以聚乙烯亚胺作为电子注入层的有机-无机复合发光器件

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摘要 聚乙烯亚胺(PEIE)能有效地提高有机-无机复合发光器件中氧化锌对发光聚合物特别是具有较低电子亲和势蓝色发光聚合物的电子注入效率, 以PEIE作为电子注入层的有机-无机复合发光器件具有与采用低功函数金属阴极的传统结构器件接近的发光效率. 有机-无机复合磷光器件的外量子效率为19.1%, 为目前该类器件的最高效率.

关键词 有机-无机复合发光器件, 电子注入层, 发光聚合物, 溶液加工方法制备小分子材料发光层

有机发光器件(OLEDs)在平板显示和固态照明等领域具有广泛的应用前景. 经过20多年的发展, 作为有机电子学领域首先应用于实用产品的技术之一, OLEDs备受学术界与工业界的重视^[1,2]. 当前OLEDs的稳定性与成本是限制其大规模产业化的关键问题. 在传统结构的OLEDs中, 用于注入电子的低功函数金属材料(如Ca, Ba等)极易受到环境中水与氧气的侵蚀, 器件需要严格封装才能正常工作^[3]. 研究表明采用金属氧化物(如TiO₂^[4], ZnO^[5-7], ZrO₂^[8], MgO, HfO₂^[9])电子注入层可以显著地提高器件的稳定性, 但金属氧化物与发光层之间较大的电子注入势垒严重地限制了电子注入效率. 不同研究小组报道采用自组装偶联材料^[10,11]、聚电解质^[12,13]、金属无机材料(如Cs₂CO₃^[5,14]和Ba(OH)₂^[15])、离子液体^[16]、碳纳米管^[17]等电子注入材料来提升电子注入效率. 采用Cs₂CO₃作为电子注入层、聚芴衍生物作为发光层的有机-无机复合发光器件的外量子效率为7%~9%^[14,15], 是迄今为止该类型器件所报道的最高效率. 但Cs₂CO₃极易吸潮, 很难在日常实验条件下应用, 另外具有较强结晶性的Cs₂CO₃与有机材料之间较大

的表面能差异导致有机发光材料薄膜形貌发生改变^[18], 在器件中产生针孔和泄漏电流. Bolink等人^[19]的研究表明在Cs₂CO₃层上制备的磷光发光层存在结晶现象, 器件无法正常工作. 为了降低Cs₂CO₃对有机发光层形貌的影响, 该研究小组采用将Cs₂CO₃共混在ZnO层中的方法来制备有机-无机复合磷光器件, 但器件的最大发光效率仅为15 cd A⁻¹, 低于采用相同发光层传统结构器件的效率^[20]. 为了进一步提高有机-无机复合磷光器件的发光效率, 电子注入材料不仅需要具有优越的电子注入和空穴/激子阻挡能力, 而且需与发光层形成良好的界面^[21]. 聚电解质材料作为界面修饰层可以有效降低金属氧化物层对有机发光层形貌的影响, 但目前应用在有机-无机复合发光器件中的具有共轭主链结构的聚电解质材料, 虽然具有较好的载流子传输特性, 但其较低能量的三线激发态可能对磷光材料激发态产生猝灭作用^[22]. 绝缘聚合物材料(如聚环氧乙烷(PEO)^[23,24]、聚乙二醇(PEG)^[25]、PEIE^[26,27]等)可以提高器件的电子注入效率, 同时这些材料还具备以下优点: (1) 在空气中比较稳定且易溶于水和酒精, 可形成均匀的超薄薄膜;

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Lei Y, Wang R X, Fan C J, et al. Hybrid organic-inorganic light-emitting diodes based on a polythyleneimine Interlayer (in Chinese). Chin Sci Bull, 2016, 61: 740-747, doi: 10.1360/N972015-00065

(2) 能够同有机发光层形成良好的界面; (3) 足够大的激发态能量可以将载流子复合形成的激发态限制在发光层内部; (4) 动态离子的缺失可减少甚至消除对有机发光层的掺杂作用, 有利于器件的驱动稳定性. 综上所述, 这些聚合物材料适合在有机-无机复合发光器件中作为电子注入层, 提高器件的发光效率.

