[Article]

doi: 10.3866/PKU.WHXB201203273

www.whxb.pku.edu.cn

利用Cs基衍生物作为n型掺杂剂改善蓝色有机发光二极管的效率

申利莹¹ 吴晓明^{1,*} 华玉林¹ 董木森¹ 印寿根¹ 郑加金²

(¹天津理工大学材料科学与工程学院, 显示材料与光电器件教育部重点实验室, 光电材料与器件天津市重点实验室, 天津 300384; ²南京邮电大学光电工程学院, 南京 210003)

摘要: 利用两种Cs基衍生物碳酸铯(Cs_2CO_3)和醋酸铯(CH_3COOCs)作为n型掺杂剂掺入到一种新型的电子传输材料2,9-二(2-萘基)-4,7-二苯基-1,10-菲咯啉(NBPhen)中来提高有机发光二极管(OLEDs)的效率. 实验结果表明: 器件的驱动电压明显降低, 并且优化后得到的Cs基n型掺杂器件(ITO/ β -NPB/CBP:5%(w)N-BDAVB/ NBPhen/NBPhen: Cs_2CO_3 (or CH_3COOCs)/Al)呈现出较好的电致发光性能, 在14 V时电流密度分别为551.80和527.88 $\text{mA}\cdot\text{cm}^{-2}$, 对应的亮度分别达到39750和39820 $\text{cd}\cdot\text{m}^{-2}$, 电流效率在亮度为10000 $\text{cd}\cdot\text{m}^{-2}$ 时分别为14.60 $\text{cd}\cdot\text{A}^{-1}$ (Cs_2CO_3 掺杂)和14.40 $\text{cd}\cdot\text{A}^{-1}$ (CH_3COOCs 掺杂), 这些参数明显优于传统器件的发光性能(ITO/ β -NPB/CBP:5%(w)N-BDAVB/NBPhen/ Cs_2CO_3 /Al, 其在14 V时电流密度为312.39 $\text{mA}\cdot\text{cm}^{-2}$, 对应的亮度为25190 $\text{cd}\cdot\text{m}^{-2}$; 电流效率在亮度为10000 $\text{cd}\cdot\text{m}^{-2}$ 时为9.45 $\text{cd}\cdot\text{A}^{-1}$). 此外, 基于有机半导体掺杂原理和器件的能级结构对n型掺杂器件效率提高的原因进行了分析.

关键词: 有机发光二极管; 碳酸铯; 醋酸铯; n型电子传输层; 电致发光性能

中图分类号: O644

Improving the Efficiency of Blue Organic Light-Emitting Diodes by Employing Cs-Derivatives as the n-Dopant

SHEN Li-Ying¹ WU Xiao-Ming^{1,*} HUA Yu-Lin¹ DONG Mu-Sen¹
YIN Shou-Gen¹ ZHENG Jia-Jin²

(¹Key Laboratory of Display Materials and Photoelectric Devices, Ministry of Education, Tianjin Key Laboratory of Photoelectric Materials and Devices, School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, P. R. China;

²College of Optoelectronics Engineering, Nanjing University of Posts and Telecommunications, Nanjing 210003, P. R. China)

Abstract: The efficiency of organic light-emitting diodes (OLEDs) was markedly improved using the novel electron transporting material 2,9-bis(naphthalen-2-yl)-4,7-diphenyl-1,10-phenanthroline (NBPhen) doped with Cs-derivatives including cesium carbonate (Cs_2CO_3) and cesium acetate (CH_3COOCs) as the n-type dopant. The operating voltage of devices containing these materials as an n-type electron transporting layer (n-ETL) was significantly reduced. Optimized devices with Cs_2CO_3 -doped or CH_3COOCs -doped n-ETL (ITO/ β -NPB/CBP:5%(w) N-BDAVB/NBPhen/NBPhen: Cs_2CO_3 (or CH_3COOCs)/Al) exhibited excellent electroluminescent performance with current densities of 551.80 and 527.88 $\text{mA}\cdot\text{cm}^{-2}$ at 14 V, corresponding brightnesses of 39750 and 39820 $\text{cd}\cdot\text{m}^{-2}$, and current efficiencies of 14.60 and 14.40 $\text{cd}\cdot\text{A}^{-1}$ at 10000 $\text{cd}\cdot\text{m}^{-2}$, respectively. These results were superior to that of conventional device (ITO/ β -NPB/CBP:5%(w)N-BDAVB/NBPhen/ Cs_2CO_3 /Al) without an n-ETL, which exhibited a current density of 312.39

