

# Characterizations of Carbide Buffer Structure at Cathode for Efficient O/PLEDs

**A** novel approach by spin-casting or thermal evaporation in vacuum of a salt-free, neutral, insulated, organic-oxide ultra-thin film as a buffer layer with an aluminum (Al) cathode was reported for fabricating high-performance organic and polymer light-emitting diodes. Introducing an organic-oxide cathode buffer layer suppresses the oxidation and the diffusion of the Al atoms into the functional polymer layer. The formation of a carbide-like (negative carbon) thin layer, which accompanies interfacial interactions as characterized by X-ray photoelectron spectroscopy, is critical to the injection of electrons through the Al cathode. The electroluminescence efficiency for the device made of organic oxide/Al cathode is of two orders of magnitude higher (14.53 cd/A) than that of Al-cathode device (0.16 cd/A)

Our recent works have demonstrated a marked improvement in the electroluminescence (EL) efficiency of "high-yellow" phenyl-substituted poly (para-phenylene vinylene) copolymer (HY-PPV)-based polymer light-emitting diodes (PLEDs) and tris-(8-hydroxyquinoline) aluminum-based organic light-emitting diodes (OLEDs) using the organic oxide/Al composite cathode.<sup>[1-5]</sup> Salt ions need not to be added to the cathode buffer layer. Introducing a thin layer of ethylene-oxide derivative into the cathode interface of O/PLEDs facilitates the injection of electrons through the Al cathode and inhibits the metal-induced quenching sites of luminescence in the light-emissive layer near the recombination zone. Additionally, the organic oxide film somewhat blocks the excitons from the metal cathode, increasing the probability of radiative recombination. In this work, the interfacial properties at the polymer/metal junction in PLEDs with and without the deposition of an ultra thin organic-oxide interlayer are studied by X-ray photoelectron spectroscopy (XPS). The vacuum thermal deposition of Al is suggested to oxidize the surface of the conjugated polymer, where introducing an ultra-thin (2~5 nm) organic-oxide buffer layer at the polymer/metal junction suppresses the oxidation of the HY-PPV. The formation of a carbide-like layer at the junction interface, which is characterized by the XPS, accompanies the interfacial reaction and is important in facilitating the injection of electrons through the Al electrode. The EL efficiency of PLED made of HY-PPV as the light-emissive layer with Al as the cathode is 0.16 cd/A, but an organic oxide/Al composite cathode increases this value by approximately two orders of magnitude to 14.53 cd/A. The improved device performance follows essentially the specific interaction of Al with ethylene-oxide groups,  $(-\text{CH}_2\text{CH}_2\text{O}-)_n$ . When silver (Ag) is used instead of Al with the organic-oxide layer as the electrode, no significant interaction occurs in the polymer/metal junction and no improvement in the device performance is observed.

