基于钙钛矿量子点的电致发光二极管研究进展

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摘要 钙钛矿量子点因其优异的光电特性, 在新型显示和固态照明等领域有着广泛的应用潜力. 近年来, 钙钛矿量子点成为光电领域的研究热点, 钙钛矿量子点发光二极管的器件效率也有了突飞猛进的发展. 本文综述了基于钙钛矿量子点的电致发光器件研究进展, 分析了制约钙钛矿量子点电致发光二极管效率的主要因素, 并对钙钛矿量子点电致发光器件效率提升的策略进行了讨论.

关键词 钙钛矿, 量子点, 电致发光, 器件性能

近年来, 金属卤化钙钛矿材料由于其优异的光学和电子特性, 在光电领域备受瞩目. 由于金属卤化钙钛矿材料兼具载流子迁移率高^[1,2]、缺陷容忍度高^[3]、带隙可调^[4]、荧光量子产率高^[4]、制造成本低^[2]等优点, 在显示和照明领域具有很大的应用潜力. 2014年, Friend课题组^[5]首次报道了基于 $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ 的绿光器件, 实现了外量子效率达0.76%, 同时可以在室温下工作的钙钛矿发光二极管. 短短数年时间, 钙钛矿发光二极管的器件性能已经有了突飞猛进的发展.

卤化物钙钛矿通常具有结构通式 ABX_3 . 其中, A和B分别是一价和二价阳离子, X是一价卤化物阴离子(Cl^- 、 Br^- 或 I^-), 一般B位阳离子通常为 Pb^{2+} 或 Sn^{2+} (Ag^{2+} 与 Bi^{2+} 为双钙钛矿), 与6个卤化物离子配位形成八面体结构, 八面体之间通过点共享的形式组成三维结构, 且A位阳离子位于八面体中心. 通过改变卤化物离子的组分^[6]和减少阳离子比例^[7], 可以调节钙钛矿的光学和电学性质. 另外, 钙钛矿的尺度和维度也可以用来

调整光学性质. 钙钛矿材料具有吸收系数大^[8]、载流子扩散距离超长^[9]、载流子迁移率高^[10]、荧光量子产率高^[11]、可全光谱调谐^[12]以及色纯度高^[13]等突出的光电特性^[13], 使其在显示和照明领域拥有很大的应用潜力^[14].

金属卤化钙钛矿为直接带隙半导体材料, 其激子结合能一般在几十meV量级, 远低于有机材料的激子结合能, 较小的激子结合使得基于多晶钙钛矿薄膜的电致发光器件中的激子不够稳定. 要实现高性能器件, 对于钙钛矿薄膜的成膜质量要求更为苛刻. 将钙钛矿材料与传统的量子点制备技术相结合, 能够得到一类新型光电材料——钙钛矿量子点^[15]. 由于空间尺寸限制量子效应, 钙钛矿量子点具有更大的激子结合能, 更利于形成稳定的激子, 从而实现高荧光量子效率和窄的发射带宽. 相比钙钛矿多晶, 钙钛矿量子点在显示和照明领域具有更大的应用潜力. 此外, 钙钛矿量子点相比于传统半导体量子点, 具有更广泛的光谱调节性和更容易的加工制造性. 合理的制备方式能够使得钙钛

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矿量子点的荧光量子效率接近100%^[16], 光谱可在400~950 nm范围内连续调节. 在过去几年时间里, 钙钛矿量子点的合成制备及其在电致发光方面的应用发展迅猛.

本文以钙钛矿量子点的电致发光器件为切入点, 讨论钙钛矿量子点的电致发光进展, 提出钙钛矿量子点在电致发光器件方面存在的问题和策略, 并展望钙钛矿量子点的应用前景

1 钙钛矿量子点电致发光进展

根据A位阳离子的不同, 钙钛矿量子点(quantum dot, QD)可分为有机-无机杂化型和全无机型两种类型. 此外, 考虑到重金属铅的毒性, 可以大致将钙钛矿量子点分为铅基钙钛矿量子点和非铅/少铅钙钛矿量子点. 本文从钙钛矿量子点的电致发光应用入手, 分别介绍有机-无机杂化铅基钙钛矿量子点、全无机铅基钙钛矿量子点和非铅/少铅钙钛矿量子点的电致发光进展.

