科学通报 2017 年 第 62 卷 第 36 期: 4256 ~ 4269
评 述
《中国科学》杂志社
SCIENCE CHINA PRESS

钙钛矿太阳能电池的稳定性

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2017-08-06 收稿, 2017-09-19 修回, 2017-09-25 接受, 2017-11-16 网络版发表
国家重点基础研究发展计划(2014CB643506 和 2013CB922104)资助

摘要 有机-无机卤化物钙钛矿太阳能电池的研究在近几年里获得了极大的突破. 然而, 电池长期的稳定性和重金属铅的毒性等问题仍未得到完全解决. 本文将讨论钙钛矿太阳能电池稳定性的影响因素, 从器件结构方面入手分析钙钛矿材料、空穴传输材料、电子传输材料以及电极对钙钛矿电池稳定性的影响, 然后根据不同结构中影响电池稳定性的因素提出对应的解决方案, 从而提升钙钛矿太阳能电池稳定性. 最后, 我们提出由n型半导体层、绝缘层和p型半导体层依次层叠构成的全无机介孔p-i-n结构框架有助于钙钛矿电池的稳定性.

关键词 太阳能电池, 钙钛矿, 稳定性

由于能源成本不断上涨和环境不断恶化, 太阳能在各行各业获得了广泛的关注. 目前太阳能的利用技术主要有太阳能光伏技术和太阳能热技术, 其中太阳能光伏技术是将太阳能直接转换为电能的一种技术. 当接受光照时, 太阳能电池产生电流输出, 对环境不会造成任何影响. 目前, 光伏发电只占全球发电量的一小部分, 但随着成本的降低, 相信太阳能光伏发电将占据越来越重要的位置.

限制太阳能电池广泛应用的主要原因是成本相对较高和光电转换率低, 晶体硅太阳能电池在过去的半个世纪中主导了光伏市场, 但晶体硅制备程序复杂、成本高, 所以人们不断追求更高效率、更简单的制备方法和更低成本的新型太阳能电池, 如有机光伏(OPV)、染料敏化太阳能电池(DSSCs)和有机-无机杂化型钙钛矿太阳能电池(PSCs)等[1].

自从2009年[2]第一次被引入DSSCs中作为吸光材料以来, 有机-无机杂化钙钛矿电池引领了太阳能电池领域的研究热潮[3~6]. 在过去的几年里, 钙钛矿太阳能电池的效率由3.8%[3]迅速增长到22.1%[7], 这是因为钙钛矿材料具有优异的性能, 包括合适的带隙(~1.5 eV)、高吸收系数(~10^4 cm^{-1}), 载流子寿命高达300 ns以及扩散长度可达到1 μm[3,4,8,9]. 如图1所示, 有机-无机杂化钙钛矿电池材料具AMX_3的化学通式和立方晶胞结构, 通常A为甲胺($CH_3NH_3^+$, MA)、乙胺($C_2H_5NH_3^+$, EA)或甲脒($HC(NH_2)_2^+$, FA), 位于立方晶胞的角的位置[11,12]; M为处在体心处的二价金属离子(Pb^{2+}或Sn^{2+})[13~16]; X是卤素阴离子(Cl^-, Br^-, I^-), 位于晶胞的面心位置[17,18]. 产品使用周期和环境影响分析结果表明, 钙钛矿太阳能电池模块的能量回收时间只需要0.22年[19], 说明作为下一代光伏材料, 钙钛矿可实现太阳能电池的低成本制造. 另外在制备工艺方面, 钙钛矿材料可使用溶液法制备纳米薄膜, 也可应用于柔性太阳能电池的制备, 因而与传统的晶体硅太阳能电池相比可大大降低制造难度和制造成本, 同时应用场景也更加广泛.

钙钛矿太阳能电池通常包含导电基底、电子传输

引用格式: 黄飞洪, 宋金魁, 廖沛哲, 等. 钙钛矿太阳能电池的稳定性. 科学通报, 2017, 62: 4256–4269
Huang F H, Song J K, Liao P Z, et al. The stability of perovskite solar cells (in Chinese). Chin Sci Bull, 2017, 62: 4256–4269, doi: 10.1360/N972017-00859

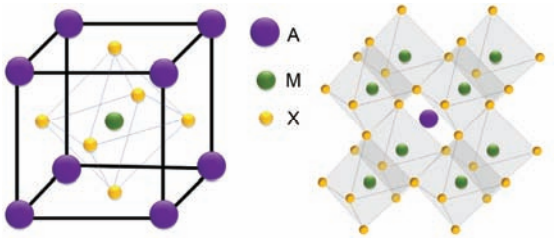

图 1 (网络版彩色)有机-无机杂化钙钛矿晶胞结构示意图. Reprinted with permission from Ref. [10], Copyright © 2016 The Royal Society of Chemistry

Figure 1 (Color online) Crystalline structure of inorganic-organic hybrid lead perovskite. Reprinted with permission from Ref. [10], Copyright © 2016 The Royal Society of Chemistry

层(electron transport layer, ETL)、钙钛矿吸光层、空穴传输层(hole transport layer, HTL)、金属电极. 根据有无介孔骨架可以分为介孔型钙钛矿电池和平板型钙钛矿电池; 根据电子传输层和空穴传输层的位置又可以分为正式太阳能电池(n-i-p型)和反式太阳能电池(p-i-n型)[20]. 具体的结构如图2所示, 钙钛矿层吸收光子后产生自由电子和空穴, 其中电子被电子传输层抽取, 空穴被空穴传输层抽取最后经过对电极与导电基底之间的回路实现电流传输.