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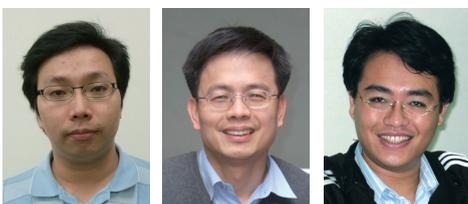
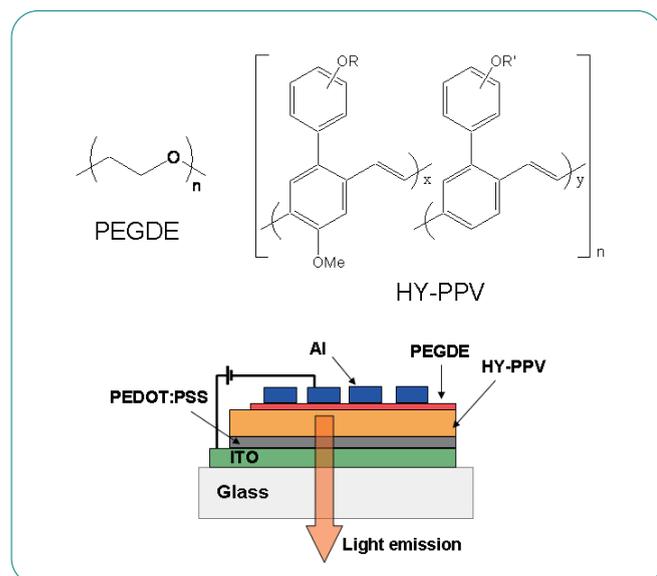
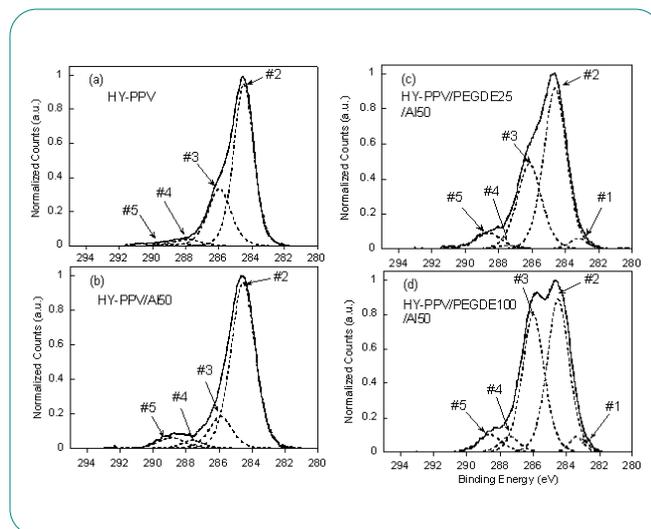


Figure 1 presents the configuration of the PLED applying the organic oxide/Al cathode structure. The device configuration herein comprises indium-tin-oxide (ITO)/glass substrate as the anode, poly(3,4-ethylenedioxythiophene): polystyrenesulfonate (PEDOT:PSS) as the hole transport layer, a "high-yellow" phenyl-substituted poly(para-phenylene vinylene) copolymer (HY-PPV) film as the light-emissive layer, a 2.5 nm thickness of poly(ethylene glycol) dimethyl ether (PEGDE) film as the interface buffer layer and the Al metal cathode electrode. The organic-oxide film was prepared by thermally evaporating a PEGDE layer onto the surface of the HY-PPV film inside a vacuum chamber ( $10^{-6}$  torr). The Al metal electrode was then evaporated on the substrates without breaking the vacuum. This process enables the thickness and the functional groups of the cathode buffer layer to be carefully controlled and also avoids the concerns of solvent compatibilities with organic layers while constructing the multi-layer structure of O/PLEDs.

Figures 2(a)-(d) present deconvolutions of the C 1s core level signals based on the minimum Gaussian peaks to yield the best fit after the background subtraction. In Fig. 2(a), peaks #2 (284.5 eV) and #3 (286.0 eV) of the



**Fig. 1:** The chemical structure of PEGDE and HY-PPV, and the configuration of PLED presented in this study.



**Fig. 2:** The deconvolutions of the normalized and corrected C 1s core level signals from (a) HY-PPV, (b) ITO/PEDOT:PSS/HY-PPV/Al(50Å) (HY-PPV/Al50 sample), (c) ITO/PEDOT:PSS/HY-PPV/PEGDE(25Å)/Al(50Å) (HY-PPV/PEGDE25/Al50 sample), and (d) ITO/PEDOT:PSS/HY-PPV/PEGDE(100Å)/Al(50Å) (HY-PPV