Received: December 28, 2011; Revised: March 27, 2012; Published on Web: March 27, 2012.

*Corresponding author. Email: wxm@mail.nankai.edu.cn; Tel: +86-13752542262.

The project was supported by the National Natural Science Foundation of China (60906022, 60676051), Natural Science Foundation of Tianjin, China (10JCYBJC01100), Scientific Developing Foundation of Tianjin Education Commission, China (2011ZD02), and Jiangsu Natural Science Development Foundation for University, China (09KJB140006).

国家自然科学基金(60906022, 60676051), 天津市自然科学基金(10JCYBJC01100), 天津市教委科学发展基金(2011ZD02)和江苏省高校自然科学基金(09KJB140006)资助项目

$\text{mA} \cdot \text{cm}^{-2}$ at 14 V, corresponding brightness of $25190 \text{ cd} \cdot \text{m}^{-2}$, and current efficiency of $9.45 \text{ cd} \cdot \text{A}^{-1}$ at $10000 \text{ cd} \cdot \text{m}^{-2}$. In addition, the reason for the increase in the efficiency of *n*-type doped devices has been analyzed based on the concept of the doping mechanism in organic semiconductors and the energy level scheme of the devices.

Key Words: Organic light-emitting diodes; Cs_2CO_3 ; CH_3COOCs ; *n*-Type electron transporting layer; Electroluminescent performance

1 Introduction

The efficient blue light emission with lower operating voltage and higher brightness is crucial to accomplishing excellent performance of white organic light-emitting diodes (WOLEDs) for the flat panel display applications as well as for the general illumination light source applications,^{1,2} which is due to the fact that an efficient blue emitter could be used as excited source for down conversion layers^{3,4} or one of the three primary colors.^{5–7} In order to achieve excellent characteristics of blue emission, a number of investigations have been actualized in the field of applying new materials^{8–10} and optimizing the structures of blue emitting layer (BEML),^{11,12} and the other efficient approaches are utilizing the *p*-type or *n*-type dopants doped into charge transport layers to form the *p/n*-type doped transport layers.^{13,14} Until recently, various *n*-type dopants (*n*-dopant), including low-work-function alkaline metals such as lithium (Li)¹⁴ and cesium (Cs),¹⁵ alkaline metal carbonates such as cesium carbonate (Cs_2CO_3)¹⁶ and rubidium carbonate (Rb_2CO_3),¹⁷ alkaline metal hydroxide such as cesium hydroxide (CsOH),¹⁸ alkaline metal nitride such as cesium azide (CsN_3),¹⁹ and alkaline metal quinoline such as 8-hydroxyquinolinolato-lithium (LiQ)²⁰, have been doped into the electron transport layers to produce the effect of *n*-type doping, which could efficiently enhance the electron injection ability at cathode/organic interfaces and increase electron conductivity of the electron transporting layer (ETL).

