Electronic structures and electron-injection mechanisms of cesium-carbonate-incorporated cathode structures for organic light-emitting devices

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In this letter, we investigate electronic structures and electron-injection mechanisms of the effective cathode structures for organic light-emitting devices incorporating cesium carbonate (Cs_2CO_3), either deposited as an individual thin injection layer or doped into the organic electron-transport layers. The electronic structures and the interface chemistry studied by ultraviolet and x-ray photoemission spectroscopy show that the enhanced electron injection is associated with strong *n*-doping effects and increase of electron concentrations in the electron-transport layer induced by Cs_2CO_3 . Since such a reaction occurs without the presence of metals, cathode structures incorporating Cs_2CO_3 may be applied to a wide range of electrode materials. © 2006 American Institute of Physics. [DOI: [10.1063/1.2192982](https://doi.org/10.1063/1.2192982)]

An effective cathode structure for efficient electron injection is critical to performances of organic light-emitting devices (OLEDs). An efficient electron injection could be achieved by using low-work-function metals, either as individual cathode layers or as *n*-type conductive dopants in the organic electron-transport layers (ETLs).^{1–6} These methods, however, require special care and equipments for handling reactive metals and thus are less convenient for fabrication. Another commonly used cathode structure that involves no reactive metals is to insert an ultrathin layer of alkali halide, such as LiF, as an electron-injection layer (EIL) between a metal cathode and an organic ETL. Since such a scheme usually involves particular chemical interaction of metal/EIL/ETL, its effectiveness is sensitive to the metal used and very often limits the choice of cathode metals to Al only. Recently, Cannon Inc. reported that cesium carbonate (Cs_2CO_3), either vacuum deposited as an individual layer over the organic ETL or codeposited with ETL, effectively facilitates electron injection from a wide range of metal electrodes.⁷ While device performances using such cathode structures are encouraging, mechanisms of this injection scheme are not understood. In this letter we investigate the electronic structures and electron-injection mechanisms of cathode structures incorporating Cs_2CO_3 using photoemission spectroscopy. Furthermore, since Cannon Inc. did not disclose the ETL used in their report, in this work we also test whether such an injection scheme is also effective with other widely used ETLs such as tris(8-hydroxyquinolate)aluminum (Alq_3).⁸

The effects of Cs_2CO_3 on electron injection from metal cathodes into Alq_3 were investigated via a series of devices structures: (1) devices using no electro-injection layer [ITO/

PEDT:PSS (20 nm)/ α -NPD (40 nm)/ Alq_3 (60 nm)/Al (device A) or Ag (device B), (2) devices using a thin layer of Cs_2CO_3 as the electron-injection layer [ITO/PEDT:PSS (20 nm)/ α -NPD (40 nm)/ Alq_3 (60 nm)/ Cs_2CO_3 (1 nm)/Al (device C) or Ag (device D)], (3) devices using Alq_3 doped with 20 wt % of Cs_2CO_3 as the electron-injection layer [ITO/PEDT:PSS (20 nm)/ α -NPD (40 nm)/ Alq_3 (40 nm)/ Alq_3 : Cs_2CO_3 (20 nm)/Al (device E) or Ag (device F)], and (4) a “benchmark” device (device G) using LiF as the electron-injection layer [ITO/PEDT:PSS (20 nm)/ α -NPD (40 nm)/ Alq_3 (60 nm)/LiF (0.5 nm)/Al]. In these devices, the conducting polymer poly(ethylene dioxythiophene)/poly(styrene sulphonate) (PEDT:PSS) and 4,4'-bis[*N*-(1-naphyl)-*N*-phenyl-amino]biphenyl (α -NPD) are used as the hole-injection and hole-transport layers, respectively.^{9,10} PEDT:PSS was prepared by spin coating and all other layers were vacuum deposited in sequence without breaking the vacuum.

Photoemission experiments were carried out in two interconnected ultrahigh-vacuum chambers, one for deposition and one for spectroscopy analysis.¹¹ Thin films of Alq_3 were prepared in the deposition chamber by thermal evaporation onto gold-coated silicon substrates. Cs_2CO_3 were deposited on Alq_3 thin films or coevaporated with Alq_3 . The core-level x-ray photoemission spectra (XPS) were measured using either Al $K\alpha$ (1486.6 eV) or Mg $K\alpha$ (1253.6 eV) photon lines. The valence-band ultraviolet photoemission spectra (UPS) were carried out with He I (21.2 eV) and He II (40.8 eV) as excitation sources. The Fermi level of the system was measured on the gold substrate before the organic deposition. The energy levels of the highest occupied molecular orbitals (HOMOs) of organic samples were determined by extrapolating the edges of the HOMO peak down to the background of the UPS spectra. The overall resolutions for XPS and UPS are 0.5 and 0.15 eV, respectively, in our system.

