

四丁基铵六氟磷酸盐对全无机 CsPbI₂Br 钙钛矿太阳电池的 多功能界面改性

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摘 要:近年来,全无机钙钛矿太阳电池(PSCs)在光伏领域受到极大的关注,与有机-无机杂化 PSCs 相比,展现出更良好的湿、热和光稳定性;尤其是宽带隙 CsPbI₂Br 钙钛矿(1.92 eV)权衡了稳定性与光吸收性能,在叠层太阳电池和柔性太阳电池中展现出巨大的应用潜力。然而,溶液法制备的 CsPbI₂Br 钙钛矿薄膜会在界面及晶界处产生各种缺陷而成为光生载流子的非辐射复合中心,同时它对水分子敏感而容易降解,从而降低器件的光电性能与稳定性。选用了一种同时具有缺陷钝化和疏水功能的界面改性剂——四丁基铵六氟磷酸盐(TBAPF₆)对 CsPbI₂Br 钙钛矿薄膜进行表面改性。结果表明, TBAPF₆ 的 PF₆⁻钝化了带正电荷的卤素空位, TBA⁺则钝化了带负电的阳离子空位,且改善了 CsPbI₂Br/碳界面的能级排列,从而提高了器件的光电性能(结构为氧化锡/ITO/CsPbI₂Br/TBAPF₆/C),最高光电转换效率达到 12.04%,开路电压为 1.24 V,短路电流密度为 14.60 mA/cm²,填充因子为 67%;同时,长烷基链和氟原子能够有效阻挡空气中水分子的入侵,在 35%~40%的湿度环境中 16 h 后保持了初始效率的 80%,在空气环境 85 °C、72 h 后保持了初始效率的 70.2%,其湿热稳定性相比于原始器件获得了极大的提升。

关键词:六氟磷酸盐;全无机钙钛矿;界面改性;缺陷钝化;疏水性

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近年来,全无机钙钛矿太阳电池(PSCs)在光伏领域受到极大的关注^[1]。与有机-无机杂化 PSCs 相比,由于卤化物钙钛矿(ABX₃, X=I、Br、Cl 等)的 A 位阳离子完全被无机铯离子(Cs⁺)取代,展现出更良好的湿、热和光稳定性;尤其是宽带隙 CsPbI₂Br 钙钛矿(1.92 eV)权衡了稳定性与光吸收性能,在叠层太阳电池和柔性太阳电池中展现出巨大的应用潜力^[2],但其功率转换效率(PCE)和稳定性仍有待进一步提升。然而,溶液法制备的 CsPbI₂Br 钙钛矿薄膜不可避免地会在界面或晶界处出现缺陷^[3-4],成为光生载流子的非辐射复合中心,从而降低了器件的光电性能^[5]。此外,金属电极容易受到从钙钛矿光吸收层迁移的卤素离子影响而被腐蚀,而普通的空穴传输层(HTL)中的吸湿性添加剂也不利于传统结构 PSCs 的稳定性。使用无 HTL、碳电极替代传统贵

金属电极的 PSCs 成为更可行的方式,这不仅是因为它们的成本更低、设备要求更低、制造工艺更简单,还由于其具备更好的疏水特性以及碳材料对卤素离子的化学惰性,解决了水分子入侵造成的不稳定问题,从而提高了器件的稳定性^[6-7]。据报道,通过离子液体对 CsPbI₂Br 钙钛矿薄膜进行表面改性,能够有效地钝化缺陷、调整界面能级排列和提高载流子抽取能力,从而提高器件的 PCE 与湿稳定性;功能性阳离子(如碱金属离子、有机胺根离子等)和阴离子(如卤素离子、醋酸根离子等)的界面改性对提高 PSCs 的效率和稳定性具有积极的作用^[8]。

本工作选用了一种同时具有缺陷钝化和疏水功能的改性剂——四丁基铵六氟磷酸盐(TBAPF₆)对 CsPbI₂Br 钙钛矿薄膜进行界面改性,从而提高全无机 CsPbI₂Br PSCs 的 PCE 和稳定性。TBAPF₆ 是一

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种具有 Lewis 碱特性的离子液体^[4,9–10], 可作为钙钛矿薄膜的掺杂剂或界面改性剂, 有利于钝化器件的缺陷^[11]。Zheng^[12]将 TBAPF₆ 作为掺杂剂应用于全无机 CsPbI₂Br₂ PSCs 上, 有效地增大了晶粒尺寸和钝化了缺陷, 从而提高了器件的 PCE 和稳定性。Xiong 等^[13]利用 TBAPF₆ 作为界面改性剂对有机–无机杂化 CH₃NH₂PbI₃ 钙钛矿薄膜表面进行处理, 不仅有效的钝化了缺陷, 还改变了钙钛矿表面能级; TBAPF₆ 改性后钙钛矿光吸收层的 Fermi 能级向导带靠近, 意味着钙钛矿光吸收层由 P 型向 N 型转变, 产生更高浓度的电子和更小的能级偏移^[4]。CsPbI₂Br 钙钛矿的湿稳定性弱于 CsPbBr₃ 和 CsPbI₂Br₂ 钙钛矿, 但吸光性能强于二者^[14]。本工作通过设置不同浓度的 TBAPF₆ 对 CsPbI₂Br 钙钛矿薄膜进行表面改性, 探究其对 CsPbI₂Br 钙钛矿的成膜质量及对全无机 CsPbI₂Br PSCs 器件光伏性能与环境稳定性(包含湿稳定性和热稳定性)的影响, 验证其有效性, 并分析其机理。

1 实验

1.1 化学试剂与原材料

碘化铅(PbI₂, 99.999% (质量分数, 下同), 辽宁优选公司), 溴化铅(PbBr₂, 99.999%, 辽宁优选公司), 碘化铯(CsI, 99.999%, 辽宁优选公司), 四丁基铵六氟磷酸盐[TBAPF₆, 98.0%, 上海阿拉丁], 二甲基亚砜(DMSO, 分析纯, 上海麦克林), 异丙醇(99.5%, 上海阿拉丁), 商用二氧化锡溶胶(SnO₂, 美国 Alfa 公司), 刻蚀氧化铟锡(ITO)导电玻璃(方阻 7–9 Ω/square, 辽宁优选公司), 商用导电碳浆(北京华敏新材料公司)。

1.2 CsPbI₂Br 钙钛矿太阳能电池组装

将 CsI、PbBr₂ 和 PbI₂ 按 1.0:0.5:0.5 摩尔比溶解在 DMSO 溶剂中, 制成浓度为 1.0 mol/L 的 CsPbI₂Br 钙钛矿前驱体溶液。分别用乙醇、丙酮、异丙醇和乙醇按顺序超声清洗蚀刻的 ITO 导电玻璃衬底各 15 min, 然后在烘箱中干燥, 再紫外线臭氧处理 25 min。将 48 μL 商用 SnO₂ 溶胶以 3 000 r/min 转速旋涂 30 s 在上述处理的 ITO 上, 随后放置在 150 °C 热台上加热 30 min, 得到 ITO/SnO₂。将 ITO/SnO₂ 紫外线臭氧处理 10 min 以去除表面有机杂质。在氮气手套箱中, 将 44 μL 钙钛矿前驱体溶液以低速 1 000 r/min 旋涂 10 s、高速 3 000 r/min 旋涂 30 s 在上述处理的 ITO/SnO₂ 上, 再在 40 °C 的热台上加热 3 min、150 °C 退火 5 min, 得到 CsPbI₂Br 薄膜。然

后, 将溶于异丙醇的浓度为 0、0.5、1.0、2.0 mg/mL 的 45 μL TBAPF₆ 溶液分别经过 4 000 r/min、30 s 旋涂在以上 CsPbI₂Br 薄膜上, 再在 120 °C 退火 10 min。最后, 采用刮刀法将商用导电碳浆刮涂在 CsPbI₂Br 钙钛矿薄膜表面, 然后在 120 °C 退火 20 min, 完成器件制备。原始器件和界面优化器件结构如图 1a 与图 1b 所示, 器件制备的工艺流程如图 1c 所示。

