

1 Dramatic efficiency improvement in phosphorescent organic 2 light-emitting diodes with ultraviolet-ozone treated 3 poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)

4 Amare Benor, Shin-ya Takizawa, Ping Chen, César Pérez-Bolivar, and
5 Pavel Anzenbacher, Jr.^{a)}
6 Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403, USA

7 (Received 24 March 2009; accepted 20 April 2009; published online xx xx xxxx)

8 The treatment of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) films by
9 ultraviolet (UV) light-ozone to improve device efficiency was investigated utilizing two simple
10 phosphorescent organic light-emitting diodes (PHOLEDs) architectures. The maximum external
11 quantum efficiency in the first device increased from 3.5% for the untreated anode to 10.5%, while
12 in the second device comprising an exciton blocking layer increased from 15.8% to 18.5%. The time
13 dependence of the UV-ozone treatment on the performance was studied. The dramatic improvement
14 in the PHOLED performance is attributed to the change in the PEDOT:PSS work function and more
15 balanced charge injection, suggesting promising easy-to-do method to improve PHOLED
16 performance. © 2009 American Institute of Physics. [DOI: 10.1063/1.3132059]

17
18 Organic light-emitting diodes (OLEDs) show promise in
19 a number of applications such as in self-luminant displays,
20 backlights for liquid crystal displays, or sources of ambient
21 light in solid state lighting.¹⁻⁵ This is due to the high lumi-
22 nance and very good power efficiency of the devices at low
23 voltages, which make the OLED technology promising from
24 the perspective of energy conservation. As a result of quan-
25 tum statistics of electron-hole recombination, which pro-
26 duces three triplet excitons per one singlet, the efficiency of
27 OLED is dramatically higher in devices that utilize phospho-
28 rescence in the so-called phosphorescent organic light-
29 emitting diode (PHOLEDs).^{6,7} However, further performance
30 improvements of the PHOLEDs are still in demand, and as a
31 result, additional improvements of the material properties
32 and processing conditions required to achieve a better
33 device performance are pursued. Of the many materials,
34 poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)
35 (PEDOT:PSS) is one of the most extensively used organic
36 material in the realization of PHOLEDs.^{8,9} The PEDOT:PSS
37 has been widely used as a material of choice for the buffer or
38 hole injection layer (HIL) between the indium tin oxide
39 (ITO) anode and the hole transport layers (HTL). Current
40 studies demonstrated that PEDOT:PSS has shown an in-
41 creased device performance compared to other widely used
42 hole injection materials including copper phthalocyanine and
43 has even the potential to entirely replace ITO used as an
44 anode in OLEDs.¹⁰ Furthermore, the easy processability
45 combined with its low cost has resulted in a widespread use
46 in OLEDs, organic photovoltaics, and organic field-effect
47 transistors. With the widespread use of PEDOT:PSS, a num-
48 ber of efforts are under way to investigate and improve its
49 properties. A common method to improve the PEDOT:PSS
50 properties is a chemical treatment either by solvents⁹ or an-
51 ionic surfactants,¹¹ both of which resulted in considerable
52 improvement of the conductivity of the polymer. Recently, a
53 method for a decrease (increase in absolute value) in the
54 work function and enhancement in conductivity of the PE-

DOT:PSS based on UV-ozone treatment was reported.^{12,13} 55
Using this method, a decrease in the work function of the 56
material is of advantage in HILs of PHOLEDs as it lowers 57
the energy barrier for charge injection into the HTL, thus 58
contributing to balanced charge injection. This simple and 59
efficient method did not attract wider attention and its use to 60
improve the efficiency of PHOLED has not been investi- 61
gated. 62