有机-无机杂化钙钛矿量子点的“A”是有机阳离子, 例如甲胺(CH_3NH_3^+)、乙胺($\text{CH}_3\text{CH}_2\text{NH}_3^+$)或甲脒($\text{HC}(\text{NH}_2)_2^+$). 1978年, Weber^[17]首次报道了有机铅卤钙钛矿材料并做了详细的表征. 2009年, Kojima等人^[18]将有机铅卤钙钛矿材料作为吸光剂应用于太阳能电池, 获得了3.8%的光电转换效率. 2014年, Galian等人^[19]首次报道了MAPbBr₃量子点发光二极管(quantum dot light-emitting diodes, QLEDs), 受限于量子点的荧光量子效率(photoluminescence quantum yield, PLQY)等, 当时的器件最大亮度仅有1 cd m⁻². 随后, Huang等人^[20]基于乳液法合成的MAPbBr₃量子点, 制备了结构为ITO/PEDOT:PSS/MAPbBr₃ QDs/TPBi/CsF/Al的QLEDs器件, 获得了2503 cd m⁻²的亮度和4.5 cd A⁻¹的电流效率(图1). 2016年, Deng等人^[21]报道了一种简单的浸涂方法(dip-coating), 可以有效地制备均匀的大面积有机金属卤化物钙钛矿量子点薄膜. 利用这种技术, 只需调整卤化物成分以及量子点的尺寸, 就可以制备蓝色、蓝绿色、绿色、橙色和红色的有机金属卤化物钙钛矿QLEDs. 蓝色、绿色和红色QLEDs最大亮度分别为2673、2398和986 cd m⁻², 外量子效率(external quantum efficiency, EQE)分别为1.38%、1.06%和0.53%, 优于同期报道的全无机钙钛矿量子点电致发光器件. Xing等人^[22]采用ITO/PEDOT:PSS/TFB/MAPbBr₃ QDs/Cs₂CO₃/Al结构, 得到了11.49 cd A⁻¹以及EQE为3.8%的优异性能(图1). Yan等人^[23]在MAPbBr₃量子点的基础上, 通过在低电压

下实现电荷平衡和抑制俄歇复合实现了高效QLEDs, 该器件显示的最大亮度为43440 cd m⁻², EQE为12.9%. Lin等人^[24]利用聚(双(4-苯基)(2,4,6-三甲基苯基)胺)(PTAA)掺杂聚(*N*-乙烯基吡啶)(PVK)作为空穴传输层, 得到最佳器件的最大亮度为7352 cd m⁻², 电流效率(current efficiency, CE)为11.1 cd A⁻¹.

与MAPbBr₃量子点相比, 有机-无机杂化甲脒卤化铅量子点在溶液和薄膜条件下表现出更好的稳定性, 是作为QLEDs发光层更明智的选择. Kim等人^[25]利用短链配体来提高基于FAPbBr₃量子点的QLEDs, 事实上, 表面配体工程在QLEDs的性能方面占据着至关重要的作用. 一方面, 表面配体可以减少表面缺陷态并提高钙钛矿量子点的稳定性; 另一方面, 其会在表面形成绝缘屏障并阻碍QLEDs内部的电荷注入和传输. 因此, 适当控制表面配体有利于钙钛矿QLEDs性能的提高. Kim等人^[25]基于FAPbBr₃正丁胺量子点制备的QLEDs电流效率为9.16 cd A⁻¹, EQE为2.5%. 2017年, Li等人^[26]利用高熔点配体合成了发光效率高、空气稳定的甲脒铅卤钙钛矿量子点. 通过卤素组分调节, 发射光谱可以在整个可见光范围(409~817 nm)内进行调节. 该工作还在器件设计时引入空穴传输层以调节器件的传输性. Han等人^[27]使用3,3-二苯丙胺溴化物(DPPA-Br)作为配体的原位LARP方法制备了高效发光的FAPbBr₃量子点, 其尺寸分布在5~20 nm, 相应的薄膜非常均匀, PLQY达到78%. 他们采用ITO/PEDOT:PSS/TFB/QDs/TPBi/LiF/Al器件结构, 获得了一种高效的纯绿色QLED, 其最大亮度为13970 cd m⁻², CE为66.3 cd A⁻¹, EQE为16.3%(图2). Zhang等人^[28]展示了一种在室温下合成的高亮度和颜色可调的FAPbBr₃ QD, 其中FAPbBr₃量子点表现出单指数衰减动力学, 基于此的QLEDs性能表现为亮度达403 cd m⁻², EQE达2.8%. 由于有机-无机杂化量子点在稳定性方面依然存在差距, 因此部分研究者转而研究稳定性相对更好的全无机钙钛矿量子点.