我们报道加入PEIE层能够有效地提高有机-无机复合发光器件中ZnO层对发光层的电子注入效率, 基于PEIE电子注入层的有机-无机复合发光器件具有与采用低功函数金属阴极的传统结构发光器件接近的发光效率. 此外, 还研究了基于溶液加工方法制备的小分子材料发光层的有机-无机复合磷光器件, 器件的最大发光效率可达 64 cd A^{-1} .

1 实验

分别以聚(2-甲氧基, 5-(2'乙基-己氧基))-对苯乙炔(MEH-PPV)、苄-三苯胺共聚物(PFA)、4,4',4"-三(N-咔唑基)三苯胺(TCTA):1,3-双((4-叔丁基苯基)-1,3,4-噁二唑基)亚苯基(OXD-7):三(2-3-(对二甲苯基)苯基)吡啶铱(TEG)作为发光层, 三氧化钼(MoO_3)作为空穴注入层, 氧化锌和聚乙烯亚胺作为电子注入层, 铟锡氧化物(ITO)和铝(Al)作为阴极和阳极, 制备了有机-无机复合发光器件, 其中所用有机材料的结构式如图1所示. 器件的制备过程如下: (1) 在ITO衬底上旋涂醋酸锌二水合物的二甲氧基乙醇溶液, 然后在

300°C 的条件下加热1 h, 制备ZnO薄膜; (2) 在惰性环境下, 在ZnO上相继旋涂PEIE的二甲氧基乙醇溶液和发光材料的氯苯溶液来制备PEIE层和发光层. 通过台阶仪来测量薄膜的厚度, 其中MEH-PPV层和PFA层的厚度均为100 nm, TCTA:OXD-7:TEG层的厚度为90 nm; (3) 将样品转移到手套箱内的高真空室中, 在TCTA:OXD-7:TEG层上蒸镀一层50 nm厚的二-[4-(N,N-二甲苯基胺基)-苯基]环己烷(TAPC)层; (4) 沉积 MoO_3 (10 nm)和Al(150 nm); (5) 对于单极性电子器件, 在MEH-PPV层上蒸镀氟化铯CsF(1 nm)和Al(100 nm)作为顶电极. 以50 nm的聚(3,4-乙烯二氧噻吩):聚苯乙炔磺酸(PEDOT:PSS)层替代发光器件中的ZnO/PEIE层来制备单极性空穴器件. 另外, 为了降低泄漏电流对器件特性的影响, 单极性载流子器件中的MEH-PPV层的厚度为300 nm. 通过膜厚检测仪来监测材料的蒸发速率和薄膜厚度, TAPC, MoO_3 , CsF, Al的蒸发速率分别为0.03, 0.02, 0.01和 0.5 nm s^{-1} . 采用程序化的Keithley 2400直流电源和Konica-Minolta CS-100A色度计测量器件的电流密度-发光亮度-电压(J - L - V)特性. 器件的电致发光光谱通过Ocean Optics USB4000-UV-VIS 光纤光谱仪进行记录. 采用Kratos Axis Ultra DLD分光仪测量样品的紫外光电子能谱(UPS)和X射线光电子能谱(XPS), He(I) 气体放电灯(21.2 eV)和Al K_α 线(1486.8 eV)分别作为UPS和XPS的激发源.