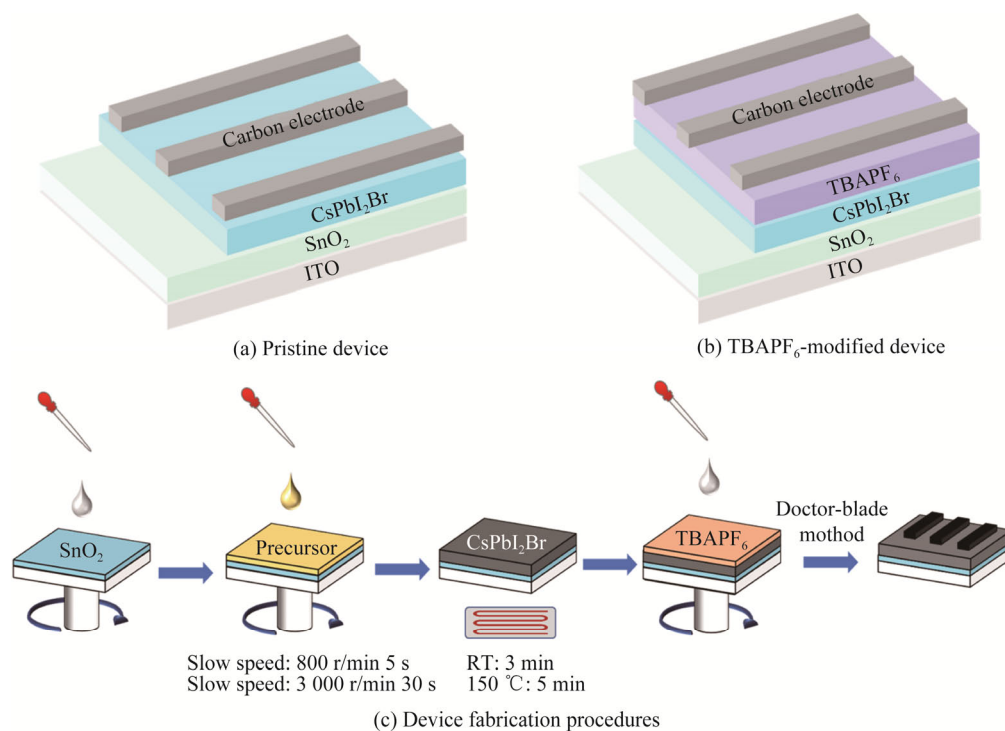
1.3 样品表征

用日本电子株式会社型号为 JSEM-5610LV 扫描电子显微镜(SEM)测试 CsPbI₂Br 钙钛矿薄膜的表面微观形貌。用德国布鲁克型号为 D8-ADVANCE 的 X 射线衍射仪(XRD)分析 CsPbI₂Br 钙钛矿薄膜的物相结构, 测试条件: Cu K_α 射线(波长为 1.54 Å), 加速电压为 30 kV, 电流为 30 mA, 扫描范围为 10°~50°。用北京中教金源型号为 3A 模拟光源、Keithley 2602A 数字源表测试器件的伏安特性曲线(*J–V*), 测试条件: 模拟标准太阳光谱(AM1.5G)、辐照强度为 100 mW/cm²。用美国赛默飞世尔型号为 Thermo ESCALAB 250XI、日本真空技术株式会社型号为 PHI5000 VersaProbe III 测试紫外光电子能谱(UPS), 测试光源能量为 21.22 eV。用日本岛津型号为 UV-3600Plus 光谱仪测试 CsPbI₂Br 钙钛矿薄膜的紫外–可见光(UV–Vis)吸收光谱, 测试波长范围为 300~800 nm。用美国爱丁堡型号为 FLS980 稳态荧光光谱仪和型号为 FLS1000 瞬态荧光光谱仪测试 CsPbI₂Br 钙钛矿薄膜的稳态光致发光(PL)与瞬态光致发光(TRPL), 测试条件: 激发光波长为 450 nm, 监测波长为 645 nm。用德国札纳型号为 PP211&CHI1030B 电化学工作站测试电化学阻抗谱(EIS), 表征电荷分离与转移特性。

2 结果与讨论

2.1 机理分析

基于密度泛函理论(DFT), 使用 GaussView 和 Gaussian 对 TBAPF₆ 进行分子建模和静电势模拟分析, 如图 2a 和图 2b 所示; TBAPF₆ 界面改性 CsPbI₂Br 钙钛矿薄膜的机理示意如图 2c 所示。图 2a 为 TBAPF₆ 的分子空间结构。由图 2a 可见, 阳离子为含有 4 个丁基的季铵根离子(TBA⁺), 阴离子为 6 个氟配位磷酸根离子(PF₆[−])。TBAPF₆ 具有 Lewis 碱特性, 其中氮元素有未配位的孤对电子, 能够通过静电作用有效地钝化未配位的 Pb²⁺^[15]; TBA⁺ 可以通过离子键和氢键与带负电荷的缺陷(如 Cs⁺空位)相互



RT is room temperature; ITO is indium tin oxide.

图 1 全无机 CsPbI₂Br 钙钛矿太阳电池的器件结构与工艺流程图

Fig. 1 Schematic of the device architecture and fabrication procedures of all-inorganic CsPbI₂Br perovskite solar cells (PSCs)

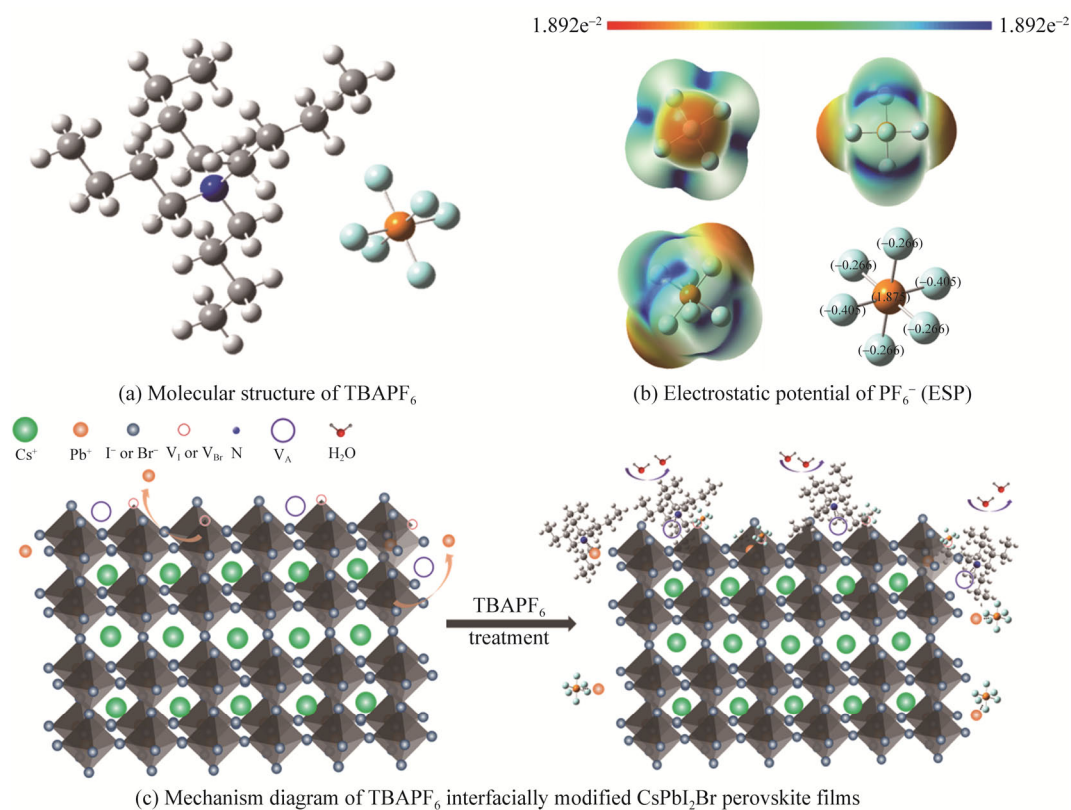


图 2 TBAPF₆ 的分子模拟与界面改性机理

Fig. 2 Molecular simulation and interfacial modification mechanism of TBAPF₆

作用^[16]。由于阴离子 PF_6^- 带负电荷, 通过静电作用钝化带正电荷的缺陷(如卤素空位), 且阴离子上的氟原子也一定程度上起到疏水作用^[17]。Zhu 等^[18]提出了一种 1,3-二甲基-3-咪唑六氟磷酸盐(DMIMPF₆)作为 $\text{CH}_3\text{NH}_2\text{PbI}_3$ 钙钛矿表面改性剂, Pb^{2+} 与 DMIMPF₆ 之间形成静电作用, DMIMPF₆ 与 PbI_2 发生化学反应: $\text{DMIMPF}_6 + \text{PbI}_2 \rightarrow \text{DMIMPbF}_3 + \text{PI}_2\text{F}_3$, 证明了 PF_6^- 可以有效地钝化钙钛矿表面 PbI_2 端的 Pb 团簇缺陷。同时, TBAPF₆ 具有高离子导电性和优异的空气稳定性^[19], 带有长烷基链的官能团能有效地抑制空气中水分子的入侵, 还起到空间位阻效应, 有效地阻碍 I^- 迁移引起的稳定性下降^[13]。

2.2 表面微观形貌表征

为探究 TBAPF₆ 界面改性剂对 CsPbI_2Br 钙钛矿

薄膜微观形貌的影响, 分别对 TBAPF₆ 界面改性前后的 CsPbI_2Br 钙钛矿薄膜进行了 SEM 测试, 如图 3 所示。由图 3a 可见, 低倍率下的未改性参考样品的表面形貌不均匀, 表面凹凸不平。放大倍数后, 如图 3b 所示, 可以明显观察到薄膜表面有多处孔洞, 晶粒间缝隙较大, 可能是由水分子对晶界腐蚀引起, 这些特征都是引起漏电流的主要原因。图 3c 为低倍率下 TBAPF₆ 改性 CsPbI_2Br 钙钛矿薄膜的表面形貌, 相比于参考样品, 薄膜更加平整均匀且致密。放大倍数后, 如图 3d 所示, 未观察到孔洞, 晶粒间缝隙明显变小。因此, 可以得出结论, TBAPF₆ 界面改性能够有效地改善 CsPbI_2Br 钙钛矿薄膜的表面形貌, 抵制空气中水分子的侵蚀, 致密的微观组织有利于提高器件光电性能和稳定性。

