

界面工程技术用于空气环境制备的高性能倒置无机钙钛矿太阳电池

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摘 要: 带隙约为 1.7 eV 的倒置无机钙钛矿太阳电池(IPSCs)由于其元素组成和优异的光、热稳定性, 有望成为下一代光伏电池的候选材料。然而, 界面处较高的缺陷态密度和能级失配导致光伏性能不如具有相同带隙的有机-无机杂化太阳电池(HPSCs), 而使用界面工程技术利用四丁基碘化铵(TBAI)对倒置器件的光吸收层表面进行处理有效降低了倒置器件的缺陷态密度, 抑制了非辐射复合, 减少了界面处的载流子积累。最终, 空气环境制备的 IPSCs 的光电转换效率(PCE)由 17.10%提升到 19.76%, PCE 提升约为 15.56%。同时, 装置的稳定性也得到提升。

关键词: 无机钙钛矿; 缺陷态密度; 能级失配; 界面工程; 非辐射复合

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无机钙钛矿太阳电池(IPSCs)因其优异的光、热稳定性逐步引起科研工作者的广泛关注^[1-3]。尤其当带隙约为 1.7 eV 时, 由于较为特殊的元素组成在很大程度上规避了相分离的风险^[4-6], 是钙钛矿/晶硅两端叠层太阳电池(TSCs)优异的顶电池候选者之一^[7-9]。然而, 目前对组成叠层的顶部电池研究聚焦于有机-无机杂化钙钛矿太阳电池。这是因为有机-无机杂化太阳电池的光电转换效率(PCE)通常比 IPSCs 高。究其原因, 主要是 IPSCs 界面处严重的非辐射复合损失。相关研究表明, 钙钛矿太阳电池表面的缺陷态密度比体内高 3 个数量级^[10]。因此对 IPSCs 界面处进行合理的调控以降低缺陷态密度、抑制非辐射复合十分必要。有望通过界面工程技术, 实现光伏性能更加优异的单结器件与叠层器件。

在以往的研究中, 研究者们开发出多种策略对 IPSCs 的界面进行处理以实现光伏性能的提升。主要包括表面重建^[11-12]、异质结构建^[13-14]、维度工程^[15-17]等。WANG 等^[11]开发了一种表面重建策略, 通过将 2-氨基-5 溴苯-甲酰胺(ABA)溶解于甲醇之中, 然后利用高速的动态旋涂结合热退火的方式对无机

钙钛矿薄膜表面进行处理。羰基(C=O)和氨基(NH₂)与未配位的 Pb²⁺协同配位, 苯环上的 Br 有助于填补卤化物空位, 抑制 Pb⁰ 的形成。重建的结果实现了对无机钙钛矿薄膜表面和体内缺陷态密度的同步管理, 非辐射复合得到有效抑制, 最终实现了倒置 IPSCs 20.38% 的 PCE, 在 65 °C 的 N₂ 环境下放置 300 h 后, ABA 处理的装置仍可以实现对其初始 PCE 有 85.98% 的保留率^[11]。LU 等^[13]通过在 CsPbI₃ 顶部引入新的两性离子有机硫化物卤化物钙钛矿, 成功地将稳健的 Pb-S 共价性引入 CsPbI₃ 异质结中。半胱胺(⁺NH₃(CH₂)₂S⁻, CYS)与 PbCl₂ 发生反应, 在 CsPbI₃ 表面形成具有更浅 Fermi 能级的新型 3D 钙钛矿, 从而构建高效的 CsPbI₃/[CYS][PbCl₂]异质结, 可以显著抑制界面能量损失, 反式 CsPbI₃ 钙钛矿太阳电池实现了 20.38% 的 PCE 且稳定性优异。HEO 等^[15]利用无机零维钙钛矿诱导表面晶格排列, 实现了高效稳定的 IPSCs。具有良好晶格应变排列的无机零维 Cs₄PbBr₆ 被用作 CsPbI₃ 上的表面锚定覆盖层。Cs₄PbBr₆ 钙钛矿促进电荷有效提取并抑制非辐射复合。基于 Cs₄PbBr₆ 的 IPSCs 实现了 21.03%

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的 PCE^[15]。尽管倒置 IPSCs 的 PCE 在诸多策略之下稳步提升^[18–21]，依然存在较大的提升空间。尤其是基于空气条件下制备的 IPSCs，这是未来面相工业化生产必须克服的阻碍。因此迫切需要一种基于界面工程的表面处理技术对空气条件下制备的 IPSCs 进行后处理以提升其界面特性。

本研究利用四丁基碘化铵(TBAI)对倒置器件的光吸收层表面进行处理。TBAI 处理后器件的缺陷态密度受到抑制，非辐射复合降低，促进了界面处载流子的高效提取和传输。最终，基于 TBAI 界面处理的空气条件下制备的 IPSCs 实现了最高的 PCE 达 19.76%，远高于参考组的 17.10%。PCE 的提升主要是由于非辐射复合受到抑制。开路电压(V_{oc})明显改善(V_{oc} 由 1.066 V 提升到 1.200 V)。此外，器件的热、湿度稳定性也有大幅度提升。在 65 °C 的 N_2 条件下放置 500 h 后，TBAI 处理的装置可以保留其初始 PCE 的 90.41%，远高于参考组的 58.82%。未封装的器件在 30%~40% 的湿度条件放置 500 h 后，TBAI 处理的装置可以实现对其初始 PCE 有 83.59% 的保留率，而参考组装置在放置 243 h 时，其 PCE 就衰减到 80%。