In this article, we would study the effect of the technology of *n*-type doped (*n*-doped) on the efficiency of blue OLEDs (BOLEDs). Firstly, we introduce a novel electron transporting material 2,9-bis(naphthalen-2-yl)-4,7-diphenyl-1,10-phenanthroline (NBPhen) doped with Cs_2CO_3 to form the *n*-type electron transporting layer (*n*-ETL) for the BOLEDs. NBPhen is a derivative of 4,7-diphenyl-1,10-phenanthroline (BPhen), however, the NBPhen shows a better thermal stability than BPhen, because the glass transition temperature (T_g) and thermogravimetric analyzer temperature (T_{TGA}) of NBPhen (105 and 370 °C (0.5% mass loss) are higher than those of BPhen (63 and 260 °C (0.5% mass loss)). Secondly, we investigate another Cs-derivative cesium acetate (CH_3COOCs) doped into the NBPhen to form the *n*-ETL, which exhibits a less-degassed procedure with low deposition temperature compared with Cs_2CO_3 (its melting point of 194 °C is lower than that of Cs_2CO_3 with 610 °C). Finally, the electroluminescent (EL) performance of Cs_2CO_3 -doped and CH_3COOCs -doped blue fluorescent devices

are compared with the conventional devices without the *n*-dopant, and relative analysis could also be put forward.

2 Experimental

Three types of devices including the conventional device (A), the Cs_2CO_3 -doped devices (B), and the CH_3COOCs -doped devices (C) fabricated in this study were as follows: device A, ITO/ β -NPB/CBP:5% (w)N-BDAVBi/NBPhen/ Cs_2CO_3 /Al; devices B, ITO/ β -NPB/CBP:5% (w)N-BDAVBi/NBPhen/NBPhen: Cs_2CO_3 /Al; devices C, ITO/ β -NPB/CBP:5% (w)N-BDAVBi/NBPhen/NBPhen: CH_3COOCs /Al.

For all devices, 40-nm-thick *N,N'*-bis(naphthalen-2-yl)-*N,N'*-bis(phenyl)-benzidine (β -NPB) and 30-nm-thick *N,N'*-dicarbazolyl-4,4'-biphenyl (CBP) doped with N-BDAVBi (doping concentration of 5% (w)) were used as hole transporting layer (HTL) and BEML, respectively. Next followed the ETL and electron injection layer (EIL) comprised of 20-nm-thick NBPhen and 1-nm-thick Cs_2CO_3 in device A. Then, in devices B and C, a 10-nm-thick NBPhen and the 10-nm-thick NBPhen doped with Cs_2CO_3 or CH_3COOCs (mass doping ratios of 4:1, 2:1, and 1:1) were employed as ETL and *n*-ETL, respectively. Finally, a 120-nm-thick cathode layer of aluminum (Al) was patterned using a shadow mask for all the devices with active area of 3 mm×3 mm. All these layers were deposited in sequence according to the device structures onto a precleaned ITO glass substrate by thermal evaporation in BOC Edwards Auto 500 thermal evaporation coating system (made in Germany & England) at a pressure of about 1×10^{-4} Pa. The deposition rates and thicknesses of the various layers were monitored using a quartz crystal oscillator. The evaporating rates were 0.1–0.2 nm·s^{−1} for organic layers and Cs-derivatives, and 0.3 nm·s^{−1} for the Al cathode. The brightness–voltage–current density (*B–V–J*) characteristics of the devices were simultaneously measured using a PR650 spectra scan spectrometer with a Keithley model 2400 programmable voltage-current source (made in America). All the measurements were carried out at room temperature in air without encapsulation.

The chemical structures of materials used in this experiment are shown in Fig.1, and the organic materials used in this work are purchased from the Aldrich with the purity of 99%.

3 Results and discussion

We firstly study the effect of the different mass ratios of Cs_2CO_3 doped into NBPhen on the EL performance of

Fig.1 Chemical structures of materials used in this experiment

BOLEDs, the comparisons for B - V - J characteristics of the Cs_2CO_3 -doped devices B with the conventional device A are shown in Fig.2. The devices B exhibit a higher current density compared with the conventional device A at the same operating voltage, because doping of Cs_2CO_3 in the NBPhen layer could effectively improve the injection and transport of electrons according to the following concept of doping in organic semiconductors,^{16,21,22} the Cs_2CO_3 will decompose into Cs_2O during thermal evaporation according to the following reaction:²³

