

Ultrahigh efficiency green polymer light-emitting diodes by nanoscale interface modification

Qianfei Xu, Jianyong Ouyang, and Yang Yang^{a)}

Department of Materials Science and Engineering, University of California, Los Angeles, Los Angeles, California 90095

Takayuki Ito and Junji Kido

School of Science and Engineering, Yamagata University, Yonezawa, Japan

(Received 25 August 2003; accepted 14 October 2003)

We report highly efficient green polymer light-emitting diodes (PLEDs) achieved by introducing a nanoscale interfacial layer, made of calcium (2) acetylacetonate [$\text{Ca}(\text{acac})_2$], between the aluminum cathode and the green polyfluorene polymer. $\text{Ca}(\text{acac})_2$ is solution processible, therefore it is ideal for the fabrication of PLEDs. It is believed that the $\text{Ca}(\text{acac})_2$ layer plays multiple roles in enhancing the device performance. Firstly, it enhances the injection of electrons, which are the minority carriers in our green polyfluorene PLEDs. Secondly, it provides a buffer layer, preventing the quenching of luminescence from the aluminum electrode. Thirdly, it behaves as a hole-blocking layer, and subsequently enhances exciton formation. Based on $\text{Ca}(\text{acac})_2$ /aluminum cathode, we obtained device efficiency as high as 28 cd/A at 2650 cd/m² brightness, which is an improvement by a more than a factor of 3 over devices using calcium/aluminum as the cathode. © 2003 American Institute of Physics. [DOI: 10.1063/1.1630848]

Polymer light-emitting diodes (PLEDs)¹ have attracted considerable attention due to their application in displays.^{2,3} Major important technological issues related to commercial applications are the quantum efficiency,⁴ device stability,⁵ and ease of fabrication. Considerable work has been devoted to getting high quantum efficiency.^{4,6} The efficiency of PLEDs is determined primarily by the efficiency of photoluminescence (PL) of the polymer film, the injection and balance of electrons and holes, and finally, the exciton formation and recombination process. In the past few years, organic LEDs have significantly improved the device efficiency by incorporating phosphorescent dopants into the device.⁷⁻⁹ On the other hand, for PLEDs, the progress in achieving high efficiency devices is somewhat behind organic LEDs (OLEDs) since the phosphorescent dopants do not work as well in the PLEDs, which is probably due to the lack of proper host polymer for the triplet dopants.^{10,11}

In this letter, we report a fluorescence (singlet) green PLED with exceptionally high efficiency. This is achieved by interfacial engineering near the cathode/polymer interface. It is known that the interfaces of the cathode/polymer contact and anode/polymer contact are crucial to device performance. In the past, the anode interface has been resolved by using a thin layer of conducting polymer to over-coat the indium tin oxide (ITO) electrode.^{12,13} In general, for the cathode interface low-work-function metals such as calcium are used to reduce the barrier height and to increase the electron injection.² However, low-work-function metals are susceptible to degradation related to oxygen and moisture. Meanwhile, the metal ions also drift easily into the polymer layer, subsequently creating defects that reduce the lifetime of the device. Moreover, the metal layer also quenches the lumines-

cence of conjugated polymers near the interface. This effect is particularly harmful to devices with electrons as minority carriers, since the recombination zone is closer to the cathode interface.

The efficiency enhancement of our device is achieved by using a nanoscale interfacial modification layer made of calcium (2) acetylacetonate [$\text{Ca}(\text{acac})_2$].¹⁴ This material was first suggested by Kambe *et al.* as the interfacial layer.¹⁴ Figure 1 shows the chemical structure of the $\text{Ca}(\text{acac})_2$ as well as the device structure. The chemical compound was synthesized in Kido's lab at Yamagata University. The same compound is also available from Aldrich Company. In our devices, glass with predeposited ITO transparent electrode was used as the substrate. A buffer layer of 50 nm poly(3,4-ethylenedioxythiophene): polystyrenesulfonate, was over-coated onto the ITO electrode as the hole injection layer. The luminescence polymer is an 80 nm green fluorine-containing co-polymer (5BTF8) consisting of 5 wt % poly(9,9-dioctylfluorene-co-benzothiadiazole) and 95 wt % poly(9,9-dioctylfluorene),^{15,16} synthesized at Kido's laboratory. The cathode contains several nanometers of $\text{Ca}(\text{acac})_2$ spin-coated from solution and over-coated with 100 nm of alumi-

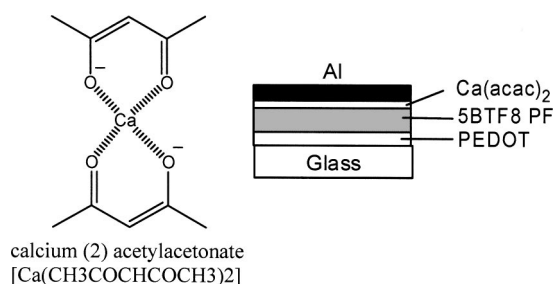


FIG. 1. The chemical structure of $\text{Ca}(\text{acac})_2$ and the device structure of the PLED in this study.