全无机型钙钛矿量子点的A位阳离子一般为Cs⁺, 具有较高的光致发光量子产率和较好的稳定性, 引起了更为广泛的关注和研究兴趣. 全无机铅基钙钛矿的发现可追溯到1958年, Møller等人^[29]首次报道了全无机钙钛矿CsPbX₃(X= Cl, Br, I)的晶体结构. 2012年, Kojima等人^[30]通过高温热注入的方式, 第一次报道了CsPbX₃纳米晶的合成. Song等人^[31]在2015年报道了第一个全无机钙钛矿电致发光器件. 他们以油酸和油胺

图1 (网络版彩色)基于MAPbBr₃量子点的器件。(a)器件结构示意图^[22]。(b)~(d)2016年乳液法MAPbBr₃量子点器件表现^[20]。(b)器件结构; (c)亮度和电流密度曲线; (d)器件EL谱

Figure 1 (Color online) Device architecture of MAPbBr₃-based QDs. (a) Schematic device structure^[22]. (b)~(d) Performance of emulsion synthesis MAPbBr₃ quantum dot devices in 2016^[20]. (b) Device structure; (c) brightness and current density as a function of driving voltage; (d) EL spectra of the device

为表面配体, 通过热注入法制备出无机钙钛矿量子点, 通过引入Cl⁻和I⁻离子使得发光峰可以在420~585 nm之间进行调节, 而且获得了60%~90%的高荧光量子产率, 特别是CsPbBr₃量子点薄膜的荧光量子产率大于85%。采用的电致发光器件结构为ITO/PEDOT:PSS(40 nm)/PVK(10 nm)/QDs(10 nm)/TPBi(40 nm)/LiF(1 nm)/Al(100 nm), 蓝光、绿光和黄光器件的发光峰分别在455、516和586 nm, EQE分别达到0.07%、0.12%和0.09%。但是, 由于表面配体油酸和油胺的电绝缘特性阻碍了QLEDs中载流子的注入与传输, 导致器件性能不佳。Zhang等人^[32]报道了一种创新的、双相的CsPbBr₃-CsPb₂Br₅量子点复合材料应用于QLEDs, 由于激子扩散长度和缺陷态密度的减少, 器件性能表现出显著的提高, 亮度为3853 cd m⁻², CE为8.98 cd A⁻¹, EQE为2.21%。Liu等人^[33]通过构建一个富卤环境, 降低了缺陷态, 提高了CsPbBr₃量子点的稳定性, 相应的QLEDs也表现出高性能, 亮度为12090 cd m⁻², CE为3.1 cd A⁻¹, EQE为1.194%。

关于红光器件, Pan等人^[34]利用双齿配体在CsPbI₃量子点合成后进行钝化, 钝化后的CsPbI₃量子点器件表现出亮度为748 cd m⁻²的红光发射, EQE达到5.02%。后来, Chiba等人^[35]通过一种阴离子交换方法, 在红光钙钛矿量子点方面取得了重大突破。在过去的几年中, 红光和绿光钙钛矿量子点电致发光器件取得了快速进展, 然而, 蓝光钙钛矿量子点电致发光器件的性能仍是一个挑战。在这一方面, Zheng等人^[36]探索了非极性溶剂可溶的有机类卤化物正十二烷基硫氰酸酯(DAT), 其可以钝化Cl空位且减少Cs量子点中存在的缺陷, 最终使得QLEDs发射蓝光并提高了器件效率。经过DAT处理的蓝色QLEDs表现出465 cd m⁻²的亮度和6.3%的最大EQE。根据Rec.2020显示标准, 这是钙钛矿量子点电致发光器件在460~480 nm范围内的纪录。Pan等人^[37]通过过饱和重结晶方法将Ni²⁺离子引入CsPbCl_xBr_{3-x}量子点中, 并调节Cl/Br元素的比例以获得高效的蓝光发射钙钛矿量子点, 相应的QLEDs呈现612 cd m⁻²的亮度和2.4%的EQE(图3)。

图2 (网络版彩色)基于FAPbBr₃量子点的LED器件性能^[27]. (a) 器件结构; (b) 不同电压下的EL光谱和CIE坐标; (c) FAPbBr₃薄膜表面的AFM图像; (d) EQE与电流密度的函数关系图和LED点亮的图片

Figure 2 (Color online) Device performance of FAPbBr₃ QDs-based LEDs^[27]. (a) Device architecture; (b) EL spectra and CIE coordinates under different voltages; (c) AFM image of the surface of FAPbBr₃ film; (d) EQE as a function of current density and lit pictures of the LEDs

图3 (网络版彩色)掺Ni²⁺的CsPbCl_xBr_{3-x}量子点的LED器件性能^[37]. (a) 基于2.5% Ni²⁺离子掺杂的CsPbCl_{0.99}Br_{2.01}量子点器件的能级; (b) 基于CsPbClBr₂量子点和2.5% Ni²⁺掺杂的CsPbCl_{0.99}Br_{2.01}量子点的EL光谱和照片; 对应器件的电流密度(c)和EQE(d)函数图

