



钙钛矿太阳能电池的内建电场调控策略研究进展

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摘要 钙钛矿太阳能电池(perovskite solar cells, PSCs)作为一种高效率、低成本的光伏器件引起了国内外学者的广泛关注. 电池内部的载流子分离和传输是器件工作的核心过程, 直接关系到器件的光电转化效率. 异质结形成的内建电场主导着载流子的行为, 其强度大小决定器件中电子和空穴的分离效率, 所以对内建电场的调控和优化可以从根本上提升电池的性能. 本文首先对钙钛矿太阳能电池中的内建电场以及载流子分离机制进行介绍, 然后对目前常见的钙钛矿太阳能电池内建电场的调控策略及其对器件性能的影响进行总结, 主要包括通过掺杂、构建三维/二维钙钛矿异质结、构建偶极层等调控钙钛矿太阳能电池的内建电场. 最后, 对钙钛矿太阳能电池的内建电场调控技术进行评价, 并对未来该领域的发展进行展望.

关键词 钙钛矿太阳能电池, 内建电场, 掺杂, 三维/二维, 偶极层

有机-无机杂化钙钛矿太阳能电池(perovskite solar cells, PSCs)是一种具有很好应用前景的光伏器件, 其中的钙钛矿光吸收层是指具有 ABX_3 结构的一类材料. 由于该材料种类繁多、制备工艺简单, 同时具有带隙灵活可调、光吸收系数高、载流子扩散距离长以及迁移率高等诸多出色的光物理特性, 现如今成为光电新能源器件的研究热点之一^[1]. PSCs从2009年3.8%的光电转化效率开始, 经过多年来世界各地研究者的努力, 其光电转化效率已经超过了25%, 同时大面积器件的效率也在不断突破, 展现出很好的应用潜力.

PSCs最早是在介孔敏化太阳能电池的基础上发展起来的, Kojima等人^[2]首次在太阳能电池的光吸收层中使用了钙钛矿材料 $CH_3NH_3PbI_3$ 替代染料分子作为敏化剂, 器件光电转化效率达到了3.81%. 2013年, Burschka等人^[3]使用连续沉积法制备出效率为15%的钙钛矿敏

化电池, 吸引了越来越多的科研人员投身于PSCs的研究工作中. 随着对载流子分离机制研究的不断深入, 钙钛矿材料具有电子和空穴的双极性传输能力和较长的载流子扩散长度, 所以在器件制备过程中可以摒弃介孔层, 钙钛矿层可以直接沉积到平面电子传输层上, 形成正置平面型结构^[4,5]. 这种结构的器件最大化地利用了钙钛矿材料的独特性质, 制作工艺简单并且成本低廉. 一些有效调控晶体生长动力学的沉积技术, 如真空闪蒸辅助溶液工艺, 可以通过改善钙钛矿薄膜质量来抑制电池迟滞效应的出现, 也有利于高效大面积器件的制备^[6]. 平面结构的PSCs也启发科研人员开发出倒置结构器件. 另外, 钙钛矿薄膜本身具有很好的空穴传输能力, 所以可以摒弃昂贵的空穴传输层, 实现无空穴传输层结构的PSCs, 这也是当前比较火热的研究方向之一^[7].

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为了进一步提高器件的效率,不仅需要针对具有宽光谱吸收、长载流子扩散长度的光活性层以及具有高载流子迁移率的电荷传输材料进行研究^[8-13],而且更加需要对器件中载流子的分离、传输与复合等物理机制进行系统而深入的探索^[14-16],这将有助于准确把握器件内部电势的分布,有望实现对载流子动力学的有效调控,甚至有望发现打破单节电池Shockley极限效率33.5%的途径^[17].

1 PSCs的载流子分离机制

PSCs由染料敏化太阳能电池发展而来.在研究初期,钙钛矿材料被认为是充当敏化剂,因此,钙钛矿电池被认为是一种敏化太阳能电池.但是,随着钙钛矿材料本身光物理特性的研究以及PSCs器件结构的演化,按照敏化太阳能电池的工作原理很难解释PSCs出色的光电转化效率. Shi等人^[18]选用无空穴传输层的PSCs,通过电流-电压曲线以及阻抗谱对PSCs的电荷转移特性进行研究,发现PSCs中的电荷转移特性符合异质结的电荷转移特性.至此,人们也开始注重PSCs的内建电场理论以及实验研究^[19-25].

1.1 PSCs异质结内建电场的形成

Jiang等人^[16]在纳米尺度使用开尔文探针力显微镜(Kelvin probe force microscope, KPFM)测定了电池截面的电位,确定了PSCs内部PN结的形成位置,解释了内部载流子的分离以及传输机制.对平面异质结PSCs进行截面的电位测定并进行电场强度分析,如图1所示,在透明电极(transparent conductive oxide, TCO)、TiO₂和钙钛矿层中存在电场,电场强度的最大值存在于TiO₂/钙钛矿界面处,并且在钙钛矿和空穴传输层(hole transport material, HTM)之间电场强度在不断减小.电场强度的分布则揭示了在PSCs内部,钙钛矿吸收层和TiO₂形成了PN结,并且与其他无机电池不同, PSCs的载流子传输主要靠漂移^[26],所以在光激发后,载流子的行为主要受内建电场的调控.通过测量空间电势的变化可以估算出空间电荷区的宽度,为对比不同电荷传输材料从钙钛矿中提取电子的能力,分别比较二氧化钛/钙钛矿界面和氧化铝/钙钛矿界面.研究指出,在暗态下,两者的空间电荷层厚度几乎一致,但在光照下,二氧化钛/钙钛矿界面的空间电荷区达到了45 nm,而氧化铝/钙钛矿界面的空间电荷区只有10 nm.通过对两种电池性能进行比较,结果发现,较宽的空间电荷区

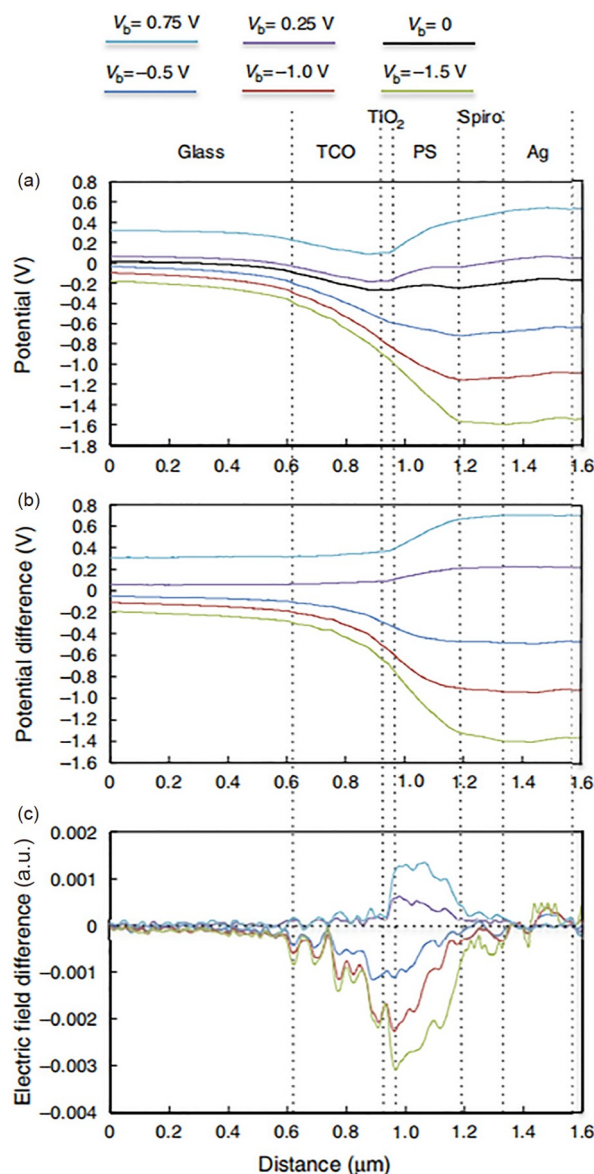


图1 平面型器件的KPFM表征^[16]. (a) 不同偏置电压下器件的电势分布. (b) 不同偏置电压下器件电势的差异. (c) 不同偏置电压下器件电场的变化

Figure 1 KPFM characterization of planar devices^[16]. (a) Potential distribution of devices under different bias voltages. (b) Differences in device potential under different bias voltages. (c) Variation of device electric field under different bias voltages

将有助于提高光生载流子的界面分离效率^[27].

Cai等人^[28]使用开尔文探针力显微镜分别对高性能的介孔型和平面型PSCs进行截面电势测定,结果表明,对于介孔型电池,电势的降落只存在于介孔TiO₂/钙钛矿混合层,在平面型电池中, TiO₂/钙钛矿界面和HTM/钙钛矿界面分别有两个明显的电势下降.这一发现与Jiang等人^[16]报道的电势下降只存在于TiO₂/钙钛

矿界面的结果不同,表明平面型PSCs内部有两个二极管结.在对两种类型的器件进行暗电流-电压测试后,依据Shockley方程得出平面型PSCs的饱和电流密度 J 以及理想因子 n 大于介孔型PSCs的相应值,说明平面型PSCs的载流子复合比介孔型PSCs严重.对于平面型电池,可以通过调控钙钛矿层的导电特性来调节内建电场的位置.