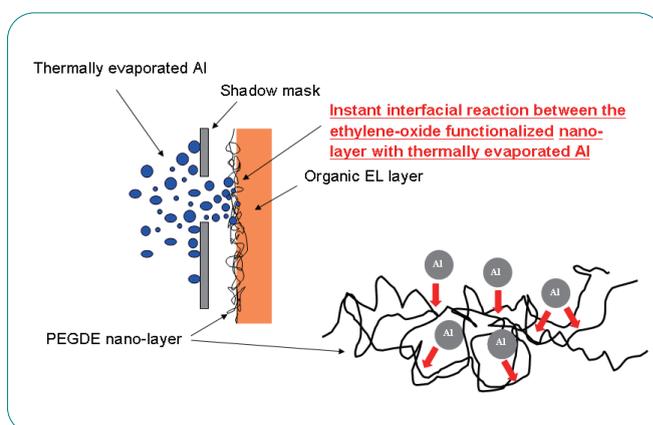
pristine HY-PPV are associated with hydrocarbon atoms (C-C and C-H) and carbon atoms attached to the oxygen (C-O) of HY-PPV molecules. The #4 (287.9 eV) peak is tentatively attributed to C=O bonds and the #5 (288.5 eV) peak is assigned to the carbon atoms in a highly oxidative environment, such as those in carboxylate ester groups. The intensity of peaks #4 and #5 in Fig. 2(a) is low, suggesting some unintentional oxidation or contamination of the polymer surface. In Figs. 2(c) and (d), the #1 (283.1 eV) peak is observed for the HY-PPV films on which had been deposited PEGDE and Al. The binding energies of carbon atoms in this range typically correspond to the carbide-like bonds. The origin or formation of the carbide-like carbons is probably correlated with the interaction between the PEGDE buffer film and Al, as will be discussed below.

In Fig. 2(b), the evaporation of a thin Al layer on an HY-PPV surface changes the relative ratio of the intensities of the deconvoluted peaks and increases the intensity of the high-energy tail in the C 1s core level spectrum above that in Fig. 2(a). The intensity of the #3 peak in Fig. 2(b)

is approximately halve, which halving accompanied by a relative increase in the #2 peak (C-C and C-H bond). This result supports the assertion that some C-O bonds at the HY-PPV surface break following the deposition of the Al layer. Furthermore, the marked increase in the intensity of the #5 peak above that in Figs. 2(b) to 2(a), associated with electron-deficient carbons, indicates the oxidation of the conjugated polymer. Very likely, many  $\text{benzene-C-O-C}^{\text{alkyl}}$  groups are transformed to the ester moieties by the addition of the second (carbonyl) oxygen to the  $\text{C}^{\text{alkyl}}$ -atom that is directly attached to the oxo-bridge in the side chain of HY-PPV. As a result, the high electron affinity of oxygen atoms causes a large chemical shift of  $\sim 4.0$  eV in the C 1s core level spectrum, which is reasonably consistent with the literature. The carbonyl-containing moieties and/or various oxidizing defects in poly(phenylene vinylene) (PPV)-based polymers are known to be the quenching sites for electroluminescence. The oxidized interface is also expected to raise the series resistance of the devices, causing the low EL efficiency of PLEDs.

When a thin layer of Al is deposited on the surface of HY-PPV covered with an ultrathin 25Å or 100Å PEGDE layer for XPS measurement, the  $\sim 50$ Å Al metal layer interferes with the penetration of the incident X-rays. The excited photoelectrons that are carried with the C 1s core level signals mainly escape from the PEGDE-rich region located directly beneath the Al layer. The PEGDE film has a higher C-O bond ratio than the HY-PPV film. As a result, in Fig. 2(c), the relative intensity of the #3 peak is higher than that of Fig. 2(a), partially because of the change in the XPS probing depth. The intensity of the #3 peak in Fig. 2(d) is even larger than that in Fig. 2(c) because of the better coverage of the thicker (100Å) PEGDE layer on the HY-PPV surface, as also suggested by a decline in the full-width-half-maximum (FWHM) of the #3 peak in Fig. 2(d). The #5 peak regarding to highly oxidized ester-like carbon species presented in Fig. 2(b) is still observed in Fig. 2(c) and 2(d), suggesting oxidation at the surface of the PEGDE-rich region induced by the deposited Al layer. Noticeably, the #1 peak at 283.1 eV is observed in both Figs. 2(c) and 2(d), revealing that the formation of a carbide-like thin layer at

the interface is accompanied by an interaction between PEGDE and Al. The reaction of the PEGDE layer with the thermally evaporated Al probably suppresses the diffusion of Al into the HY-PPV layer, potentially inhibiting further oxidation or generation of metal-induced EL quenching sites in the HY-PPV layer near the recombination zone. Figure 3 schematically presents the diffusion of Al atoms into the HY-PPV layer during vacuum thermal deposition, in which the inhibition of diffusion of Al atoms by the PEGDE buffer at the polymer/meal junction.