图1 有机材料的分子结构式

Figure 1 Chemical structures of organic materials

2 分析与讨论

2.1 发光器件中PEIE层的功能

首先研究PEIE层厚度不同的器件的发光特性,并同未添加PEIE层器件的发光特性进行了比较.图2(a)给出器件的发光效率-电流密度特性.当PEIE层的厚度从2 nm增加到6 nm时,器件的发光效率从 1.3 cd A^{-1} 增加到 2.5 cd A^{-1} .本文报道的发光效率为10~12个器件测量结果的平均值,发光效率的误差范围为10%~15%.PEIE层的厚度为10 nm时,器件具有最佳的发光效率(2.7 cd A^{-1}).继续增加PEIE层的厚度至20 nm时,器件的发光效率为 1.3 cd A^{-1} .未添加PEIE层器件的发光效率为 0.28 cd A^{-1} ,约是PEIE厚度为10 nm器件发光效率的1/10,表明加入PEIE层能够显著地提高器件的发光效率.厚度较小的PEIE层可能还未形成连续薄膜,影响其电子注入和空穴阻挡作用. PEIE层较高的体电阻和低电子迁移率降低了20 nm PEIE层器件的发光效率.图2(b)给出未添加PEIE层器件和PEIE厚度为10 nm器件的 J - L - V 特性.同未添加PEIE层的器件相比,添加PEIE层器件的启亮电压提高约0.2 V,该结果与Bolink等人^[5]所报道的加入 Cs_2CO_3 电子注入层导致器件启亮电压增加的结果相类似,启亮电压的变化可能是源于加入电子注入层造成器件内建电势的改变.此外,在相同的驱动电压下,PEIE器件具有更低的电流密度和更高的发光亮度.例如,在电压为5 V时,两类器件的电流密度分别为 404 和 560 mA cm^{-2} ;同时,PEIE器件的发光亮度(9300 cd m^{-2})约为未添加PEIE层器件发光亮度(1700 cd m^{-2})的5倍.图2(c)给出器件的能级图.由于 MoO_3 的功函数约为 6.9 eV ^[28],空穴可以有效地从 MoO_3 层注入到MEH-PPV层.然而,ZnO导带能级(-3.6 eV)^[15]和MEH-PPV最低未占有轨道(LUMO)能级(-2.7 eV)^[29]之间存在着较大的电子注入势垒,电子注入比较困难.加入PEIE层能有效地减小ZnO/MEH-PPV界面的电子注入势垒,提高电子注入效率和器件的发光效率.

2.2 器件发光效率提高的机理

为了探究器件发光效率提高的机理,研制了单极性载流子器件,其中单极性空穴器件的结构为ITO/PEDOT:PSS/MEH-PPV/ MoO_3 /Al.分别采用

图2 (网络版彩色)采用不同厚度PEIE层器件的发光效率-功率效率-电流密度特性(a),未添加PEIE层器件和PEIE厚度为10 nm器件的 J - L - V 特性(b)和器件能级图(c)

Figure 2 (Color online) Luminance efficiency-power efficiency-current density characteristics of the devices with varied PEIE layer thickness (a), J - V - L characteristics of the devices with a 10 nm PEIE layer or without a PEIE layer (b) and energy level diagram of the devices (c)

ITO/PEDOT:PSS和 MoO_3 /Al作为空穴注入电极,单极性空穴器件的 J - V 关系如图3(a)所示,器件具有接近

图3 (网络版彩色)采用不同注入电极的单极性空穴器件(a)和单极性电子器件(b)的*J-V*特性

Figure 3 (Color online) *J-V* characteristics of the hole-only devices (a) and electron-only devices (b) using different injection contacts

的空穴电流密度,这是因为具有较高功函数的PEDOT:PSS和 MoO_3 都能与MEH-PPV形成空穴注入的欧姆接触^[30,31].单极性电子器件的结构为ITO/ZnO/PEIE/MEH-PPV/CsF/Al,其中PEIE层的厚度为10 nm.器件的*J-V*特性如图3(b)所示.从ITO/ZnO/PEIE注入的电子电流密度接近于从CsF/Al注入的电子电流密度,说明ITO/ZnO/PEIE电子注入电极具有与广泛采用的CsF/Al电子注入电极接近的电子注入能力.比较图3(a)和(b)可知,在相同电压下,电子电流密度比空穴电流密度低100~400倍,这主要是由于在MEH-PPV中存在电子陷阱,导致其电子迁移率低于空穴迁移率约2个数量级^[32].尤为重要的是,在相同驱动电压下未添加PEIE层的单极性电子器件的电流密度相对于有PEIE层器件的电子电流密度低约1个数量级.上述结果表明,加入PEIE层可以有效地改善ZnO层对MEH-PPV层的电子注入效率.