Cs_2O behaves as a kind of *n*-type semiconductor with an estimated bandgap of 1.9 eV.²⁴ Therefore, a charge transfer from electron donor Cs_2O to matrix NBPhen induces generation of free charge carriers, resulting in an increase of electrical conductivity for the *n*-ETL. Furthermore, the Fermi level of the NBPhen doped with Cs_2O layer could be shifted towards the transport states, leading to efficient carrier's tunnel injection across Al/*n*-ETL interface. Namely, an effective *n*-doping could be produced. From Fig.2, it could be obviously found that the maximum brightness of $39750 \text{ cd} \cdot \text{m}^{-2}$ has been obtained at 14 V in the devices B with the optimum NBPhen: Cs_2O mass doping ratio of 2:1, whereas it is $25190 \text{ cd} \cdot \text{m}^{-2}$ for conventional device A at 14 V.

However, Cs_2CO_3 need a higher evaporating temperature (around 500 °C under the vacuum), which is much higher than that of organic materials NBPhen. As a result, the co-deposition of NBPhen and Cs_2CO_3 in the thermal evaporation chamber could result in the out-gassing of the organic molecules at-

tached on the chamber wall during the evaporation, and the evaporation chamber may require frequent cleaning accordingly. In order to solve the complexity of manufacturing process for these devices, another Cs-derivative CH_3COOCs with lower deposition temperature has been investigated, and it is doped into NBPhen to form the *n*-ETL instead of the Cs_2CO_3 .

Furthermore, to optimize the doping ratio of CH_3COOCs -doped NBPhen, we also fabricated a series of CH_3COOCs -doped devices C. The B - V - J characteristics of the devices C with different mass doping ratios in the *n*-ETL are shown in Fig.3. It is also illustrated that the devices C with CH_3COOCs -doped NBPhen as *n*-ETL present a lower operating voltage and a higher brightness compared with those of the device A, and the doping ratio of CH_3COOCs -doped NBPhen could finally be optimized to 2:1. The decrease in the operating voltage for the devices C is attributed to producing an effect of *n*-doping similarly with Cs_2CO_3 -doped *n*-ETL. In other words, the active alkali metal Cs can be achieved by thermal decomposition during evaporation of alkali metal acetates CH_3COOCs according to the following reaction:²⁵

Doping Cs in electron transport layer NBPhen would occur the electron transfer from Cs to NBPhen because Cs is a well-known *n*-doping material with a work function of 2.3 eV,¹⁹ which is energetically above the lowest unoccupied molecular orbital (LUMO) level of 3.2 eV for NBPhen. Thereby, the structure of CH_3COOCs -doped with NBPhen is suitable for producing an effective *n*-doping effect.^{18,19} The devices C

Fig.2 B - V - J characteristics of the devices A and B

Fig.3 B - V - J characteristics of the devices A and C

Fig.4 η - B characteristics of the devices A and B (a) and the devices A and C (b)

would be capable of achieving much higher current density and EL output at the same operating voltage compared with those of the device A. For instance, the optimum device C (2:1) presents the maximum brightness of 39820 cd·m⁻² at the current density of 527.88 mA·cm⁻² (14 V), which is greatly improved by 58% (brightness) and 69% (current density) compared with the brightness of 25190 cd·m⁻² at the current density of 312.39 mA·cm⁻² (14 V) for the device A. The turn-on voltage of the optimum devices C has been lowered to 3.4 V compared with the value of 4.9 V in device A.

From Fig.4, the current efficiency (η) of the Cs₂CO₃-doped devices B and CH₃COOCs-doped devices C are markedly higher than that of the conventional device A, and the doping ratio is optimized to 2:1. At the brightness of 10000 cd·m⁻², the current efficiencies of optimum devices B and C are 14.60 and 14.40 cd·A⁻¹, respectively, which are improved by 54% and 52% compared with the conventional device A (9.45 cd·A⁻¹ at 10000 cd·m⁻²). These results clearly indicated that the current efficiency of BOLEDs could be markedly improved by co-evaporating NBPhen with Cs₂CO₃ or CH₃COOCs as *n*-ETL, and CH₃COOCs with lower deposition temperature could be considered as an alternative for the effective *n*-dopant besides Cs₂CO₃.