Here, we report the use of UV-ozone exposure of 63
PEDOT:PSS for the efficiency improvement of PHOLEDs. 64
The impact of the UV-ozone plasma treatment of the 65
PEDOT:PSS HIL is demonstrated on two PHOLEDs that 66
differ by the degree of the device optimization and charge 67
balance. Thus, the unoptimized device I comprises of 68
ITO/PEDOT:PSS/4,4'-bis[*N*-(1-naphthyl)-*N*-phenylamino] 69
biphenyl (α -NPD) / 1,3,5-tris(*N*-phenylbenzimidazol- 70
2-yl)benzene (TPBI) doped with 6% Iridium(III)bis(2- 71
phenylpyridinato-*N*,*C*^{2'})acetylacetonate [Ir(ppy)₂(acac)]/ 72
CsF/Al. The device II differs from device I by a more opti- 73
mized charge balance as it comprises an electron/exciton- 74
blocking layer (EBL) of 4,4',4''-tris(*N*- 75
carbazolyl)triphenylamine (TCTA). The device II architec- 76
ture was as follows: ITO/PEDOT:PSS/ α -NPD/TCTA/TPBI: 77
6% Ir(ppy)₂(acac)/CsF/Al (see Fig. 1). The ITO (R_{\square} 78
 $\sim 10 \Omega/\square$) on glass was used as an anode. The device fab- 79
rication was performed by combination of spin-coating (PE- 80
DOT:PSS, Baytron) and resistive evaporation.¹⁴ The outline 81
of the device architectures is shown in Fig. 1. 82

In both PHOLED types (devices I and II), the 83
PEDOT:PSS layers were treated by UV-ozone plasma for a 84
period of time of 2, 4, and 8 min, respectively, and compared 85
to control devices, in which the PEDOT:PSS layer was left 86
untreated. 87

Figure 2 shows the characteristics of device I recorded at 88
0, 2, 4, and 8 min of UV-ozone treatment. As shown in Fig. 89
2(a), the luminous efficiency of the device is significantly 90
improved upon the UV-ozone treatment of the PEDOT:PSS, 91
as compared to the control devices without the UV-ozone 92
treatment. The luminous efficiency of the device increases 93

^{a)}Electronic mail: pavel@bgsu.edu.

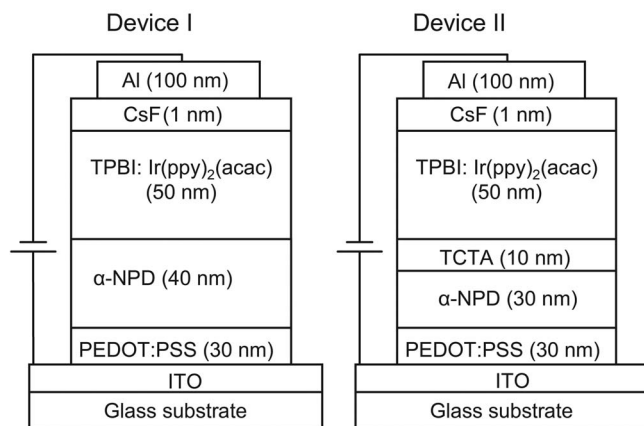


FIG. 1. A schematic cross-section of the two PHOLEDs: device I (left) and device II (right).

94 with the UV-ozone time exposure, i.e., from 12.5 cd/A at 0
95 min to 25 cd/A after an 8 min exposure. Thus, the maximum
96 luminous efficiency was improved by more than 100%. With
97 a prolonged UV-ozone treatment beyond 8 min, the effi-
98 ciency decreases. To get more insight about the device effi-