1.2 PSCs异质结内建电势的测试方法

1.2.1 Mott-Schottky方法

内建电场在太阳能电池的工作过程中发挥很大的作用,根据经验公式 $V_D = (E_{fn} - E_{fp}) / q$ 可以计算出异质结的电势差,其中 E_{fn} 和 E_{fp} 分别为n型半导体和p型半导体的费米能级,费米能级之差即为平衡时电子从n型半导体导带到p型半导体导带所需要克服的功.通过PN结的电容特性,可以对内建电势进行定量推导.根据半导体物理中异质结理论,PN结的电容可以描述为^[29]

$$\frac{1}{C^2} = \frac{2}{q} \left(\frac{1}{\varepsilon_f N_{A1}} + \frac{1}{\varepsilon_2 N_{D2}} \right) (V_D - V), \quad (1)$$

其中, ε_1 、 ε_2 分别为受主和施主半导体的介电常数, N_{A1} 和 N_{D2} 分别为受主浓度和施主浓度, V_D 为异质结耗尽电势.对于具有单个PN结的钙钛矿电池,一般情况下施主浓度 N_{D2} 远大于p型光吸收层的受主浓度 N_{A1} ,所以可得简化单边异质结电压-电容特性,其模型为Mott-Schottky模型:

$$\frac{1}{C^2} = \frac{2}{q\varepsilon_f N_{A1}} (V_D - V). \quad (2)$$

在以上式(1)和(2)中,可以得出 $\frac{1}{C^2}$ 与电压 V 有着良好的线性关系,据此关系可以推出异质结的耗尽电势以及半导体介电常数和掺杂浓度.

1.2.2 电吸收光谱法

电吸收光谱技术利用了二次Stark效应的非线性光学表征方法,可以对内建电势进行测量^[30].将调制的外加偏置电压施加于太阳能电池上,调节光活性化合物的吸收.测量外加电场作用下透过率的相对变化 $\Delta T/T$, $\Delta T/T$ 与三阶非线性电介质磁化率的虚部和电场的平方成正比:

$$-\frac{\Delta T}{T} = \Delta\alpha \cdot d \propto \text{Im}\chi^{(3)}(h\nu) \cdot E^2, \quad (3)$$

其中, α 为吸光系数, d 为薄膜的厚度, $h\nu$ 为光子的能量.外加电场由直流电场 E_{dc} 和频率为 ω 的交流电场 $E_{ac}\cos(\omega t)$ 组成,则电池中的电场为内建电场和外加电场的叠加,所以电吸收光谱信号 $\Delta T/T$ 满足:

$$\frac{\Delta T}{T} \propto \text{Im}\chi^{(3)} \left\{ E_{dc}^2 + [E_{dc} - E_{bi}]E_{ac}\cos(\omega t) + E_{ac}^2 \frac{1}{2} [1 + \cos(2\omega t)] \right\}, \quad (4)$$

式(4)表示在频率 ω 下电吸收光谱信号 $\Delta T/T$ 随直流偏置电压呈线性变化,当外加偏置电压可以补偿内建电势差时,信号强度为0,由此可以得出内建电势差.

1.2.3 开尔文探针显微镜测试法

KPFM通过探针与样品电接触可以形成接触电势差,探针和样品之间可以视为电容器.在探针上施加可以平衡接触电势差的直流偏置电压以获得接触电势差的值^[31],一般选择功函数稳定的金属对探针表面电势进行标定,根据测得的接触电势差获得样品的电势分布^[32].使用偏置电压补偿法,通过KPFM可以对器件横截面的电势进行准确的定量测量^[33].在器件的两端施加偏置电压 V_{bias} 来对异质结两端的电势差 V_{bi} 进行补偿,找到恰好能够抵消异质结电压的偏置电压,此时异质结两端的电势相等,那么外加的偏置电压则为异质结两端内建电势差.这种方法可以避免分子细节以及表面态所导致的测量误差,对内建电势的测量可以直接得出可视化的结果,使用KPFM测量内建电势的结果与Mott-Schottky方法求得的结果基本一致.

Mott-Schottky分析法、电吸收光谱法等属于内建电势的间接测试方法,已经被广泛应用于钙钛矿太阳能电池内建电势的测量.开尔文探针显微镜测试是一种具有纳米级分辨率的功能成像技术,可以在不接触样品的情况下,直接绘制出所测样品的局部表面电势,也可以用来测量太阳能电池相邻层之间的电势差.对于器件的开路电压、内建电势和电极电势差,可以给出定量准确的测量,通过偏置电压补偿的测量方法,其测量结果与暗电流-电压曲线拟合法以及Mott-Schottky法基本一致.KPFM不同于其他测量方法的优点在于可以通过成像的方法,不需要额外的计算推导,直接给出所测样品中所测点的电势,并且在探测环境敏感的材料方面有明显的优势.

2 PSCs的内建电场调控策略

根据PSCs的内部机理基础性研究成果,更多科研

人员将研究重心放在对内建电场调控的工作上, 以提升电池内部载流子的分离和传输能力进而提高器件性能^[34]. 能级调控与异质结设计工程则是这方面的重要方法之一. 通过优化钙钛矿层的能级结构并构建更加强大的内建电场, 进而加速载流子的传输和转移, 最终可以提升PSCs的性能. PSCs的载流子分离和传输调控策略在不断的研究中逐渐走向成熟, 多种方法已经被实验证明在优化内建电场方面有很好的表现.

2.1 通过掺杂调控PSCs的内建电场

在PSCs中, 掺杂会影响载流子的扩散长度、界面势垒、接触电阻和电荷复合率, 这些因素都会影响器件的性能^[35]. 许多与掺杂有关的成分工程或添加剂已经被证明对PSCs的性能有很大改善. 通过掺杂对器件内建电场进行调控是一种十分有效的手段, 根据平面型PSCs双异质结的结构, 对电子传输层、钙钛矿吸收层、空穴传输层进行掺杂, 可以调控其功函数, 从而实现内建电场大小的调控.

2.1.1 钙钛矿吸收层掺杂

钙钛矿材料可以通过改变卤化物和有机铵盐组分调节其半导体特性, 材料的组成成分变化可能会导致载流子浓度和类型的差异^[36]. Cai等人^[28]进一步研究了钙钛矿掺杂对器件PN结的影响, 用富含MAI(p型掺杂)与富含PbI₂(n型掺杂)前驱体溶液制备的介孔型和平面型PSCs进行了KPFM测试. 结果表明, 对于介孔型电池, 在两种掺杂情况下, 钙钛矿的组成和掺杂浓度对PN结位置的影响可以忽略不计. 对于平面型电池, 富含MAI的前驱体在TiO₂/钙钛矿界面出现了显著的电势下降, 富含PbI₂的器件在HTM/钙钛矿界面上有显著的电势变化, 说明在平面PSCs中前驱体的化学成分组分会影响PN结的电势分布和位置. 根据电势的分布情况, 富含MAI的器件开路电压取决于二氧化钛和钙钛矿薄膜的费米能级差异, 富PbI₂的器件开路电压取决于HTM和钙钛矿薄膜的费米能级差异, 说明在平面型器件中对钙钛矿的不同导电类型掺杂可以调控PN结内建电场的位置以及大小.

Li等人^[37]通过精确地调节混合卤素无机钙钛矿CsPbX₃的卤素比例, 发现钙钛矿的价带最大值(valence band maximum, VBM)随溴化物的增加而逐渐升高, 满足梯度能级取向, 如图2(a)所示, 实现了对无机钙钛矿纳米晶能带结构的连续调节, 制备了一种MAPbI₃-CsPbX₃梯度异质结无空穴传输层PSCs. 利用MAPbI₃和

CsPbX₃形成异质结, 使钙钛矿价带发生偏移导致内建电场形成, 提供了额外的空穴驱动力. 更重要的是, 溴化物比例的增加会使无机钙钛矿的带隙逐渐变宽, 使梯度异质结中受体和给体的费米能级之间的差异变大, 增大了异质结内建电场强度, 极大地增强了钙钛矿光吸收层内电子-空穴对分离效率, 提升了PSCs的电流密度和开路电压, 实现了11.33%的光电转换效率. Zhuang等人^[38]研究了多功能镧系元素掺杂CsPbBrCl₂量子点对高效稳定MAPbI₃ PSCs的协同效应, 通过引入4种Ln³⁺(Yb³⁺、Ce³⁺、Eu³⁺、Sm³⁺)掺杂的CsPbBrCl₂量子点, 发现Ln³⁺的引入不仅提高了结晶度, 还可以形成比Pb-I键更强的Ln-I键, 调节功函数, 增强内建电场强度, 优化能带对齐. 实验发现, Sm³⁺钙钛矿量子点具有最佳性能, 其钙钛矿的能级结构如图2(b)所示, 掺杂后器件的开路电压从1.13 V提高到1.20 V, 光电转化效率从18.54%提高到22.52%. Chen等人^[39]报告了一种通过掺杂具有高极化率的有机电材料聚偏二氟乙烯(dab-coHReO₄, PVDF:DH)来提高FA_{0.92}MA_{0.08}PbI₃钙钛矿内建电场的有效方法. PVDF:DH的极化会形成一个额外的电场并且永久保持与PSCs内建电场一致的方向, 内建电场的叠加可以更充分地驱动载流子的分离和传输, 经过处理后的器件光电转化效率达到了24.35%(认证的效率为23.45%). 在碳电极PSCs中, Zou等人^[40]通过p型有机小分子2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane(F4-TCNQ)掺杂钙钛矿, 使器件中的载流子分离更加高效, 从而使相应的碳电极器件效率显著提升.