^{a)}Electronic mail: yangy@ucla.edu

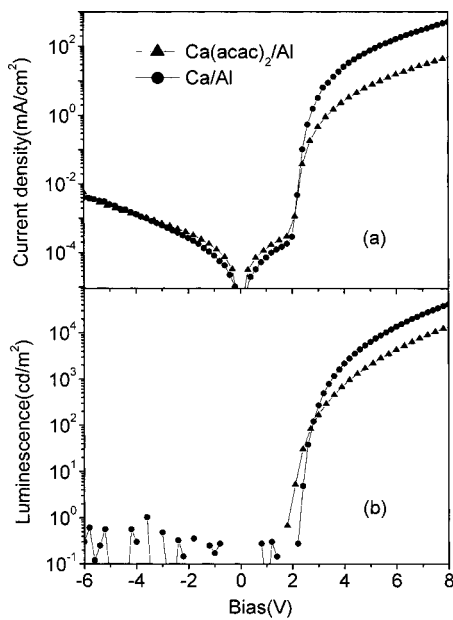


FIG. 2. The I - V curves (a) and the L - V curves (b) of the two sets of devices using Ca/Al and Ca(acac)₂/Al as the cathode, respectively. The lower current density of the device using Ca(acac)₂/Al as the cathode is probably due to the inert surfactant that we used to improve the adhesion of the Ca(acac)₂.

num deposited by thermal evaporation under 1×10^{-6} Torr vacuum. The Ca(acac)₂ solution is 0.2 wt % solution in ethoxyethanol solvent with polyoxyetholene(12) tridecyl ether [C₁₃H₂₇(OCH₂CH₂)_nOH] as surfactant to enhance the adhesion to the 5BTF8 polymer. In order to compare the device performance and understand the device operating mechanism, similar devices but using Ca/Al as cathode were made as reference devices. The PLED characterization was carried out by a Keithley 2400 source-measure unit and a calibrated silicon photodiode. The brightness is further measured using a Photo Research PR650 spectrophotometer. The photovoltaic measurement was performed under illumination supplied by a Thermo Oriol 150 W solar simulator (AM1.5G). All devices were tested in nitrogen ambient. The UV-visible absorption spectrum was measured by a HP 8453 spectrophotometer. The PL spectrum was measured by a Jobin-Yvon Spex Fluorolog-3 double-grating spectrofluorometer. The excitation wavelength for the polymer thin film was chosen as 390 nm based on UV-visible absorption spectra in which the absorption peak is around 360 nm. The green emission shows a main peak at 534 nm in the PL spectra. The devices made from this polymer have CIE coordinate number at $x = 0.396$, $y = 0.581$.

The I - V and light-voltage (L - V) curves for these two sets of devices are shown in Figs. 2(a) and 2(b), respectively. The results of using Ca(acac)₂ as an electron injection layer were exciting: we got maximum device efficiency as high as 28 cd/A at 2650 cd/m² for Ca(acac)₂-based devices, while for the Ca-based devices, we obtained maximum efficiency equal to 8.9 cd/A at 1165 cd/m². The luminescence efficiency versus current plot for both devices is shown in Fig. 3.

Comparing these two sets of devices, it is found that both devices show similar current (I) turn-on voltage (V_{I-on}) around 1.8 V, which is the voltage at which majority carrier injection occurs. It suggests that the majority carriers for

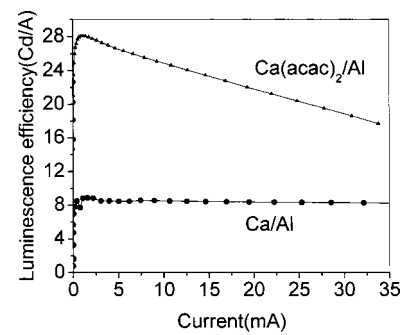


FIG. 3. The luminescence efficiency versus current curves of both devices. The device with Ca(acac)₂/Al as the cathode shows a much higher efficiency.

these devices are holes and that injection is determined by the anode interface; therefore, these two sets of devices show the same V_{I-on} voltage. However, the device using Ca/Al as cathode has higher injection current at larger voltages; we will discuss this issue in a later part of this letter. On the other hand, it is shown in the L - V curves that the light turn-on voltage (V_{L-on}) of the Ca(acac)₂-based device is almost same as its V_{I-on} voltage, while for the device using Ca/Al as cathode, the V_{L-on} voltage is around 2.2 V, which is 0.4 V higher than its V_{I-on} . For our device, the V_{L-on} is mainly determined by the minority carrier (electron) injection in our devices. For the device with Ca(acac)₂/Al cathode, lower light V_{L-on} voltage indicates that it is easier for electron injection into the polymer layer by using Ca(acac)₂ as an interfacial layer. This phenomenon is also discussed later in this letter.