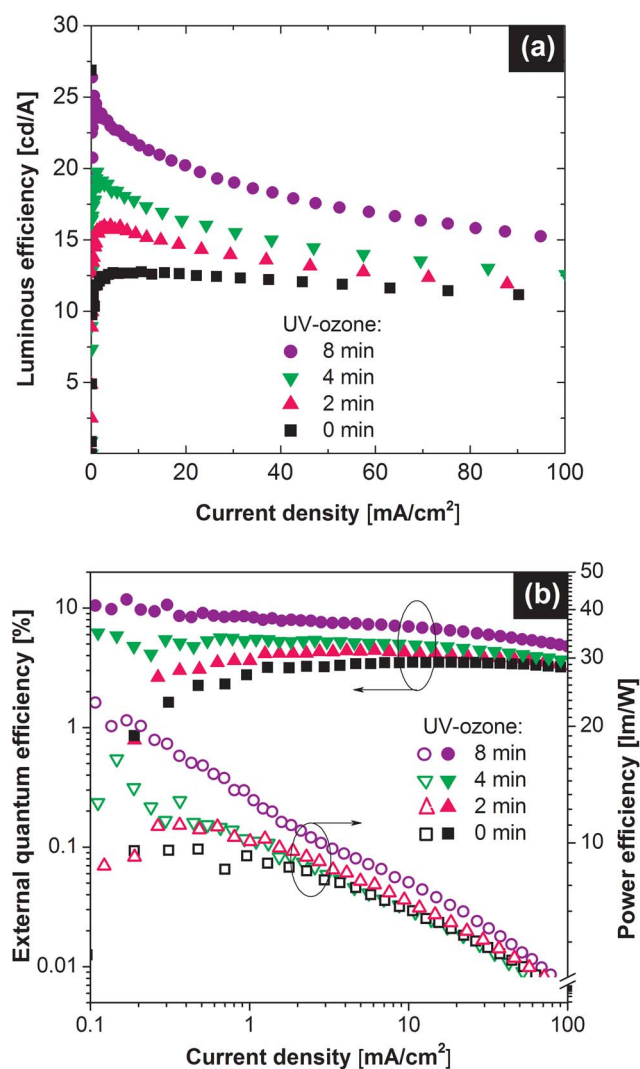


FIG. 2. (Color online) (a) Luminous efficiency-current density characteristics of device I. (b) EQE and power efficiency of device I at 0, 2, 4, and 8 min, respectively, of UV-ozone exposure.

ciency improvement, the external quantum and power effi- 99
ciencies of the devices have been investigated. Figure 2(b) 100
shows the external quantum efficiency (EQE) and power effi- 101
ciency as a function of current density in device I. Here, the 102
performance improvement follows the same trend as that of 103
the luminous efficiency and reaches maximum at 8 min of 104
the UV-ozone exposure. In both cases, Figs. 2(a) and 2(b), 105
the efficiency peaks at 8 min of the UV-ozone exposure. 106
Notably, the maximum EQE of the device increased from 107
3.5% to 10.5% as a result of just the 8 min UV-ozone treat- 108
ment. The overall improvement in EQE by threefold com- 109
pared to the control device was achieved without using ad- 110
ditional layers or a dopant. 111

Device I, perhaps due to inherent charge imbalance, ap- 112
pears to be easy to improve. Naturally, we were curious 113
whether an advanced device with higher efficiency could 114
also be improved using the same method. To investigate the 115
applicability of this method, improved devices comprising an 116
additional EBL of TCTA (10 nm) sandwiched between the 117
 α -NPD HTL and emissive layer of TPBI doped with 6% of 118
Ir(ppy)₂(acac) were fabricated (devices II). TCTA is used 119
here as an EBL, expected to prevent triplet exciton diffusion 120
from the emissive layer to the adjacent α -NPD layer of lower 121
triplet energy.¹⁵ The dramatic improvement in the perfor- 122
mance of the device with TCTA EBL layer suggests that the 123
charge recombination zone in the devices utilizing untreated 124
PEDOT:PSS is located closer to the α -NPD layer. 125

Figure 3 shows characteristics of device II recorded at 0 126
and 8 min of UV-ozone exposure. When the control devices 127
I and II (with untreated HIL) are compared, device II with 128
TCTA EBL displays luminance efficiency of 57 cd/A compar- 129
ed to 12.5 cd/A recorded for device I, which corresponds 130
to maximum EQEs of ca. 16% and 4%, respectively. Al- 131
though the incorporation of the TCTA layer in device II in- 132
creases the device efficiency, the UV-ozone treatment of the 133
PEDOT:PSS HIL in device II resulted in a further improved 134
device performance, following the same trend observed for 135
device I (Fig. 3). Thus, the 8 min UV-ozone treatment of the 136
PEDOT:PSS in device II resulted in a maximum luminous 137
efficiency of 68 cd/A compared to the control device that 138
showed only 57 cd/A. Furthermore, the EQE and power effi- 139
ciency of the devices were found likewise improved [Fig. 140
3(b)]. The maximum EQE of device II at 8 min UV-ozone 141
treatment is 18.5% compared to the 15.8% recorded for de- 142
vice II without UV-ozone treatment, corresponding to an in- 143
crease of 17%. 144