在倒置PSCs中, 对其内部异质结的电场调控同样具有重要的意义. Li等人^[41]提出一种通过表面硫化构建异质结制备高效反式PSCs的方法. 研究表明, 在钙钛矿表面Pb-S键强于Pb-I键, 对富含Pb的钙钛矿薄膜表面进行硫化, 可提高钙钛矿界面处的费米能级, 如图2(c)所示, 并为电子的提取提供额外的背面场, 如图2(d)所示. 通过时间分辨荧光光谱(time-resolved fluorescence spectrum, TRPL)表征, 发现经过硫化处理的钙钛矿中载流子有更长的寿命, 表明Pb-S键的形成减少了一些非辐射复合, 增加了载流子的传输能力. 通过莫特-肖特基测试分析, 经过硫化处理后的倒置PSCs内建电场强度为1.21 V(对照组1.07 V), 电池的开路电压为1.19 V(对照组1.09 V), 光电转化效率为24.3%, 相比于对照组的21.8%有很大的提升. 强Pb-S键可以稳定钙钛矿异质结并使其拥有更好的内建电场, 显著提升了电

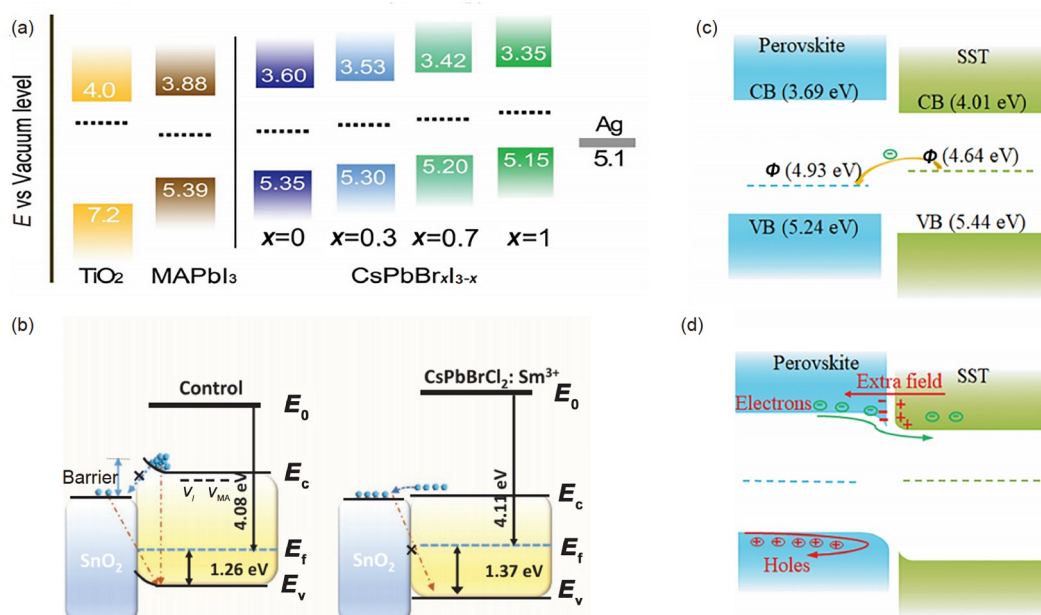


图 2 (网络版彩色)钙钛矿层掺杂对器件的影响. (a) MAPbI₃-CsPbX₃梯度异质结能带结构. Reprinted with permission from Ref. [37], Copyright © 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) 标样器件和掺杂Sm³⁺器件的能级结构. Reprinted with permission from Ref. [38], Copyright © 2022 Wiley-VCH GmbH. (c) 硫化处理后钙钛矿的能级结构. Φ为钙钛矿的费米能级. (d) 钙钛矿表面的背面场形成, 由于费米能级的差异, 正电荷在钙钛矿表面积累, 导致能带弯曲和背电场的形成. Reprinted with permission from Ref. [41], Copyright © 2022 the American Association for the Advancement of Science

Figure 2 (Color online) The effect of doping perovskites on devices. (a) Band structure of MAPbI₃-CsPbX₃ gradient heterojunctions. Reprinted with permission from Ref. [37], Copyright © 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Energy level structures of the control device and the Sm³⁺-doped device. Reprinted with permission from Ref. [38], Copyright © 2022 Wiley-VCH GmbH. (c) Energy level structure of perovskites after sulfide treatment. Φ is the Fermi level of perovskites. (d) The formation of the back surface field on the surface of perovskites. Due to the difference in the Fermi level, positive charges accumulate on the surface of perovskites, resulting in the formation of band bending and back electric field. Reprinted with permission from Ref. [41], Copyright © 2022 the American Association for the Advancement of Science

池的开路电压和光电转化效率.

2.1.2 电子传输层掺杂

电子传输层(electron transport material, ETM)是PSCs器件中的重要组成部分, 对电池中内建电场的优化起到关键性作用. 电子传输层掺杂的一般原理是通过n型掺杂, 降低电子传输层的功函数, 使费米能级上移, 并与钙钛矿吸收层形成更强大的内建电场, 有助于载流子的分离和传输.

早在2014年, Zhou等人^[42]对TiO₂进行钌掺杂, 使其费米能级和钙钛矿更加匹配, 实现了19.3%的光电转化效率. Wang等人^[43]将Ru掺杂到致密的TiO₂电子传输层中调节其能级结构. 随着Ru的加入, Ti-O键变得很弱, 其中的Ti⁴⁺被Ru⁴⁺所取代进而形成了Ti-O-Ru结构, 扩大了钙钛矿层和电子传输层的准费米能级分裂, 形成了更加强大的内建电场. 对于1%(mol) Ru⁴⁺的掺杂, 器件的开路电压从1.06 V上升到了1.11 V, 光电转化效率从原来的14.83%上升到了18.35%. Guo等人^[44]采用了一

种远程等离子体溅射技术沉积Nb, 使其对电子传输层SnO₂进行掺杂, 这增强了器件的内建电场. 由于晶格中的Sn位点被Nb⁵⁺取代, 导致载流子浓度提高. 通过紫外光电子能谱(ultraviolet photo-electron spectroscopy, UPS)测试发现, 如图3(a)所示, 随着Nb掺杂水平的增加, SnO₂的功函数减小, 费米能级逐渐上移并接近导带, 掺杂之后的SnO₂价带更深, 如图3(b)所示, 为空穴向电子传输层的移动提供势垒, 抑制界面处载流子的复合. 更重要的是, 经过掺杂后的SnO₂由于载流子浓度的不断增加, n型半导体的导电特性更为突出, 导致与p型钙钛矿吸收层CsPbBr₃形成了单边异质结, 因此造成了空穴传输层一侧的电势提升, 有助于载流子的分离. 经过掺杂处理后, 器件光电转化效率从3.73%上升到了8.54%. 近期的研究结果显示, 二氧化钛通过氮掺杂可以使电子传输层的能级和钙钛矿更加匹配, 同时显著增加了电子传输层的迁移率, 从而实现了高填充因子的大面积PSCs制备.

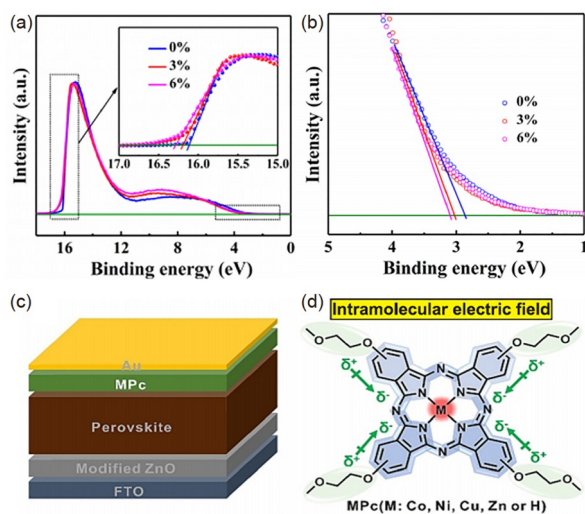


图3 电荷传输层掺杂对器件的影响。(a) Nb掺杂SnO₂的UPS曲线。(b) 不同Nb含量沉积的掺杂对SnO₂薄膜VBM的影响。Reprinted with permission from Ref. [44], Copyright © 2021 Zhengzhou University. (c) 用MPcs为HTM的钙钛矿太阳能电池。(d) MPcs的结构和分子内的电场方向。Reprinted with permission from Ref. [48], Copyright © 2021 Wiley-VCH GmbH