**Fig. 3:** The reaction of PEGDE layer with thermally evaporated Al suppresses the diffusion of Al into the light-emissive polymer layer, potentially inhibiting oxidation and generation of metal-induced EL quenching sites near the recombination zone. The instant interfacial reaction is proposed.

The performance of HY-PPV-based PLED is optimized at a PEGDE buffer layer thickness of 45Å with an Al cathode (HY-PPV/PEGDE45/Al800 device). The EL intensity of the HY-PPV/PEGDE45/Al800 device exceeds 85,000 cd/m<sup>2</sup> when biased at  $\sim 10.0$  V. The maximum luminous efficiency is approximately 14.53 cd/A at 6.80V, 7794.02 cd/m<sup>2</sup>. However, the EL intensity of the HY-PPV/Al800 device biased at  $\sim 10.0$  V is only 641.80 cd/m<sup>2</sup> and the maximum luminous efficiency is  $\sim 0.16$  cd/A at 8.61V, 288.44 cd/m<sup>2</sup>. Moreover, the light turn-on voltage of the HY-PPV/PEGDE45/Al800 device was reduced to  $\sim 2.50$  V from the corresponding value of the HY-PPV/Al800 device, which was about 3.50 V. This result also infers that

the voltage for the effective injection of minority carriers was brought forward to the lower electrical bias, in which the shift results from the interfacial dipoles or the decline in the metal work function when the PEGDE buffer layer is introduced at the HY-PPV/Al junction.

In conclusions, this study demonstrates the oxidation of both the surface of the conjugated polymer and the Al metallic layer upon the thermal evaporation of Al cathode occurs in a vacuum ( $10^{-6}$  torr). The oxidation substantially worsens the performance of PLEDs, but can be suppressed by applying an ultra-thin PEGDE buffer layer at the HY-PPV/Al interface. The polymer/metal junctions of HY-PPV-based PLEDs with and without introducing the PEGDE buffer layer are investigated by the high-resolution XPS. The use of the PEGDE/Al cathode improves the EL intensity and luminous efficiency of HY-PPV-based PLED by approximately two orders of magnitude over those when Al is used as the device cathode. The balanced charge injection and probably the high radiative recombination efficiency in the active layer of HY-PPV/PEGDE45/Al800 device contribute to the enhanced EL efficiency. This work discussed the origins of the functionalized organic-oxide buffer layer in the fabrication of high-performance PLEDs: the steps for preparing the salt-free, neutral interfacial layer can be easily integrated into the manufacturing procedure. ◆

### Experimental Station

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### Publications

1. T. F. Guo, F. S. Yang, Z. J. Tsai, T. C. Wen, S. N. Hsieh, and Y. S. Fu, *Appl. Phys. Lett.* **87**, 013504 (2005).
2. T. F. Guo, F. S. Yang, Z. J. Tsai, T. C. Wen, S. N. Hsieh, Y. S. Fu, and C. T. Chung, *Appl. Phys. Lett.* **88**, 113501 (2006).
3. T. F. Guo, F. S. Yang, Z. J. Tsai, G. W. Feng, T. C. Wen, S. N. Hsieh, C. T. Chung, and C. I. Wu, *Appl. Phys. Lett.* **89**, 051103 (2006).
4. T. F. Guo, F. S. Yang, Z. J. Tsai, T. C. Wen, C. I. Wu, and C. T. Chung, *Appl. Phys. Lett.* **89**, 053507 (2006).
5. T. H. Lee, J. C. A. Huang, G. L. Pakhomov, T. F. Guo, T. C. Wen, Y. S. Huang, C. C. Tsou, C. T. Chung, Y. C. Lin, and Y. J. Hsu, *Adv. Funct. Mater.* **18**, 3036 (2008).

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