Finally, the further explanation of the increase in current efficiency for *n*-doped BOLEDs compared with the conventional device A is analyzed based on the energy level scheme of devices. Fig.5 shows the schematic energy level diagram of devices

Fig.5 Schematic energy level (unit in eV) diagram of devices B and C

es B and C. As shown in Fig.5, for device A (the devices A, B, and C have the same energy levels of ITO/HTL/BEML/ETL, besides that of the *n*-ETL), we could conclude that the holes may be directly trapped at the doping site of N-BDAVB due to existing a lower injection barrier about 0.1 eV at the NPB/N-BDAVB interface compared with that of 0.5 eV for the NPB/CBP interface. However, the electron injection barriers are 0.6 and 0.5 eV for the interfaces of NBPhen/CBP and NBPhen/N-BDAVB, respectively. Therefore, the holes can be easily injected into BEML compared to electrons. At the same time, considering the preferable hole transport property of N-BDAVB,¹¹ the holes would become the majority carriers in BEML accordingly. As a result, the conventional device A exhibits a lower current efficiency due to the unbalanced number of carriers between holes and electrons. However, for the *n*-doped devices B and C, we have demonstrated that the ability of electrons injection and transport could be markedly increased by employing Cs₂CO₃ or CH₃COOCs as *n*-dopant, and the magnitude of electron injected into BEML would increase correspondingly. As a result, the carrier injection would be balanced and the combination rate in the BEML region should be improved, then the current efficiency of *n*-doped OLEDs could be greatly enhanced.

4 Conclusions

In summary, we demonstrate that the EL performance of BOLEDs could be markedly increased by employing Cs₂CO₃ or CH₃COOCs as *n*-dopant doped into a novel electron transporting material NBPhen to produce an effective effect of *n*-type doping. Moreover, the experiment results indicate that CH₃COOCs with lower deposition temperature could replace Cs₂CO₃ as an effective *n*-dopant, which would facilitate the manufacturing process of co-evaporating for the temperature difference between organic materials and inorganic materials. The optimum devices B and C exhibit higher current efficien-

cies of 14.60 and 14.40 $\text{cd} \cdot \text{A}^{-1}$ at the brightness of 10000 $\text{cd} \cdot \text{m}^{-2}$, respectively, which are improved by 54% and 52% compared with the device A (9.45 $\text{cd} \cdot \text{A}^{-1}$ at 10000 $\text{cd} \cdot \text{m}^{-2}$). The results obviously reveal that introducing the *n*-ETL (NBphen: Cs-derivative) in OLEDs not only efficiently reduces the electron injection barrier, but also powerfully increases the carrier density for current conduction. Therefore, a higher efficiency for *n*-doped devices could be achieved based upon the balance of carrier injection and the improvement of the carrier combination rate in the BEML region.