尽管实验室中钙钛矿太阳能电池的效率取得可喜的发展, 但稳定性严重抑制其应用. 与液态电解质型太阳能电池相比[21,22], 全固态电池的稳定性已经有了很大的提升[23]. 然而, 有机-无机杂化钙钛矿太阳能电池的稳定性在水汽与光照环境中, 仍需要进一步改进和提高. 研究表明, PSCs的不稳定性主要与钙钛矿材料和传输材料之间界面的退化有关[19,24~30], 同时钙钛矿材料对水、氧气、紫外线、温度和电荷传输材料中掺杂剂都比较敏感[19,25~28], 也加速了器件衰减过程. 为了实现高效率和稳定的钙钛矿太阳能电池, 研究者必须寻找降低钙钛矿太阳能电池的衰减速度的方法, 提高器件稳定性. 本文总结了钙钛矿太阳能电池中不同结构部分对器件稳定性的影响, 然后对各部分给出针对性的优化建议, 旨在提高钙钛矿太阳能电池的稳定性.

1 钙钛矿材料对电池稳定性的影响

在钙钛矿太阳能电池中, 钙钛矿吸光层是最核心的部分, 其稳定性直接影响着钙钛矿太阳能电池的稳定性.

根据前驱体溶液(MAI和PbI_2)是一次沉积还是分两步顺序沉积在基底上, 可以将制备$MAPbI_3$晶体的方法分为一步法和两步法. 其操作流程如图3所示, 通常一步法是将前驱体溶液按比例混合制备成钙钛矿溶液之后一次性沉积在基底上, 然后退火就可得到钙钛矿薄膜. 两步法是先将PbI_2沉积在基底上, 退火后再将MAI沉积在基底上, 最后退火得到钙钛矿薄膜. 在一步法沉积过程中, 由于有多个$MAPbI_3$晶相导致难以形成最佳的单晶钙钛矿薄膜[29], 而利用两步法沉积的钙钛矿薄膜因为残余的有机物会混合在晶体中难以确保所得的$MAPbI_3$的纯度[30]. 钙钛矿晶体和界面处的缺陷可能捕获光生电荷或加剧离子迁移[32], 因此保持$MAPbI_3$良好的晶体性质对于提升器件性能和稳定性至关重要. 研究者发现水在两步法制备钙钛矿薄膜的过程中起到了意料之外的作用, 少量水与*N*,*N*-二甲基甲酰胺(DMF)的协同作用可以获得更大的晶粒以及缺陷更少的钙钛矿薄膜, 从而有望提升器件的效率与稳定性[33].

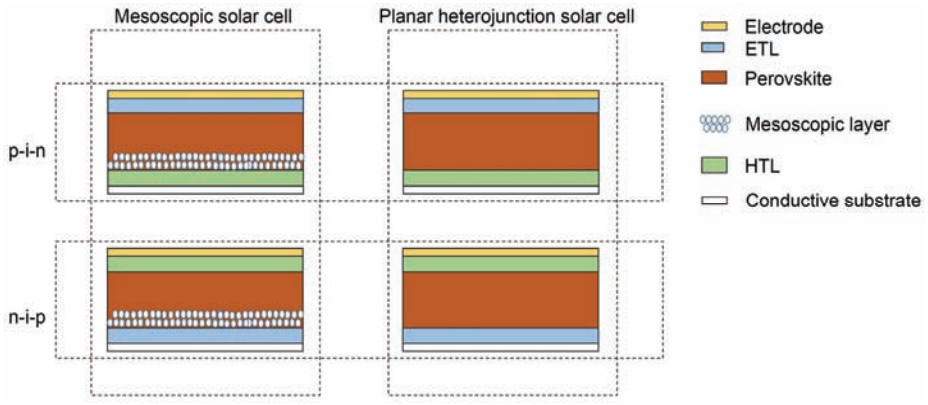

图 2 (网络版彩色)不同类型钙钛矿太阳能电池结构示意图

Figure 2 (Color online) Diagram of different types of perovskite solar cell structure

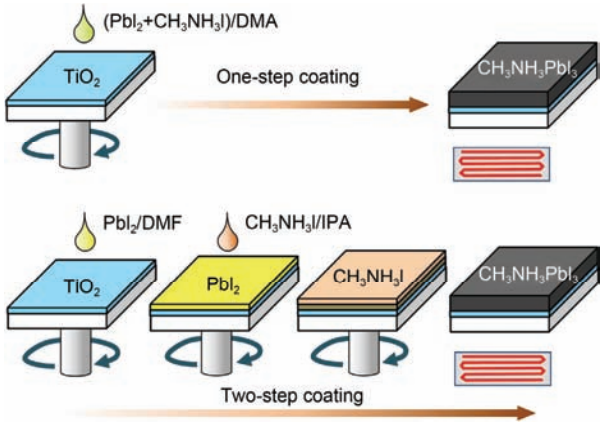

图 3 (网络版彩色)一步法和两步法制备钙钛矿薄膜的流程. Reprinted with permission from Ref. [31], Copyright © 2014 Nature Publishing Group