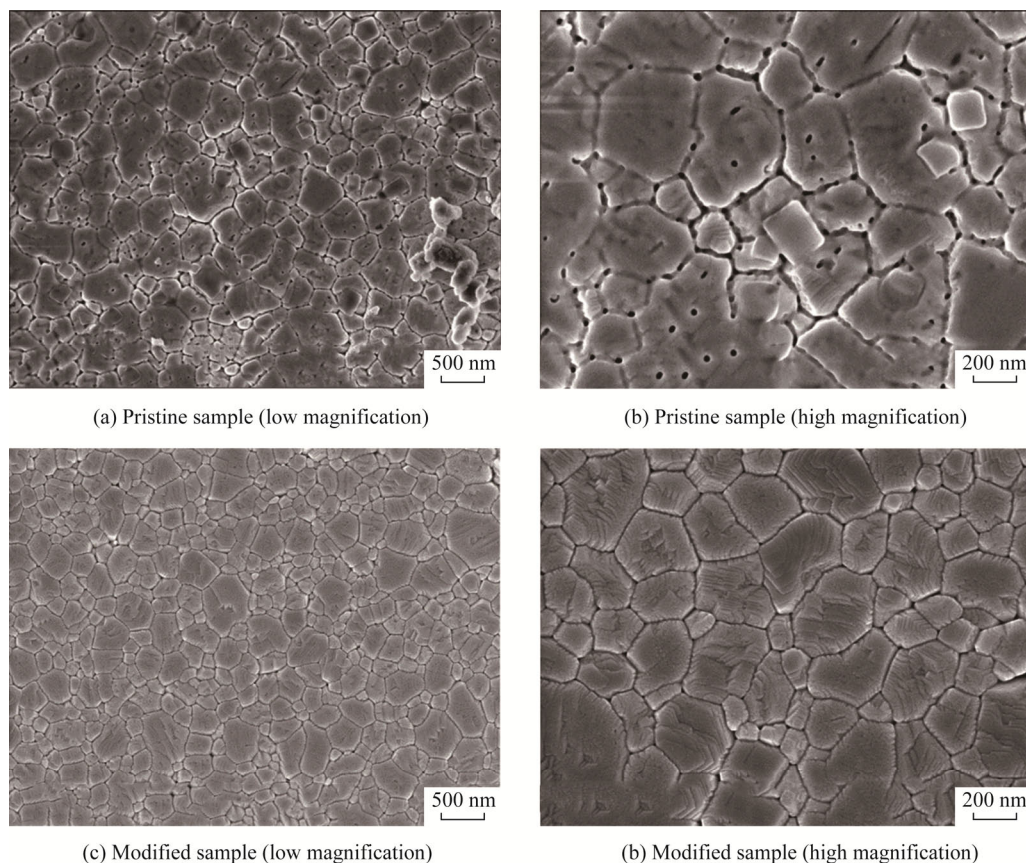


图 3 原始和 TBAPF₆ 改性 CsPbI_2Br 钙钛矿薄膜的 SEM 照片

Fig. 3 SEM images of the pristine and TBAPF₆ modified CsPbI_2Br perovskite films

2.3 物相结构表征

为了探究 TBAPF₆ 改性前后 CsPbI_2Br 钙钛矿薄膜的物相结构变化, 对不同浓度 TBAPF₆ 处理的样品进行了 XRD 分析, 如图 4 所示。由图 4a 可见, 不同浓度 TBAPF₆ 处理的样品都存在 2θ 为 14.5° 和 29.6° 附近的特征衍射峰, 分别对应 CsPbI_2Br 钙钛矿相的(100)和(200)晶面, 表明了 CsPbI_2Br 钙钛矿晶

体的形成^[20]。随着 TBAPF₆ 浓度的增加, CsPbI_2Br 钙钛矿薄膜的特征峰强度明显上升, 当浓度增加到 1.0 mg/mL 时, 特征衍射峰的强度达到最高值; 当 TBAPF₆ 浓度继续增加时, 特征峰强度有所下降。如图 4b 所示, 当放大最优浓度改性的样品和参考样品的(100)和(200)晶面的特征峰时, 可以看出经过优化后样品的特征峰强度远远超出参考样品。由

XRD 谱可以看出, TBAPF₆ 改性的 CsPbI₂Br 钙钛矿薄膜的特征衍射峰强度明显地增强和半高宽变小, 表明结晶性得到了明显的改善, 当 TBAPF₆ 浓

度为 1.0 mg/mL 时达到最优的效果。

2.4 器件的光电性能表征

图 5a 为不同浓度 TBAPF₆ 改性 CsPbI₂Br PSCs

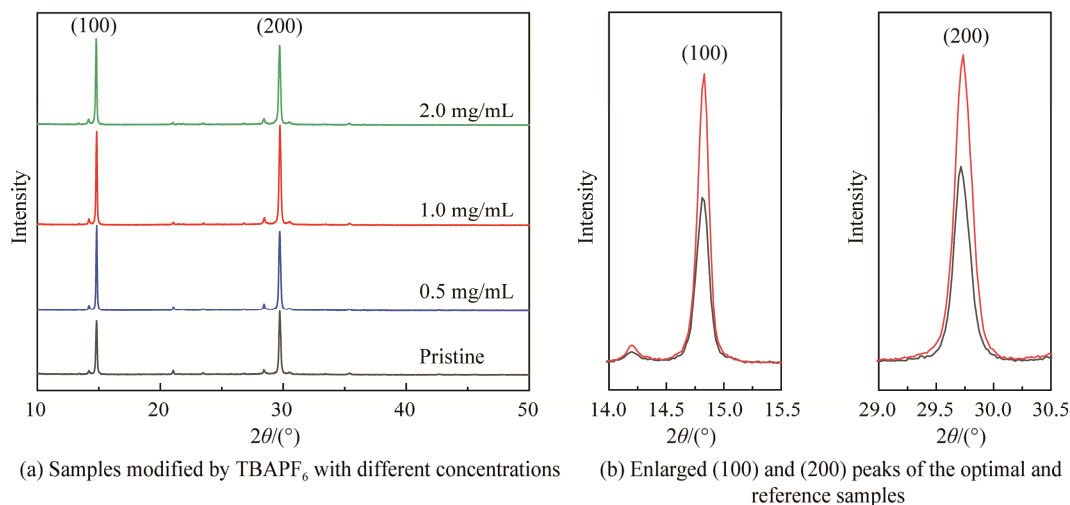
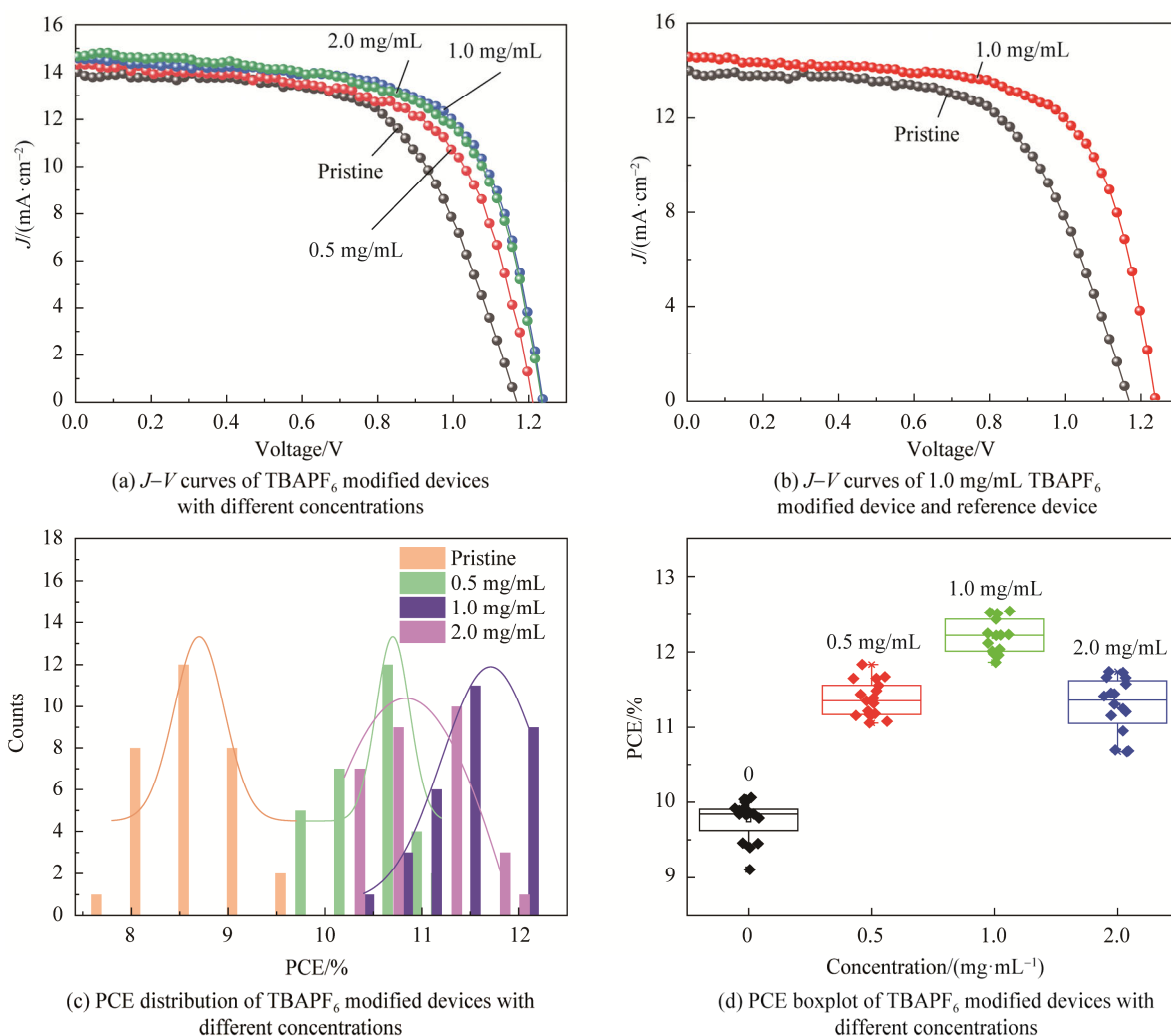


图 4 不同浓度 TBAPF₆ 改性 CsPbI₂Br 钙钛矿薄膜的 XRD 谱

Fig. 4 XRD spectra of CsPbI₂Br perovskite films modified by TBAPF₆ with different concentrations



PCE is power conversion efficiency.