Figure 3 (Color online) Performance of LED devices CsPbCl_xBr_{3-x} quantum dots doped with Ni²⁺^[37]. (a) Band level of the QDs based on 2.5% Ni²⁺ ions doped CsPbCl_{0.99}Br_{2.01}; (b) the EL spectra and photos of the LEDs based on CsPbClBr₂ QDs and 2.5% Ni²⁺ doped CsPbCl_{0.99}Br_{2.01} QDs, respectively; current density (c) and EQE (d) of the corresponding devices

为了实现同时具有高效率 and 优异稳定性的量子点电致发光器件, 混合阳离子已经被研究作为构建高效钙钛矿QLEDs的有效策略. Cho等人^[38]首次报道了 $\text{MA}_{1-x}\text{Cs}_x\text{PbBr}_3$ 量子点的合成以及基于 $\text{MA}_{0.7}\text{Cs}_{0.3}\text{PbBr}_3$ 量子点的QLEDs, 其最大亮度为 24510 cd m^{-2} , CE为 4.1 cd A^{-1} , EQE为1.3%. Zhang等人^[39]利用混合阳离子 $\text{FA}_{0.8}\text{Cs}_{0.2}\text{PbBr}_3$ 量子点制备QLEDs, 获得了 55005 cd m^{-2} 的亮度, 电流效率为 10.09 cd A^{-1} , EQE为2.80%. Zhang等人^[40]利用红光的 $\text{FA}_{0.87}\text{Cs}_{0.13}\text{PbI}_3$ 纳米晶来制备QLEDs, 结果显示, 亮度为 218 cd m^{-2} , EQE为15.8%.

钙钛矿量子点是成为下一代光源和显示器的发射体. 到目前为止, Pb^{2+} 仍然是钙钛矿量子点 ABX_3 结构通式中最常见的B位阳离子, 因为它具有更高的稳定性和优异的量子效率. 然而, Pb^{2+} 的固有毒性对环境不友好, 这是一个棘手的问题. 根据《有害物质限制法》(RoHS), 要求全部或部分替代 Pb^{2+} 以控制QLEDs中的重金属剂量^[41]. 因为电子维度的不平衡, 钙钛矿量子点的光学性质和稳定性在替换其他非铅类金属离子后将发生显著变化. 在这里, 强烈期望在原子水平上对组分调节后的结构重组有一个彻底的理解. 据报道, 密度泛函理论(density functional theory, DFT)为筛选合理的分子设计提供了强有力的支持, 这取决于对带隙和热力学稳定性的估量^[42,43]. 尽管有不少关于非铅/少铅钙钛矿量子点制备和光致发光的研究报道, 非铅/少铅钙钛矿量子点电致发光进展仍然十分落后.

目前, 毒性较小的 Sn^{2+} 离子是最合适的替代品, 已广泛应用于太阳能电池^[44,45]. 然而, 关于Sn基钙钛矿QLEDs的研究报道很少. Zhang等人^[46]证明了部分 Sn^{2+} 离子取代的 $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ 量子点具有减轻毒性的作用, 并首次将其应用于QLEDs, 器件性能达到了 5495 cd m^{-2} 的亮度, CE达到 3.60 cd A^{-1} . 随着Sn含量的增加, 钙钛矿量子点的带隙和发射峰发生蓝移. 值得注意的是, 过量添加Sn会导致亮度快速衰减, 从而导致器件性能下降. 2017年, Wang等人^[47]提出了一种简便的热注入方法, 用稳定的 Sn^{4+} 部分取代 Pb^{2+} , 同时, 将 $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ 的光致发光量子产率从45%提高到83%. 利用 $\text{CsPb}_{0.67}\text{Sn}_{0.33}\text{Br}_3$ 量子点薄膜制备了结构为ITO/PEDOT:PSS/TFB/QDs/TPBi/LiF/Al的电致发光器件, 最大亮度为 12500 cd m^{-2} , 电流效率CE、功率效率和EQE分别为 11.63 cd A^{-1} 、 6.76 lm W^{-1} 和4.13%, 启亮电压为3.6 V, 电致发光光谱峰值位于517 nm, 这是目前Sn基钙钛矿量子点的最优电致发光器件报道. 2020年, Ma等

人^[48]首次报道了 $\text{Cs}_3\text{Sb}_2\text{Br}_9$ 量子点在室温下的电注入紫外发射, 电致发光光谱峰值为408 nm, 这是目前钙钛矿量子点电致发光器件的最短波长, 其器件结构为ITO (110 nm)/ZnO(80 nm)/PEI/ $\text{Cs}_3\text{Sb}_2\text{Br}_9$ (40 nm)/TCTA (50 nm)/ MoO_3 /Al(70 nm), EQE为0.206%(图4). 此外, 该器件表现出良好的工作稳定性, 在长时间运行6 h后, 可以保持几乎90%的初始电致发光性能, 并且电流密度不会随着运行时间而上升. 无铅 $\text{Cs}_3\text{Sb}_2\text{Br}_9$ 量子点在实现环境友好和稳定的紫色发光二极管方面具有一定的潜力.

