Highly Efficient Hybrid Inorganic–Organic Light-Emitting Diodes by using Air-Stable Metal Oxides and a Thick Emitting Layer

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During the last two decades, considerable progress has been made with the device efficiency and lifetime of organic light-emitting diodes (OLEDs), enabling their application in flat-panel displays and solid-state lighting. To realize high-performance, full-color OLED devices as commercial products, it is necessary to further improve the power efficiency and lifetime of the devices. To date, research in this direction has focused on the fabrication of multilayered devices with the goal of overcoming low device efficiencies and short operation lifetimes in small-molecule-based OLEDs [1] and polymer light-emitting diodes (PLEDs) [2]. However, production costs are critical for competition with existing panel displays, such as liquid-crystal displays, and current lighting devices, such as fluorescent lamps. In this regard, the simplification of OLEDs without loss of the optimized performance becomes very important [3]. In addition, air-stable solution-processed LEDs without air-sensitive charge injection materials are important for realizing roll-to-roll mass production of flexible OLEDs, because it is difficult to apply conventional encapsulation techniques to the production of flexible OLEDs [4–7].

Strategies for fabricating simplified air-stable devices without a thin low-work-function metal (i.e., Ca or Ba) beneath the Al electrode have proven to be flawed when applied to conventional structures (Figure 1a), because most of the holes can recombine with electrons near the Al electrode, leading to significant quenching of the excitons [6, 7]. Therefore, it is of particular importance to incorporate air-stable, efficient charge injection contacts into the devices. Although several approaches using ionic polymers that are soluble in polar solvents have been employed [5], they have required conventional encapsulation techniques for stable operation because of their strong susceptibility to moisture.

A recent promising approach towards overcoming these issues is to use inorganic metal oxides as charge injection contacts (Figure 1b). These are attractive because of their good transparency in the visible range of the spectrum, good charge transport properties, and excellent air stability [8–15]. Most recent studies have reported hybrid inverted PLEDs in which n-type metal oxides, such as titanium oxide (TiO₂) [8–11] or zirconium oxide (ZrO₂) [12], are employed as bottom electron injection contacts on top of indium tin oxide (ITO) or fluorine-doped tin oxide (FTO), and thermally evaporated molybdenum trioxide (MoO₃) is used as the top hole injection layer beneath a Au positive electrode (Figure 1b, with or without a Cs₂CO₃ layer [8–14]). The problem with hybrid PLEDs has been their relatively low luminous efficiency, attributed to the high current density flowing through the device without radiative electron–hole recombination [8–13].

As shown in Table 1, Mori et al. reported the fabrication of hybrid PLEDs using poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) as emitting layer and TiO₂ as electron injection contact. These devices showed a maximum brightness of 700 cd m⁻² at 6 V and a maximum luminous efficiency of the device in the 1021 range.
order of 0.1 cd A$^{-1}$. Bolink et al. used ZnO instead of TiO$_2$ in an otherwise identical device structure. This device exhibited a greatly improved device performance (luminous efficiency of ca. 1.3 cd A$^{-1}$ and a maximum brightness of 6500 cd m$^{-2}$).[9] Kabra et al. reported that the inclusion of poly(2,7-(9,9-di-n-octylfluorene)-alt-(1,4-phenylene(4-sec-butylphenyl)limino)-1,4-phenylene) (TFB) between F8BT and MoO$_3$ improved the luminous efficiency to up to 2.8 cd A$^{-1}$ with the structure ITO/ZnO (120 nm)/F8BT (80 nm)/TFB (60 nm)/MoO$_3$ (10 nm)/Au (50 nm).[11] The improvement was attributed to the role of the TFB layer in reducing any probable exciton quenching at the F8BT/MoO$_3$ interface.[11] Actually, an important advance in the performance of hybrid PLEDs was recently achieved by adding an electron-injecting and hole-blocking Cs$_2$CO$_3$ layer on top of the n-type metal oxide layer (ZnO).[13] Bolink et al. achieved a high luminous efficiency of 8 cd A$^{-1}$ by using the structure ITO/ZnO/Cs$_2$CO$_3$ (4 nm)/Super Yellow (80 nm)/MoO$_3$/Au (70 nm).[11] A great jump in the efficiency of hybrid PLEDs was accomplished by the Friend group.[14] They reported a maximum luminance efficiency of 22.7 cd A$^{-1}$ in a hybrid structure of ITO/ZnO (70 nm)/Cs$_2$CO$_3$ (7 nm)/F8BT (1200 nm)/MoO$_3$ (10 nm)/Au (50 nm), as shown in Figure 1d. This advance was achieved with a very thick emitting layer (1200 nm). On the other hand, the luminous efficiency of the thin hybrid device with structure ITO/ZnO (70 nm)/Cs$_2$CO$_3$ (7 nm)/F8BT (200 nm)/MoO$_3$ (10 nm)/Au (50 nm) was much lower, 11.8 cd A$^{-1}$ (Figure 1b).

