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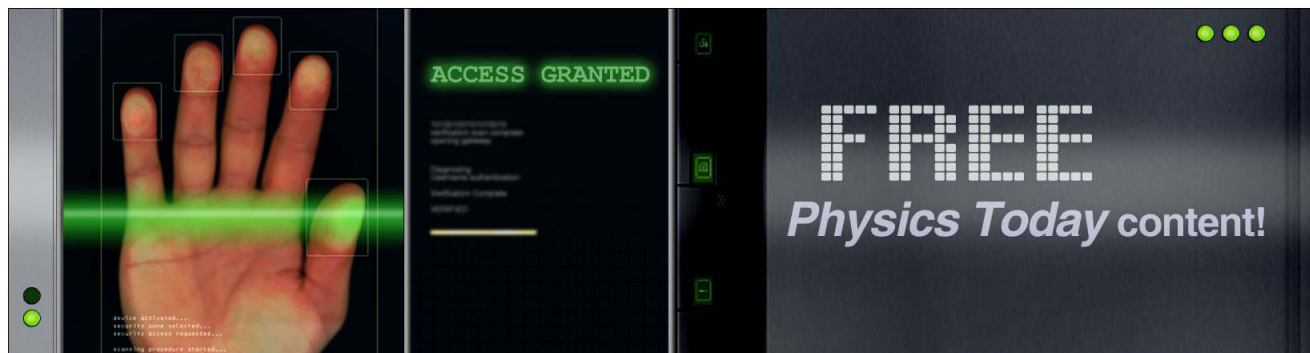
High performance polymer light-emitting diodes with N-type metal oxide/conjugated polyelectrolyte hybrid charge transport layers

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We present an interfacial engineering strategy employing n-type-metal-oxide/conjugated-polyelectrolyte (CPE) hybrid charge-transport layers for highly efficient polymer light-emitting diodes (PLEDs). The hybrid metal-oxide/CPE layer facilitates electron-injection, while blocking hole-transport, and thereby maximizes electron-hole recombination within the emitting layer. A series of metal-oxide/CPE combinations were tested in inverted PLEDs (FTO/metal-oxide/CPE/ F8BT/MoO$_3$/Au). Specifically, HfO$_2$/CPE double layer achieved an electroluminescence (EL) efficiency of up to 25.8 cd/A (@ 6.4 V, one of the highest values reported for fluorescent PLEDs). © 2011 American Institute of Physics. [doi:10.1063/1.3653962]

Over the past several decades, semiconducting-polymer-based light-emitting diodes (PLEDs) have been extensively used for solution processible and mechanically flexible displays.[1] To achieve highly efficient PLEDs with stable lifetimes, bandgap engineering at the interface between inorganic electrodes and a semiconducting polymer is a major concern.[2] Since carrier injection in polymeric semiconducting devices is generally retarded at the layer interfaces, a low-barrier contact is crucial for achieving high device performance in PLEDs.[3,4] An ohmic contact with low contact resistance is highly desired for barrier-free carrier injection and transport.

Recently, MoO$_3$ deposited on a Au anode demonstrated an unprecedented ohmic hole-injection[5–7] into a widely commercialized green-light-emitting polymer, poly(9,9′-dioctyl-fluorene-co-benzo-thiadiazole) (F8BT). Such a combination facilitates hole injection at the anode interface. In contrast, n-type metal oxides (ZnO or TiO$_2$) deposited on a transparent cathode (InSnO (ITO) or SnO$_2$:F (FTO)) reveal significant electron-injection barriers to the lowest unoccupied molecular orbital (LUMO) of F8BT.[8,9] To date, various charge-injection/transport layers, including semiconducting polymers,[10,11] self-assembled monolayers,[12] ionic liquids,[13] metals,[14] metal halides,[15] and metal oxides,[16–18] have been employed to promote the electron injection. Nevertheless, considerable room for performance improvement still remains.

Here, we demonstrate an interfacial engineering design at the cathode employing various n-type-metal-oxide/conjugated-polyelectrolyte (CPE) hybrid charge-transport layers.