最近, Wang等人^[49]利用一种改进的热注入法制备了稳定的深蓝纳米晶 Cs_2CuI_5 , 具有高达87%的绝对PLQY, 并以 Cs_2CuI_5 为发光层首次成功制备了电驱动的深蓝无铅LED. 器件结构为ITO/NiO/ $\text{Cs}_3\text{Cu}_2\text{I}_5$ QD/TPBi/LiF/Al, 发光峰位于445 nm, EQE达到1.12%(图4), 可与性能最好的铅卤钙钛矿蓝色LED相媲美. 另外, $\text{Cs}_3\text{Cu}_2\text{I}_5$ 对于环境中的水氧也表现出了杰出的稳定性, 研究结果强调了无毒的 $\text{Cs}_3\text{Cu}_2\text{I}_5$ 纳米晶作为稳定蓝色发光体的巨大潜力.

2 钙钛矿量子点电致发光器件存在的问题和解决方法

钙钛矿量子点薄膜的PLQY与QLEDs的性能密切相关. 尽管利用配体钝化表面可以提高量子点溶液的PLQY, 但薄膜中配体的绝缘性质阻碍了电荷的注入及传输, 并对QLEDs的性能产生负面影响, 因此合适的配体选择和有效的配体交换在构建高效的QLEDs中起到重要的作用. 此外, 调整器件结构使得能级更加匹配也可以提高器件的综合效率, 这也是另一种提高QLEDs性能的主要方法. 现将钙钛矿量子点电致发光器件存在的问题和解决方法进行进一步的讨论.

2.1 长链配体引起的电荷传输差的问题

事实上, 在量子点合成过程中, 引入限制量子点尺寸的长链绝缘配体会大大降低量子点薄膜的电荷传输特性. 为了改善全无机量子点薄膜的电荷传输特性, Li等人^[50]提出, 通过控制表面配体密度来实现电荷传输性能的改善. 利用正己烷/乙酸乙酯混合溶剂调节清洗溶剂极性, 对量子点进行可控制的清洗, 实现表面配体密度循环调控, CsPbBr_3 量子点光致发光量子效率和薄膜均匀性都有显著提升, 电致发光器件的EQE达到6.27%, 并且器件性能具有良好的重复性, 40个电致发

图4 (网络版彩色)非铅量子点的器件特性^[49]. (a) 基于 $\text{Cs}_3\text{Sb}_2\text{Br}_9$ 量子点的器件结构示意图; (b) 器件的*I-V*和亮度-电压曲线, 插图为7.0 V下工作的发射单元的照片; (c) 该器件在不同电压下的EQE^[48]. (d) 基于 Cs_2CuI_5 量子点的器件结构示意图; (e) 该器件EQE与偏置电压的依赖关系; (f) 不同电压下的EL光谱, 插图显示器件的相应照片

Figure 4 (Color online) Device characteristics of lead free quantum dots^[49]. (a) Schematic device structure of the $\text{Cs}_3\text{Sb}_2\text{Br}_9$ QDs-based LEDs. (b) *I-V* and luminance-voltage curves of the device. The inset displays the photograph of the emitting unit operated at 7.0 V. (c) EQE of the device at different bias voltages^[48]. (d) Schematic of LEDs fabricated using Cs_2CuI_5 QD. (e) Dependence of EQE of the device on bias voltages. (f) EL spectra at different applied voltages. The insets display the corresponding photographs of the device

光器件的平均EQE为5.4%.

2018年, Dai等人^[51]以共轭烷基胺——3-苯基-丙烯-1-胺(PPA)为配体, 制备了 MAPbBr_3 量子点, 解决了长烷基链配体的引入导致量子点薄膜电荷传输差的问题. 基于PPA配体合成的 MAPbBr_3 量子点电致发光器件的最大电流效率CE为 9.08 cd A^{-1} , 是传统正辛胺量子点(OA-QDs)器件电流效率的8倍. 上述工作提出, 利用共轭配体进行钙钛矿量子点制备是提高钙钛矿量子点电荷传输性的一条有效思路. 有机-无机杂化钙钛矿量子点的稳定性较差, 国内外部分科研团队将研究方向转移到更为稳定的全无机钙钛矿量子点电致发光的研究上.