1 实验

1.1 原料

N,N-二甲基甲酰胺(DMF, 纯度 99.5%)、二甲基亚砜(DMSO, 纯度 99.5%)、甲醇(纯度 99.5%)、异丙醇(IPA, 纯度 99.5%)、氯苯(CB, 纯度 99.5%)均购买自 Sigma-Aldrich 公司。碘化铯(CsI, 纯度 99.5%)、碘化氢铅($HPbI_3$, 纯度 99.5%)、溴化铅($PbBr_2$, 纯度 99.5%)、[6,6]-苯基 C_{61} 丁酸甲酯($PC_{61}BM$, 纯度 99%)、2,9-二甲基-4,7-联苯-1,10-菲罗啉(BCP, 纯度 99.5%)均购自西安宝莱特科技有限公司。四丁基碘化铵(TBAI, 纯度 99.5%)购自北京伊诺凯科技有限公司。聚[3-(4-羧基丁基)噻吩-2,5-二基] (P3CT)购自北京百灵威科技有限公司。聚[3-(4-甲氨基丁基)噻吩-2,5-二基] (P3CT-N)按照之前报道过的方法合成^[22]。

1.2 样品制备

本工作所制备的 IPSCs 为 pin 型结构，具体制备方法如下：氟掺杂氧化锡(FTO)玻璃基底依次在玻璃清洗剂、去离子水、异丙醇溶液中超声清洗 15 min，使用前将 FTO 衬底紫外臭氧处理 20 min。随后，将 10.0 mg/mL 的 NiO_x 水溶液，以 2000 r/min 的旋转速度旋涂于臭氧处理后的 FTO 玻璃表面，旋涂时间为 30 s，并在 130 °C 的空气环境中退火

20 min。待冷却至室温后，将 0.5 mg/mL 的 P3CT-N(甲醇溶液)以 4000 r/min 的转速旋涂于退火后的 NiO_x 表面并于空气环境 130 °C 退火 10 min，要特别注意的是，P3CT-N 滴加到 NiO_x 表面后，需要等待其自由扩散开后，静置 3~5 s 再开始旋涂，这有助于 P3CT-N 和 NiO_x 之间更好的界面接触。按照摩尔比 $n(CsI) : n(HPbI_3) : n(PbBr_2) = 3.00 : 2.85 : 0.15$ 的比例进行无机钙钛矿前驱液的配制，所用溶剂为 DMF : DMSO = 1 : 1 的混合溶剂，无机钙钛矿前驱液的浓度为 0.8 mol， N_2 环境下搅拌至完全溶解后，以 2500 r/min 的转速旋涂于 70 °C 预热的 P3CT-N 表面，旋涂时间为 25 s，并于湿度约为 20% 的空气环境中 190 °C 的热板上退火约 5~8 min。将退火后的薄膜转移至 N_2 氛围手套箱之中，以 6000 r/min 的转速动态旋涂 60 μL 的浓度为 2.0 mg/mL 的 TBAI (液体环境为 IPA)溶液，旋涂时间为 30 s，随后 80 °C 退火 5 min。利用蒸发设备在 TBAI 表面热蒸发 0.5 nm 的 MgF_2 。随后以 2000 r/min 的转速将 20.0 mg/mL 的 $PC_{61}BM$ (液体环境为 CB)旋涂 30 s 作为电子传输层，以 5000 r/min 的转速将 0.5 mg/mL 的 BCP (液体环境为 IPA)旋涂 30 s 作为空穴阻挡层。最后，利用蒸发设备在 BCP 表面蒸发 80.0 nm 的 Ag 作为金属电极。

1.3 样品表征

对 Control(无 TBAI)和 TBAI 等薄膜进行的紫外-可见光吸收测试采用 Varian Carry 500 (Shimadzu, 日本)。时间分辨光致发光(TRPL)光谱使用 FLS980 进行测试(Edinburgh Instruments, 美国)。器件的电流-电压特性由 Keithley 2400 Source meter(光焱科技 Enlitech, 中国)在 AM 1.5G 照明下测试，采用带有 KG-5 滤光片的硅标准电池校准光强，测试时所用金属掩膜面积为 0.075 5 cm²，以减少散射光的影响。样品形貌使用 FEI NanoSEM650(Thermo Fisher Scientific, 美国)型扫描电子显微镜(SEM)表征。外量子效率(EQE)测量使用 Enlitech (QE-R)测试(光焱科技 Enlitech, 中国)，水接触角测试利用 POWEREACH JC-2000C1 进行表征(上海中晨 POWEREACH, 中国)。Mott-Schottky 测试 (M-S) 由 Metrohm Autolab (PGSTAT204)(Metrohm, 瑞士)进行表征。