Figure 3 (Color online) One-step and two-step spin-coating procedures for perovskite formation. Reprinted with permission from Ref. [31], Copyright © 2014 Nature Publishing Group

前面已经提到了$MAPbI_3$薄膜的稳定性取决于多种环境因素, 包括温度、光照、氧气和水分[34]. 其中水被认为是钙钛矿分解的重要因素, 有研究表明水分子会促进钙钛矿分解成CH_3NH_2, HI和PbI_2, 然后在光照或氧气的作用下HI进一步分解, 从而进一步加速钙钛矿的分解过程[25]. 具体的反应方程如式(1)~(4)所示:

$$CH_3NH_3PbI_3 \xleftrightarrow{H_2O} CH_3NH_3I(aq) + PbI_2 \quad (1)$$

$$CH_3NH_3I(aq) \leftrightarrow CH_3NH_2aq) + HI(aq) \quad (2)$$

$$4HI(aq) + O_2 \leftrightarrow 2I_2(s) + 2H_2O \quad (3)$$

$$2HI(aq) \xleftrightarrow{h\nu} H_2\uparrow + I_2(s) \quad (4)$$

因此, 在潮湿空气中具有高稳定性的新型钙钛矿材料是解决该问题的最直接方法, 本课题组[35]利用Br部分取代$MAPbI_3$中的I, 制备的$MAPbI_3Br$钙钛矿太阳能电池稳定性获得了极大提高, 通过测试发现, 即使存放300 h以上效率也能保持在较高水平, 短路电流密度基本保持不变, 这表明钙钛矿中利用Br取代I有助于提高钙钛矿材料的稳定性.

另外, 通过使用适当的封装来避免钙钛矿薄膜与这些环境接触也可以提高器件的稳定性. 但是$MAPbI_3$本身具有热不稳定性和晶体结构的不稳定性, 因此很难保证器件的长期稳定[36,37].

在热不稳定性方面, $MAPbI_3$粉末的热重分析结果表明, 温度达到250 ℃时开始有明显的质量损失[38], 通常认为是HI和CH_3NH_2的升华导致的. 这似乎表明在钙钛矿电池中钙钛矿吸光层应该具有很好的热稳定性. 然而, 通过其他的测试方法发现, $MAPbI_3$实际在85 ℃时就已经发生了分解[36], 虽然在该温度下分解速度相对缓慢(24 h分解率<10%), 但在长时间范围内材料的稳定性仍比较差.

分析钙钛矿分解原因发现, 钙钛矿薄膜热不稳定性很大程度上是由有机阳离子的不稳定引起, 因此通过替换有机阳离子的方式制备全无机钙钛矿材料可以在一定程度上解决钙钛矿薄膜的热稳定性问题. Cs阳离子作为被广泛关注的离子之一, 早在1893年就报道了采用Cs阳离子制备的全无机钙钛矿具有优异的稳定性[39]. 其中最常见的材料为$CsPbI_3$和$CsPbI_3$, 它们在温度达到其熔点(约460 ℃)时也不会分解[40], 采用$CsPbI_3Br$制备的太阳能电池具有很好的热稳定性[41,42].

另外, 采用离子半径和相对质量更大的有机阳离子取代MA也可以在一定程度上提高钙钛矿的热稳定性, 比如常见的FA阳离子, 早期研究者就发现$FAPbI_3$在180 ℃下仍能在60 min内不分解, 与之相对照的$MAPbI_3$则几乎完全分解[43], 而在相同的分解速度的前提下, $FAPbBr_3$所需要的温度比$MAPbBr_3$要高50 ℃左右[44], 这些结果都表明, 在热稳定方面, 使用FA阳离子的钙钛矿材料要远好于使用MA阳离子的钙钛矿. 而使用混合有机-无机阳离子的$FA_{0.83}Cs_{0.17}Pb(I_{1-x}Br_x)_3$钙钛矿薄膜在130 ℃的环境中仍能保持6 h不分解[45]. 综合考虑电池效率和稳定性等因素, 目前基于FAI的钙钛矿材料被认为是MAI钙钛矿材料的理想替代物[43], 还有其他一些有机阳离子基团也被证明添加到$MAPbI_3$可以提高器件的稳定性, 如乙基碘化铵(EAI)[46]和5-铵戊酸碘化物(5-AVA)[47].

然而, 人们在实际的器件稳定性测试中发现, 使用$FAPbI_3$吸光层的钙钛矿电池的稳定性要差于使用$MAPbI_3$吸光层的钙钛矿电池. 对此, 利用热重分析(TGA)、傅里叶变换红外光谱(FTIR)、X光衍射图像(XRD)等测试方法发现, $FAPbI_3$薄膜的热稳定性优于$MAPbI_3$. 这主要是因为在$FAPbI_3$中FA阳离子和卤化物阴离之间形成了较强的氢键, 因此有机离子的电负性也会对钙钛矿材料的稳定性产生影响. 在器件稳定性测试中, 为了避免TiO_2对钙钛矿的影响, 本课题组[48]制备了氧化铟锡(ITO)/Perovskite/空穴传输层(HTM)/Au型无电子传输层的电池, 在含水分的空气中, $FAPbI_3$钙钛矿电池的效率较高但稳定性较差, 但在干燥空气中$FAPbI_3$钙钛矿电池的效率和稳定性都

要好于$MAPbI_3$钙钛矿电池, 因此发现$FAPbI_3$的亲水性会影响其在潮湿空气中的稳定性, 而通过适当的封装隔绝空气能提高$FAPbI_3$钙钛矿电池的稳定性.