蓝光全无机钙钛矿量子点电致发光器件相对落后于红、绿电致发光器件, Dong等人^[52]报道了一种双极性壳结构的钙钛矿量子点设计策略. 其中, 双极性壳由内层阴离子和外部极性溶剂分子及阳离子构成, 外壳被静电吸附到带负电荷的内壳上, 这种方法导致强束缚的钙钛矿量子点结构, 可以大大降低配体密度, 提高载流子迁移率($0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). 其报道的4 nm小尺寸

CsPbBr_3 蓝光钙钛矿量子点薄膜的光致发光量子效率超过90%, 实现了EQE为12.3%的蓝光电致发光器件, 用该策略制备的7 nm CsPbBr_3 绿光量子点电致发光器件效率高达22%.

2018年, 曾海波团队Song等人^[53]探索了有机-无机杂化配体钝化量子点的表面缺陷态并增强载流子的注入. 结果表明, ZnBr_2 钝化 CsPbBr_3 量子点, 与原始量子点相比, 量子点薄膜的辐射复合明显增强且电传输特性提高. 钝化后的量子点对应的电致发光器件结构为ITO/PEDOT:PSS/PVK/QDs/TPBi/LiF/Al, 实现了16.48%的EQE, 与未钝化量子点的器件效率相比提高了近40%.

在红光全无机钙钛矿量子点电致发光器件方面, Chiba等人^[35]于2018年用含 Γ 的碘铵盐对纯 CsPbBr_3 量子点进行阴离子交换, 制备出649 nm发射的深红钙钛矿量子点, 并实现了21.3%的红光钙钛矿量子点电致发光器件. 阴离子交换后的量子点为11 nm左右尺寸均一的立方晶体, 在甲苯中的光致发光量子效率为80%, 而阴离子交换前 CsPbBr_3 量子点的光致发光量子效率仅

为38%,这主要是由于阴离子缺陷在离子交换过程中的有效抑制.其采用的器件结构为ITO/PEDOT:PSS(40 nm)/poly-TPD/QDs/TPBi(50 nm)/LiF(1 nm)/Al(100 nm),由于大量的阴离子缺陷,原始CsPbBr₃量子点器件的EQE只有0.17%.离子交换是实现钙钛矿量子点高效发光的一种很有前景的技术.

最近, Xu等人^[54]报道了一种对量子点薄膜的双边钝化策略,在量子点薄膜的上下界面引入一层有机分子,可以有效降低薄膜的缺陷密度,抑制非辐射复合速率.钝化后的量子点薄膜PLQY达到79%,用此薄膜作为发光层制备的器件达到了18.7%的最大外量子效率和75 cd A⁻¹的电流效率.器件结构为ITO/PEDOT:PSS/PTAA/QDs/TPBi/LiF/Al.此外, QLEDs的工作寿命提高了20倍,达到15.8 h.这项报道突出了界面钝化对于高效和稳定的量子点光电器件的重要性.器件性能如图5所示.

2.2 器件中电荷注入的不平衡性

通过降低配体密度或钝化减少缺陷提高量子点的荧光量子产率,可以有效地提升电致发光器件性能.此外,通过调整器件各功能层能级和钙钛矿发光层的匹

配程度,从而提升器件中的电子空穴平衡性,可以实现器件性能的进一步改善. Shi等人^[55]报道了一种全溶液制备的全无机CsPbBr₃ LED器件.该工作中,发光层为CsPbBr₃量子点, ZnO和NiO纳米粒子分别为电子传输层和空穴传输层.具体的器件结构为ITO/NiO/QDs/ZnO/Al,得到的最大亮度为6093.2 cd m⁻², CE为7.96 cd A⁻¹, EQE为3.79%.更重要的是,此钙钛矿QLEDs在空气下长时间工作依然具有出色的稳定性,即使不封装,也能在高湿度(75%, 12 h)和高工作温度(393 K, 三次加热/冷却循环)下工作.这项为实现能够在恶劣环境下工作的钙钛矿QLED铺平了道路.

Li等人^[26]在电致发光器件设计时,在PEDOT:PSS和钙钛矿量子点发光层之间引入TFB和PVK聚合物空穴传输层,从而增强空穴注入,改善器件内部的载流子平衡性.其中,引入PVK聚合物空穴传输层的器件实现了4.07% EQE的绿光电致发光器件,最大电流效率为20.3 cd A⁻¹,最大亮度达到33993 cd m⁻²,发光峰位置在545 nm,器件性能如图6所示.曾海波课题组^[50]将PVK替换为poly-TPD,这是因为poly-TPD的空穴迁移率(约1×10⁻⁴ cm² V⁻¹ s⁻¹)比PVK(约1×10⁻⁶ cm² V⁻¹ s⁻¹)高出两个数量级,使得空穴注入效率提高,改善了器件的