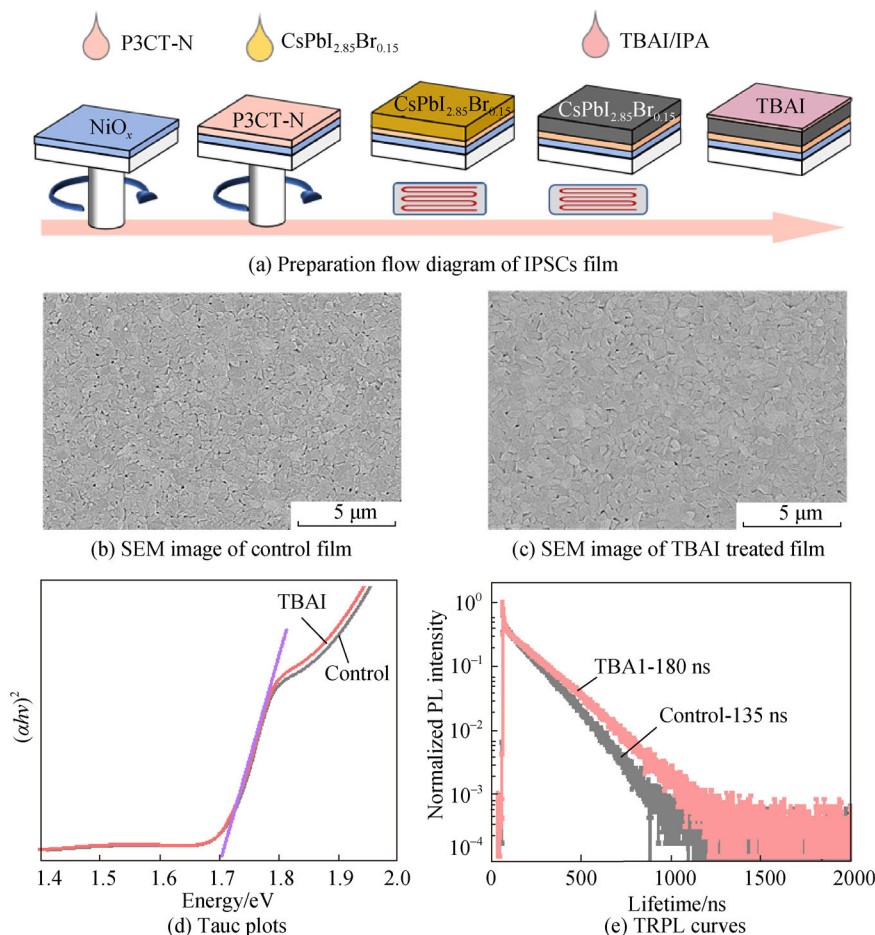
2 结果与讨论

2.1 无机钙钛矿薄膜的表面特性

利用图 1a 所示的流程图进行无机钙钛矿薄膜的制备。经 TBAI 界面处理与否的薄膜如图 1b 和图 1c 所示。相比之下，TBAI 处理的薄膜的颗粒更加

饱满且孔洞明显减少, 这些孔洞将作为非辐射复合的中心^[23-25], 严重制约着器件光伏性能的提升。由图 1d 可见, TBAI 后处理并不会改变无机钙钛矿

$\text{CsPbI}_{2.85}\text{Br}_{0.15}$ 的带隙。TRPL 测试的结果表明 TBAI 处理的薄膜具有更长的载流子寿命, 表明非辐射复合受到抑制^[26-27], 与 SEM 的结果相对应。



P3CT-N is poly[3-(4-(methylamino)butyl)thiophene-2,5-diyl]; TBAI is the devices with petrabutylammonium iodide; IPA is isopropyl alcohol; α is absorption coefficient; h is planck constant; ν is incident photon frequency; Control is the device without TBAI.

图 1 IPSCs 薄膜的制备流程图以及 Control 组与 TBAI 组的 SEM 照片、tauc 谱和 TRPL 曲线

Fig. 1 Preparation flow diagram of IPSCs film, the SEM imagine, tauc plots and TRPL curves for TBAI device and Control device

2.2 TBAI 对 IPSCs 光伏性能的影响

图 2a 为 IPSCs 的结构示意图, 参考组和实验组的区别仅在于是否在 $\text{CsPbI}_{2.85}\text{Br}_{0.15}$ 表面利用 TBAI 进行后处理。由图 2b 与表 1 可见, 参考组的 V_{OC} 仅为 1.066 V, 经过 TBAI 表面修饰后显著提升到 1.200 V, 器件的 PCE 也由 17.10%大幅度提升到 19.76%。为探明 V_{OC} 的提升机制, 进行了 Mott-Schottky 测试(图 2c), TBAI 处理的装置展示出 1.196 V 的内建电场, 远高于参考组的 1.038 V, 更大的内建电场意味着更强的载流子分离驱动力, 对应着更高的 V_{OC} ^[28-29]。图 2d 的 EQE 测试结果表明, Control 和 TBAI 处理的器件积分电流密度分别为 19.44 mA/cm^2 和 19.61 mA/cm^2 , 与 $J-V$ 测试的结果匹配良好。对 TBAI 处理的器件进行 300 s 的稳态功率输出(SPO)效率测试, 在 400 s 的时间内, 器