Figure 3 The effect of doping the charge transport layer on the device. (a) UPS curve of Nb-doped SnO₂. (b) VBM edges of Nb-doped SnO₂ films deposited with different Nb contents. Reprinted with permission from Ref. [44], Copyright © 2021 Zhengzhou University. (c) Scheme illustration of PSCs with MPcs as HTMs. (d) Structures of MPcs and direction of the intramolecular electric field. Reprinted with permission from Ref. [48], Copyright © 2021 Wiley-VCH GmbH

2.1.3 空穴传输层掺杂

空穴传输层对PSCs同样有着至关重要的作用，通过掺杂同样可以调节其能级结构，从而实现对PSCs内建电场的调控。

在正置器件中，Seo等人^[45]使用Zn-TFSI₂作为p型掺杂剂代替了传统的Li-TFSI添加到空穴传输层spiro-OMeTAD中，实现了器件光伏性能和稳定性的大幅度提升。掺杂后的HTM相对于标样费米能级有明显的下降，说明Zn-TFSI₂有更高的p型掺杂水平。通过莫特-肖特基计算内建电场，结果表明，Zn-TFSI₂掺杂后的器件内建电场比Li-TFSI高80 mV。由于掺杂后的PSCs具有更好的载流子分离和传输效率，器件的效率从19.48%上升到21.52%，开路电压由1.10 V上升到了1.15 V。Liu等人^[46]在空穴传输层PEDOT:PSS中掺杂p型有机小分子F4-TCNQ作为钙钛矿太阳能电池的空穴传输层，相对于未掺杂的空穴传输层，经过UPS测试，薄膜的功函数从5.08 eV增加到5.18 eV，使空穴传输层的费米能级下移，扩大了费米能级分裂，器件的光电转化效率从

13.2%提升到17.2%。

Jiang等人^[47]在PSCs的空穴传输层spiro-OMeTAD中添加了二维(two-dimensional, 2D)过渡金属硫化物花状的MoS₂纳米晶体，掺杂剂对HTM中的Li⁺有较强的吸附能力，可以抑制Li⁺在HTM中的迁移，修饰HTM的性能。UPS测试表明，与原始的spiro-OMeTAD相比，经过MoS₂处理后，其费米能级向下移动，并且价带更接近于CH₃NH₃PbI₃的最高占据分子轨道(highest occupied molecular orbital, HOMO)，这意味着MoS₂的引入增强了器件的内建电场。最终器件的光电转化效率从17.79%上升到20.18%，开路电压从1.05 V上升到1.10 V。Yu等人^[48]通过修饰酞菁金属配合物(metal phthalocyanines, MPcs)作为PSCs的空穴传输层，如图3(c)所示，在4个甲氧基单元修饰的镍酞菁(Ni phthalocyanine, NiPc)中形成了较强的分子内偶极子，如图3(d)所示，使得酞菁分子内形成较强的内建电场，大幅度提升了空穴传输层载流子的传输效率。基于该酞菁金属配合物作为空穴传输层的PSCs效率达到了认证的21.03%。Lin等人^[49]通过对空穴传输层spiro-OMeTAD添加双(氟磺酰基)甲酰亚胺(potassium bis(fluorosulfonyl)imide, K-FSI)使spiro的HOMO能级明显降低，HTM与钙钛矿层有更好的能级匹配，器件实现了21.02%的光电转化效率。

在倒置器件中，同样可以通过掺杂对空穴传输层的功函数进行调节，比较典型的有通过F4-TCNQ对PTAA进行掺杂，实现器件性能的显著提升。在无机空穴传输材料中，2015年，Chen等人^[11]对氧化镍通过Li和Mg掺杂，在提升其空穴迁移率的同时，其能级也与钙钛矿更加匹配，并以此制备了当时认证效率最高的大面积PSCs。

2.2 通过构建三维/二维钙钛矿异质结调控PSCs的内建电场

对于二维钙钛矿材料，Goldsmith容许因子对其中有机阳离子的限制较为宽松，二维卤化物钙钛矿材料通常是通过结合大尺寸的有机阳离子来实现^[50,51]，常见的离子如图4所示。大量研究表明，二维或准二维钙钛矿材料在提升电池的稳定性方面有巨大的潜力，但是其具有较宽的光学带隙且不利于电荷的传输，所以器件的性能远远低于三维(three-dimensional, 3D)PSCs^[52,53]。将2D钙钛矿层叠加在3D钙钛矿光吸收层的表面上可以钝化表面缺陷，形成的2D/3D双层钙钛矿异质结可以形成更加强大的内建电场，显著提升器件的

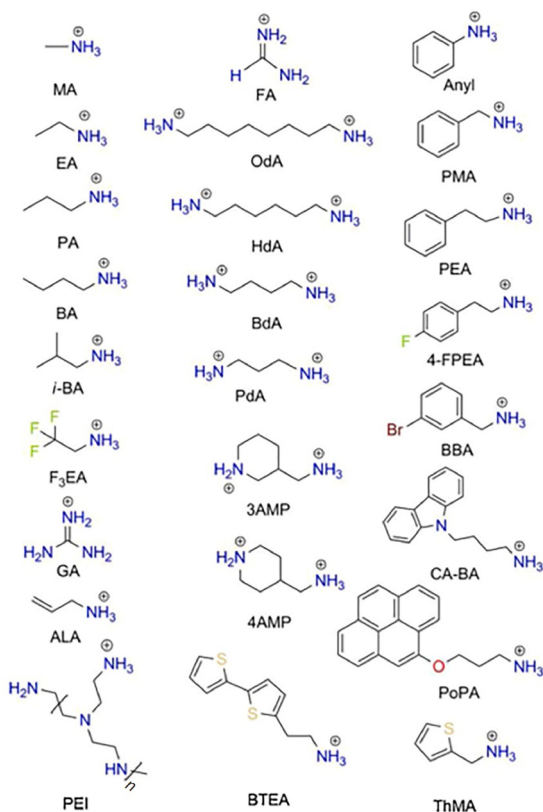


图4 (网络版彩色)2D钙钛矿不同的有机阳离子. Reprinted with permission from Ref. [58], Copyright © 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Figure 4 (Color online) Different organic cations in 2D perovskites. Reprinted with permission from Ref. [58], Copyright © 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

效率和稳定性^[54-60],如表1所示。

Jang等人^[61]通过无溶液固相面内生长的方式生长稳定且高度结晶的二维 $(C_4H_9NH_3)_2PbI_4$ 膜,形成完整的2D/3D钙钛矿异质结。2D/3D钙钛矿异质结增强了内建电场,提高了器件的开路电压。通过UPS表征,3D钙钛矿吸收层的费米能级略低于导带和价带中线,证明其是p型半导体。2D钙钛矿材料 $(BA)_2PbI_4$ 已经通过开尔文探针显微镜测定为p型半导体,费米能级更低,则2D电场诱导层和3D光吸收层组成了p-p型同型异质结。较厚的2D钙钛矿层将会形成更宽的耗尽区,这样会进一步增强内建电场的强度,有利于电池中载流子的分离和传输。结果显示,通过固相面内生长法制备的2D/3D同型异质结PSCs效率相比之前的22.39%提升到了24.59%,开路电压由原来的1.098 V提高到1.185 V,并且证明了开路电压随2D钙钛矿层厚度增加而变大的现象,说明增大内建电场有利于提高电池的效率 and 开路

电压。He等人^[62]引入了异戊基碘化铵(PNAI)大型有机阳离子铵盐,通过热处理原位生长二维钙钛矿,最优成分的2D/3D钙钛矿异质结可以显著提升器件的开路电压。Wang等人^[63]提出一种通过咪唑氢溴酸盐(IABr)处理无MA PSCs的方法,在 $FA_{0.9}Cs_{0.1}PbI_3$ 薄膜上构建了2D钙钛矿,形成了2D/3D异质结。实验发现,IABr诱导了2D钙钛矿 $(C_3H_5N_2)_2PbI_2Br_2$ 的生成。通过UPS测试,经过IABr处理后,2D钙钛矿的费米能级从-4.71 eV降低到-4.92 eV,进一步增强了准费米能级的分裂,最大限度地减少了器件中的开路电压损失。该构建2D/3D异质结的方法导致PSCs的转化效率由21.61%上升到23.25%,开路电压由原来的1.120 V提升到1.172 V。

值得注意的是,在目前报道的高效率器件中,大部分钙钛矿层都需要经过长链有机铵盐处理,在钝化界面缺陷的同时改变其能级结构,从而显著提升PSCs的效率和稳定性。

2.3 通过构建偶极层调控PSCs的内建电场

当大量的正负电荷不对称地分布在薄层中时,会形成电偶极层,可以近似为大量的电偶极矩,导致正电荷侧到负电荷侧电势突然下降,这会使界面处的真空能级急剧移动。电偶极层间的电偶极矩可以显著地改变电池功能层的功函数,如图5(a)^[77]所示。在满足能级匹配的条件下,增加钙钛矿两侧的功函数差异可以增大器件的内建电场,从而实现载流子的高效分离^[78]。