Figure 2 show a schematic energy band diagram of the hybrid PLEDs. The lowest unoccupied molecular orbital (LUMO) of MoO$_3$ is lower than the highest occupied molecular orbital (HOMO) of F8BT,[15] which enables excellent hole injection from Au to F8BT. However, electron injection is limited by the energy barrier between ZnO and F8BT (0.9 eV). The Cs$_2$CO$_3$ layer can assist electron injection from ZnO to F8BT and block holes at the interface. Therefore, the hole current in the device follows the space-charge limited current.[14] As depicted in Figure 2, the holes accumulate near the Cs$_2$CO$_3$ layer and the accumulated holes induce more electrons to be injected into the F8BT. As a result, efficient electron–hole recombination occurs. The thin device (200 nm F8BT) shows a lower luminous efficiency than the thick device (1200 nm F8BT; see Table 1) because a number of the generated excitons are quenched near the Cs$_2$CO$_3$ interface, as confirmed by a measurement of the absolute photoluminescence quantum yield.[14] Therefore, the deposition of a thick emitting layer in the devices broadened the exciton density profile, thereby minimizing exciton quenching.

It should be noted that the high luminous efficiency achieved by the use of a thick emitting layer was also observed in conventional devices with the structure ITO/PEDOT:PSS (70 nm)/F8BT (1450 nm)/Ca/Al; the luminous efficiency of which was as high as 21.7 cd A$^{-1}$. In this conventional structure, electron injection is efficient whereas hole injection is limited due to the energy barrier between PEDOT:PSS and F8BT (Figure 1a and c). Therefore, significant quenching is induced by the PEDOT:PSS layer because the recombination zone is located near the layer. The thick ambipolar emitting layer broadens the recombination zone away from the quenching zone in both conventional and hybrid inverted PLEDs.

Lee also reported a great improvement in the luminous efficiency of a hole-dominant PLED with a laminated Au cathode by reducing the exciton quenching at the cathode.[26] A self-assembled monolayer was employed as a space layer to prevent exciton quenching near the Au layer. In this device, the hole space charges were dominant, which induced spatial redistribution of the internal electric field near the Au. Therefore, more electrons are injected by assistance of hole space charges, even in devices with a Au cathode.

We conclude that management of the exciton density profiles by widening the recombination zone and accumulating space charges near the charge injection contacts leads to great improvements in simple-structured PLEDs. High luminous efficiencies in devices with a micrometer-thick emitting layer have great advantages with respect to processing, for practical mass production of flat-panel or flexible displays and lighting devices, because the thick layer definitely improves the producational efficiency.
duction yield of the devices and allows for much more simplified, large-area film deposition and patterning processes, such as screen printing, doctor-blade printing, and gravure printing (rather than ink-jet printing), which are essential processes for low-cost flexible displays and solid-state lighting. However, although a very high efficiency was achieved from hybrid PLEDs, comparable to state-of-art PLEDs, the hybrid devices require further improvements in terms of power efficiency, which is crucial for real applications to panel displays and solid state lightings. In addition, the operational lifetime of the hybrid PLEDs should be studied in depth for real practical applications.

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