采用紫外光电子能谱方法(UPS)分别测量了ZnO

和ZnO/PEIE样品的功函数.图4(a)给出样品UPS谱图的二次电子截止边.ZnO的功函数为3.8 eV,而加入PEIE层后,功函数降低了1.2 eV.功函数降低是因为PEIE层具有较强的体偶极矩或能够形成界面偶极层.此外,还采用X-射线光电子能谱分析了界面偶极层的产生机制,图4(b)给出了ZnO/PEIE样品的N1s核心能级谱图.ZnO/PEIE样品N1s谱的峰值位于399.2 eV,来源于中性胺,几乎未观察到束缚能位于401 eV的质子化胺的发射,表明界面偶极层的产生主要来源于中性胺^[26].

2.3 器件电子注入效率同发光材料亲和势之间的关系

为了探究PEIE层电子注入效率同发光聚合物电子亲和势之间的关系,选择了具有较高LUMO能级的蓝色发光聚合物PFA(能级结构见图2(c))来制备发光器件.图5给出器件的发光特性.器件的启亮电压(2.8 V)

图4 (网络版彩色)ZnO和ZnO/PEIE样品的紫外光电子光谱(a)和ZnO/PEIE样品的N 1s核心能级谱图(b)

Figure 4 (Color online) UPS measurements of ZnO and ZnO/PEIE samples (a) and N 1s core level spectrum of ZnO/PEIE sample (b)

非常接近于PFA的光子能量与电子电荷之比,表明器件中的电子注入势垒很小.器件的发光效率(4.1 cd A^{-1})与采用低功函数金属阴极传统器件的发光效率相近^[33,34].发光来自PFA层^[33],两个发光光谱峰分别位于452和486 nm,来源于激发态到基态不同振动能级的跃迁,色坐标为(0.17, 0.24).上述结果表明:对于具有较低电子亲和势的PFA, PEIE仍然可以作为有效的电子注入层来实现较好的发光效率.

2.4 小分子磷光器件的发光特性

同目前普遍采用的 Cs_2CO_3 电子注入层^[5,14]相比, PEIE具有与有机材料接近的表面能并可形成均匀的薄膜,对器件中与其相邻的有机发光层的形貌影响

较小,因此PEIE非常适合与磷光材料发光层特别是与小分子材料发光层相匹配来制备高效率的有机-无机复合发光器件.采用空穴传输材料TCTA和电子传输材料OXD-7作为共主体材料, TEG作为磷光材料来制备发光层.在发光层与 MoO_3 层之间加入50 nm的TAPC层,由能级图6(a)可知, TAPC具有高于发光层材料的LUMO能级^[35],可有效地阻挡电子而将载流子复合区域限制在发光层中,并降低 MoO_3 对发光的猝灭效应^[36].另外, TAPC具有较高的三线态能量(2.87 eV)还可以作为激子阻挡层.发光层中TCTA和OXD-7的三线态能量分别为2.78和2.7 eV^[35],高于TEG的三线态能量2.3 eV^[37],能够将形成的三线态激发态限制在TEG上.图6(b)~(d)给出TCTA同OXD-7的含量比为1:1器件的发光特性. TEG掺杂浓度为10%的器件约在4.5 V启亮,当发光亮度为 1000 cd m^{-2} 时,驱动电压为10.3 V.器件的最大发光效率为 64 cd A^{-1} ,外量子效率为19.1%.器件的发光效率为目前有机-无机复合发光器件的最高效率^[4-17],为文献中采用 $\text{ZnO}:\text{Cs}_2\text{CO}_3$ 电子注入层器件发光效率的4倍^[19].这主要是由于PEIE具有良好的电子注入和空穴/激子阻挡特性,特别是在PEIE层上能够制备成膜质量较好的TCTA:OXD-7:TEG发光层.器件发光光谱的峰值位于530 nm,发光来自于TEG.图6给出TEG掺杂浓度不同器件的发光效率-电流密度特性.发光器件的最大发光效率均在 60 cd A^{-1} 左右,说明TEG掺杂浓度并未显著地影响器件的发光效率.这可能是由于TCTA:OXD-7:TEG发光层具有较平衡的空穴和电子传输特性,以及TEG较均匀分散在TCTA:OXD-7中减弱了浓度猝灭效应.