Canil等人^[79]利用了自组装的小分子单分子层(self assembled monolayer, SAM)在钙钛矿表面感应出了稳定的偶极子,从而对钙钛矿的功函数进行了调整,并且提供了一个通用的方法,可以直接选择分子的种类和沉积条件来调控钙钛矿的功函数,并调整了与电荷传输材料界面的能级对准。实验通过调整沉积的溶液浓度控制表面覆盖,进而调整钙钛矿的功函数。电偶极子的正电荷端接触样品称为正电偶极子,负电荷端接触样品称为负电偶极子。通过开尔文探针测试发现,正偶极子处理后的样品功函数会增加,负偶极子处理的样品功函数会下降,如图5(b)所示。对于ETM,一般使用负偶极子进行处理,处理后可以使ETM的功函数降低;对于HTM,一般使用正偶极子进行处理,处理后可以使HTM的功函数增加;但对于钙钛矿层,使用负偶极子可以增强HTM/钙钛矿界面的内建电场,正偶极子可以增强ETM/钙钛矿的内建电场。在选择合适的电偶极层材料时,应根据具体情况而定,目的在于使钙钛矿层

表1 不同种类2D/3D的PSCs性能参数表^{a)}

Table 1 Summary of performance parameters of different types of 2D/3D perovskite solar cells

钙钛矿材料	器件结构	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE(%)	文献
(BA) ₂ PbI ₄ -(FAPbI ₃) _{0.95} (MAPbBr ₃) _{0.05}	FTO/SnO ₂ /PVK/spiro-OMeTAD/Au	1.19	24.70	0.84	24.59	[61]
(PNA) ₂ FA _{n-1} Pb _n I _{3n+1} -(CsPbI ₃) _x (FAPbI ₃) _y (MAPbBr) _{1-x-y}	FTO/SnO ₂ /PVK/spiro-OMeTAD/Au	1.16	23.82	0.82	22.62	[62]
IA ₂ PbI ₂ Br ₂ -FA _{0.9} Cs _{0.1} PbI ₃	FTO/SnO ₂ /PVK/spiro-OMeTAD/Au	1.17	24.57	0.81	23.25	[63]
(DA ₂ PbI ₄) _{0.05} -MAPbI ₃	ITO/PEDOT:PSS/PVK/PC ₆₁ BM/LiF/Ag	1.05	22.95	0.79	19.09	[64]
Gua _{0.1} [Cs _{0.1} (FA _{0.83} MA _{0.17}) _{0.9} Pb(I _{0.83} Br _{0.17}) ₃]	ITO/SnO ₂ /PVK/spiro-OMeTAD/MoO ₃ /Ag	1.19	23.66	0.75	21.21	[65]
(MA _{0.44} FA _{0.56})Pb(I _{0.67} Cl _{0.33}) ₃ -(ThMA) ₂ PbI ₄	ITO/SnO ₂ /PVK/spiro-OMeTAD/MoO ₃ /Ag	1.16	22.36	0.81	21.49	[66]
EDBEPbI ₄ -MAPbI ₃	FTO/SnO ₂ /PVK/spiro-OMeTAD/Au	1.13	23.53	0.79	21.06	[67]
FA _{0.79} MA _{0.16} Cs _{0.05} PbI _{2.5} Br _{0.5} -(PA) ₂ PbI ₄	FTO/c-TiO ₂ /m-TiO ₂ /PVK/spiro-OMeTAD/Au	1.06	21.90	0.74	17.23	[68]
PEA ₂ MA _{n-1} Pb _n I _{3n+1}	FTO/c-TiO ₂ /m-TiO ₂ /PVK/spiro-OMeTAD/Ag	1.08	21.91	0.83	19.10	[69]
BA _{0.09} (FA _{0.83} Cs _{0.17}) _{0.91} Pb(I _{0.6} Br _{0.4}) ₃	FTO/SnO ₂ /PC ₆₁ BM/PVK/spiro-OMeTAD/Au	1.18	19.80	0.73	17.20	[70]
MA ₃ Bi ₂ I ₉ -MAPbI ₃	FTO/c-TiO ₂ /PVK/spiro-OMeTAD/Au	1.09	23.03	0.76	18.97	[71]
(CEA ₂ PbX ₄) _{0.005} -[(Cs _{0.1} FA _{0.9})Pb(I _{0.9} Br _{0.1}) ₃] _{0.995}	FTO/c-TiO ₂ /m-TiO ₂ /PVK/spiro-OMeTAD/Au	1.10	22.77	0.79	20.08	[72]
PEA ₂ PbI ₄ -Cs _{0.05} (FA _{0.83} MA _{0.17}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃	FTO/c-TiO ₂ /PVK/spiro-OMeTAD/Au	1.11	22.89	0.73	18.51	[73]
IBA ₂ FAPb ₂ I ₇ -FAPbI ₃	FTO/c-TiO ₂ /m-TiO ₂ /(3D/2D) PVK/ spiro-OMeTAD/Au	1.11	25.40	0.81	22.70	[74]
SBLC based-MAPbI ₃	ITO/TAA/PVK/PCBM/BCP/Ag	1.19	22.36	0.76	20.14	[75]
(AVA) ₂ PbI ₄ -MAPbI ₃	FTO/c-TiO ₂ /m-TiO ₂ /(3D/2D) PVK/ spiro-OMeTAD/Au	1.06	22.30	0.76	18.00	[76]

a) V_{oc} , 开路电压; J_{sc} , 短路电流; FF, 填充因子; PCE, 光电转化效率

两侧内建电场最大化。溶液浓度的增加对功函数的影响也会变大, 通过改变溶液的浓度, 功函数的变化幅度在几百meV, 这为通过构建偶极层来调控PSCs的内建电场提供了方法和思路。Huang等人^[80]发现一系列碱性碳酸盐能有效降低导电玻璃氧化铟锡(indium tin oxide, ITO)的功函数, 并且发现Cs₂CO₃由于其可以形成层间最强的偶极矩, 所制备的器件性能良好。Zuo等人^[81]通过3-氨基丙酸的SAM修饰电子传输层ZnO, 通过UPS测试发现, ZnO的功函数降低了0.65 eV, 增强了电子的选择性收集并且减少了电荷的复合, 器件获得了优越的光电转化效率。Ok等人^[82]通过在空穴传输层NiO和钙钛矿层间插入含苯恶嗪和咪唑的小分子, 小分子层偶极矩的正电荷端指向NiO, 负电荷端指向钙钛矿, 所形成相对于HTM的正偶极层使NiO的功函数变大, 增大了器件内建电场的强度, 如图5(c)所示。Lee等人^[83]提出可以同时增加两个电极的功函数差异, 从而提升载流子的分离和传输能力, 进而提高电池的光电转换效率, 最终获得了19.4%的光电转换效率。

Wang等人^[84]通过引入电偶极分子二甲胺基(PTFCN)和三氟化物(CF₃BACl)增加阴极和阳极之间

功函数差($\Delta\mu_1$)和钙钛矿薄膜上下表面之间的功函数差($\Delta\mu_2$)来最大化内建电场, 如图5(d)所示, 内建电场的协同强化提高了电荷的传输和收集。含氨基聚合物PTFCN通过侧链向电极表面的优先取向降低了ITO的功函数, 提升了其费米能级。这是由于该过程产生了部分质子化的氮, 形成了永久负偶极矩^[85,86], 从而使真空能级向下移动。使用CF₃BACl可以降低钙钛矿层的费米能级, 由于CF₃BACl的三氟化物和氨基团通过苯环共价键合, 可以提供较大的正偶极矩来提高钙钛矿的功函数^[87], CF₃BACl不仅提供了偶极效应来调节钙钛矿的表面电位, 而且提供了疏水性三氟化物基团, 并使未封装的PSCs在储存2000 h后仍保持初始效率的95%以上。经过处理后的器件具有更长的载流子寿命和长度, 器件的效率从17.87%上升到20.57%, 实现了使用电偶极子进行内建电场的双重增强, 大大提高了PSCs的器件性能。Liu等人^[88]在电子传输层SnO₂和钙钛矿层之间添加了1-丁基-3-甲基咪唑四氟硼酸盐([BMIM]-BF₄), 由于四氟硼酸阴离子与不饱和Sn⁴⁺之间的库仑相互作用, 形成了负偶极子层, 降低了电子传输层的表面功函数, 扩大了费米能级劈裂, 进而增强了内建电场,