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FIG. 1. *I-V* characteristics of devices A–G.

The current-voltage (*I-V*) characteristics of devices A–G are shown in Fig. 1. Without an appropriate injection scheme, devices A and B show poor *I-V* characteristics. With a thin layer of Cs_2CO_3 inserted between Alq_3 and cathode metals (devices C and D) the currents are increased by over two orders of magnitude, comparable to or even higher than that obtained with the LiF/Al cathode structure (i.e., the benchmark scheme, device G). Moreover, *I-V* characteristics are further improved with coevaporation of Cs_2CO_3 and Alq_3 as part of the ETL (i.e., devices E and F). It is interesting to note that in contrast to LiF , which only works effectively with Al , Cs_2CO_3 is effective for both Al and Ag cathodes. Previous studies have shown that the formation of an effective cathode with LiF/Al is due to the release of Li ions from LiF into the Alq_3 matrix and consequent formation of Alq_3^- anion through the chemical reaction between LiF and Al .^{11–14} Such reactions require the presence of Al and may not occur with other metals. Here, the fact that Cs_2CO_3 also works effectively for metals other than Al implies different reaction mechanisms. To understand the mechanisms, we thus further studied the interfacial chemistry and energy levels in these cathode structures with photoemission spectroscopy.

Figure 2 shows the UPS spectra near the onset and the valence bands with incremental Cs_2CO_3 deposition on Alq_3 , which allows us to investigate energy structures and chemical reactions at the interfaces. The nominal thickness is obtained from the quartz oscillator calibrated with densities and geometric factors. 1 Å of Cs_2CO_3 is equivalent to $2.5 \times 10^{14} \text{ cm}^{-2}$ molecules on the surface. For pristine Alq_3 , the edge of HOMO is about 1.5 eV below the Fermi level

FIG. 2. The UPS spectra near the onset and valence bands as a function of incremental deposition of Cs_2CO_3 on Alq_3 . The surface state is indicated by the arrow in the inset.

FIG. 3. Evolution of energy band diagrams, from left to right, with incremental deposition of Cs_2CO_3 on Alq_3 .

and the ionization energy is 5.8 eV, which is consistent with the reported data.^{15–18} With as little as 0.1 Å Cs_2CO_3 deposited on the Alq_3 surfaces, the onset of UPS spectra, which represents the vacuum level of the sample, is lowered by 1.2 eV. The abrupt lowering of the vacuum levels indicates charge exchanges and a strong dipole field at the interfaces with Cs_2CO_3 .^{19,20} The valence-band features of the Alq_3 are still clearly seen in the UPS spectrum, yet with HOMO and other peaks rigidly shifting toward lower binding energies by 1.1 eV with respect to the Fermi level. Given the band gap of Alq_3 being 2.8 eV, the Fermi level is only 0.2 eV below the lowest unoccupied molecular orbital (LUMO) (Fig. 3), indicating that the Alq_3 film becomes *n*-doped with Cs_2CO_3 deposition. The influence of Cs_2CO_3 on electronic structures of Alq_3 is quite different from that of LiF . In the $\text{Alq}_3/\text{LiF}/\text{Al}$ cathode structure, the *n*-doping effect of Alq_3 only occurs with the subsequent deposition of Al , which reacts with LiF and forms AlF_3 .^{11–14} The Li atoms are then released into the Alq_3 matrix and generate Li^+ cation and Alq_3^- anion, resulting in *n*-doped Alq_3 . In contrast, the photoemission results here show that 0.1 Å Cs_2CO_3 alone (without subsequent metal deposition) can induce strong *n*-doping effects in Alq_3 . Such characteristics would render this scheme rather insensitive to cathode metals, as already observed in the device results. With increasing Cs_2CO_3 coverage, the HOMO of Alq_3 shifts further toward the lower binding energy, along with a similar shift of the vacuum level. Some surface states are also observed at the top of HOMO after 2 Å of Cs_2CO_3 depositions. Furthermore, the energy level of Alq_3 HOMO is more than 2.8 eV below the Fermi level with Cs_2CO_3 coverage larger than 0.5 Å, suggesting heavily *n*-doped Alq_3 surfaces. The Fermi level being more than 2.8 eV (optical absorption band gap) above the HOMO of Alq_3 may be due to the fact that photoemission data involve the molecular anion-cation gap, which is typically 0.5–1.5 eV larger than the optical gap of neutral molecules.^{21,22} Therefore, the Fermi level could still be below the LUMO of Alq_3 in this case. The energy-level diagrams of Alq_3 with incremental deposition of Cs_2CO_3 are summarized in Fig. 3, illustrating that the Fermi level at the interface can move close to, or even above, LUMO with a thin layer of Cs_2CO_3 . As a result, the electron-injection barrier, i.e., the energy difference between the Fermi level of the electrode and the LUMO at the interface, is greatly reduced.