件的平均 SPO 效率为 19.36%, 曲线的波动可以忽略不计(图 2e)。

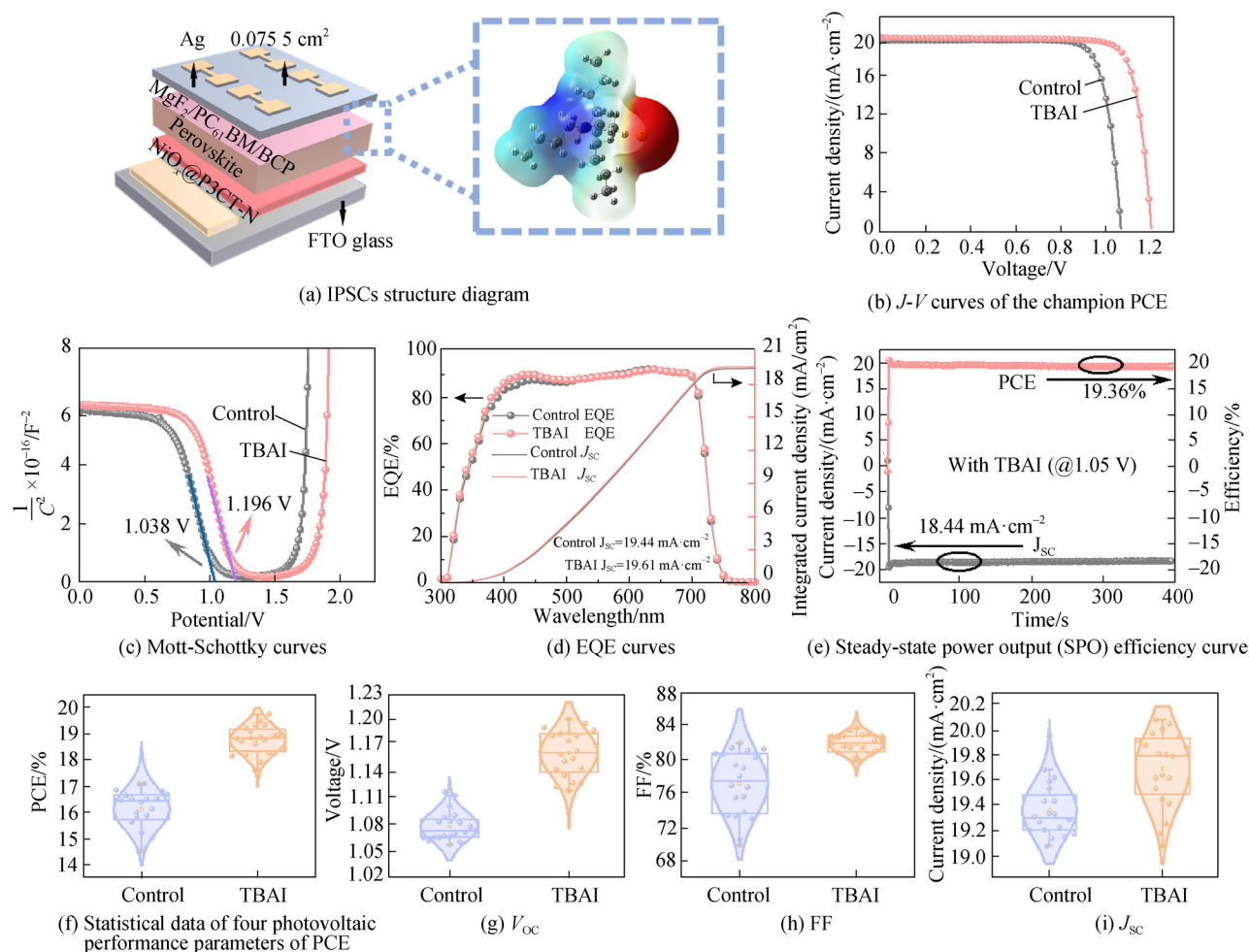
表 1 control 组与 TBAI 组中最佳效率的参数

Table 1 Parameters of the optimal efficiency for the control group and the TBAI group

Sample	PCE/%	V_{OC}/V	$J_{SC}/(\text{mA}\cdot\text{cm}^{-2})$	FF/%
Control	17.10	1.066	19.57	81.93
TBAI	19.76	1.200	19.88	82.76

PCE is power conversion efficiency; V_{OC} is open-circuit voltage; J_{SC} is short-circuit current density; FF is fill factor.

对 20 个独立的子电池的 4 个光伏性能参数进行统计并绘制对应的箱式分布示意图, 如图 2f~图 2i 所示, 在 TBAI 界面处理后, 器件的各个参数均提升明显, 排除了实验偶然性的影响, 验证了 TBAI 后处理的积极作用。



PC₆₁BM is phenyl-C61-butyric acid methyl ester; BCP is bathocuproine; FTO is fluorine-doped tin oxide; IPSCs is inorganic perovskite solar cells; EQE is external quantum efficiency.

图2 IPSCs结构示意图以及Control组与TBAI组中PCE、 V_{OC} 、FF、 J_{sc} 统计数据和Control组与TBAI组最高效率的 J - V 曲线、莫特-肖特基测试曲线、EQE曲线和稳态功率输出(SPO)效率曲线

Fig. 2 IPSCs structure diagram, as well as the PCE, V_{OC} , FF and J_{sc} statistical data in control group and TBAI group, and the highest efficiency control group and TBAI group of J - V curves, Mott-Schottky curves, EQE curves, and steady-state power output (SPO) efficiency curves.

