **8**(1), 173 (2008).
- ¹⁶A. Dimiev, D. V. Kosynkin, A. Sinitiskii, A. Slesarev, Z. Sun, and J. M. Tour, *Science* **331**(6021), 1168 (2011).
- ¹⁷J. Kalinowski, W. Stampor, J. Mezyk, M. Cocchi, D. Virgili, V. Fattori, and P. Di Marco, *Phys. Rev. B* **66**(23), 235321 (2002).
- ¹⁸J. Kalinowski, W. Stampor, J. Szymtkowski, D. Virgili, M. Cocchi, V. Fattori, and C. Sabatini, *Phys. Rev. B* **74**(8), 085316 (2006).
- ¹⁹L. J. Cote, F. Kim, and J. Huang, *J. Am. Chem. Soc.* **131**(3), 1043 (2009).