密度泛函理论计算和实验数据表明, 由于Pb-Br/Cl具有更高的键能, 因此通过引入溴和氯($MAPbBr_3$/$MAPbCl_3$)替代碘化物也可以提高稳定性, 但这些化合物不太适合高效率的太阳能电池[49].

在晶体结构方面, AMX_3晶体并非只有钙钛矿相一种结构, 还可能形成光电转换能力较差的非钙钛矿相的结构, 常见的钙钛矿相包括立方晶相、四方晶相和正交晶相, 非钙钛矿相主要为斜方晶相[24,50~52]. 这些晶体结构之间是有可能相互转化的. 本课题组[53]研究温度对钙钛矿电池的影响时发现, $MAPbI_3$在160 K时会发生相变导致低于160 K时电池的电压和电流输出都会有极大的下降, 因此如何保持晶体稳定在钙钛矿相也成为钙钛矿太阳能电池稳定工作的关键因素.

通过理论计算发现, 对于杂化卤化物钙钛矿AMX_3, 可以使用容忍因子t来大概描述钙钛矿晶体结构的稳定性情况: $t=\frac{r_A+r_x}{\sqrt{2(r_M+r_x)}}$. 其中, r_A, r_M, r_x分别表示A, M, X 3种离子的离子半径, 当t在一定范围内时才可能稳定地保持钙钛矿相. t=1为立方晶相; 0.7<t<0.9为四方晶相或者正交晶相[54~57]. 通常情况下$FAPbI_3$的容忍因子为0.89, 因此在常温下可以保持在钙钛矿相, 由于热稳定问题, 研究者尝试使用更大的FA离子与更小的Br离子来部分取代MA离子与碘离子, 如经过优化得到的$FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$结构的材料, 其容忍因子达到1.01, 稳定性大大增强, 电池光电转换效率也达到了20%以上[58]. 另外, 态密度计算表明$MASrI_3$相比于$MAPbI_3$是更稳定的钙钛矿相材料[59], 因此用Sr取代Pb不仅可以获得更稳定的晶相, 同时也可以减少钙钛矿中Pb的污染. 本课题组[60]通过溶液法制备的$MASr_aPb_{1-a}(I_xBr_x)_3$太阳能电池获得了16.3%的效率, 同时稳定性也获得了较大的提升, 通过测试和分析发现, Sr的掺入可以抑制Pb^0的生成从而提高材料的稳定性, 同时Sr取代Pb也会导致导带能级上移, 提高激子结合能和束缚态密度.

全无机钙钛矿太阳能电池具有优异的热稳定性, 其中Cs取代MA的钙钛矿材料最为常见, 但在不同温度下, 这些材料会表现出不同的晶相, 如$CsPbBr_3$在常温下为正交晶相, 当温度达到88 ℃之后会转变为四方晶相, 当温度达到130 ℃时会转变为斜方晶相[61,62]; 而$CsPbI_3$与$CsPbBr_3$正好呈现出相反的性质, 在常温下$CsPbI_3$稳定地处于斜方晶相, 当温度升高到300 ℃时会转变为立方晶相[40,63], 因此纯$CsPbI_3$或$CsPbBr_3$都难以保持为钙钛矿相, 通过将这两种材料混合制备成的$CsPb(I_xBr_{1-x})_3$钙钛矿材料具有极好的稳定性, 制备的电池效率也达到了9.84%[42].

2 空穴传输材料(HTM)对电池稳定性的影响

研究者通过大量的研究发现, 空穴传输材料也显著影响着钙钛矿太阳能电池的稳定性[64,65]. 空穴传输材料在空穴传输和防止电子空穴复合方面有着重要作用. 目前为止, 人们引进了许多半导体聚合物和小分子材料作为钙钛矿电池中的空穴传输材料[65~69], 其中spiro-OMeTAD是迄今为止最为成功的[19]. Spiro-OMeTAD由于分子间距太大导致空穴传输率较低[16,70,71], 因此人们使用4-叔丁基吡啶(4-tert-butylpyridine, TBP)和三氟甲烷磺酰亚胺锂(trifluoromethane sulfonimide lithium salt, Li-TFSI)作为掺杂剂来提高电荷传输性能[25,72], Li-TFSI在调节spiro-OMeTAD的极性方面也起到了重要作用, 增加$MAPbI_3$和空穴传输层之间的接触面. 然而, 这类添加剂也会带来一些不良影响: (1) TBP是类似于γ-丁内酯(GBL)的极性溶剂, 它可以溶解钙钛矿, 导致太阳能电池稳定性下降; (2) spiro-OMeTAD自身的分解对长期稳定性有负面作用; (3) Li离子具有亲水性, 导致钙钛矿电池在有水分环境下的降解速度加快[73].