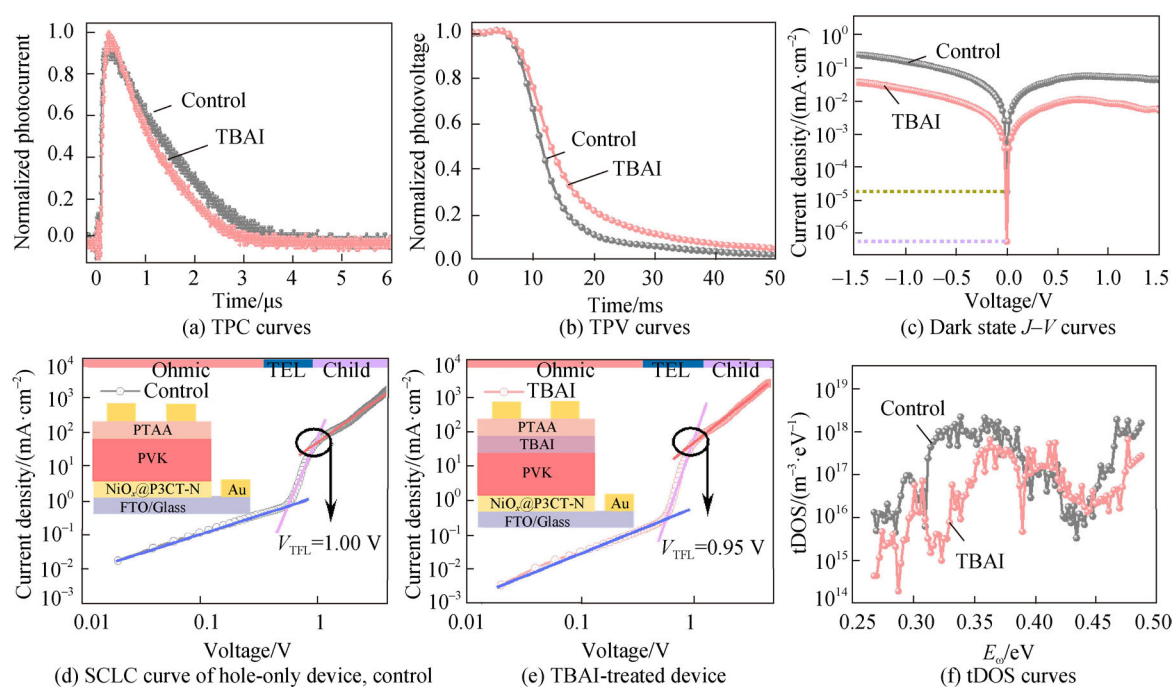
2.3 TBAI提升IPSCs光伏性能的机理分析

为探明TBAI的作用机制,进行了一系列的电学性能测试分析,首先利用瞬态光电流(TPC)和瞬态光电压(TPV)测试分析薄膜的缺陷态密度变化。图3a的TPC测试结果表明,TBAI处理的IPSCs电子抽取更快,有效的减少了电荷积累。图3b的TPV测试结果表明,TBAI处理的IPSCs具有更低的电荷缺陷态密度和更长的载流子复合寿命,这主要是由于TBAI分子和CsPbI_{2.85}Br_{0.15}相互作用,最终的作用效果使得薄膜的表面状态得到改善,孔洞减少,缺陷态密度降低。图3d的暗态 J - V 测试同样可以验证这一结论。构建了纯空穴器件对2种薄膜的缺陷态密度进行空间电荷限制电流(SCLC)测试,对SCLC结果进行分析计算易得Control和TBAI处理

的装置的陷阱填充限制电压 V_{TFL} 分别为1.00 V和0.95 V,对应的缺陷态密度分别为 $1.68 \times 10^{16} \text{ cm}^{-3}$ 和 $1.56 \times 10^{16} \text{ cm}^{-3}$,TBAI的后处理降低了薄膜的缺陷态密度,抑制了非辐射复合。图3f的总态密度(tDOS)测试表明在整个区间内相比于控制组而言,实验组的缺陷态密度均有所降低,与SCLC的测试结果一致。