图 5 不同浓度 TBAPF₆ 改性 CsPbI₂Br PSCs 器件的光伏性能

Fig. 5 Photovoltaic performance of CsPbI₂Br PSCs modified by TBAPF₆ with different concentrations

在 AM1.5G 光照下(100 mW/cm^2)的电流密度–电压 (J - V)曲线, 光伏性能参数如表 1 所示。由图 5a 和表 1 可见, 随着浓度的增加, 器件的光伏性能参数呈现先增加后减少的趋势。未改性的原始器件展现出 1.16 V 的开路电压(V_{oc}), 14.02 mA/cm^2 的短路电流密度(J_{sc}), 60% 的填充因子(FF), PCE 达到 9.93% 。当 TBAPF₆ 浓度从 0 增加到 1.0 mg/mL 时, 器件的各种光伏参数达到最佳值, 最高 PCE 达到 12.04% , V_{oc} 为 1.24 V , J_{sc} 为 14.60 mA/cm^2 , FF 为 67% , PCE、 V_{oc} 、 J_{sc} 、FF 分别提高了 21% 、 24% 、 6.9% 、 11.7% 。其中, V_{oc} 提升最明显, 说明 TBAPF₆ 起到了良好的钝化缺陷的效果; J_{sc} 都有所提升, 说明 CsPbI₂Br 钙钛矿光吸收层的薄膜质量得到了改善; PCE 和 FF 提升为器件综合的表现, 这主要得益于表面形态的改善、表面缺陷的减少、载流子非辐射复合降低和载流子迁移率的提高。

为了检验重复性, 设置基于不同浓度 TBAPF₆ 的器件各 30 个, PCE 值统计如图 5b 和箱线图 5c。由图 5b 和图 5c 可见, 优化器件的整体 PCE 分布明显高于原始器件, 其中 0.5 mg/mL 浓度优化器件的 PCE 主要分布在 $11.0\% \sim 11.5\%$ 区间, 个别能达到 11.5% 以上; 1.0 mg/mL 浓度优化器件的 PCE 明显上升, 主要分布在 12% 左右, 是器件 PCE 整体分布最优的, 最高达到 12.04% ; 2.0 mg/mL 浓度优化器件的 PCE 主要分布在 $11.0\% \sim 11.8\%$ 区间, 略微下降, 虽然

整体分布明显比上述各浓度器件要低, 但仍然优于原始器件, 因此将 1.0 mg/mL 设置为本工作界面改性剂的最佳浓度; 相较于优化器件, 原始器件的 PCE 主要分布在 $7\% \sim 10\%$ 区间。不同浓度优化器件性能的一致性意味着 TBAPF₆ 界面改性效果的可重复性, 证明 TBAPF₆ 对器件的效率有明显的优化作用。

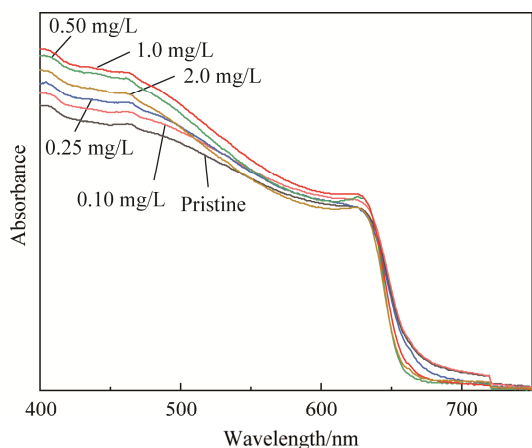
表 1 不同浓度 TBAPF₆ 改性 CsPbI₂Br PSCs 器件的光伏性能参数

Table 1 Photovoltaic parameters of CsPbI₂Br PSCs modified by TBAPF₆ with different concentrations

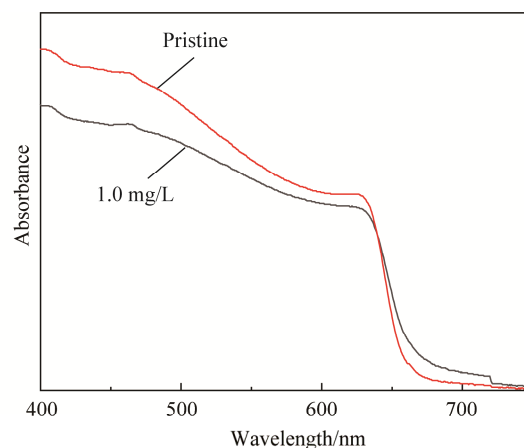
Concentration/($\text{mg} \cdot \text{mL}^{-1}$)	V_{oc}/V	$J_{sc}/(\text{mA} \cdot \text{cm}^{-2})$	FF/%	PCE/%
Pristine	1.16	14.02	0.60	9.93
0.5	1.21	14.33	0.64	11.08
1.0	1.24	14.60	0.67	12.04
2.0	1.23	14.68	0.65	11.73

V_{oc} is open circuit voltage; J_{sc} is short circuit current density; FF is fill factor.

图 6a 为不同浓度 TBAPF₆ 改性 CsPbI₂Br 钙钛矿薄膜在可见光范围内的吸收谱($400 \sim 800 \text{ nm}$)。由图 6a 可见, 随着 TBAPF₆ 浓度的增加, CsPbI₂Br 薄膜对应的光吸收能力逐渐加强, 当浓度为 1.0 mg/mL 时, 对应的光吸收能力最大, 如图 6b 所示。当浓度为 2.0 mg/mL 时, 光吸收能力下降; 不同浓度 TBAPF₆ 界面改性 CsPbI₂Br 薄膜在 645 nm 附近都有一个吸收限, 对应了 CsPbI₂Br 钙钛矿的带隙宽度 (1.92 eV), 这与 PL 测试结果一致。



(a) TBAPF₆ modified CsPbI₂Br films with different concentrations



(b) 1.0 mg/mL TBAPF₆ modified and pristine CsPbI₂Br films

图 6 不同浓度 TBAPF₆ 改性 CsPbI₂Br 钙钛矿薄膜的可见光吸收光谱

Fig. 6 Visible light absorption spectra of CsPbI₂Br perovskite films modified by TBAPF₆ with different concentrations

为了深入了解 TBAPF₆ 界面改性对 CsPbI₂Br 钙钛矿薄膜能级结构的影响, 对优化前后的样品进行了 UPS 测试, 并分析其价带顶(E_v)、导带底(E_c)和 Fermi 能级(E_F)的位置。UV-Vis 吸收光谱 Tauc Plot 如图 7a 和图 7b 所示, 得到对照组和优化组的光学

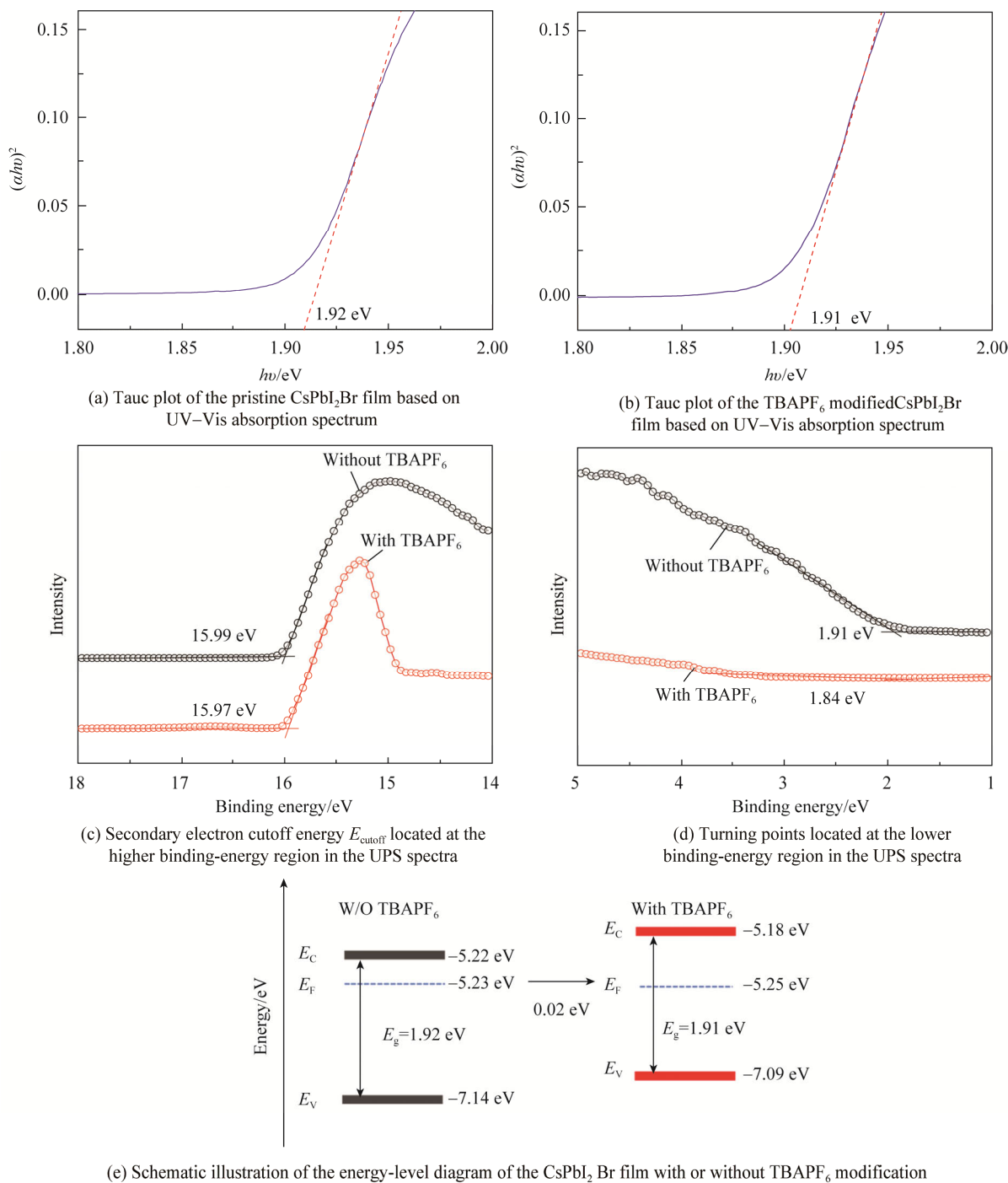
带隙(E_g)分别为 1.92 eV 和 1.91 eV , 可知优化后带隙略微降低, 吸收光谱产生一定的红移。图 7c 为 UPS 高结合能区对照组和优化组的二次电子截止能量 (E_{cutoff}), 分别为 15.99 eV 和 15.97 eV , 依据式(1)可计算出 E_F 分别为 -5.23 eV 和 -5.25 eV , 其中 21.22 eV