因此, 很多研究工作集中在寻找spiro-OMeTAD的替代物上, 尤其是无需掺杂的材料, 研究者测试了大量的p型有机小分子作为钙钛矿电池中的空穴传输材料[74~76], 虽然这些材料在合成的难度和纯度方面有很大的优势, 但在器件性能方面却很难比得上spiro-OMeTAD. 作为spiro-OMeTAD的替代物, 具有导电性和疏水性的聚合物也引起了研究者的关注, 其器件性能也接近spiro-OMeTAD的水平[77,78]. 除了有机的空穴传输材料, 类似于CuSCN[79], CuI[64]和NiO[80]等无机材料也是低成本以及高稳定性的空穴传输材料. 其中NiO由于具有理想的能级, 高载流子迁移率以及制备方法简单多样, 是最具有应用前景的空穴传输材料之一. 除了寻找spiro-OMeTAD的替代物, Aitola等人[81]也通过向spiro中掺入单臂碳纳米管提高spiro的导电性同时提高器件的稳定性. 另外,

无空穴传输材料的电池结构也获得了人们的大量关注, 虽然目前效率还有待提高, 但稳定性方面获得了巨大提升[82,83].

3 电子传输材料(ETM)对电池稳定性的影响

通常人们会使用n型金属氧化物作为电子传输材料, 作为钙钛矿太阳能电池中的电子传输材料, 它具有很多优点, 例如稳定性好、透明度高以及良好的电子传输与空穴阻挡效果, 但其同时也会对钙钛矿晶体造成破坏, 从而降低电池的稳定性. TiO_2是应用最广泛的n型金属氧化物[35,84~86], 一些实验表明当使用TiO_2作为电子传输层时, PSC器件性能会快速衰减, 即使封装在惰性气体中也会这样[87,88]. 排除$MAPbI_3$和spiro-OMeTAD在光照下的不稳定性的影响之后, 研究者认为TiO_2颗粒中的氧缺位会形成电子势阱与来自钙钛矿中的光生电子结合导致器件性能的下降. 图4演示了假设的结合机制, TiO_2颗粒表面的氧缺位是很强的给电子位点, 并且很容易吸附氧原子. UV光照激发TiO_2中的电子形成电子-空穴对, TiO_2价带中的空穴在氧吸附位点与电子复合, 导致氧原子吸附, 在这种情况下, TiO_2导带中的自由电子和TiO_2表面的带正电荷的氧缺位点结合, 在重p掺杂的spiro-OMeTAD中过量的空穴将容易与自由电子重新结合.

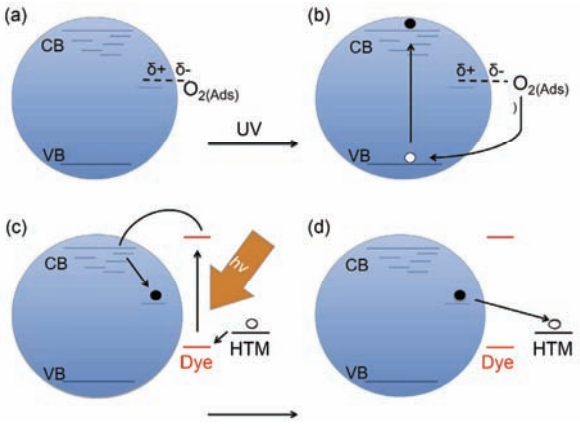

图 4 (网络版彩色)紫外线下钙钛矿的降解机制. (a) 空位上的氧吸收, (b) TiO_2 中的空穴与氧位点上的电子结合, (c) HTM中的空穴与TiO_2上留下的自由电子结合, (d) HTM中的空穴与染料中的自由电子结合. Reprinted with permission from Ref. [19], Copyright © 2013 Nature Publishing Group

Figure 4 (Color online) Degradation mechanism under UV illustration. (a) Oxygen absorption on the vacancy. (b) Recombination of holes in TiO_2 with electrons on oxygen site. (c) Recombination of holes in HTM with the free electron left on TiO_2. (d) Recombination of holes in HTM with electrons reduced by dye. Reprinted with permission from Ref. [19], Copyright © 2013 Nature Publishing Group

同时, 来自吸光材料中的光生电子被氧缺位位点捕获. 最后, HTM中的空穴将与被捕获的电子复合. 过量氧的存在可以补充这些氧缺位位点, 从而减少电子势阱的数量[19].

因此阻止紫外光对电子传输层和钙钛矿的照射可以有效地缓解TiO_2导致的钙钛矿分解. 其中荧光下转换法是最简单可行的方法之一, 通过荧光物质将紫外光转换为可见光, 不仅可以降低紫外光对电池的影响, 同时也可以提高电池对光子的利用率, 本课题组[89]利用非稀土荧光材料($Sr_4Al_{14}O_{25}:Mn^{4+}$, 0.5%Mg)作为转换层旋涂在FTO外侧, 从而减少了紫外光对电池稳定性的影响, 同时电池的效率相对未旋涂荧光材料的样品获得了10%的提升.