图5 (网络版彩色)双边钝化器件特性^[54]. (a) 双边钝化器件结构示意图; (b) 钝化分子TSPO1, DPEPO, TPPO和DMAC-DPS的分子结构. 原始器件和双边钝化器件的电流密度和亮度(c)、电流效率(d)和EQE(e)的比较

Figure 5 (Color online) Characteristics of bilateral-passivated device^[54]. (a) The schematic diagram of device structure with bilateral passivation. (b) The molecular structures of the passivation molecules TSPO1, DPEPO, TPPO and DMAC-DPS. The comparison of current density and luminance (c), current efficiency (d) and EQE (e) of original device and bilateral-passivated device

图6 (网络版彩色)基于FAPbBr₃量子点的两种不同基质材料发光二极管的EL性能^[26]。(a) PVK制备的绿色QD-LED在电压升高时的EL光谱变化;(b) 电流密度(J)和亮度(L)与驱动电压(V)的关系图;(c) 电流效率和外部量子效率与亮度的关系图

Figure 6 (Color online) EL performance of two different FAPbBr₃ QD-based LEDs with different host materials^[26]. (a) Evolution of EL spectra of green QD-LED made from PVK with increasing voltage; (b) current density (J) and luminance (L) versus driving voltage (V); (c) current efficiency (η_A) and external quantum efficiency (η_{EQE}) versus luminance

载流子平衡性。类似地, Zhang等人^[56]在空穴传输层间插入一层全氟离子聚合物(perfluorinated ionomer, PFI)以提高空穴注入效率, 器件亮度为1377 cd m⁻², 电流效率为0.19 cd A⁻¹, EQE为0.06%。

2018年, Sargent团队^[23]报道了一种基于胶体MAPbBr₃量子点的高效LED, 该QLEDs通过实现电荷平衡并抑制低驱动电压下的俄歇复合而实现。特别地, 器件采用ITO/PEDOT:PSS/QDs/B3PYMPM:TPBi/B3PYMPM:Cs₂CO₃/Al结构, 最大亮度为43440 cd m⁻², EQE为12.9%。这一报道将极大地促进未来钙钛矿量子点LED的发展。Khan等人^[57]通过引入Li掺杂的TiO₂纳米粒子作为电子传输层, 优化了基于CsPbBr₃量子点QLEDs的器件结构和能级排列。与3 V启亮且电流效率为5.6 cd A⁻¹的基准器件相比, 电子传输层为Li掺杂的TiO₂纳米粒子的器件启亮电压为2 V, 并且电流效率提高到15.2 cd A⁻¹。

在最近的工作中, Fang等人^[58]使用10 nm尺寸的均匀CsPbBr₃量子点, 基于PTAA聚合物空穴注入层, 通过使用双电子传输层结构进一步改善电致发光器件中的电子空穴注入平衡性。器件结构为ITO/PEDOT:PSS (40 nm)/PTAA (18 nm)/QDs (20 nm)/TPBi (5 nm)/PO-T2T (35 nm)/LiF (1 nm)/Al (100 nm), 实现了21.63%的EQE,

电致发光器件的发光峰为520 nm, 电致发光光谱半峰宽为18 nm, 是目前效率最高的钙钛矿QLED之一。另外, 与对比器件相比, 电荷传输平衡性的改善可以提高器件寿命近20倍。这项工作进一步强调了控制电注入器件中载流子的平衡性对于构建高性能QLED的重要性。

3 分析与展望

钙钛矿材料激子结合能一般只有几十meV^[59], 量子点的量子限域效应可以使激子结合能显著增大, 更容易实现高荧光量子产率, 因此, 钙钛矿量子点在显示和照明领域具有更大的应用潜力。配体在钙钛矿量子点的合成过程中起到关键的作用, 因此, 配体工程对于实现高性能电致发光器件至关重要。一方面, 配体可以限制钙钛矿量子点的空间维度, 获得较大的激子结合能^[60], 避免在量子点成膜过程中重新聚集^[61]。理想的配体在实现上述功能的同时, 希望获得的量子点表面缺陷密度降低, 特别是降低卤素空位^[62,63]。通过引入较大空间位阻的配体, 可以降低钙钛矿量子点结晶速度, 减少缺陷的形成^[64]。另一方面, 配体本身参与电致发光器件的载流子注入和传输过程, 显著影响电致发光器件的性能。对于电注入器件, 希望通过配体工程调控量