为 He 离子能量, 可以看出优化前后 Fermi 能级 E_F 从 -5.23 eV 下移到 -5.25 eV, 下降了 0.02 eV, 改性后 E_F 越靠近价带, 说明 CsPbI₂Br 钙钛矿薄膜由 N 型向 P 型转变^[21]。

$$E_F = 21.22 - E_{\text{cutoff}} \quad (1)$$

图 7d 为 UPS 低结合能区转折点对应 E_v 与 E_F 的能级差, 分别位于 1.90 eV 和 1.84 eV, 可计算出

对照组和优化组的 E_v 分别为 -7.14 eV 和 -7.09 eV; 依据 E_g 值, 可计算出对照组和优化组的 E_c 分别为 -5.22 eV 和 -5.18 eV; 依照 E_v 、 E_c 和 E_F 位置, 绘制出优化前后能带结构变化图, 如图 7e 所示。由此可以看出, 经过 TBAPF₆ 界面改性后, E_v 上移 0.05 eV, 这使 CsPbI₂Br/碳电极界面的能级偏移减小, 有效降低了 V_{oc} 损失, 促进了钙钛矿与碳电极之间的空穴传输^[16]。

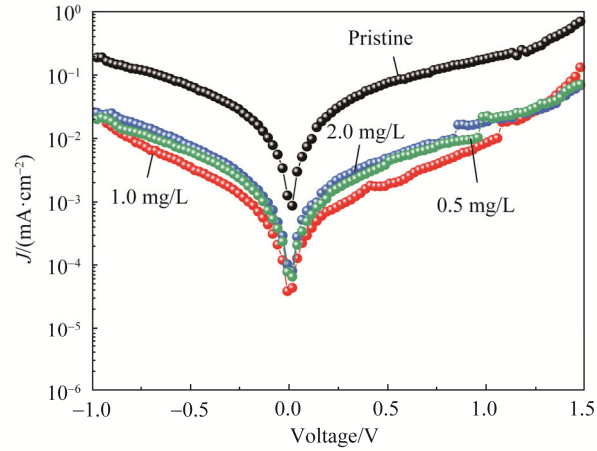


E_c is conduction band minimum; E_F is Fermi level; E_v is valence band maximum; UPS is ultraviolet photoelectron spectra.

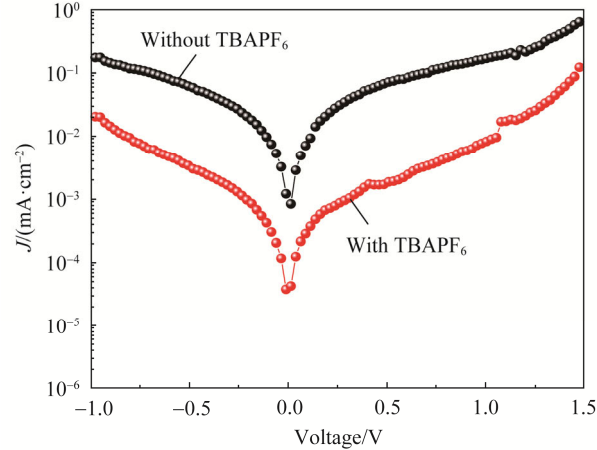
图 7 未改性与 1.0 mg/mL TBAPF₆ 改性 CsPbI₂Br 钙钛矿薄膜的能带结构
Fig. 7 Band structures of the pristine and 1.0 mg/mL TBAPF₆ modified CsPbI₂Br perovskite films

2.5 器件的电荷分离和转移特性表征

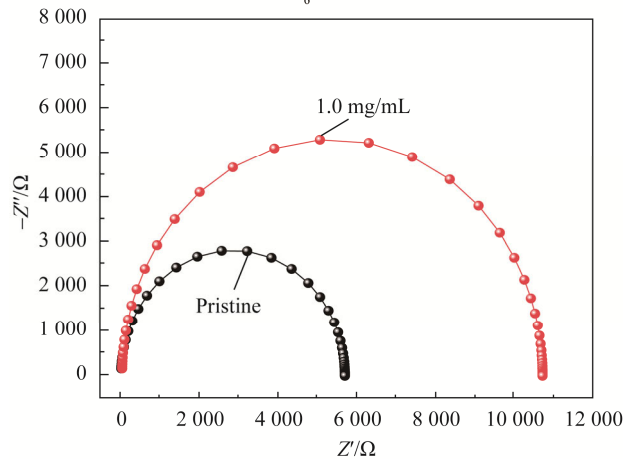
如图 8a 所示, 对原始器件和不同浓度 TBAPF₆ 界面改性的器件进行了暗电流测量。结果显示, 经



(a) Dark J - V curves for pristine and TBAPF₆ modified devices with different concentrations



(b) Dark J - V curves for the pristine and 1.0 mg/mL TBAPF₆ modified devices



(c) Nyquist plot curves of the pristine and 1.0 mg/mL TBAPF₆

图 8 原始器件与不同浓度 TBAPF₆ 改性器件的电荷分离和转移特性

Fig. 8 Charge separation and transfer characteristics of the pristine and TBAPF₆ modified devices with different concentrations

过 TBAPF₆ 处理后器件的暗电流密度均低于原始器件的暗电流密度, 证明经过优化的器件可以有效降低载流子复合机率。随着 TBAPF₆ 浓度的增加, 暗电流密度随之降低; 当浓度增加到 1.0 mg/mL 时, 器件的暗电流密度最低; 浓度再增加时, 暗电流密度略有上升, 但始终低于原始器件的暗电流密度。当 TBAPF₆ 浓度为 1.0 mg/mL 时, 优化器件达到最佳的效果, 远低于参考器件接近 2 个数量级, 如图 8b 所示, 这证明 TBAPF₆ 界面改性可以有效地抑制漏电流和降低缺陷密度。

为评估 CsPbI₂Br PSCs 中电荷传输和复合情况, 进行了 EIS 测量, 结果如图 8 所示, 其中图 8a 与图 8b 为暗电流 J - V 曲线、图 8c 为 Nyquist 图, 表 2 总结了等效电路模型拟合的数据。经过最佳浓度为 1.0 mg/mL TBAPF₆ 改性的 CsPbI₂Br 器件呈现出最低的串联电阻 R_s 和最高的复合电阻 R_{rec} 值; 与参考器件相比, 虽然界面改性的器件的串联电阻没有降低, 但是复合电阻得到了很大的提升, 可以推断出在 CsPbI₂Br/TBAPF₆ 界面处, TBAPF₆ 界面改性可以有效缓解钙钛矿光吸收层载流子非辐射性复合和提高载流子迁移率, 这与暗电流测量和 PL 测量的结果一致。

表 2 原始器件与 1.0 mg/mL 浓度 TBAPF₆ 改性器件基于等效电路模型拟合的数据

Table 2 Fitted data of the pristine and 1.0 mg/mL TBAPF₆ modified devices based on equivalent circuit model

Concentration/(mg·mL ⁻¹)	R_s/Ω	R_{rec}/Ω	C/nF
Pristine	48.47	5 653	9.648×10^{-9}
1.0	72.28	10 624	9.747×10^{-9}

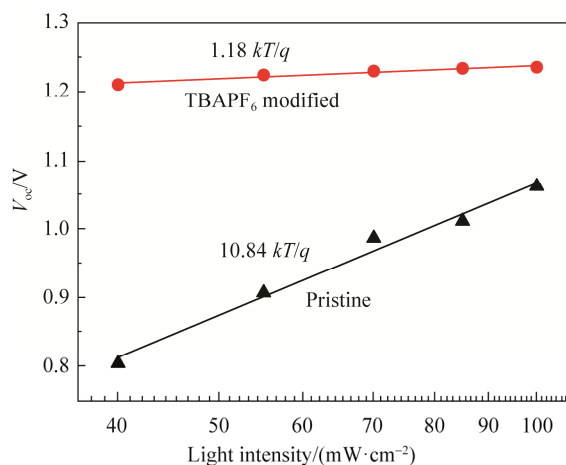
R_s is series resistance; R_{rec} is recombination resistance; C is capacitance.