To gain insight into the operating mechanism of the devices and the improvement of the device performance, photovoltaic measurements were carried out to compare the open-circuit voltage (which is related to the built-in potential) as well as the short-circuit current of the devices.^{17,18} Since the dark current here is not negligible, we subtract the dark current to show the true photoinduced current.^{17,18} The photovoltaic results are shown in Fig. 4. The V_{oc} for both devices are the same, which is approximately 2.0 V, equal to the difference between work functions of ITO and Ca. On the other hand, the I_{sc} is higher for the device with Ca/Al cathode. This result is rather important in understanding the function of the Ca(acac)₂/Al electrode. The same V_{oc} suggests that the Ca(acac)₂/Al cathode indeed has the same work

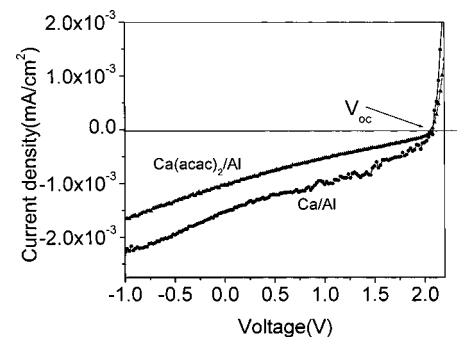


FIG. 4. The I - V curves of the photovoltaic results of both devices. The current shown in the figure is the photocurrent minus the dark current. V_{oc} is similar in both devices suggests that the Ca(acac)₂/Al cathode has a similar work function as the pure Ca cathode.

function as the Ca/Al cathode. Since our devices have been exposed to air for almost 1 min when we transferred the samples from the glove box to vacuum chamber, we believe that there was a small amount of oxygen trapped in the surface of the thin films. In this case, after Al deposited, it was easy to form a very thin layer of Al_2O_3 at the interface. Based on the literature,^{19,20} metal acetylacetonate complexes react readily with metal oxides, and we believe that $\text{Ca}(\text{acac})_2$ exchanges metal with Al or Al_2O_3 . The released Ca^{2+} ions become dopants for the polyfluorene in the interfacial layers. This doping can significantly reduce the electron injection barrier (similar to the Ca electrode) and increase the electron injection.¹⁷ Moreover, compared to devices with Ca/Al cathode, the number of doped ions and the depth of doping were dramatically reduced. Cao *et al.* reported that the reduction in electroluminescence (EL) efficiency is closely related to the doping level and the depth of the doped region.¹⁰ Therefore, in our device with $\text{Ca}(\text{acac})_2/\text{Al}$ cathode, the pronounced improvement of the device performance is also attributed to different doping effect of the ions. Similar cathode systems, using metal chelates and aluminum electrode, have been applied to small molecule-based OLEDs.²¹

The reduction of I_{sc} for the device with $\text{Ca}(\text{acac})_2/\text{Al}$ cathode suggests that the thin $\text{Al}(\text{acac})_2$ layer also behaves as a buffer layer (thin insulating layer) which slightly reduces the I_{sc} . This buffer layer, however, plays an important role in enhancing the PLED performance. It is a wide-gap insulator that can block the holes and, in the meantime, prevent PL quenching due to the Al electrode. Since the device recombination zone is close to the cathode, this buffer layer is particularly important to protect the polymer. As a result, the luminescence efficiency of the device is improved dramatically at the same current density compared to the device with Ca/Al as the cathode, which leads to much higher luminescent efficiency. In the meantime, due to the hole-blocking capability, the accumulated holes can also effectively “pull” the electrons into the polymer layer, which may be the reason that the current is injected into the device at a lower voltage in the device with $\text{Ca}(\text{acac})_2/\text{Al}$ cathode.²² Eventually, at high voltage where tunneling is the dominating charge injection mechanism, the Ca/Al electrode is better for injection of the electrons, which results in higher current density in case of devices with a Ca/Al cathode.

In summary, we have demonstrated a very high efficiency green PLED by using a nanoscale interfacial layer to modify the cathode interface. The $\text{Ca}(\text{acac})_2$ layer is solution processible and, when over-coated with a layer of Al, they form an ideal cathode for the green polyfluorene PLEDs. This layer plays multifunctional roles for the PLEDs: (a) it reduced the electron injection barrier height, (b) it prevents

the quench of luminescence near the cathode, and (c) it behaves as a hole-blocking layer that subsequently might have helped the injection of electrons by Coulomb attraction force.²² As a result, the efficiency of our green devices was improved dramatically. The luminescence efficiency achieved was as high as 28 cd/A. This is the probably the highest efficiency ever achieved in the fluorescence singlet devices, including OLEDs and PLEDs. The adhesion of the $\text{Ca}(\text{acac})_2$ layer to the conjugated polymer has not been optimized as yet. With better material research, we anticipate that even higher device efficiency is possible.

One of the authors (Y.Y.) is indebted to financial support from the Office of Naval Research, Air Force of Scientific Research, and the National Science Foundation. Technical discussions with Dr. Qibing Pei of SRI and Dr. Yijian Shi of UCLA are also deeply appreciated.

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