2.4 TBAI对IPSCs稳定性的影响

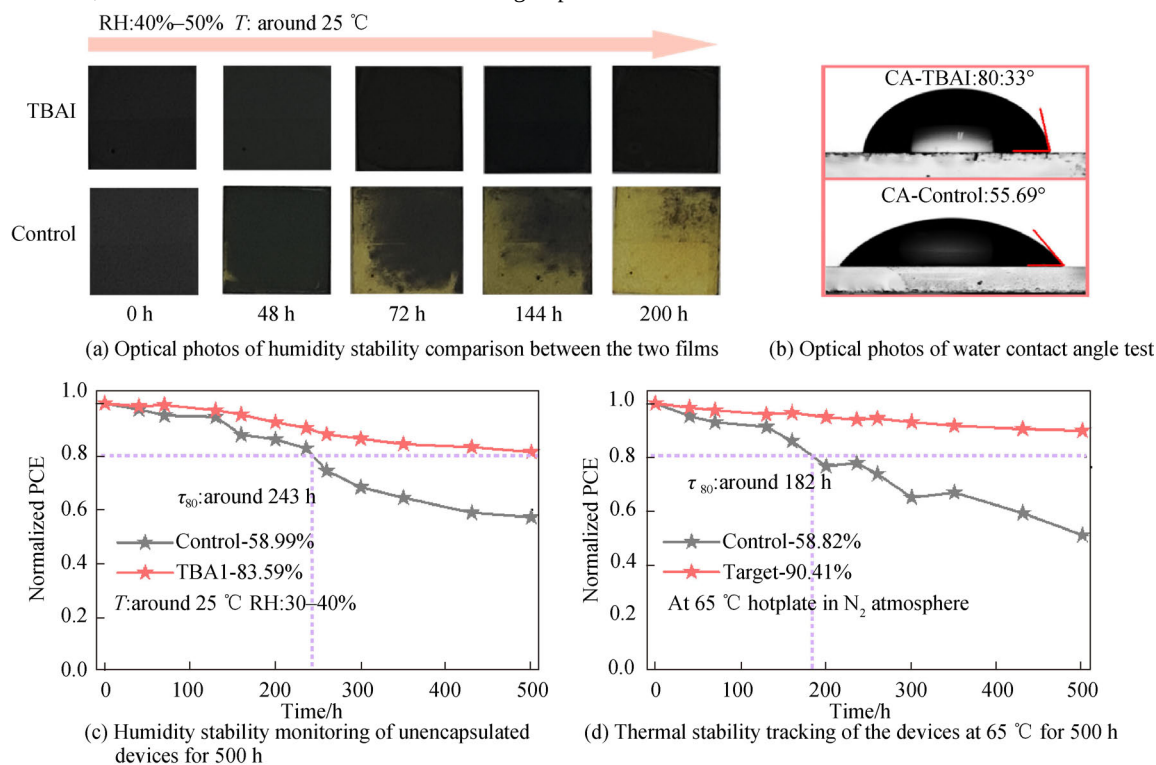
在特定条件下对2种薄膜的湿度稳定性进行监测,在潮湿的空气中放置72 h时,Control组薄膜已经出现明显的分解现象,而实验组几乎没有变化(图4a)。图4b的水接触角测试可以解释这一现象,经过TBAI处理之后薄膜水接触角由 55.69° 增加到 80.33° ,水接触角度的增加意味着更强的疏水能力。图4c记录了未封装的2种器件在500 h



PTAA is a poly (triaryl amine) semiconductor; PVK is perovskite film; SCLC is space-charge-limited current; V_{TFL} is trap filling voltage; tDOS is the changes of density of defect states; E_0 is energetic profile.

图 3 控制组与 TBAI 组器件的瞬态光电流(TPC)曲线、瞬态光电压(TPV)曲线、暗态 $J-V$ 曲线、纯空穴器件的 SCLC 测试曲线、tDOS 曲线

Fig. 3 Transient photocurrent (TPC) curves, transient photovoltage (TPV) curves, dark $J-V$ curves, SCLC curves of pure hole devices, and tDOS curves of the control and TBAI group



RH is relative humidity; CA- TBAI is water contact angle of TBAI device; CA-Control is water contact angle of control device ; τ_{80} is time of normalized PCE descending to 80%.

图 4 控制组和 TBAI 组的膜湿度稳定性对比的光学照片、水接触角测试的光学照片、未封装器件 500 h 的湿度稳定性监测曲线和 500 h 的 65 °C 热稳定性追踪曲线

Fig. 4 Comparison of optical photos of humidity stability, optical photos of water contact angle test, humidity stability monitoring of unencapsulated devices for 500 h and thermal stability tracking of the devices at 65 °C for 500 h, of the control and TBAI group

时间内湿度稳定性的变化情况, TBAI 处理的器件在 500 h 时仍可以实现对其初始 PCE 有 83.59% 的保留率, 而 Control 器件在大概 243 h 时, PCE 的保留率已经低于 80%。在 65 °C 的 N₂ 条件下放置 500 h 后, TBAI 处理的装置可以保留其初始 PCE 的 90.41%, 远高于参考组的 58.82%。综合以上稳定性测试的结果, TBAI 的界面处有效增强了 IPSCs 的湿度和热稳定性, 这是由于阳离子 TBA⁺ 具有强大的插层能力, 可以交换 Cs⁺, 在表层形成一维 TBAPbI₃ 层对钙钛矿层进行保护, 从而增强器件的稳定性^[30]。

3 结论

IPSCs 界面处缺陷态密度非常高, 非辐射复合损失严重, 严重制约着器件光伏性能的进一步提升。本工作利用 TBAI 对 CsPbI_{2.85}Br_{0.15} 表面进行后处理, 提升了薄膜的结晶质量, 有效降低了缺陷态密度, 抑制了非辐射复合, 减少了界面处不必要的载流子积累。最终, 基于该界面工程处理的空气条件下制备的 IPSCs 样品中最高 PCE 达到了 19.76%, V_{OC} 高达 1.200 V。为在空气条件下制备高效稳定的 IPSCs 提供了新方法, 有助于推进其实用化进程。

参考文献:

- [1] WANG J G, CHE Y H, DUAN Y W, et al. 21.15%-efficiency and stable γ -CsPbI₃ perovskite solar cells enabled by an acyloin ligand[J]. *Adv Mater*, 2023, 35(12): 2210223.
- [2] WU W W, XIONG H, DENG J H, et al. Rotatable skeleton for the alleviation of thermally accumulated defects in inorganic perovskite solar cells[J]. *ACS Energy Lett*, 2023, 8(5): 2284–2291.
- [3] XU C Z, ZHANG S C, FAN W Q, et al. Pushing the limit of open-circuit voltage deficit via modifying buried interface in CsPbI₃ perovskite solar cells[J]. *Adv Mater*, 2023, 35(7): 2207172.
- [4] WANG S L, QI S S, SUN H R, et al. Nanoscale local contacts enable inverted inorganic perovskite solar cells with 20.8 % efficiency[J]. *Angew Chem Int Ed*, 2024, 63(19): e202400018.
- [5] XU T F, XIANG W C, KUBICKI D J, et al. Simultaneous lattice engineering and defect control via cadmium incorporation for high-performance inorganic perovskite solar cells[J]. *Adv Sci*, 2022, 9(36): e2204486.
- [6] LIU T R, ZHAO X M, ZHONG X J, et al. Improved absorber phase stability, performance, and lifetime in inorganic perovskite solar cells with alkyltrimethoxysilane strain-release layers at the perovskite/TiO₂ interface[J]. *ACS Energy Lett*, 2022, 7(10): 3531–3538.
- [7] YUAN J F, ZHANG D, DENG B B, et al. High efficiency inorganic perovskite solar cells based on low trap density and high carrier mobility CsPbI₃ films[J]. *Adv Funct Mater*, 2022, 32(47): 2209070.
- [8] ZHANG J R, CHE B, ZHAO W G, et al. Polar species for effective dielectric regulation to achieve high-performance CsPbI₃ solar cells[J]. *Adv Mater*, 2022, 34(41): e2202735.
- [9] WANG S L, SUN H R, WANG P Y, et al. Small molecule regulatory strategy for inorganic perovskite solar cells with 368 mV of V_{OC} deficit and its application in tandem devices[J]. *Adv Energ Mater* 2024, 14 (26), 2400151.
- [10] NI Z Y, BAO C X, LIU Y, et al. Resolving spatial and energetic distributions of trap states in metal halide perovskite solar cells[J]. *Science*, 2020, 367(6484): 1352–1358.
- [11] WANG S L, WANG P Y, SHI B, et al. Inorganic perovskite surface reconfiguration for stable inverted solar cells with 20.38% efficiency and its application in tandem devices[J]. *Adv Mater*, 2023, 35(28): e2300581.
- [12] CHU X B, YE Q F, WANG Z H, et al. Surface *in situ* reconstruction of inorganic perovskite films enabling long carrier lifetimes and solar cells with 21% efficiency[J]. *Nat Energy*, 2023, 8: 372–380.
- [13] LU C Y, GUO X M, ZHANG W X, et al. Efficient inverted CsPbI₃ solar cells with Pb–S contained organosulfide-halide perovskite heterojunction[J]. *Adv Funct Mater*, 2024, 34(39): 2403563.
- [14] ZHANG S A, ZHANG L, TIAN Q W, et al. Spontaneous construction of multidimensional heterostructure enables enhanced hole extraction for inorganic perovskite solar cells to exceed 20% efficiency[J]. *Adv Energy Mater*, 2022, 12(1): 2103007.
- [15] HEO J H, PARK J K, LEE H J, et al. Inorganic-derived 0D perovskite induced surface lattice arrangement for efficient and stable all-inorganic perovskite solar cells[J]. *Adv Mater*, 2024, 36(45): 2408387.
- [16] HEO J H, ZHANG F, PARK J K, et al. Surface engineering with oxidized Ti₃C₂T_x MXene enables efficient and stable p-i-n-structured CsPbI₃ perovskite solar cells[J]. *Joule*, 2022, 6(7): 1672–1688.
- [17] TAN S, YU B C, CUI Y Q, et al. Temperature-reliable low-dimensional perovskites passivated black-phase CsPbI₃ toward stable and efficient photovoltaics[J]. *Angew Chem Int Ed*, 2022, 61(23): e202201300.
- [18] XU T F, XIANG W C, YANG J J, et al. Interface modification for efficient and stable inverted inorganic perovskite solar cells[J]. *Adv Mater*, 2023, 35(31): e2303346.
- [19] LI T X, LI W, WANG K, et al. Ambient air processed inverted inorganic perovskite solar cells with over 21 % efficiency enabled by multifunctional ethacridine lactate[J]. *Angew Chem Int Ed*, 2024, 63(36): e202407508.
- [20] LI T X, WANG K, TONG Y, et al. *In situ* dehydration condensation of self-assembled molecules enables stabilization of CsPbI₃ perovskites for efficient photovoltaics[J]. *Adv Funct Mater*, 2024, 34(51): 2409621.
- [21] WANG Z Z, XU T F, LI N, et al. Interfacial engineering with trivalent cations for efficient and stable inverted inorganic perovskite solar cells[J]. *Energy Environ Sci*, 2024, 17(19): 7271–7280.
- [22] LU C Y, LI X D, GUO X M, et al. Efficient inverted CsPbI₃ perovskite solar cells fabricated in common air[J]. *Chem Eng J*, 2023, 452: 139495.
- [23] LUO M, WANG S L, ZHU Z, et al. Novel cathode buffer layer enabling over 21.6%/20.9% efficiency in wide bandgap/inorganic perovskite solar cells[J]. *Nano Energy*, 2024, 121: 109162.
- [24] JIANG Y, XU T F, DU H Q, et al. Organic-inorganic hybrid nature enables efficient and stable CsPbI₃ based perovskite solar cells[J]. *Joule*, 2023, 7(12): 2905–2922.
- [25] YANG M, MO K W, ZHU X L, et al. Controlling nucleation and crystallization of CsPbI₃ perovskites for efficient inverted solar cells[J]. *Small*, 2024, 20(28): 2310749.
- [26] WANG S L, WANG P Y, CHEN B B, et al. Suppressed recombination for monolithic inorganic perovskite/silicon tandem solar cells with an approximate efficiency of 23%[J]. *eScience*, 2022, 2(3): 339–346.
- [27] FU S, LI X D, WAN J Y, et al. *In situ* stabilized CsPbI₃ for