为了进一步探究 TBAPF₆ 界面改性 CsPbI₂Br PSCs 器件中光生载流子复合情况, 对 TBAPF₆ 优化器件和原始器件进行了可变光强测试, 并绘制了改性前后 J_{sc} 和 V_{oc} 输出作为光照强度的函数, 如图 9 所示。根据式(2)和式(3)可知, 器件的 V_{oc} 、 J_{sc} 与光照强度成正相关, 对应的斜率反映界面处电子与空穴的复合方式, 证明载流子非辐射复合的抑制效果。由图 9a 可见, 优化器件的 V_{oc} 与光强(I)的斜率为 $1.18 kT/q$, 原始器件的 V_{oc} 与 I 斜率为 $10.84 kT/q$; 由图 9b 可见, 优化器件的 J_{sc} 与 I 斜率为 0.928, 原始器件的 J_{sc} 与 I 斜率为 0.860。优化后器件的 V_{oc} 与 I 的斜率值变小很多, 表明优化器件的缺陷得到有效钝化, 抑制了载流子非辐射复合概率; 而 J_{sc} 与 I 的斜率越接近于 1, 表明双分子复合更加可以忽略^[22]。

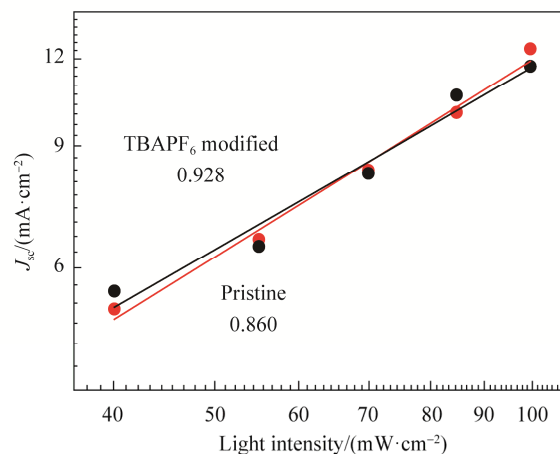
$$J_{sc} \propto I^\alpha \alpha \leq 1 \quad (2)$$

$$V_{OC} = \frac{nkT \ln(I)}{q} + \text{constant} \quad (3)$$

其中: α 、 n 为理想因子; k 、 T 、 I 、 q 分别为 Boltzmann 常数、温度、光强、电量。



(a) V_{OC} as a function of light intensity for the pristine and 1.0 mg/mL TBAPF₆ modified devices



(b) J_{sc} as a function of light intensity for the pristine and 1.0 mg/mL TBAPF₆ modified devices

k is Boltzmann constant; T is temperature; q is quantity of electric charge.

图 9 原始器件与 1.0 mg/mL 浓度 TBAPF₆ 改性器件的 J_{sc} 、 V_{OC} 与光照强度的函数关系

Fig. 9 V_{OC} and J_{sc} as a function of light intensity for the pristine and 1.0 mg/mL TBAPF₆ modified devices

通过 PL 和 TRPL 探究了 TBAPF₆ 改性对 CsPbI₂Br 薄膜中载流子复合和激子寿命的影响。如图 10a 所示, 经过 TBAPF₆ 表面改性 CsPbI₂Br 薄膜表现出更强的光致发光峰, 进一步揭示 TBAPF₆ 处理降低了缺陷态密度并抑制了载流子非辐射复合, 与前面讨论的暗电流测量和 EIS 测量相一致。此外, 相应的 TRPL 衰减曲线用双指数函数拟合, 如图 10b 所示, 相应的拟合参数列于表 3。时间寿命较短的 τ_1 归因于表面缺陷态复合, 称为单分子复合; 时间寿命较长的 τ_2 归因于体相的复合过程, 也称之为双分子复合^[23]。根据式(4)计算出平均载流子寿命(τ_{ave}),

可以观察到一个明显的现象, TBAPF₆ 改性的 CsPbI₂Br 薄膜拥有比原始薄膜(34.67 ns)更长的平均载流子寿命(78.09 ns), 表明通过 TBAPF₆ 改性延长载流子的寿命和抑制缺陷相关的电荷复合。因此, 可以进一步验证优化后器件的 V_{OC} 增加是由于钙钛矿光吸收层的载流子非辐射复合减少。

$$\tau_{ave} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i} \quad (4)$$

式中: A_i 为衰减幅值($i=1$ 或 2); τ_i 为载流子寿命($i=1$ 或 2)。

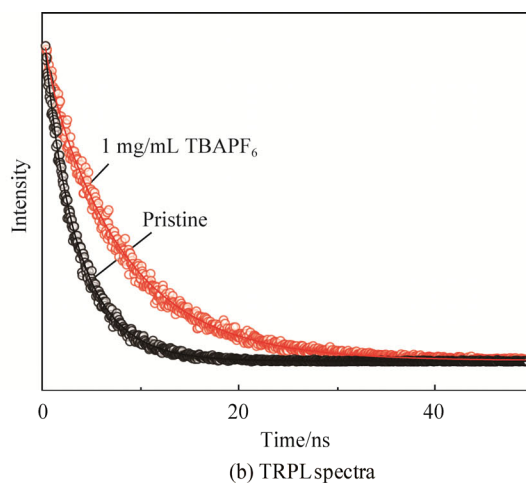
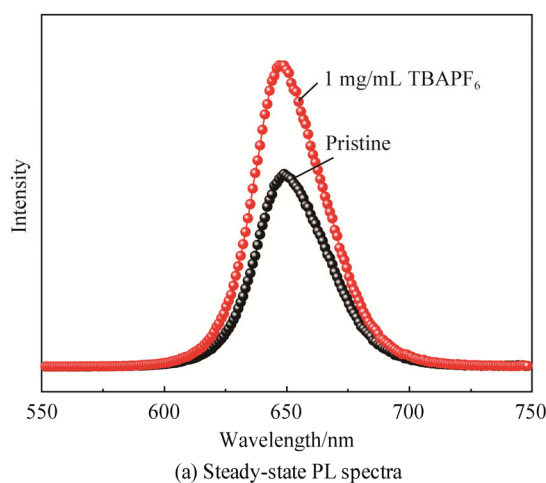


图 10 未改性与 1.0 mg/mL 浓度 TBAPF₆ 改性 CsPbI₂Br 钙钛矿薄膜的稳态 PL 谱和瞬态 TRPL 谱

Fig. 10 Steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra of the pristine and 1.0 mg/mL TBAPF₆ modified CsPbI₂Br perovskite films

表 3 未改性与 1.0 mg/mL 浓度 TBAPF₆ 改性 CsPbI₂Br 薄膜的 TRPL 谱拟合平均载流子寿命

Table 3 Fitted average carrier lifetime from time-resolved photoluminescence (TRPL) spectra of the pristine and 1.0 mg/mL TBAPF₆ modified CsPbI₂Br films

Concentration/(mg·mL ⁻¹)	A ₁ /%	τ ₁ /ns	A ₂ /%	τ ₂ /ns	τ _{ave} /ns
Pristine	157.34	1.63	817.15	3.93	34.67
1.0	62.00	4.84	927.16	8.10	78.09

A₁ and A₂ represent decay amplitude; τ₁ represents the carrier lifetime derived from surface defective state recombination; τ₂ represents the carrier lifetime derived from bulk recombination; τ_{ave} represents the average carrier lifetime.

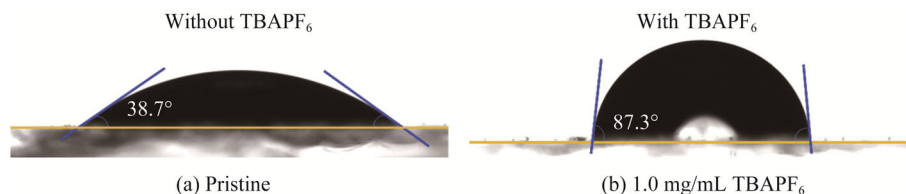


图 11 未改性与 1.0 mg/mL 浓度 TBAPF₆ 改性 CsPbI₂Br 钙钛矿薄膜的水接触角
Fig. 11 Contact angles of the pristine and 1.0 mg/mL TBAPF₆ modified CsPbI₂Br perovskite films

为进一步验证改性前后 CsPbI₂Br 钙钛矿薄膜的湿稳定性,进行了 UV-Vis 吸收光谱在 35%~40%湿度条件下经过 72 h 随时间连续变化的测试,如图 12 所示。由图 12 可见,未改性 CsPbI₂Br 钙钛矿薄膜的光吸收能力随着时间延长而减弱非常明显,而 1.0 mg/mL 浓度 TBAPF₆ 改性 CsPbI₂Br 钙钛矿薄膜的光吸收能力随着时间延长而减弱比较缓慢,这进一步证实了经过 TBAPF₆ 改性后 CsPbI₂Br 钙钛矿薄膜的湿度稳定性得到了显著提升。

在潮湿的空气环境中,水分子会促使 CsPbI₂Br 从钙钛矿立方相(α)转变为非钙钛矿相(δ)^[23],因此

2.6 环境稳定性测试

为了探究 TBAPF₆ 改性对 CsPbI₂Br 钙钛矿薄膜疏水性能的影响,对未改性与 1.0 mg/mL 浓度 TBAPF₆ 改性 CsPbI₂Br 钙钛矿薄膜的水接触角进行了测试,测试结果如图 11 所示。由图 11 可见,未改性 CsPbI₂Br 钙钛矿薄膜的水接触角为 38.15°±0.55°,而 1.0 mg/mL 浓度 TBAPF₆ 改性 CsPbI₂Br 钙钛矿薄膜的水接触角为 86.85°±0.45°,后者的水接触角比前者增大 48.70°,由此证明 TBAPF₆ 改性 CsPbI₂Br 钙钛矿薄膜的疏水性显著提高,这可以有效阻挡空气中水分子入侵,从而增强湿稳定性。