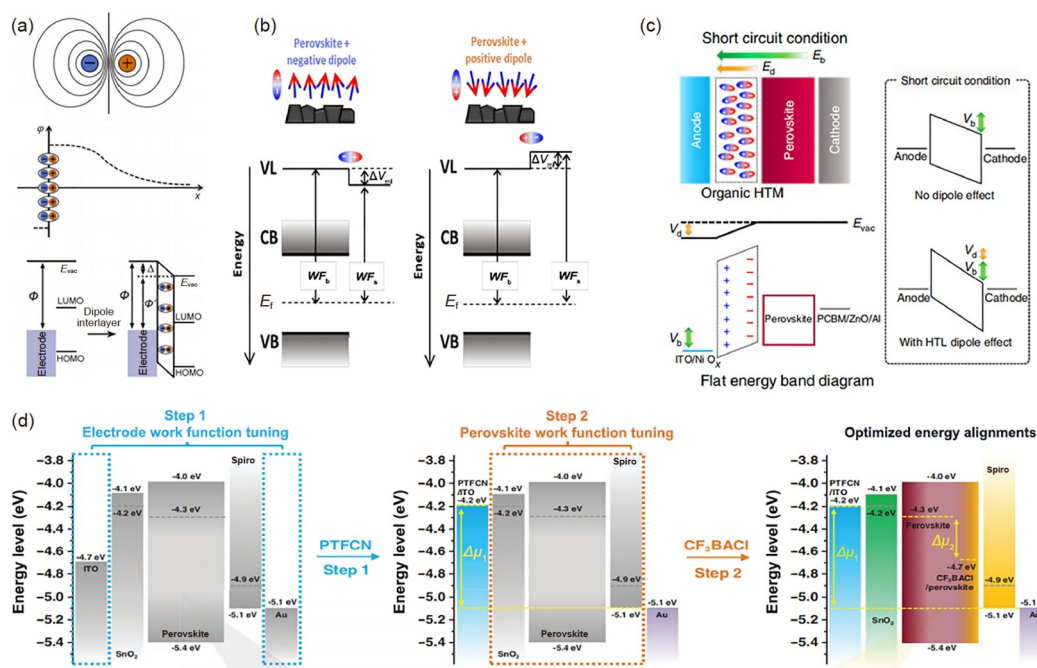


图 5 (网络版彩色)电偶极子的原理和作用。(a) 电偶极子影响电极功函数的原理, 界面偶极子诱导真空能级(E_{vac})下移 Δ , $\Phi'=\Phi-\Delta$ 为表观功函数。Reprinted with permission from Ref. [77]. Copyright © 2020 American Chemical Society. (b) 正负电偶极子对钙钛矿功函数的影响^[79]。(c) 有机HTM偶极效应器件能级图^[82]。 V_b 和 E_b 分别为内建电势和内建电场; V_d 和 E_d 分别表示HTM的偶极效应对内建电势和内建电场的改善。(d) 电偶极分子PTFCN和 CF_3BACl 处理后器件的能级结构示意图^[84]。 $\Delta\mu_1$ 为阴极和阳极的功函数差异, $\Delta\mu_2$ 为钙钛矿上表面和下表面的功函数差异。 Reprinted with permission from Ref. [84]. Copyright © 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Figure 5 (Color online) Principles and effects of electric dipoles. (a) The principle of electric dipoles affecting the work function of electrodes. The interface dipole induces vacuum energy level (E_{vac}) to downshift Δ . $\Phi'=\Phi-\Delta$ is the apparent work function. Reprinted with permission from Ref. [77]. Copyright © 2020 American Chemical Society. (b) The effect of positive and negative electric dipoles on the work function of perovskites^[79]. (c) Energy-level diagrams of the device about the dipole effect of organic HTM^[82]. V_b and E_b : Built-in potential and electric field; V_d and E_d : Improved built-in potential and electric field by the dipole effect of HTM. (d) Schematic diagram of the energy level structure of the device after treatment with electric dipole molecules PTFCN and CF_3BACl ^[84]. $\Delta\mu_1$ is the work function difference between the cathode and the anode, and $\Delta\mu_2$ is the work function difference between the upper and lower surfaces of the perovskite. Reprinted with permission from Ref. [84]. Copyright © 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

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3 总结与展望

PSCs是极具应用前景的新型光伏器件, 经过数年来研究者的不懈努力, 其光电转化效率从3.8%上升到了如今的25.7%, 未来还有无限可能。载流子的分离和传输是PSCs的核心要素, 这是光能转化为电能的关键之处。本综述首先对PSCs的电荷分离机制进行总结和评述, 指出了PSCs中的内建电场对器件光电转化效率的重要性。其次, 对目前常见的PSCs内建电场的调控策略进行总结, 主要包括以下3方面。

(1) 通过掺杂调控PSCs的内建电场。在掺杂调控PSCs的内建电场方面, 可以看出, 目前高效率器件的电子传输层和空穴传输层通常都需要进行掺杂, 在提升其迁移率的同时使其能级和钙钛矿更加匹配, 再结

合钙钛矿层的掺杂和缺陷钝化, 方可实现其最优的光电转化效率。

(2) 通过构建三维/二维钙钛矿异质结调控PSCs的内建电场。在2D/3D异质结方面, 该方法是目前高效率PSCs普遍采用的方法, 也是调控其内建电场最为有效的策略。但是2D钙钛矿吸收层的厚度对载流子的传输影响很大, 如何处理好吸收层厚度与电池性能之间的关系也是今后研究所要关注的方面。

(3) 通过构建偶极层调控PSCs的内建电场。在电池界面处添加电偶极子可以改变原本电池各层的功函数差异, 这些修饰材料本身具有独特的化学性质, 可以产生偶极效应, 增大异质结两侧的费米能级差异, 进而增强电池的内建电场。电偶极子材料的理想选择还会对电池内建电场进行协同加强, 这些材料往往还具有一些缺陷钝化、增强器件疏水性和稳定性的额外功能。

但是, 寻求有效电偶极子材料来调节各层的能级结构以优化电池内建电场的工作也是较为复杂且富有挑战性的, 往往需要人工合成目标材料, 其成本较高。为促进PSCs的商业化, 采用大面积的印刷技术还会造成薄膜厚度的较大波动, 所以发明对薄膜厚度形态不敏感的电偶极子材料十分重要。

进PSCs的商业化, 采用大面积的印刷技术还会造成薄膜厚度的较大波动, 所以发明对薄膜厚度形态不敏感的电偶极子材料十分重要。

参考文献

- 1 Yin W J, Yang J H, Kang J, et al. Halide perovskite materials for solar cells: A theoretical review. *J Mater Chem A*, 2015, 3: 8926–8942
- 2 Kojima A, Teshima K, Shirai Y, et al. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *J Am Chem Soc*, 2009, 131: 6050–6051
- 3 Burschka J, Pellet N, Moon S J, et al. Sequential deposition as a route to high-performance perovskite-sensitized solar cells. *Nature*, 2013, 499: 316–319
- 4 Liu M, Johnston M B, Snaith H J. Efficient planar heterojunction perovskite solar cells by vapour deposition. *Nature*, 2013, 501: 395–398
- 5 Docampo P, Ball J M, Darwich M, et al. Efficient organometal trihalide perovskite planar-heterojunction solar cells on flexible polymer substrates. *Nat Commun*, 2013, 4: 2761
- 6 Shockley W, Queisser H J. Detailed balance limit of efficiency of p-n junction solar cells. *J Appl Phys*, 1961, 32: 510–519
- 7 Liao J F, Wu W Q, Jiang Y, et al. Understanding of carrier dynamics, heterojunction merits and device physics: Towards designing efficient carrier transport layer-free perovskite solar cells. *Chem Rev*, 2020, 49: 354–381
- 8 Bai S, Wu Z, Wu X, et al. High-performance planar heterojunction perovskite solar cells: Preserving long charge carrier diffusion lengths and interfacial engineering. *Nano Res*, 2014, 7: 1749–1758
- 9 Qin S, Lu C, Jia Z, et al. Constructing monolithic perovskite/organic tandem solar cell with efficiency of 22.0% via reduced open-circuit voltage loss and broadened absorption spectra. *Adv Mater*, 2022, 34: 2108829
- 10 Jiang Q, Zhang X, You J. SnO₂: A wonderful electron transport layer for perovskite solar cells. *Small*, 2018, 14: 1801154
- 11 Chen W, Wu Y, Yue Y, et al. Efficient and stable large-area perovskite solar cells with inorganic charge extraction layers. *Science*, 2015, 350: 944–948
- 12 Zhu L F, Shi J J, Li D M, et al. Effect of mesoporous TiO₂ layer thickness on the cell performance of perovskite solar cells (in Chinese). *Acta Chim Sin*, 2015, 73: 261–266 [朱立峰, 石将建, 李冬梅, 等. 多孔TiO₂层厚度对钙钛矿太阳能电池性能的影响. 化学学报, 2015, 73: 261–266]
- 13 Yang L, Zhang J B. Recent progress of doping strategies for organic hole transport materials in perovskite solar cells (in Chinese). *Chin Sci Bull*, 2021, 66: 2793–2801 [杨丽, 张金宝. 钙钛矿太阳能电池中有机空穴传输材料掺杂方法研究进展. 科学通报, 2021, 66: 2793–2801]
- 14 Niu G S, Zhuang J, Luan Y G, et al. Research progress on defects and interfacial passivation layers in hybrid perovskite solar cells (in Chinese). *Chin Sci Bull*, 2020, 66: 2179–2201 [牛国盛, 庄晶, 栾乙刚, 等. 杂化钙钛矿太阳能电池中缺陷与界面钝化层的研究进展. 科学通报, 2020, 66: 2179–2201]
- 15 Garrett J L, Tennyson E M, Hu M, et al. Real-time nanoscale open-circuit voltage dynamics of perovskite solar cells. *Nano Lett*, 2017, 17: 2554–2560
- 16 Jiang C S, Yang M, Zhou Y, et al. Carrier separation and transport in perovskite solar cells studied by nanometre-scale profiling of electrical potential. *Nat Commun*, 2015, 6: 8397
- 17 Peng J, Chen Y, Zheng K, et al. Insights into charge carrier dynamics in organo-metal halide perovskites: From neat films to solar cells. *Chem Soc Rev*, 2017, 46: 5714–5729
- 18 Shi J, Dong J, Lü S, et al. Hole-conductor-free perovskite organic lead iodide heterojunction thin-film solar cells: High efficiency and junction property. *Appl Phys Lett*, 2014, 104: 063901
- 19 Zhao L, Sun X, Yao Q, et al. Field-effect control in hole transport layer composed of Li:NiO/NiO for highly efficient inverted planar perovskite solar cells. *Adv Mater Inter*, 2022, 9: 2101562
- 20 Belisle R A, Nguyen W H, Bowring A R, et al. Interpretation of inverted photocurrent transients in organic lead halide perovskite solar cells: Proof of the field screening by mobile ions and determination of the space charge layer widths. *Energy Environ Sci*, 2017, 10: 192–204
- 21 Li G, Guo F, Zhou X, et al. Performance optimization of homojunction perovskite solar cells by numerical simulation. *Superlattices Microstruct*, 2021, 156: 106922
- 22 Han D, Yuan Q, Slanina Z, et al. Enhancing built-in electric field and defect passivation through gradient doping in inverted CsPbI₂Br perovskite solar cells. *Sol RRL*, 2021, 5: 2000629
- 23 Li H, Li F, Shen Z, et al. Photoferroelectric perovskite solar cells: Principles, advances and insights. *Nano Today*, 2021, 37: 101062
- 24 Sandberg O J, Kurpiers J, Stolterfoht M, et al. On the question of the need for a built-in potential in perovskite solar cells. *Adv Mater Interfaces*, 2020, 7: 2000041