3 结论

PEIE可以有效提高有机-无机复合发光器件中ZnO层对发光聚合物特别是具有较低电子亲和势的蓝色发光聚合物的电子注入效率,以PEIE作为电子注入层的有机-无机复合发光器件具有与采用低功函数金属阴极的传统结构器件相近的发光效率.由于PEIE层具有与有机发光层良好的兼容性,基于溶液加工方法制备的小分子材料发光层的有机-无机复合磷光器件的外量子效率可达19.1%,为目前该类器件的最高效率.我们的研究不仅大幅度地提高了有机-无机复合发光器件的发光效率,对未来该类器件效率和稳定性的进一步研究也具有一定的参考意义.

图5 (网络版彩色)以PFA作为发光层器件的 J - V 特性(a)、发光效率-电流密度特性(b)和发光光谱(c)

Figure 5 (Color online) J - V - L (a), luminance efficiency-current density properties (b) and EL spectrum (c) of the PFA devices

图 6 (网络版彩色)以小分子材料作为发光层的有机-无机复合发光器件能级图(a)、 J - L - V 特性(b)、TEG浓度不同器件的发光效率-电流密度特性 (c)和发光光谱(d)

Figure 6 (Color online) Energy level diagram (a), J - L - V (b), luminance efficiency-current density characteristics (c) and EL spectrum (d) of the devices using small-molecule emissive layer

参考文献

- 1 Tang C W, VanSlyke S A. Organic electroluminescent diodes. Appl Phys Lett, 1987, 51: 913-915
- 2 Burroughes J H, Bradley D D C, Brown A R, et al. Light-emitting-diodes based on conjugated polymers. Nature, 1990, 347: 539-541
- 3 Aziz H, Popovic Z, Tripp C P, et al. Degradation processes at the cathode/organic interface in organic light emitting devices with Mg:Ag cathodes. Appl Phys Lett, 1998, 72: 2642-2644
- 4 Morii K, Ishida M, Takashima T, et al. Encapsulation-free hybrid organic-inorganic light-emitting diodes. Appl Phys Lett, 2006, 89: 183510
- 5 Bolink H J, Coronado E, Orozco J, et al. Efficient polymer light-emitting diode using air-stable metal oxides as electrodes. Adv Mater, 2009, 21: 79-82
- 6 Youn H, Yang M Y. Solution processed polymer light-emitting diodes utilizing a ZnO/organic ionic interlayer with Al cathode. Appl Phys Lett, 2010, 97: 243302
- 7 Bolink H J, Coronado E, Repetto D, et al. Air stable hybrid organic-inorganic light emitting diodes using ZnO as the cathode. Appl Phys Lett, 2007, 91: 223501
- 8 Tokmoldin N, Griffiths N, Bradley D D C, et al. A hybrid inorganic-organic semiconductor light-emitting diode using ZrO₂ as an electron-injection layer. Adv Mater, 2009, 21: 3475-3478
- 9 Bolink H J, Brine H, Coronado E, et al. Hybrid organic-inorganic light emitting diodes: Effect of the metal oxide. J Mater Chem, 2010, 20: 4047-4049