Ito等人[26]通过研究$MAPbI_3$太阳能电池在光照下的稳定性, 提出了光照条件下TiO_2诱导PSCs降解的另外一种机制. 他们研究了2种不同结构的器件: FTO/TiO_2/$MAPbI_3$/CuSCN/Au(A) 和 FTO/TiO_2/Sb_2S_3/$MAPbI_3$/CuSCN/Au(B). 如图5(a)所示, 在12 h光照之后, 装置B在不封装的情况下效率仍维持在65%, 而装置A的稳定性在5 h内急剧下降并且在12 h内衰减到0左右. 因此可以认为TiO_2/$MAPbI_3$界面处的Sb_2S_3层提高了器件的稳定性. 在诸如反射吸收谱、XRD图、光谱响应(IPCE)光谱和傅里叶变换红外光谱的综合分析之后, 他们提出了$MAPbI_3$在光照下降解的机理, 如图5(b)和(c)所示, 经过一夜光照后, 没有Sb_2S_3层的电池中的$MAPbI_3$降解为PbI_2和CH_3NH_2, HI气体, 而另一方面, 有Sb_2S_3层的电池由于Sb_2S_3层的保护作用减缓了$MAPbI_3$的降解过程, 因此$MAPbI_3$的分解发生在TiO_2/$MAPbI_3$界面处. 作为典型的n型半导体, TiO_2广泛应用为环境净化的光催化剂[72~75], TiO_2具有很强的电子提取能力, 因此, TiO_2从碘化物阴离子提取电子促进了$MAPbI_3$的分解.

式(5)~(8)解释了TiO_2可能发生的反应. 首先, 通过TiO_2提取I^-的价电子导致$MAPbI_3$被分解, 产生了I_2, 然后I_2在TiO_2/$MAPbI_3$界面处被提取的电子还原. 因此在TiO_2/$MAPbI_3$之间插入Sb_2S_3阻挡层可以在光照下显著地增强器件的稳定性.

$$CH_3NH_3PbI_3 \leftrightarrow PbI_2 + CH_3NH_2\uparrow + HI\uparrow \quad (5)$$

$$2I^- \leftrightarrow I_2 + 2e^- \quad (6)$$

$$3CH_3NH_3^+ \leftrightarrow 3CH_3NH_2\uparrow + 3H^+ \quad (7)$$

$$I_2 + I^- + 3H^+ + 2e^- \leftrightarrow 3HI\uparrow \quad (8)$$

从这些现象可以发现, 改变二氧化钛表面的化

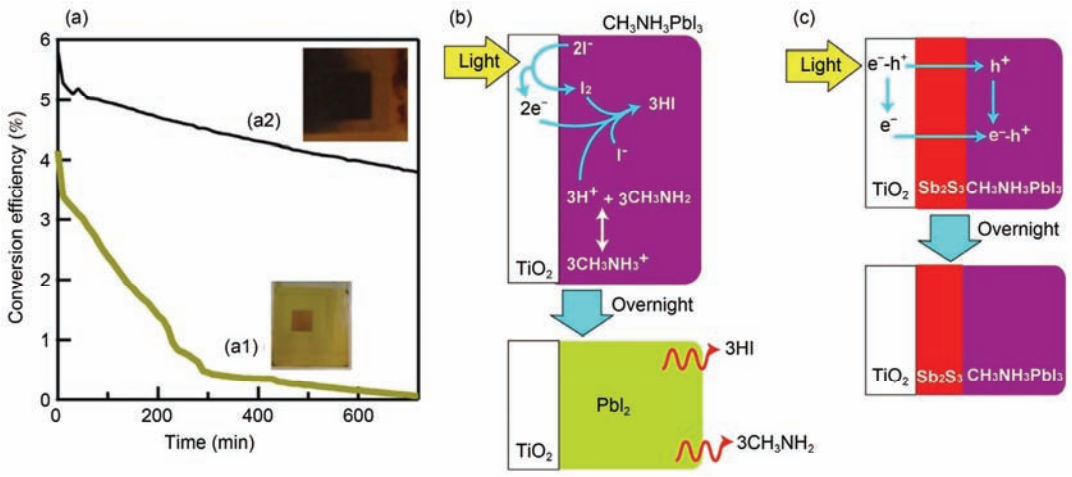

图 5 (网络版彩色)加入Sb_2S_3层之后的器件稳定性表现与原理分析. (a) 封装后在空气中照射12 h过程中电池的效率变化曲线. (a1) 样品电池(FTO/TiO_2/Sb_2S_3/$MAPbI_3$/CuSCN/Au), (a2) 参比电池(FTO/TiO_2/$MAPbI_3$/CuSCN/Au). (b) FTO/TiO_2/$MAPbI_3$/CuSCN/Au结构在光照下的载流子传输过程和衰减机理; (c) FTO/TiO_2/Sb_2S_3/$MAPbI_3$/CuSCN/Au结构在光照下的载流子传输过程. Reprinted with permission from Ref. [10], Copyright © 2016 The Royal Society of Chemistry

Figure 5 (Color online) Device stability performance after adding Sb_2S_3 layer and its principle analysis. (a) Variation of photo-energy conversion efficiencies of solar cells during light exposure (AM 1.5, 100 mW/cm^2) without encapsulation in air for 12 h. (a1) FTO/TiO_2/Sb_2S_3/$MAPbI_3$/CuSCN/Au, (a2) FTO/TiO_2/$MAPbI_3$/CuSCN/Au. Degradation scheme of $MAPbI_3$ perovskite solar cells during light exposure test without (b) and with (c) Sb_2S_3 layer. Reprinted with permission from Ref. [10], Copyright © 2016 The Royal Society of Chemistry