- 25 Shi J, Li Y, Li Y, et al. Eliminating the electric field response in a perovskite heterojunction solar cell to improve operational stability. *Sci Bull*, 2021, 66: 536–544
- 26 Luque A, Hegedus S. Handbook of Photovoltaic Science and Engineering. New York: John Wiley & Sons, 2011
- 27 Xing G, Mathews N, Sun S, et al. Long-range balanced electron- and hole-transport lengths in organic-inorganic $\text{CH}_3\text{NH}_3\text{PbI}_3$. *Science*, 2013, 342: 344–347
- 28 Cai M, Ishida N, Li X, et al. Control of electrical potential distribution for high-performance perovskite solar cells. *Joule*, 2018, 2: 296–306
- 29 Sze S M, Ng K K. Physics of Semiconductor Devices. 3rd ed. New York: John Wiley & Sons, 2006
- 30 Zimmermann B, Glatthaar M, Niggemann M, et al. Electroabsorption studies of organic bulk-heterojunction solar cells. *Thin Solid Films*, 2005, 493: 170–174
- 31 Kang Z, Si H, Shi M, et al. Kelvin probe force microscopy for perovskite solar cells. *Sci China Mater*, 2019, 62: 776–789
- 32 Wang Y B, Cui D Y, Zhang C Y, et al. Recent advances in perovskite solar cells: Space potential and optoelectronic conversion mechanism (in Chinese). *Acta Phys Sin*, 2019, 68: 158401 [王言博, 崔丹钰, 张才益, 等. 钙钛矿太阳能电池研究进展: 空间电势与光电转换机制. 物理学报, 2019, 68: 158401]
- 33 Chen Q, Mao L, Li Y, et al. Quantitative operando visualization of the energy band depth profile in solar cells. *Nat Commun*, 2015, 6: 7745
- 34 Dymshits A, Henning A, Segev G, et al. The electronic structure of metal oxide/organo metal halide perovskite junctions in perovskite based solar cells. *Sci Rep*, 2015, 5: 1–6
- 35 Edri E, Kirmayer S, Mukhopadhyay S, et al. Elucidating the charge carrier separation and working mechanism of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite solar cells. *Nat Commun*, 2014, 5: 1–8
- 36 Wang Q, Shao Y, Xie H, et al. Qualifying composition dependent p and n self-doping in $\text{CH}_3\text{NH}_3\text{PbI}_3$. *Appl Phys Lett*, 2014, 105: 163508
- 37 Li B, Zhang Y, Zhang L, et al. Graded heterojunction engineering for hole-conductor-free perovskite solar cells with high hole extraction efficiency and conductivity. *Adv Mater*, 2017, 29: 1701221
- 38 Zhuang X, Sun R, Zhou D, et al. Synergistic effects of multifunctional lanthanides doped CsPbBrCl_2 quantum dots for efficient and stable MAPbI_3 perovskite solar cells. *Adv Funct Mater*, 2022, 32: 2110346
- 39 Chen W, Liu S, Li Q, et al. High-polarizability organic ferroelectric materials doping for enhancing the built-in electric field of perovskite solar cells realizing efficiency over 24%. *Adv Mater*, 2022, 34: 2110482
- 40 Zou Y, Yu W, Tang Z, et al. Improving interfacial charge transfer by multi-functional additive for high-performance carbon-based perovskite solar cells. *Appl Phys Lett*, 2021, 119: 151104
- 41 Li X, Zhang W, Guo X, et al. Constructing heterojunctions by surface sulfidation for efficient inverted perovskite solar cells. *Science*, 2022, 375: 434–437
- 42 Zhou H, Chen Q, Li G, et al. Interface engineering of highly efficient perovskite solar cells. *Science*, 2014, 345: 542–546
- 43 Wang S, Liu B, Zhu Y, et al. Enhanced performance of TiO_2 -based perovskite solar cells with Ru-doped TiO_2 electron transport layer. *Sol Energy*, 2018, 169: 335–342
- 44 Guo R, Zhao Y, Zhang Y, et al. Significant performance enhancement of all-inorganic CsPbBr_3 perovskite solar cells enabled by Nb-doped SnO_2 as effective electron transport layer. *Energy Environ Mater*, 2021, 4: 671–680
- 45 Seo J Y, Kim H S, Akin S, et al. Novel p-dopant toward highly efficient and stable perovskite solar cells. *Energy Environ Sci*, 2018, 11: 2985–2992
- 46 Liu D, Li Y, Yuan J, et al. Improved performance of inverted planar perovskite solar cells with F4-TCNQ doped PEDOT:PSS hole transport layers. *J Mater Chem A*, 2017, 5: 5701–5708
- 47 Jiang L L, Wang Z K, Li M, et al. Flower-like MoS_2 nanocrystals: A powerful sorbent of Li^+ in the spiro-OMeTAD layer for highly efficient and stable perovskite solar cells. *J Mater Chem A*, 2019, 7: 3655–3663
- 48 Yu Z, Wang L, Mu X, et al. Intramolecular electric field construction in metal phthalocyanine as dopant-free hole transporting material for stable perovskite solar cells with >21% efficiency. *Angew Chem Int Edit*, 2021, 60: 6294–6299
- 49 Lin Z, Li J, Li H, et al. A novel dopant for spiro-OMeTAD towards efficient and stable perovskite solar cells. *Sci China Mater*, 2021, 64: 2915–2925
- 50 Dou L. Emerging two-dimensional halide perovskite nanomaterials. *J Mater Chem C*, 2017, 5: 11165–11173
- 51 Saparov B, Mitzi D B. Organic-inorganic perovskites: Structural versatility for functional materials design. *Chem Rev*, 2016, 116: 4558–4596
- 52 Smith I C, Hoke E T, Solis-Ibarra D, et al. A layered hybrid perovskite solar-cell absorber with enhanced moisture stability. *Angew Chem Int Edit*, 2014, 53: 11232–11235
- 53 Proppe A H, Wei M, Chen B, et al. Photochemically cross-linked quantum well ligands for 2D/3D perovskite photovoltaics with improved photovoltage and stability. *J Am Chem Soc*, 2019, 141: 14180–14189
- 54 Yoo J J, Wieghold S, Sponseller M C, et al. An interface stabilized perovskite solar cell with high stabilized efficiency and low voltage loss. *Energy Environ Sci*, 2019, 12: 2192–2199