- 10 Park J S, Lee B R, Lee J M, et al. Efficient hybrid organic-inorganic light emitting diodes with self-assembled dipole molecule deposited metal oxides. *Appl Phys Lett*, 2010, 96: 243306
- 11 Hsieh S N, Chen S P, Li C Y, et al. Surface modification of TiO_2 by a self-assembly monolayer in inverted-type polymer light-emitting devices. *Org Electron*, 2009, 10: 1626–1631
- 12 Choi H, Park J S, Jeong E, et al. Combination of titanium oxide and a conjugated polyelectrolyte for high-performance inverted-type organic optoelectronic devices. *Adv Mater*, 2011, 23: 2759–2763
- 13 Bolink H J, Brine H, Coronado E, et al. Ionically assisted charge injection in hybrid organic-inorganic light-emitting diodes. *ACS Appl Mater Interfaces*, 2010, 2: 2694–2698
- 14 Kabra D, Lu L P, Song M H, et al. Efficient single-layer polymer light-emitting diodes. *Adv Mater*, 2010, 22: 3194–3198
- 15 Lu L P, Kabra D, Friend R H. Barium hydroxide as an interlayer between zinc oxide and a luminescent conjugated polymer for light-emitting diodes. *Adv Funct Mater*, 2012, 22: 4165–4171
- 16 Brine H, Sánchez-Royo J, Bolink H. Ionic liquid modified zinc oxide injection layer for inverted organic light-emitting diodes. *Org Electron*, 2013, 14: 164–168
- 17 Park J S, Lee J M, Lee S K, et al. A ZnO/n-doped carbon nanotube nanocomposite charge transport layer for high performance optoelectronics. *J Mater Chem*, 2012, 22: 12695–12700
- 18 Hsiao C C, Hsiao A E, Chen S A. Design of hole blocking layer with electron transport channels for high performance polymer light-emitting diode. *Adv Mater*, 2008, 20: 1982–1988
- 19 Bolink H J, Brine H, Coronado E, et al. Phosphorescent hybrid organic-inorganic light-emitting diodes. *Adv Mater*, 2010, 22: 2198–2201
- 20 Yang X H, Neher D. Polymer electrophosphorescence devices with high power conversion efficiencies. *Appl Phys Lett*, 2004, 84: 2476–2478
- 21 Sessolo M, Bolink H J. Hybrid organic-inorganic light-emitting diodes. *Adv Mater*, 2011, 23: 1829–1845
- 22 Huang F, Wu H B, Wang D, et al. Novel electroluminescent conjugated polyelectrolytes based on polyfluorene. *Chem Mater*, 2004, 16: 708–716
- 23 Guo T F, Yang F S, Tsai Z J, et al. High-performance polymer light-emitting diodes utilizing modified Al cathode. *Appl Phys Lett*, 2005, 87: 013504
- 24 Zhang F L, Ceder M, Ingalas O. Enhancing the photovoltage of polymer solar cells by using a modified cathode. *Adv Mater*, 2007, 19: 1835–1838
- 25 Deng X Y, Lau W M, Wong K Y, et al. High efficiency low operating voltage polymer light-emitting diodes with aluminum cathode. *Appl Phys Lett*, 2004, 84: 3522–3524
- 26 Zhou Y, Fuentes-Hernandez C, Shim J. A universal method to produce low-work function electrodes for organic electronics. *Science*, 2012, 336: 327–332
- 27 Kyaw A K K, Wang D H, Gupta V, et al. Efficient solution-processed small-molecule solar cells with inverted structure. *Adv Mater*, 2013, 25: 2397–2402
- 28 Meyer J, Hamwi S, Kroger M, et al. Transition metal oxides for organic electronics: Energetics, device physics and applications. *Adv Mater*, 2012, 24: 5408–5427
- 29 Holt A L, Leger J M, Carter S A. Electrochemical and optical characterization of p- and n-doped poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]. *J Chem Phys*, 2005, 123: 044704
- 30 Lu M, Bruyn P D, Nicolai H T, et al. Hole-enhanced electron injection from ZnO in inverted polymer light-emitting diodes. *Org Electron*, 2012, 13: 1693–1699
- 31 Craciun N I, Brondijk J J, Blom P W M. Diffusion-enhanced hole transport in thin polymer light-emitting diodes. *Phys Rev B*, 2008, 77: 035206
- 32 Tsai M J, Meng H F. Electron traps in organic light-emitting diodes. *J Appl Phys*, 2005, 97: 114502
- 33 Harkema S, Kicken R A H J, Langeveld-Voss B M W, et al. Tuning the voltage dependence of the efficiency of blue organic light-emitting diodes based on fluorene-amine copolymers. *Org Electron*, 2010, 11: 755–766
- 34 Laquai F, Hertel D. Influence of hole transport units on the efficiency of polymer light emitting diodes. *Appl Phys Lett*, 2007, 90: 142109
- 35 Fu Q, Chen J S, Shi C S, et al. Solution-processed small molecules as mixed host for highly efficient blue and white phosphorescent organic light-emitting diodes. *ACS Appl Mater Interfaces*, 2012, 4: 6579–6586
- 36 Kabra D, Song M H, Wenger B, et al. High efficiency composite metal oxide-polymer electroluminescent devices: A morphological and material based investigation. *Adv Mater*, 2008, 20: 3447–3452
- 37 Rehmann N, Hertel D, Meerholz K, et al. Highly efficient solution-processed phosphorescent multilayer organic light-emitting diodes based on small-molecule hosts. *Appl Phys Lett*, 2007, 91: 103507