From the hole-only devices and a sandwich device uti- 145
lizing only PEDOT:PSS, one can see that the conductivity of 146
the PEDOT:PSS layer increases compared to the untreated 147
HIL. At the same time, the hole current in the OLEDs was 148
found to decrease with the UV-ozone treatment. This is ex- 149
plained by the decrease from -5.2 to -5.4 eV in the 150
PEDOT:PSS work function determined by x-ray photoelec- 151
tron and Raman spectroscopy to be 0.2–0.25 eV (Refs. 12 152
and 13) and simultaneous increase in conductivity.¹² As a 153
result, the barrier for hole injection from the ITO anode into 154
the PEDOT:PSS is increased while the barrier for hole trans- 155
port from PEDOT:PSS to α -NPD is decreased. As a result, 156
we observe decrease in the overall current density in the 157
devices utilizing the UV-ozone treated PEDOT:PSS. The im- 158
portant fact, however, is that due to aforementioned drop in 159
the current density upon UV-ozone treatment, the maximum 160

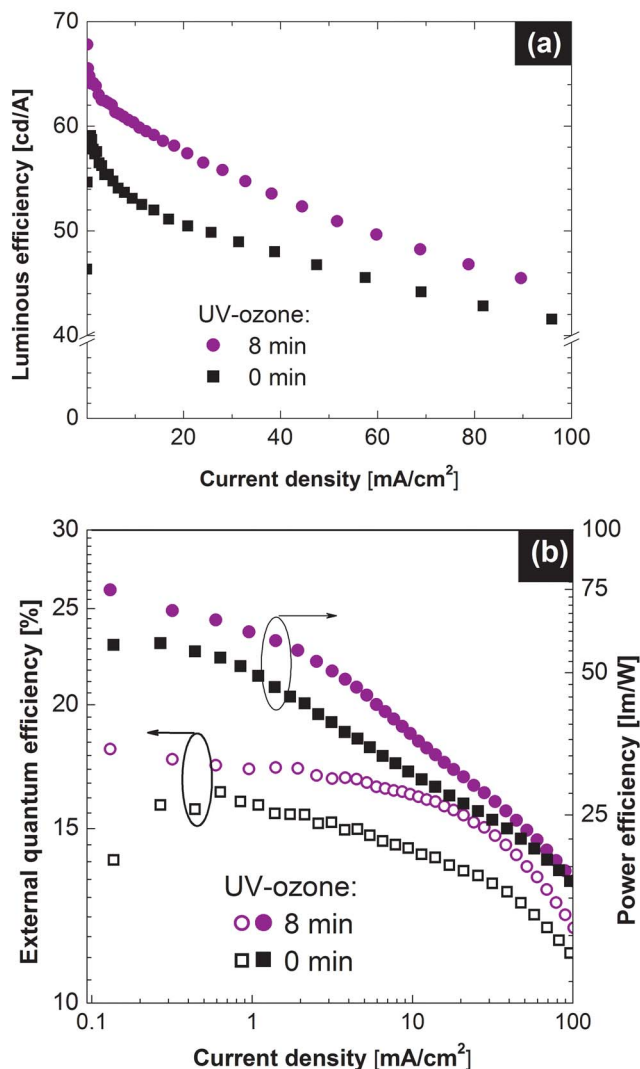


FIG. 3. (Color online) (a) Luminous efficiency-current density characteristics of device II. (b) EQE and power efficiency of device II at 0 and 8 min of UV-ozone exposure.

luminance is achieved at significantly lower current densities compared to the untreated ones. Since the device efficiency is inversely proportional to current density, the actual efficiency of the devices is dramatically improved. Specifically, the untreated version of device I at max luminance displayed current density of 2000 mA/cm^2 , while the UV-ozone treated at 8 min displayed only 375 mA/cm^2 . Similarly, the untreated version of device II displayed 950 mA/cm^2 , while the treated one displayed 520 mA/cm^2 . Thus, the UV-ozone treatment of the PEDOT:PSS HIL results in more balanced charge distribution and a better charge utilization in the devices.