- air-fabricated inverted inorganic perovskite photovoltaics with wide humidity operating window[J]. *Adv Funct Mater*, 2022, 32(14): 2111116.
- [28] WANG X T, WANG Y, CHEN Y T, et al. Efficient and stable CsPbI₃ inorganic perovskite photovoltaics enabled by crystal secondary growth[J]. *Adv Mater*, 2021, 33(44): e2103688.
- [29] SUN H R, WANG S L, QI S S, et al. Surface defects management by *in situ* etching with methanol for efficient inverted inorganic perovskite solar cells[J]. *Adv Funct Mater*, 2023, 33(23): 2213913.
- [30] LIU X, WANG X, ZHANG T, et al. Organic tetrabutylammonium cation intercalation to heal inorganic CsPbI₃ perovskite[J]. *Angew Chem Int Ed*, 2021, 60(22): 12351–12355.

Interface Engineering Technology for High-Performance Inverted Inorganic Perovskite Solar Cells Prepared in Air

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Extended Abstract

Introduction The inverted inorganic perovskite solar cells (IPSCs) with a bandgap of 1.7 eV are prospective candidates for the next generation of photovoltaic cells due to their elemental composition and unparalleled light and thermal stability. However, the higher defect state density and energy level mismatch at the interface result in an inferior photovoltaic performance to that of organic-inorganic hybrid perovskite solar cells (HPSCs) with the same bandgap. In this paper, tetrabutylammonium iodide (TBAI) was used to treat the surface of the optical absorption layer of the inverted device. The interface engineering technique can effectively reduce the density of defect states in the inverted device, suppress non-radiative recombination, and decrease the carrier accumulation at the interface. Finally, the photoelectric conversion efficiency (J) of IPSCs prepared in air is increased from 17.10% to 19.76%, and the PCE is increased by 15.56%. In addition, the stability of the device is also considerably improved.

Method The NiO_x solution was spun on the surface of FTO glass and annealed at 130 °C for 20 min. After cooling to room temperature, the P3CT-N solution was spun coated on the surface of the annealed NiO_x and annealed in air at 130 °C for 10 min. Afterwards, the prepared perovskite precursor liquid was spun coated on the surface of P3CT-N preheated at 70 °C, and annealing on a hot plate at 190 °C for 5–8 min. The annealed films were transferred to a N₂ atmosphere glove box for dynamic spin coating of TBAI (IPA) solution, and then annealed at 80 °C for 5 min. MgF₂ was thermally evaporated on the surface of TBAI by an evaporation equipment. PC₆₁BM (CB) was spun as the electron transport layer, and BCP (IPA) was spun as the hole barrier layer. Finally, the evaporation device vaporized Ag with the thickness of 80.0 nm on the surface of the BCP as a metal electrode.

Results and discussion The SEM images show that the particles of TBAI treated films are fuller and the holes significantly reduce. These holes are the center of non-radiative recombination, seriously restricting the improvement of photovoltaic performance of devices. The results of UV-absorption test indicate that TBAI post-treatment does not change the bandgap of inorganic perovskite CsPbI_{2.85}Br_{0.15}. The results of TRPL test show that the TBAI-treated films have a longer carrier lifetime, indicating that the non-radiative recombination is inhibited. Based on the results of the Mott-Schottky test, the TBAI-treated device demonstrates a built-in electric field of 1.196 V, which is much higher than that of the reference group (*i.e.*, 1.038 V), and a larger built-in electric field means a more intense carrier separation drive, corresponding to a higher V_{OC} . The steady-state power output (SPO) efficiency of the TBAI treated device is tested for 300 s, and the average SPO efficiency of the device is 19.36% for over 400 s. A pure hole device is constructed to analyze the defect state density of the two films. The V_{TFL} values of the control and TBAI treated devices are 1 V and 0.95 V, respectively, and the corresponding defect state densities are 1.68×10^{16} and 1.56×10^{16} cm⁻³, respectively. The TBAI post-treatment reduces the defect state density of the films, inhibiting non-radiative recombination. The humidity stability of the two films is monitored under specific conditions. The decomposition the films in the control group appears when the films in the control group are in humid air for 72 h, while that in the experimental group almost constancy.

Conclusions The defect state density at the interface of IPSCs was high, and the non-radiation recombination loss was serious, thus restricting the further improvement of the photovoltaic performance of the device. In this paper, TBAI was used to post-treated the surface of CsPbI_{2.85}Br_{0.15}, which improved the crystal quality of the film, effectively reduced the density of defect states, inhibited non-radiative recombination, and reduced unnecessary carrier accumulation at the interface. IPSCs prepared in air treated by this interface engineering achieved a champion PCE of 19.76% with a V_{OC} of 1.200 V. This work could provide a method for preparing highly efficient and stable IPSCs in air, thus promoting the practical process.

Key words inorganic perovskite; defect state density; energy level mismatch; interface engineering; non-radiative recombination