学性质对器件的稳定性有着重要的作用, 例如Al掺杂技术[90]和钝化二氧化钛表面来减少缺陷和复合[91]; 也可以通过阻止氧化钛与钙钛矿的直接接触避免二氧化钛分解钙钛矿, 例如ZrO/TiO_2核-壳结构[92]和在二氧化钛与钙钛矿之间插入阻挡层[26,93]. 此外, 有研究表明器件的稳定性也部分取决于TiO_2的形态、孔隙率和结晶度. 例如, 含有无定形TiO_x作为电子传输材料的器件的效率会衰减[94]. 同时, TiO_2需要在500℃下烧结, 使得其与柔性基板的兼容性较差并且需要消耗大量的能量; 可以利用PCBM等有机n型有机电子传输材料取代二氧化钛从而提高器件的稳定性和柔性基板的兼容性[93,95]. 本课题组使用PFN-2TNDI[96]和N-PDI[97]作为电子传输材料取代二氧化钛制备的n-i-p型钙钛矿电池均取得了良好的效率稳定性. Wang等人[98]利用n掺杂的富勒烯作为电子传输层制备出n-i-p型器件也取得了良好的稳定性.

而在无机的电子传输层的替代材料方面, Snaith课题组[99]研究证明, 通过低温处理的Al_2O_3电子传输材料取代TiO_2可以保持较高的效率, 同时提升器件的稳定性. Wang等人[100]利用CeO_x作为电子传输材料也取得了很高的效率和稳定性. ZnO由于具有更高的电子迁移率以及可以在低温情况下沉积, 被认为是TiO_2的有效替代物并在钙钛矿太阳能电池中被广泛研究. 除了正常的ZnO纳米结构之外, ZnO量子点通过对光生载流子的限制增强了器件性能, 为未来钙钛矿太阳能电池的发展开辟了新的研究途径. 此外, 这些器件对氧和水有更高的稳定性[101]. 值得注意的是, 本质上ZnO属于化学性质不稳定的物质, 容易与弱酸和弱碱发生反应, 同时也可能腐蚀钙钛矿[102], 因而一些研究人员在无机钙钛矿太阳电池中使用金属硫化物和其他的金属氧化物作为电子传输材料[103~105], 这也为提高钙钛矿太阳能电池的稳定性和进一步寻找相关的无机半导体材料提供了重要信息.

4 电极材料对电池稳定性的影响

电极是钙钛矿太阳能电池中不可缺少的一部分, 除了可以传导电子之外, 致密的电极也可以起到隔绝钙钛矿与空气的作用, 从而减少空气对器件的影响, 但电极材料在有的情况下也会影响钙钛矿电池的稳定性. 金是钙钛矿太阳能电池中常用的电极材料, 通常使用热蒸发的方法将其沉积在电池上. 然而, 金由于昂贵而且在蒸发沉积的过程中只有一小部分金最终沉积到器件上, 造成大量的浪费. 对于规模商业应用, 降低成本是很关键的一步. 因此, 银和铝相比金而言是更好的选择. 然而, 银和铝作为电极与钙钛矿膜接触容易生成卤化物, 影响电极的导电

性能, 导致电荷收集效率降低, 可能会降低器件稳定性; 同时钙钛矿内的卤素原子缺位也会导致钙钛矿稳定性降低[106,107]. 因此, 研究者在电荷传输材料与电极之间引入金属氧化物或聚合物的超薄层作为缓冲层, 也可以增强电极的稳定性和改善电荷收集效率. 如Kevin课题组[108]将铝掺杂的氧化锌透明导电玻璃(AZO)作为缓冲层插入到富勒烯衍生物(PCBM)与电极之间(图6), 不仅阻止了钙钛矿与电极的直接接触, 还隔绝了水汽并抑制了MAI的逃逸, 从而极大地提高了器件的稳定性; Ma等人[109]使用铜铟锡纳米晶体(CISNCs)作为插入层也提高了器件的稳定性, 这种缓冲层还可以减小器件工作时的金属迁移导致的不稳定性[88,108]. 有研究者尝试使用铜或者其他种类的电极来替换银和铝电极, 也取得了不错的效果[107].

碳材料由于具有优异的导电性、良好的化学稳定性和合适的能级水平, 已经通过丝网印刷技术应用于钙钛矿太阳能电池中[110]. 但是在这类太阳能电池中, 绝大部分的光生电流是由少子扩散到PN结产生的. 由于这种浓差扩散是一个相对较慢的过程, 所以光生电荷的收集效率受到限制. 本课题组[111]设计了一种介孔无机氧化物p-i-n结构器件, 实现了高效稳定的钙钛矿太阳能电池(图7). 器件中, 无机氧化物扮演电荷传输层角色的同时构筑p-i-n异质结, 目的是为了增大耗尽层的物理长度, 增加这个区域内光生电子-空穴对的收集[112,113]. 电容-电压测试表明, 常规PN结电池的电荷迁移在低偏压和高偏压区间分别表现为欠缺区和扩散区行为. 而无机绝缘氧化物的加入形成的p-i-n结构器件在欠缺区和扩散区形成一个电荷过渡区间[114,115], 该结果表明钙钛矿光生电荷在异质结产生电场作用下进行漂移输运, 保证了载流子的高效收集. 研究结果表明, 采用$MAPbI_3$作为光活性层器件的光电转换效率达到15%, 是同类型钙钛矿电池报道的最高效率[111]. 因为电荷传输层采用无机氧化物和背电极采用碳电极材料, 该结构器件40℃光照1000 h后效率衰减小于20%(图8). 我们应用电化学交流阻抗研究p-i-n结构钙钛矿太阳能电池, 提出电路模型明确钙钛矿p型选择性电极界面电荷积累限制器件性能作用, 指出降低界面电荷复合和增加电子传输层传输能力是提高器件性能的关键[116~118].