Figures 1(a) and 1(b) present the chemical structures of F8BT and the CPE, cationic poly(9,9′-bis(6″-N,N,N-trimethylammoniumhexyl)fluorene-co-alt-phenylene) with bromide counterions (FPQ-Br),[19,20] and the PLED device architecture employed in this work. The device consists of an F8BT polymer light-emitting layer sandwiched between the FTO/n-type-metal-oxide (ZnO, HfO$_2$, ZrO$_2$, or MgO) transparent cathode and MoO$_3$/Au metallic anode. As mentioned above, while the anode interface has ohmic hole-injection,[5–7] the cathode interface has a significant electron-injection barrier. The cathode interface was modified by employing several metal-oxide/CPE hybrid transport layers. A detailed energy-level diagram for each device component layer is illustrated in Figure 1(c). The valence bands of n-type metal oxides were obtained from ultraviolet photoemission spectroscopy (UPS) measurements (Fig. S1 in Ref. 23). The samples were prepared by electron-beam-evaporated n-type metal-oxide films on 70 nm-thick gold coated silicon substrates. The valence band could be obtained from the difference between the inelastic cutoff and the Fermi edge. Except semiconducting ZnO (~3.4 eV), dielectric ZrO$_2$ (~5.1 V), HfO$_2$ (~5.5 eV), and MgO (~7.6 eV) exhibited band gaps larger than 5 eV.[23] The conduction band could be calculated from the valence band and the band gap of each n-type metal oxide. In Figure S2 (in Ref. 23), smooth surface morphologies of the n-type metal oxides were measured by atomic force microscopy.

The light-emitting characteristics of the PLEDs with various n-type-metal-oxide/CPE hybrid charge-transport layers are presented in Figure 2. Figures 2(a) and 2(b) show the bipolar injection current (J) and luminance (L) against the applied voltage (V). The PLED devices with the hybrid transport layers exhibited the lower turn-on voltages than those with single metal-oxide layers. Figures 2(c) and 2(d)

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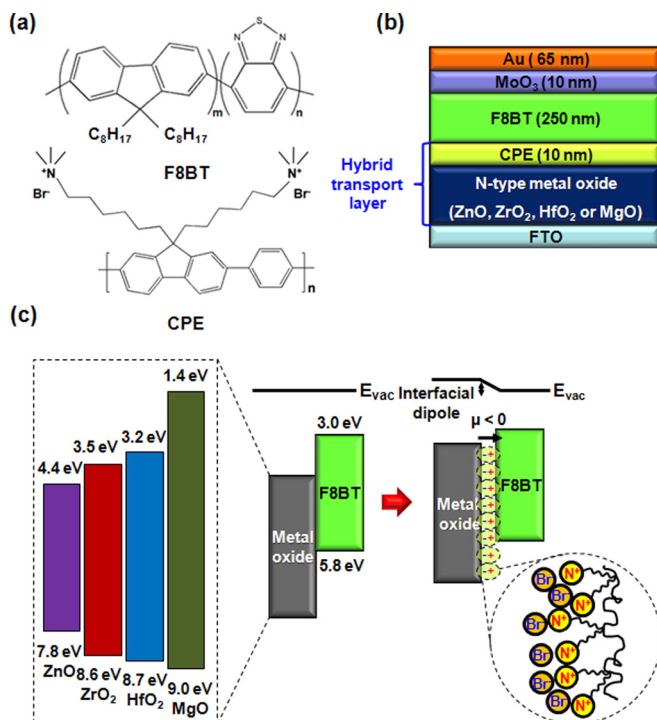c)Electronic mail: mhsong@unist.ac.kr.

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FIG. 1. (Color online) (a) Chemical structures of F8BT and CPE. (b) Device architecture of inverted PLEDs. (c) Schematic energy-level diagrams at the n-type-metal-oxide/F8BT junction with and without the CPE having negative dipoles.

TABLE I. Detailed device characteristics of inverted PLEDs with various interfacial charge-transport layers.

Device configuration	Bias @ 1000 cd/m^2	$\eta_{EL, max}$ (cd/A) @ bias	$\eta_{EL, max}$ (lm/W) @ bias
ZnO	7.8 V	2.2 @ 10.4 V	0.7 @ 10.4 V
ZrO$_2$	13.4 V	5.6 @ 13.8 V	1.3 @ 13.8 V
HfO$_2$	8.4 V	5.5 @ 9.2 V	1.9 @ 8.8 V
MgO	15.4 V	2.9 @ 14.8 V	0.6 @ 14.8 V
ZnO/CPE	7.8 V	11.9 @ 9.4 V	10.1 @ 9.4 V
ZrO$_2$/CPE	8.4 V	15.8 @ 7.6 V	6.8 @ 7.2 V
HfO$_2$/CPE	7.4 V	25.8 @ 6.4 V	12.6 @ 6.4 V
MgO/CPE	17.4 V	7.7 @ 7.6 V	3.2 @ 7.6 V