Figure 4 shows the UPS spectra of pristine Alq_3 and Alq_3 doped with two different Cs_2CO_3 concentrations ($\text{Alq}_3:\text{Cs}_2\text{CO}_3$ of 64:1 and 16:1 weight ratios). As in the case

FIG. 4. The UPS spectra near the onset and valence bands for pristine Alq₃ and Alq₃ doped with two Cs₂CO₃ concentrations (Alq₃:Cs₂CO₃ of 64:1 and 16:1 weight ratios).

of thin Cs₂CO₃ on Alq₃, with Cs₂CO₃ doping the valence-band features of Alq₃ can still be clearly distinguished, and yet shift rigidly to higher binding energies as compared to that of pristine Alq₃. There also occur extra states at the top of the Alq₃ HOMO with the presence of Cs₂CO₃ in the matrix. These extra states in the forbidden gap might provide a ladder for carrier injection across the interfacial regions. With Cs₂CO₃ doping, the energies of Alq₃ HOMO are lowered by 0.9 and 1.3 eV for the mixing ratios of 1/64 and 1/16, respectively. With even higher concentrations, the Fermi levels saturate at the vicinity of the Alq₃ LUMO level. In comparing the Fermi levels of samples with Cs₂CO₃ inserted at the interfaces or doped in the Alq₃ matrix, it is found that the electron-injection barriers are similar and negligibly small for both cases. Lower device voltages observed for devices E and F, with Cs₂CO₃ doped in Alq₃, thus may be associated with enhanced conduction due to increased carrier concentrations. Therefore, doping Cs₂CO₃ in the Alq₃ matrix not only reduces the electron-injection barrier but also increases the carrier concentration for current conduction.

The chemistry of Cs₂CO₃ and Alq₃ was further investigated with XPS. First, a sample with Cs₂CO₃ deposited on the Au substrate is measured with XPS and the core-level intensities of Cs, C, and O verify that Cs₂CO₃ does not decompose during the evaporation. Thereby, all the characteristics observed in devices or in photoemission spectroscopy are results of interaction between Cs₂CO₃ and Alq₃, not from other species, for instance, Cs decomposed from Cs₂CO₃. Figure 5 shows the XPS Cs 3*d* core-level spectra of Cs₂CO₃ deposited on Au and Alq₃ as well as Cs₂CO₃ codeposited with Alq₃. The Cs 3*d*_{3/2} and 3*d*_{5/2} peaks of Cs₂CO₃ on Au appear at binding energies of 741.2 and 727.3 eV, respectively. For Cs₂CO₃ doped in Alq₃ and Cs₂CO₃ deposited on Alq₃, the Cs 3*d* peaks both shift to higher binding energy by about 2 eV. The large difference in binding energies of Cs 3*d* core levels in these samples indicates a substantial chemical reaction between Cs₂CO₃ and Alq₃. The higher binding energies of the Cs 3*d* core levels in the samples with Alq₃ indicate additional positive charges surrounding the Cs atoms and a portion of the electrons being transferred to the host materials (Alq₃). The increase of the electron concentration in the Alq₃ matrix would move the Fermi level close to LUMO of Alq₃, consistent with the UPS results. Overall, both XPS and UPS show that the reactions between Cs₂CO₃ and Alq₃ occur without presence of cathode metals. Thus the enhancement of electron injection brought by Cs₂CO₃ is

FIG. 5. The XPS spectra associated with Cs 3*d* core levels of Cs₂CO₃ on Au and Alq₃ and Cs₂CO₃ doped in Alq₃ matrix.

rather independent of the cathode metals used, substantially different from mechanisms of the conventional Alq₃/LiF/Al cathode.

In summary, we investigate the electronic structures and mechanisms of the effective cathode structures incorporating Cs₂CO₃ either as an individual thin layer or doped into the organic electron-transport layer. The electronic structures and the interface chemistry studied by photoemission spectroscopy show that the enhanced electron injection is associated with *n*-doping effects and increase of electron concentrations. Since such a reaction occurs without the presence of metals, cathode structures incorporating Cs₂CO₃ may be applied to a wide range of electrode materials.

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