References

- (1) Kamtekar, K. T.; Monkman, A. P.; Bryce, M. R. *Adv. Mater.* **2010**, *22*, 572.
- (2) D'Andrade, B. W.; Forrest, S. R. *Adv. Mater.* **2004**, *16*, 1585.
- (3) Ji, W. Y.; Zhang, L. T.; Gao, R. X.; Zhang, L. M.; Xie, W. F.; Zhang, H. Z.; Li, B. *Opt. Express*. **2008**, *16*, 15489.
- (4) Yuan, Y. B.; Li, S.; Wang, Z.; Xu, H. T.; Zhou, X. *Opt. Express*. **2009**, *17*, 1577.
- (5) Zhang, Z. Q.; Wang, Q.; Dai, Y. F.; Liu, Y. P.; Wang, L. X.; Ma, D. G. *Org. Electron.* **2009**, *10*, 491.
- (6) Qi, X. F.; Srotsky, M.; Forrest, S. *Appl. Phys. Lett.* **2008**, *93*, 193306.
- (7) Ma, T.; Jiang, Y. D.; Yu, J. S.; Lou, S. L.; Li, L.; Zhang, Q. *Acta Phys. -Chim. Sin.* **2008**, *24*, 977. [马涛, 蒋亚东, 于军胜, 娄双玲, 李璐, 张清. 物理化学学报, **2008**, *24*, 977.]
- (8) Su, S. J.; Gonmori, E.; Sasabe, H.; Kido, J. *Adv. Mater.* **2008**, *20*, 4189.
- (9) Huang, H.; Fu, Q.; Zhuang, S. Q.; Liu, Y. K.; Wang, L.; Chen, J. S.; Ma, D. G.; Yang, C. L. *J. Phys. Chem. C* **2011**, *115*, 4872.
- (10) Wang, Z. Q.; Xu, C.; Wang, W. Z.; Duan, L. M.; Li, Z.; Zhao, B. T.; Ji, B. M. *New J. Chem.* **2012**, *36*, 662.
- (11) Wang, Y.; Hua, Y. L.; Wu, X. M.; Zhang, L. J.; Hou, Q. C.; Guan, F.; Zhang, N.; Yin, S. G.; Cheng, X. M. *Org. Electron.* **2008**, *9*, 692.
- (12) Seo, J. H.; Lee, K. H.; Seo, B. M.; Koo, J. R.; Moo, S. J.; Park, J. K.; Yoon, S. S.; Kim, Y. K. *Org. Electron.* **2010**, *11*, 1605.
- (13) Gebeyehu, D.; Walzer, K.; He, G.; Pfeiffer, M.; Leo, K.; Brandt, J.; Gerhard, A.; Stöbel, P.; Vestweber, H. *Synth. Met.* **2005**, *148*, 205.
- (14) Kido, J.; Matsumoto, T. *Appl. Phys. Lett.* **1998**, *73*, 2866.
- (15) Oyamada, T.; Sasabe, H.; Adachi, C.; Murase, S.; Tominaga, T.; Maeda, C. *Appl. Phys. Lett.* **2005**, *86*, 033503.
- (16) Wu, C. I.; Lin, C. T.; Chen, Y. H.; Chen, M. H.; Lu, Y. J.; Wu, C. C. *Appl. Phys. Lett.* **2006**, *88*, 152104.
- (17) Leem, D. S.; Kim, S. Y.; Kim, J. J.; Chen, M. H.; Wu, C. I. *Electrochem. Solid-State Lett.* **2009**, *12*, 8.
- (18) Wang, F. X.; Xiong, T.; Qiao, X. F.; Ma, D. G. *Org. Electron.* **2009**, *10*, 266.
- (19) Yook, K. S.; Jeon, S. O.; Min, S. Y.; Lee, J. Y.; Yang, H. J.; Noh, T.; Kang, S. K.; Lee, T. W. *Adv. Funct. Mater.* **2010**, *20*, 1797.
- (20) Ma, J. W.; Xu, W.; Jiang, X. Y.; Zhang, Z. L. *Synth. Met.* **2008**, *158*, 810.
- (21) Pfeiffer, M.; Leo, K.; Zhou, X.; Huang, J. S.; Hofmann, M.; Werner, A.; Nimoth, J. B. *Org. Electron.* **2003**, *4*, 89.
- (22) Walzer, K.; Maennig, B.; Pfeiffer, M.; Leo, K. *Chem. Rev.* **2007**, *107*, 1233.
- (23) Chen, S. Y.; Chu, T. Y.; Chen, J. F.; Su, C. Y.; Chen, C. H. *Appl. Phys. Lett.* **2006**, *89*, 053518.
- (24) Band, A.; Albu-Yaron, A.; Livneh, T.; Cohen, H.; Feldman, Y.; Shimon, L.; Popovitz-Biro, R.; Lyahovitskaya, V.; Tenne, R. *J. Phys. Chem. B* **2004**, *108*, 12360.
- (25) Ganzorig, C.; Fujihira, M. *Appl. Phys. Lett.* **2004**, *85*, 4774.