show the device electroluminescence (EL) efficiency (η_{EL}) plotted against the current density and EL spectra of the PLEDs with structure of FTO/n-type-metal-oxide/CPE/F8BT/MoO$_3$/Au, respectively. While the devices with a single metal-oxide layer revealed a luminance efficiency of 2.2-5.6 cd/A, the device with the n-type-metal-oxide/CPE hybrid charge-transport layer exhibited a dramatically improved efficiency of 7.7-25.8 cd/A (approximately a 4-fold increase for all metal oxides). In particular, the device with HfO$_2$/CPE layer presented the highest efficiency of 25.8 cd/A at 6.4 V. The detailed device characteristics are summarized in Table I.
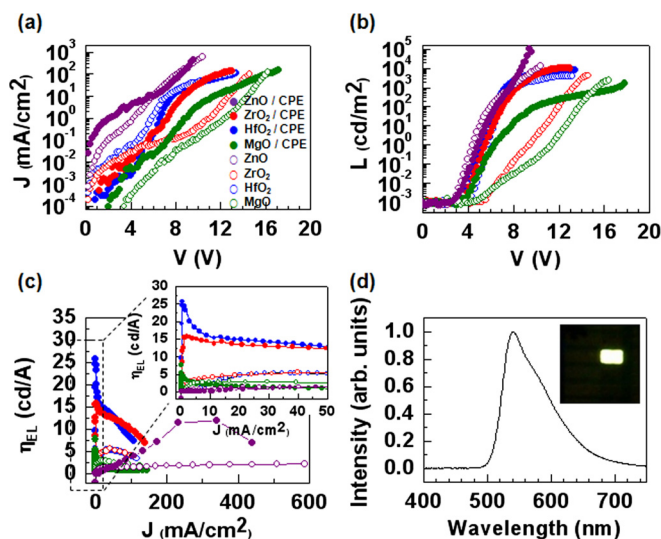

FIG. 2. (Color online) (a) *J-V*, (b) *L-V*, and (c) η_{EL}-*J* for various cathodic charge-transport layers. (d) EL spectra of inverted PLEDs.

The enhanced device performance with the n-type-metal-oxide/CPE hybrid transport layer is believed to be largely due to the spontaneous polarization of CPE.[21] The energy band diagrams for n-type-metal-oxide/F8BT junctions with and without the CPE layer are illustrated in Figure 1(c) under flat band conditions. In the absence of an applied electric field, mobile ions are attracted to the metal-oxide interface with a high dielectric constant ($\varepsilon_r = 8.0$) rather than that of F8BT with a lower dielectric constant ($\varepsilon_r = 2.9$).[22,23] Moreover, the preference for the CPE polymer backbone to interact with the hydrophobic organic F8BT interface leads to the spontaneous polarization. Given that the negative dipoles pointing away from the metal-oxide surface are aligned, the band edge of the metal-oxide surface shifts closer to the local-vacuum-level of the F8BT. Thus, the conduction band at the metal-oxide surface and the corresponding electron-injection barrier effectively decrease. The UPS measurement of the n-type-metal-oxide/CPE hybrid layers confirmed that the CPE lowers the conduction band at the metal-oxide surfaces by 0.8-1.45 eV (Fig. S1 in Ref. 23).

The influence of the metal-oxide/CPE bilayer on electron-injection efficiency could be straightforwardly confirmed by the electron-only device (Fig. S3(a) in Ref. 23) characteristics. Figure S3(b) (in Ref. 23) shows the *J-V* characteristics of the electron-only devices. The device with the n-type-metal-oxide/CPE hybrid layer reached an electron-injection current density of 2 mAcm^{-2} at 8.6 V for ZnO, at 10.5 V for HfO$_2$, at 12.9 V for ZrO$_2$, and at more than 15 V for MgO, respectively. In contrast, the devices with a single-metal-oxide-layer (without CPE) reached the same current density at significantly higher voltages (13.1 V for ZnO and more than 15 V for HfO$_2$, ZrO$_2$, and MgO). These results along with UPS measurements confirm that the negative dipoles within the CPE layer promoted the electron injection.