CsPbI₂Br PSCs 器件在潮湿的条件下光伏性能也会迅速下降。为此,对未改性与 1.0 mg/mL 浓度 TBAPF₆ 改性 CsPbI₂Br PSCs 器件在室温、暗态、35%~40%湿度条件下进行了标准化 PCE 随时间演变的测试,结果如图 13 所示。由图 13 可见,未改性 CsPbI₂Br PSCs 器件的 PCE 值在 3 h 内已出现明显的下降,8 h 后的 PCE 下降到 20%,10 h 后下降为零;1.0 mg/mL 浓度 TBAPF₆ 改性 CsPbI₂Br PSCs 器件能够在 7 h 后保持初始 PCE 值的 90%,16 h 后保持初始 PCE 值的 80%,表现出了良好的湿稳定性,这证明了经过 TBAPF₆ 界面改性后器件的湿稳定性也得到了显著提升。

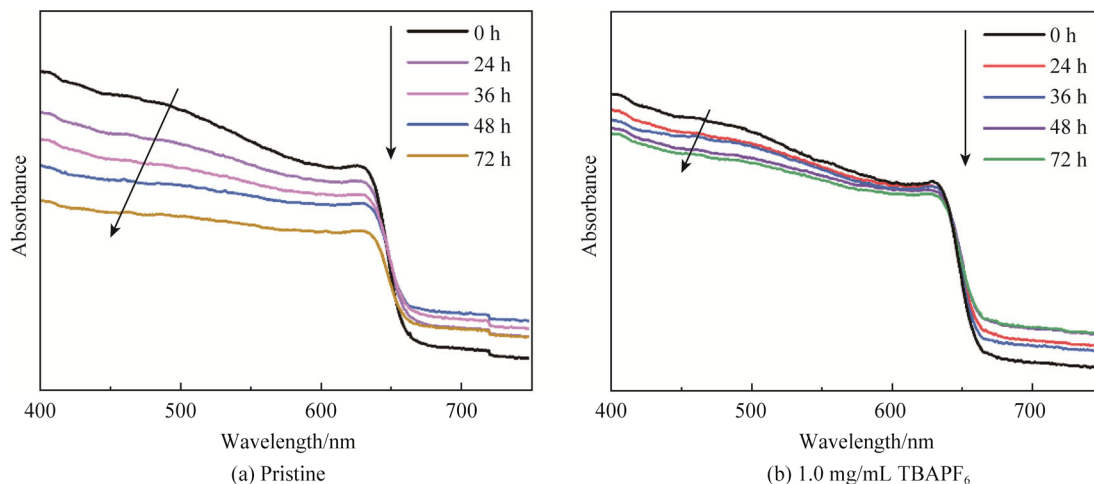


图 12 未改性与 1.0 mg/mL 浓度 TBAPF₆ 改性 CsPbI₂Br 钙钛矿薄膜在 35%~40%湿度条件下 UV-Vis 的时间演变
Fig. 12 Temporal evolution of standardized UV-Vis of the pristine and 1.0 mg/mL TBAPF₆ modified CsPbI₂Br perovskite films at 35%–40% humidity

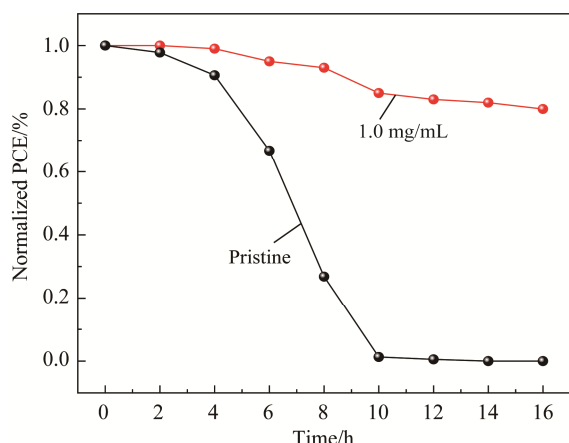


图 13 无封装原始器件与 1.0 mg/mL 浓度 TBAPF₆ 改性 CsPbI₂Br 器件在 35%~40% 湿度条件下标准化 PCE 的时间演变

Fig. 13 Temporal evolution of standardized PCE of the pristine and 1.0 mg/mL TBAPF₆ modified CsPbI₂Br devices without encapsulation at 35%~40% humidity

为了表征器件的热稳定性,对原始器件与 1.0 mg/mL 浓度 TBAPF₆ 改性 CsPbI₂Br PSCs 器件在暗态、空气环境、85 °C 条件下进行了标准化 PCE 随时间演变的测试,结果如图 14 所示。由图 14 可见,原始器件的 PCE 值在 24 h 后只保留了原来的 23.9%; 1.0 mg/mL 浓度 TBAPF₆ 改性 CsPbI₂Br PSCs 器件能够在 72 h 后保持初始 PCE 值的 70.2%,由此可见,器件的热稳定性获得了很大的增强。

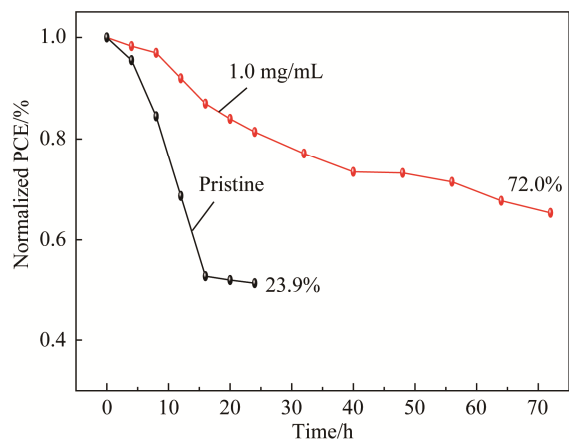


图 14 无封装原始器件与 1.0 mg/mL 浓度 TBAPF₆ 改性 CsPbI₂Br 器件在空气环境 85 °C 标准化 PCE 的时间演变

Fig. 14 Temporal evolution of standardized PCE of the pristine and 1.0 mg/mL TBAPF₆ modified CsPbI₂Br devices without encapsulation at 85 °C in air

3 结论

1) TBAPF₆ 界面改性剂不仅能有效钝化 CsPbI₂Br

钙钛矿薄膜的表面缺陷,减少载流子非辐射复合,而且可以改善 CsPbI₂Br/碳电极界面的能级排列,促进载流子传输,还能够起到疏水作用,从而提高全无机 CsPbI₂Br PSCs 的 PCE 和稳定性。

2) TBAPF₆ 表面改性 CsPbI₂Br 薄膜,微观组织更加平整致密、结晶度更高。带隙 E_g 略微变小,光吸收能力增强; E_f 更接近价带,意味着向 P 型转变; E_v 向上移动,有利于 CsPbI₂Br/碳电极界面的空穴传输。稳定光致发光强度更强,平均载流子寿命更长;暗电流减小,复合电阻增大,说明优化后器件的缺陷得到有效钝化,降低了载流子非辐射复合的概率。分子建模和静电势模拟表明, TBAPF₆ 的 PF₆⁻ 通过静电作用钝化了带正电荷的卤素空位, TBA⁺ 则通过离子键和氢键钝化了带负电的 Cs⁺ 空位;带有长烷基链的官能团和氟原子能有效阻碍空气中水分子的入侵,从而提高器件的湿稳定性。

3) TBAPF₆ 浓度为 1.0 mg/mL 时,器件获得最佳效率,ITO/SnO₂/CsPbI₂Br/TBAPF₆/C 结构的 PSCs 器件的 PCE、 V_{oc} 、 J_{sc} 、FF 分别为 12.04%、1.24 V、14.60 mA/cm²、67%,在 35%~40% 的湿度环境中 16 h 后保持了初始效率的 80%,在空气环境 85 °C、72 h 后保持了初始效率的 70.2%,其湿热稳定性相比于原始器件获得了极大的提升。

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Multifunctional Interface Modification of Tetrabutylammonium Hexafluorophosphate to All-Inorganic CsPbI₂Br Perovskite Solar Cells

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Extended Abstract

Introduction The all-inorganic wide-band gap CsPbI₂Br perovskite (1.92 eV) trades off stability and light absorption performance, showing a great application potential in tandem solar cells and flexible solar cells. However, its power conversion efficiency (PCE) and stability still need to be further improved. Usually, the CsPbI₂Br perovskite films derived from solution process will inevitably generate various defects at interfaces or grain boundaries as non-radiative recombination centers for photogenerated carriers, and they are sensitive to water molecules to degrade, thus reducing the photovoltaic performance and stability of the devices. It was reported that the interface modification of functional cations (*i.e.*, alkali metal ions, organic amine ions, *etc.*) and anions (*i.e.*, halogen ions, acetic acid ions, *etc.*) had a positive effect on improving the efficiency and stability of perovskite solar cells (PSCs).

In this paper, a modifier tetrabutylammonium hexafluorophosphate (TBAPF₆) with both defect passivation and hydrophobic functions was used to modify the interface of CsPbI₂Br/Carbon for the improvement of the PCE and stability of hole-free carbon-based CsPbI₂Br PSCs with an architecture of indium tin oxide (ITO)/SnO₂/CsPbI₂Br/TBAPF₆/Carbon. TBAPF₆ as an ionic liquid with the Lewis base properties was used as a dopant or an interfacial modifier of perovskite films, which was conducive to passivating the defects of devices. The surface modification of CsPbI₂Br perovskite films was carried out at different concentrations of TBAPF₆, and its effect on the film quality of CsPbI₂Br perovskite and the photovoltaic performance and environmental the stability (including wet and thermal stability) of CsPbI₂Br PSCs devices was investigated.