量子点薄膜的电荷传导能力, 增强量子点薄膜的电荷注入^[65], 例如配体密度、长度控制、配体交换以及选择导电有机官能团^[66,67]。

此外, 可以进一步通过其他钝化过程, 降低配体动态吸附脱附、快速结晶引起的缺陷, 提高量子点薄膜的辐射效率。钙钛矿材料的带边电子结构主要由BX₆骨架决定。以MAPbI₃为例, 导带底主要由Pb原子的6p轨道形成, 价带顶主要由I的5p轨道和Pb的6s轨道杂化形成的反键态组成^[68]。卤素原子轨道在带边跃迁过程中十分重要。位于量子点表面的卤素空位^[61,69]引起的表面缺陷对电致发光的影响很大, 特别是由于量子点比表面积高, 卤素空位引起的表面缺陷影响就更大。因此, 对表面缺陷的钝化十分重要, 可以进一步通过表面涂层、有机/无机(卤素)盐^[53,62,63,65,70,71]、阴离子交换策略^[35]等方式实现钙钛矿量子点表面缺陷的钝化。

从电致发光器件结构设计的角度, 需要改善量子点薄膜成膜质量, 获得平整、无孔洞的钙钛矿量子点薄膜, 降低电致发光器件的漏电流。关注钙钛矿量子点器件中的载流子注入平衡性, 通过器件传输层和阻挡层设计, 改善器件各功能层之间的能级匹配性, 实现载流子平衡性注入。同时需要注意, 有机传输层的三线态能级过低可能导致器件发光层激子能量泄漏。上述策略可有效提升钙钛矿量子点电致发光器件的性能。目前, 钙钛矿量子点电致发光器件在红、绿光色已经实现了20%以上的外量子效率^[58,72], 蓝光器件的外量子效率也突破了12%^[52]。除了进一步提高器件的效率以外, 激子辐射机制、器件稳定性、环境友好型量子点器件等方面需要更多的关注和进一步的研究。总之, 由于钙钛矿量子点的优异光电特性, 相信其在显示和照明领域具有广阔的应用潜力和价值。

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Summary for “基于钙钛矿量子点的电致发光二极管研究进展”

Advances on perovskite quantum dot electroluminescent devices

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Perovskite materials display great potential in the optoelectronic applications and are considered as one of the most promising optoelectronic materials due to the advantages such as high color-rendering index, wide color gamut, excellent charge-transport properties, adjustable band gap, high photoluminescence quantum efficiency, low manufacturing cost, and compatibility with flexible/stretchable devices. Applying perovskite QDs as phosphors in white light down-converted light-emitting diode (LED) or emitter materials in active matrix-QLEDs to obtain high efficiency and wide color gamut is significantly promising for next-generation high-definition information displays and high-quality lighting sources applications. In this paper, the evolution of device performance of perovskite QDs-based LEDs has been demonstrated. Significant enhancement of device performance has been realized through appropriate ligand choice and effective ligand exchange together with modifying device architectures. Meanwhile, numerous encouraging achievements have been achieved via inhibition of non-radiative recombination and enhancement of exciton binding energy, since the first perovskite LED was reported in 2014. Due to the quantum effect limited by space size, perovskite quantum dots have higher exciton binding energy, easily achievable high fluorescence quantum efficiency and narrow emission bandwidth.

Because of the excellent photoelectric characteristics, perovskite quantum dots have a wide application potential in new display and solid state lighting. However, for the commercial applications, further efforts are required to elucidate the physical mechanisms and improve the device performance of perovskite QLEDs. Besides, the poor stability of perovskite QLEDs in ambient and harsh conditions has attracted a wide concern, and simultaneously, several strategies have been explored to circumvent this issue, including compositional engineering, surface engineering, matrix encapsulation and device encapsulation. Although significant advances have been made in this regard, the lifetime of perovskite QLEDs remains far away from the commercial requirements. Further strategies to stabilize perovskite QDs and prevent their decomposition are in demand. Encapsulation technology of such kind of devices should be further investigated. Moreover, to avoid the toxicity problem, stable lead-free metal halide analogues with high optoelectronic performance are also needed. Furthermore, colloidal perovskite QDs can maintain functionality under tensile strains, opening new possibilities for their applications in flexible/stretchable electronics to satisfy the future development trend of QLEDs.

In recent years, perovskite quantum dots have become an important issue in the field of photoelectricity. The device performance of perovskite quantum dot light-emitting diode has advanced considerably. In this paper, the research progress of perovskite quantum dot electroluminescence devices is reviewed, the main factors restricting the electroluminescence performance of perovskite quantum dots are analyzed, and in view of the problems in devices: Poor charge transport caused by long-chain ligands, non-radiative quenching of excitons caused by surface defects, and imbalance of charge injection in devices, the improvement strategies are discussed separately.

Due to the quantum effect limited by space size, perovskite quantum dots have higher exciton binding energy, easily achievable high fluorescence quantum efficiency and narrow emission bandwidth. Compared with perovskite orebody materials, perovskite quantum dots have greater application potential in the field of display and lighting. And we are convinced that a highly efficient and stable perovskite QDs-based LED will be fulfilled in the near future.

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