Figure 3(a) shows the energy-level diagram and EL spectra of the devices for evaluating the hole-blocking behavior of n-type metal-oxide layers employed in this work. The devices include the two light-emitting polymer layers of F8BT (green-light-emitting polymer) and poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) (Fig. S4 in Ref. 23, blue-light-emitting polymer). The devices revealed the hole-dominant characteristics with the ohmic PFO/MoO$_3$ anode contact. If the metal oxide layer inserted between the two light-emitting polymers efficiently blocks the holes, the electron and hole recombination should occur within the PFO
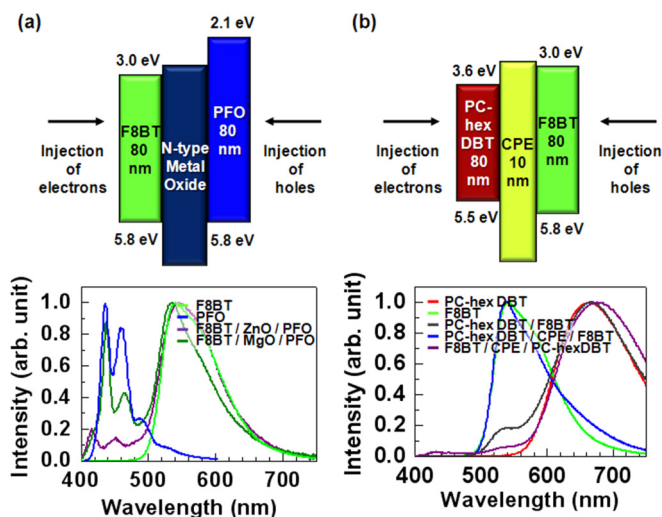
FIG. 3. (Color online) Schematic energy-level diagrams and EL spectra of the devices for evaluating the hole-blocking behavior of (a) single n-type-metal-oxide-layer in a device configuration of FTO/n-type-metal-oxide/F8BT/n-type-metal-oxide/PFO/MoO$_3$/Au and (b) CPE layer in a configuration of FTO/ZnO/PC-hexDBT/CPE/F8BT/MoO$_3$/Au.

layer and blue light should be emitted. The devices with a ZnO or MgO layer emitted both blue and green light, simultaneously, suggesting that the single metal-oxide layer is insufficient for hole-blocking. We note that the MgO layer with a deeper valance band (~9.0 eV) blocks holes more effectively than the ZnO layer (~7.8 eV) based on the EL spectra.

Figure 3(b) shows the energy-level diagram and EL spectra of the devices for evaluating the hole-blocking behavior of the CPE layer. The devices include two light-emitting polymer layers of poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5 -(4′,7′-bis(4-hexylthiophen-2-yl)-2′,1′,3′-benzothiadiazole)] (PC-hexDBT) (Fig. S4 in Ref. 23, red-light-emitting polymer) and F8BT. Without the CPE layer, the device emitted red light due to the hole-dominant device characteristics and energy transfer from F8BT to PC-hexDBT. In contrast, when the CPE layer was inserted between the PC-hexDBT and F8BT layers, green light was dominantly emitted. This suggests that the CPE layer effectively blocked the hole transport from the F8BT layer into the PC-hexDBT layer, and therefore, the injected electrons and holes dominantly recombined within the F8BT layer. We note that the device with the reversed order of light-emitting polymers and intermediate CPE layer exhibited red light again. The EL spectrum almost overlaps with that of the PC-hexDBT single-emitting-layer device, demonstrating an effective hole-blocking by the CPE layer, even though it still contains small part of geen-light emission. Along with the facile electron injection, the effective hole-blocking of the hybrid transport layer constitutes highly selective carrier-transport. We note that the amphiphilic FPQ-Br layer was deposited by spin casting onto the hydrophobic PC-hexDBT or F8BT layers after a brief UV/O$_3$ treatment. This treatment induced the spontaneous polarization in the CPE layer without influencing the light-emitting characteristics of PC-hexDBT or F8BT.

In summary, we demonstrated an interfacial engineering strategy employing n-type-metal-oxide/CPE hybrid double layers. The hybrid transport layer effectively blocks hole-transport as well as significantly enhances electron injection

such that electron-hole recombination can be optimized within a light-emitting layer. Furthermore, this approach is generally applicable to various combinations of metal oxides and CPEs for optimizing the charge injection/transport and improving the contact problem between hydrophilic metal oxides and hydrophobic organic layers. We note that the HfO$_2$ layer demonstrates the highest efficiency among the various n-type metal oxides employed in this work, due to the well-matched energy levels with F8BT, which optimize the hole-blocking and carrier injection so as to maximize the carrier recombination within the 250 nm-thick F8BT layer. Our charge-selective interfacial engineering offers a new design scheme for optimizing the carrier injection and recombination, which is potentially advantageous for various organic-semiconductor-based devices.

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