Hybrid organic-inorganic light-emitting diodes based on a polythylenimine interlayer

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Implementation of a polyethylenimine ethoxylated (PEIE) interlayer significantly enhances electron injection efficiency from ZnO into light emitting polymers including a blue light emitting polymer with relatively low electron affinity, verified by comparison of current density-voltage characteristics of the electron-only devices with or without a PEIE interlayer. Ultraviolet photoelectron spectroscopy measurements reveal that PEIE forms interfacial dipoles and reduces the work function of ZnO by ca. 1.2 eV, thus facilitating electron injection into light emitting polymers. Neutralized amines rather than protonated amines are responsible for the formation of interfacial dipoles as manifested by N1s core level spectra of the ZnO/PEIE sample. Luminance efficiency of hybrid organic-inorganic light emitting devices employing PEIE interlayer is similar to that of the analogous conventional devices with low work-function metal cathode due to electron injection promoting and hole/exciton-blocking properties of PEIE. Compared to Cs_2CO_3 , PEIE, which possesses similar surface energy to the organic materials and can form homogeneous film, is expected to collaborate with the adjoining organic layers, without significantly interrupting their morphology, especially for those containing low molecular weight components such as phosphorescent emitters. We envisage that this valuable tribute enables the use of small molecule light emitting materials for device fabrication and is particularly beneficial for the effective introduction of phosphorescent emitters into the emission layer of organic-inorganic light emitting devices. Phosphorescent hybrid organic-inorganic light emitting devices with solution-processed 4,4',4''-tris(carbazol-9-yl)triphenyl-amine (TCTA): 1,3-bis[(4-tert-butylphenyl)-1,3,4-oxadiazolyl]phenylene (OXD-7): Ir-complex emission layer show the maximum luminance efficiency of 64 cd/A and external quantum efficiency of 19.1%, which represent the best efficiency for organic-inorganic light emitting devices reported so far and are approximately 4 times higher than those of the analogous devices using Cs_2CO_3 electron injection layer. The luminance efficiency of the devices is rather independent of Ir-complex concentration, indicating balanced hole and electron transport in the emission layer and broad emission zone due to the use of hole-transporting TCTA and electron-transporting OXD-7 as the co-hosts, together with the confinement of the emission zone inside the emission layer and homogeneous dispersion of Ir-complex into the TCTA: OXD-7 host. Furthermore, the efficiency roll-off at high luminance is rather small, for example, the luminance efficiency at 10000 cd/m^2 is 62 cd/A, maintaining 97% of the maximum luminance efficiency. Our findings enrich the organic materials for the preparation of organic-inorganic light emitting devices and pave the way for the future improvement of device efficiency and stability.

hybrid organic-inorganic light emitting devices, electron injection interlayer, light emitting polymers, solution-processed small molecule emissive layer

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