- 55 Jung E H, Jeon N J, Park E Y, et al. Efficient, stable and scalable perovskite solar cells using poly(3-hexylthiophene). *Nature*, 2019, 567: 511–515
- 56 Hu Y, Schlupf J, Wussler M, et al. Hybrid perovskite/perovskite heterojunction solar cells. *ACS Nano*, 2016, 10: 5999–6007
- 57 Cho Y, Soufiani A M, Yun J S, et al. Mixed 3D-2D passivation treatment for mixed-cation lead mixed-halide perovskite solar cells for higher efficiency and better stability. *Adv Energy Mater*, 2018, 8: 1703392
- 58 Ortiz-Cervantes C, Carmona-Monroy P, Solis-Ibarra D. Two-dimensional halide perovskites in solar cells: 2D or not 2D? *ChemSusChem*, 2019, 12: 1560–1575
- 59 Mahmud M A, Duong T, Peng J, et al. Origin of efficiency and stability enhancement in high-performing mixed dimensional 2D-3D Perovskite solar cells: A review. *Adv Funct Mater*, 2022, 32: 2009164
- 60 Wu G, Liang R, Ge M, et al. Surface passivation using 2D perovskites toward efficient and stable perovskite solar cells. *Adv Mater*, 2022, 34: 2105635
- 61 Jang Y W, Lee S, Yeom K M, et al. Intact 2D/3D halide junction perovskite solar cells via solid-phase in-plane growth. *Nat Energy*, 2021, 6: 63–71
- 62 He M, Liang J, Zhang Z, et al. Compositional optimization of a 2D-3D heterojunction interface for 22.6% efficient and stable planar perovskite solar cells. *J Mater Chem A*, 2020, 8: 25831–25841
- 63 Wang C, Wang X, He Z, et al. Minimizing voltage deficit in methylammonium-free perovskite solar cells via surface reconstruction. *Chem Eng J*, 2022, 444: 136622
- 64 Huang X, Cui Q, Bi W, et al. Two-dimensional additive diethylammonium iodide promoting crystal growth for efficient and stable perovskite solar cells. *RSC Adv*, 2019, 9: 7984–7991
- 65 Wu S, Li Z, Zhang J, et al. Efficient large guanidinium mixed perovskite solar cells with enhanced photovoltage and low energy losses. *Chem Commun*, 2019, 55: 4315–4318
- 66 Cho Y, Soufiani A M, Yun J S, et al. Mixed 3D-2D passivation treatment for mixed-cation lead mixed-halide perovskite solar cells for higher efficiency and better stability. *Adv Energy Mater*, 2018, 8: 1703392
- 67 Li P, Zhang Y, Liang C, et al. Phase pure 2D perovskite for high-performance 2D-3D heterostructured perovskite solar cells. *Adv Mater*, 2018, 30: 1805323
- 68 Yao D, Zhang C, Zhang S, et al. 2D-3D mixed organic-inorganic perovskite layers for solar cells with enhanced efficiency and stability induced by n-propylammonium iodide additives. *ACS Appl Mater Interfaces*, 2019, 11: 29753–29764
- 69 Li M H, Yeh H H, Chiang Y H, et al. Highly efficient 2D/3D hybrid perovskite solar cells via low-pressure vapor-assisted solution process. *Adv Mater*, 2018, 30: 1801401
- 70 Chen Y, Sun Y, Peng J, et al. Tailoring organic cation of 2D air-stable organometal halide perovskites for highly efficient planar solar cells. *Adv Energy Mater*, 2017, 7: 1700162
- 71 Hu Y, Qiu T, Bai F, et al. Highly efficient and stable solar cells with 2D $\text{MA}_3\text{Bi}_2\text{I}_9$ /3D MAPbI_3 heterostructured perovskites. *Adv Energy Mater*, 2018, 8: 1703620
- 72 Liu G, Zheng H, Xu X, et al. Introduction of hydrophobic ammonium salts with halogen functional groups for high-efficiency and stable 2D/3D perovskite solar cells. *Adv Funct Mater*, 2019, 29: 1807565
- 73 Chen P, Bai Y, Wang S, et al. *In situ* growth of 2D perovskite capping layer for stable and efficient perovskite solar cells. *Adv Funct Mater*, 2018, 28: 1706923
- 74 Liu Y, Akin S, Hinderhofer A, et al. Stabilization of highly efficient and stable phase-pure FAPbI_3 perovskite solar cells by molecularly tailored 2D-overlayers. *Angew Chem Int Edit*, 2020, 59: 15688–15694
- 75 Hu J, Wang C, Qiu S, et al. Spontaneously self-assembly of a 2D/3D heterostructure enhances the efficiency and stability in printed perovskite solar cells. *Adv Energy Mater*, 2020, 10: 2000173
- 76 Ye T, Bruno A, Han G, et al. Efficient and ambient-air-stable solar cell with highly oriented 2D@3D perovskites. *Adv Funct Mater*, 2018, 28: 1801654
- 77 Chen Q, Wang C, Li Y, et al. Interfacial dipole in organic and perovskite solar cells. *J Am Chem Soc*, 2020, 142: 18281–18292
- 78 de Bruyn P, van Rest A H P, Wetzelaer G A H, et al. Diffusion-limited current in organic metal-insulator-metal diodes. *Phys Rev Lett*, 2013, 111: 186801
- 79 Canil L, Cramer T, Fraboni B, et al. Tuning halide perovskite energy levels. *Energy Environ Sci*, 2021, 14: 1429–1438
- 80 Huang J, Li G, Yang Y. A semi-transparent plastic solar cell fabricated by a lamination process. *Adv Mater*, 2008, 20: 415–419
- 81 Zuo L, Gu Z, Ye T, et al. Enhanced photovoltaic performance of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells through interfacial engineering using self-assembling monolayer. *J Am Chem Soc*, 2015, 137: 2674–2679
- 82 Ok S A, Jo B, Somasundaram S, et al. Management of transition dipoles in organic hole-transporting materials under solar irradiation for perovskite solar cells. *Nat Commun*, 2018, 9: 4537
- 83 Lee J H, Kim J, Kim G, et al. Introducing paired electric dipole layers for efficient and reproducible perovskite solar cells. *Energy Environ Sci*,

- 2018, 11: 1742–1751
- 84 Wang W, Chen P, Chiang C, et al. Synergistic reinforcement of built-in electric fields for highly efficient and stable perovskite photovoltaics. [Adv Funct Mater](#), 2020, 30: 1909755
- 85 Yeo J S, Kang M, Jung Y S, et al. In-depth considerations for better polyelectrolytes as interfacial materials in polymer solar cells. [Nano Energy](#), 2016, 21: 26–38
- 86 Schlapak R, Armitage D, Saucedo-Zeni N, et al. Preparation and characterization of dense films of poly(amidoamine) dendrimers on indium tin oxide. [Langmuir](#), 2007, 23: 8916–8924
- 87 Wang F, Geng W, Zhou Y, et al. Phenylalkylamine passivation of organolead halide perovskites enabling high-efficiency and air-stable photovoltaic cells. [Adv Mater](#), 2016, 28: 9986–9992
- 88 Liu D, Zheng H, Wang Y, et al. Vacancies substitution induced interfacial dipole formation and defect passivation for highly stable perovskite solar cells. [Chem Eng J](#), 2020, 396: 125010

Summary for “钙钛矿太阳能电池的内建电场调控策略研究进展”

Progress on strategies to control the built-in electric field of perovskite solar cells

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Perovskite solar cells (PSCs) are high-efficiency and low-cost photovoltaic devices that have been extensively studied by researchers around the world. The carrier separation and transport inside the solar cell is the key process of the device operation, which is directly related to the photoelectric conversion efficiency (PCE) of the device. The built-in electric field formed by the heterojunction dominates the behavior of carriers, and its strength determines the separation efficiency of electrons and holes in the device. Therefore, regulating and optimizing the built-in electric field can fundamentally improve the performance of the solar cells. Much work is focusing on the built-in electric field for the fabrication of high-efficiency devices. According to previous results, this paper firstly introduces some fundamental experiments on the heterojunctions and the mechanism of carrier separation and transport of PSCs. Secondly, the regulation strategies of the built-in electric field commonly used in perovskite solar cells and their effects on device performance are summarized. The following are the most common built-in electric field control strategies: (1) Tuning the built-in electric field of perovskite solar cells by doping. The method of doping to control the built-in electric field is to add appropriate impurities according to different conductive properties of the materials. According to the structure of planar perovskite solar cells, doping the electron transport layer, hole transport layer, and perovskite layer of PSCs with different doping materials can change the position of the Fermi level and further enlarge the splitting of the Fermi level which can assist in the separation and transport of carriers. (2) Tuning the built-in electric field of perovskite cells by constructing 3D/2D perovskite heterojunctions. Fabrication of 3D/2D heterojunctions can not only improve the PCE of perovskite solar cells, but also improve its stability, so this method is more popular among researchers. The construction of 3D/2D perovskite heterojunctions can expand the splitting of the Fermi level to form a more powerful built-in electric field. This method can increase the separation and transport efficiency of carriers, and improve the PCE and open the circuit voltage of the device. (3) Tuning the built-in electric field of perovskite cells by constructing a dipole layer. Electric dipoles have the property of changing the work function of materials. Using them can effectively adjust the energy level structure of perovskite solar cells, expand the work function difference, and increase the built-in electric field strength to achieve the effect of enhancing carrier separation and transport efficiency. The above three methods are relatively popular control strategies for the built-in electric field of perovskite solar cells and this paper systematically analyzes and summarizes them. In the end, we evaluate the built-in electric field regulation technologies of perovskite solar cells, and look forward to the future development of this field. Enhancing the built-in electric field of perovskite solar cells is the key to improving the PCE of the device. In the future, more research should be devoted to the study of the built-in electric field of perovskite solar cells.

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