The UV-ozone induced changes may be both chemical and physical, resulting from oxidation along with possible

re-alignment of the polymer chains due to UV excitation and partial etching of the PEDOT:PSS surface known to increase surface roughness as demonstrated previously for oxygen-mediated reactive ion etching, respectively.⁸ The absence of further improvement beyond 8 min of UV-ozone exposure might be due to the saturation in change in the work function of the material as a function of time.¹² However, our observations suggest that the partial removal of the PEDOT:PSS material and thinning of the polymer anode with increased probability of pinhole defects are also contributing to this effect.

In summary, we have studied the utility of UV-ozone exposure of the PEDOT:PSS hole-injection layer for the efficiency improvement of PHOLEDs. This study shows that a dramatic increase in the device efficiency may be observed in unoptimized devices. We have demonstrated a 100% increase in the device performance in simple, two-layer green PHOLEDs. Here, a threefold EQE increase from 3.5% to 10.5% was realized without any changes to the device architecture. In the case of the optimized devices the increase in the performance is modest, typically 2.5%–2.8% in the additional increase in the EQE. Nevertheless, a respectable increase in EQE from 15.8% to 18.5% was realized, without any change in the device architecture as well. The improvement of the device performance seems to be mainly originated from the decrease (increase in absolute value) in the work function and conductivity of the PEDOT:PSS film by UV-ozone exposure. This simple and versatile method can be used as an easy-to-do method to improve the performance of simple PHOLEDs.

¹K. Müllen and U. Scherf, *Organic Light Emitting Devices: Synthesis, Properties and Applications* (Wiley, Weinheim, 2006).

²K. Walzer, B. Maennig, M. Pfeiffer, and K. Leo, *Chem. Rev. (Washington D.C.)* **107**, 1233 (2007).

³Z. Kafafi, *Organic Electroluminescence*, (CRC, Boca Raton, 2005).

⁴B. D'Andrade, *Nat. Photonics* **1**, 33 (2007).

⁵P. Anzenbacher, Jr., V. Montes, and S. Takizawa, *Appl. Phys. Lett.* **93**, 163302 (2008).

⁶H. Yersin, *Highly Efficient OLEDs with Phosphorescent Materials* (Wiley, Weinheim, 2008).

⁷M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, *Nature (London)* **395**, 151 (1998).

⁸Y. Zhou, Y. Yuan, J. Lian, J. Zhang, H. Pang, L. Cao, and X. Zhou, *Chem. Phys. Lett.* **427**, 394 (2006).

⁹J. Ouyang, Q. Xu, C.-W. Chu, Y. Yang, G. Li, and J. Shinar, *Polymer* **45**, 8443 (2004).

¹⁰K. Fehse, K. Walzer, K. Leo, W. Lövenich, and A. Elschner, *Adv. Mater. (Weinheim, Ger.)* **19**, 441 (2007).

¹¹B. Fan, X. Mei, and J. Ouyang, *Macromolecules* **41**, 5971 (2008).

¹²C. Tengstedt, A. Kancirzewska, M. P. Jong, S. Braun, W. R. Salaneck, and M. Fahlman, *Thin Solid Films* **515**, 2085 (2006).

¹³Y.-J. Lin, F.-M. Yang, C.-Y. Huang, W.-Y. Chou, J. Chang, and Y.-C. Lien, *Appl. Phys. Lett.* **91**, 092127 (2007).

¹⁴V. Montes, R. Pohl, J. Shinar, and P. Anzenbacher, Jr., *Chem.-Eur. J.* **12**, 4523 (2006).

¹⁵S. H. Kim, J. Jang, K. S. Yook, and J. Y. Lee, *Appl. Phys. Lett.* **92**, 023513 (2008).