Methods Lead iodide (PbI₂, 99.999%, in mass fraction, the same below, Advanced Election Technology Co., Ltd.), lead bromide (PbBr₂, 99.999%, Advanced Election Technology Co., Ltd.), cesium iodide (CsI, 99.999%, Advanced Election Technology Co., Ltd.), tetrabutylammonium hexafluorophosphate (TBAPF₆, 98%, Aladdin Co.), dimethyl sulfoxide (DMSO, analytical reagent, Sigma-Aldrich Co.), tin (IV) oxide colloid (SnO₂, Alfa Co.), isopropanol (99.5%, Aladdin Co.), ITO-etched glass (square resistance 7–9 Ω/square, Advanced Election Technology Co., Ltd.), and conductive carbon paste (Huamin New Material Technology Co., Ltd.).

1.0 mol/L CsPbI₂Br perovskite precursor was prepared *via* dissolving CsI, PbBr₂, and PbI₂ at a molar ratio of 1.0:0.5:0.5 in

DMSO. The ITO-etched glass substrates were cleaned with ethanol, acetone, isopropanol, and ethanol under ultrasonication for 15 min and dried in an oven, and then treated with UV ozone for 25 min. The SnO₂ colloid precursor was spin-coated onto ITO glass substrates at 3 000 r/min for 30 s and then put on a hot plate in ambient air at 150 °C for 30 min. After 10 min for UV ozone, 44 μ L perovskite precursor solution was deposited on the SnO₂ layer through a spin-coating process at 1 000 r/min for 10 s and then 3 000 r/min for 30 s in anitrogen-filled glove box. After the spin-coating process, the obtained films were placed on a hot plate at 40 °C for 3 min and then annealed at 150 °C for 5 min. Afterwards, 45 μ L TBAPF₆ solution in isopropanol (IPA) with different concentrations (*i.e.*, 0, 0.5, 1.0 and 2.0 mg/mL) was spin-coated on the CsPbI₂Br films at 4 000 r/min for 30 s and then annealed at 120 °C for 10 min, respectively. Finally, the carbon electrode was deposited on top of the device by a doctor-blading method and then the prepared device was completed after annealing at 120 °C for 20 min.

The morphology of the absorber layers was observed by a model JSEM-5610LV field-emission scanning electron microscope (SEM, JEOL Co., Japan). The X-ray diffraction (XRD) pattern was recorded by a model AXS X-ray diffractometer (Bruker Co., Germany) with Cu K α radiation ($\lambda=1.54$ Å). The current density–voltage (J – V) curves of devices were obtained by a model Keithley 2400 source meter under an illumination of AM 1.5G (100 mW/cm²) with cell area controlled at 0.09 cm² by a black metal mask. The ultraviolet photoelectron spectra (UPS) were determined by a model ESCALAB 250XI ultraviolet photoelectron spectroscope (Thermo Co., USA) and a model PHI 5 000 Versa Probe III (ULVAC-PHI, Inc., Japan), and the test light source energy was 21.22 eV. The UV–Vis absorption spectra were recorded by a model UV-3600plus spectrophotometer (Shimadzu Co., Japan) in a wavelength range from 300 to 800 nm at room temperature. The steady-state photoluminescence (PL) was obtained by a model FLS1000 UltraFast fluorescence spectrometer (Edinburgh Co., UK) with an excitation wavelength of 450 nm at room temperature. The time-resolved photoluminescence (TRPL) spectra were obtained on a model Delta Flex fluorescence spectrometer (HORIBA Scientific Co., Japan) using a time-dependent single photon counting method. The electrochemical impedance spectroscopy (EIS) were carried out with a model PP211&CHI1030B electrochemical workstation under illumination with a bias at 0 V in a frequency range of 1 Hz–2 MHz.

Results and discussion Based on density functional theory, the Gauss View and Gaussian were used to conduct molecular modeling and electrostatic potential simulation analysis for TBAPF₆. The cation is a quaternary ammonium ion (TBA⁺) containing 4 butyl groups, and the anion is 6 fluorophosphate ion (PF₆[−]). TBAPF₆ has the Lewis base properties, in which nitrogen has some uncoordinated lone pair electrons, which can effectively passivate the uncoordinated Pb²⁺ through electrostatic action. TBA⁺ can interact with negatively charged defects such as Cs⁺ vacancies through ionic and hydrogen bonds. Since anion PF₆[−] is negatively charged, positively charged defects (such as halogen vacancies) are passivated by electrostatic action, and fluorine atoms on the anion also play a hydrophobic role to a certain extent.

The effect of TBAPF₆ interface modifier on the surface morphology of CsPbI₂Br perovskite films was analyzed by SEM. The surface morphology of the pristine sample is uneven and rugged. Clearly, there are many pinholes on the surface of the film and cannelures between the grains possibly due to the corrosion of water molecules on the grain boundaries. These characteristics are the main causes of leakage current. Compared with the pristine film, the surface morphology of TBAPF₆-modified film is more smooth, uniform and dense. There are few pinholes on the surface and no cannelures between grains. Therefore, TBAPF₆ modification can effectively improve the surface morphology of CsPbI₂Br perovskite films to prevent the erosion of water molecules in air, and the dense microstructure is conducive to improving the photovoltaic performance and stability of the devices. The phase composition of CsPbI₂Br perovskite films treated at different concentrations of TBAPF₆ was analyzed by XRD. Clearly, all the samples have characteristic diffraction peaks with 2θ of 14.5° and 29.6°, corresponding to the planes (100) and (200) of perovskite phase. The characteristic peak intensity increases significantly with the increase of TBAPF₆ concentration. When the concentration increases upto 1.0 mg/mL, the characteristic diffraction peak intensity reaches the maximum value. However, the characteristic peak intensity decreases when the concentration of TBAPF₆ further increases.

The pristine device has a PCE of 9.93%, with an open circuit voltage (V_{oc}) of 1.16 V, a short circuit current density (J_{sc}) of 14.02 mA/cm², and a fill factor (FF) of 60%. As TBAPF₆ concentration increases from 0 to 1.0 mg/mL, the device with an architecture of ITO/SnO₂/CsPbI₂Br/TBAPF₆/carbon exhibits the maximum PCE of 12.04%, with V_{oc} of 1.24 V, J_{sc} of 14.60 mA/cm², and FF of 67%. To test the repeatability, 30 devices based on different concentrations of TBAPF₆ were set up. The overall PCE distribution of the modified device is significantly greater than that of the pristine device. The PCE distribution of the modified device at 0.5 mg/mL is mainly in a range of 11.0%–11.5%, and some can reach more than 11.5%. The PCE of 1.0 mg/mL modified device increases, mainly distributes 12%, which is the optimum overall distribution of PCE (*i.e.*, 12.04%). The PCE of 2.0 mg/mL modified device is mainly distributed in a range of 11.0%–11.8%, which decreases slightly. Compared with the optimized device, the PCE of the pristine device is mainly distributed in a range of 7%–10%. Therefore, 1.0 mg/mL TBAPF₆ is an optimal concentration of the interface modifier.

The optical band gap (E_g) of the pristine and 1.0 mg/mL TBAPF₆-modified CsPbI₂Br perovskite films is 1.92 eV and 1.91 eV, respectively. The Fermi level (E_f) of the pristine and modified samples can be calculated as −5.23 eV and −5.25 eV, respectively, which drops from −5.23 eV to −5.25 eV before and after modification, and is closer to the valency band, indicating that CsPbI₂Br perovskite film changes from N-type to P-type semiconductor. The valence maximum (E_v) moves up by 0.05 eV, which reduces the energy level shift of the CsPbI₂Br/carbon electrode interface, thus effectively reducing V_{oc} loss and promoting the hole transfer between perovskite and carbon electrode.

At last, in the humidity environment of 35%–40%, 80% of the initial efficiency of the optimal 1.0 mg/mL TBAPF₆ modified device is maintained after 16 h, and in air at 85 °C after 72 h, 70.2% of the initial efficiency is maintained, indicating that the moisture and thermal stability are greatly improved, compared with the pristine device.

Conclusions The results showed that TBAPF₆ interface modification agent could effectively passivate the surface defects of CsPbI₂Br perovskite films, reduce the non-radiative recombination of carriers, improve the energy level arrangement of CsPbI₂Br/carbon electrode interface, and promote the carrier transport. It played a hydrophobic role. Thus, the PCE and stability of all inorganic hole-free carbon-based CsPbI₂Br PSCs were improved. The microstructure of TBAPF₆ modified CsPbI₂Br films was more smooth and dense with a higher crystallinity. The E_g decreased slightly, and the light absorption capacity increased. The E_f was closer to the valence band, indicating the transition from N-type to P-type semiconductor. The upward movement of E_v was conducive to the hole transfer at the CsPbI₂Br/carbon electrode interface. The steady-state photoluminescence intensity was more intense, indicating a longer average carrier lifetime. The decrease of dark current and the increase of recombination resistance indicated that the defects of the modified device were effectively passivated, and the probability of carrier non-radiative recombination was reduced. The molecular modeling and electrostatic potential simulation showed that PF₆[−] of TBAPF₆ passivated the positively charged halogen vacancies through electrostatic action, while TBA⁺ passivated the negatively charged Cs⁺ vacancies through ionic and hydrogen bonding. Some functional groups with long alkyl chains and fluorine atoms effectively prevented the intrusion of water molecules in air, thus improving the wet stability of the devices. The optimal 1.0 mg/mL TBAPF₆ modified device exhibited a champion PCE of 12.04%, with V_{oc} of 1.24 V, J_{sc} of 14.60 mA/cm², and FF of 67%, demonstrating the superior moisture and thermal stability, compared with the pristine device.

Keywords hexafluorophosphate; all-inorganic perovskite; interface modification; defect passivation; hydrophobicity