采用碳对电极的电池制作方式受到碳膜厚度(~10 μm) 限制, 只能采用滴涂+浸泡的方式渗透制备, 难以调控钙钛矿薄膜形貌、晶体、界面等关键参数. 在上述器件物理机制研究基础上, 本课题组[119,120]提出单壁碳纳米管等掺杂的方法, 降低NiO纳米薄膜厚度(~1 μm)、保持电荷抽取能力, 实现新型高效电池(~14.7%). 与使用过量溶剂进行旋涂制备的技术相比, 丝网印刷在制造过程中很少会有材料浪费, 且所用溶剂和黏合剂对环境无害. 更重要的是, 空白基底可以通过去除低效的光敏层并重新浸渍新的光敏层的方法来实现重复利用. 因此, 基于碳的无HTM钙钛矿器件正在受到越来越多的关注和研究[121,122].

5 总结与展望

钙钛矿太阳能电池已经在光电转换效率上取得了巨大的进步, 但稳定性仍是全球研究者所需要研

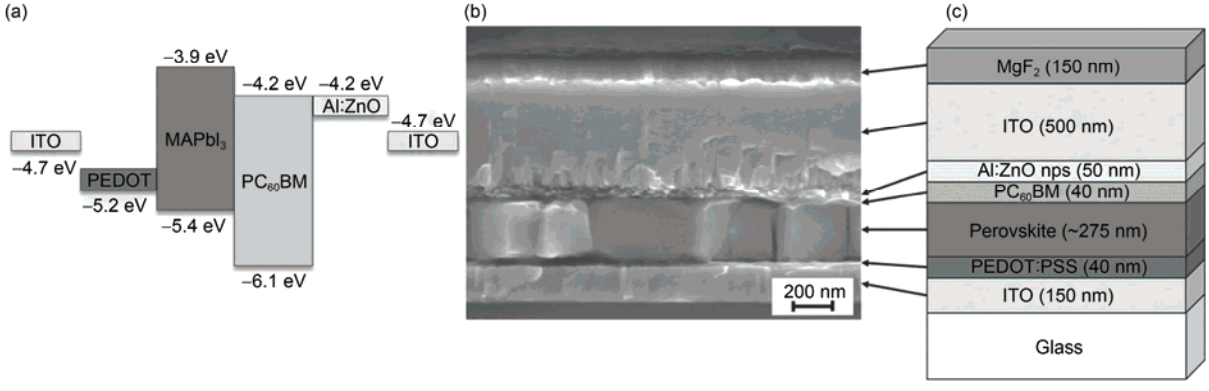

图 6 插入ITO的电池结构示意图. (a) 电池器件中不同层的能级结构示意图; (b) 电池截面扫描电子显微镜(SEM)图; (c) 电池各层结构示意图. Reprinted with permission from Ref. [106], Copyright © 2016 Wiley

Figure 6 Semi-transparent inverted perovskite device architecture. (a) Energy level diagram of different layers; (b) cross-sectional SEM; (c) illustrative schematic of the device architecture. Reprinted with permission from Ref. [106], Copyright © 2016 Wiley

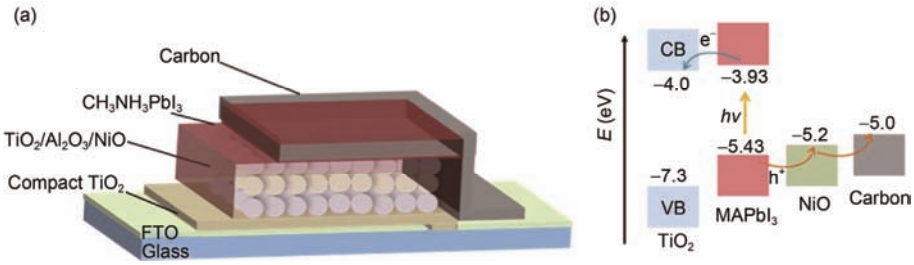

图 7 (网络版彩色)碳电极太阳能电池结构示意图. (a) $TiO_2/Al_2O_3/NiO/C(MAPbI_3)$电池结构示意图; (b) 电池器件的能级结构示意图. Reprinted with permission from Ref. [111], Copyright © 2015 Elsevier

Figure 7 (Color online) Structure diagram with carbon electrode. (a) Schematic representation of the $TiO_2/Al_2O_3/NiO/C(MAPbI_3)$ based device. (b) Energy band diagram of the fabricated device configuration. Reprinted with permission from Ref. [111], Copyright © 2015 Elsevier

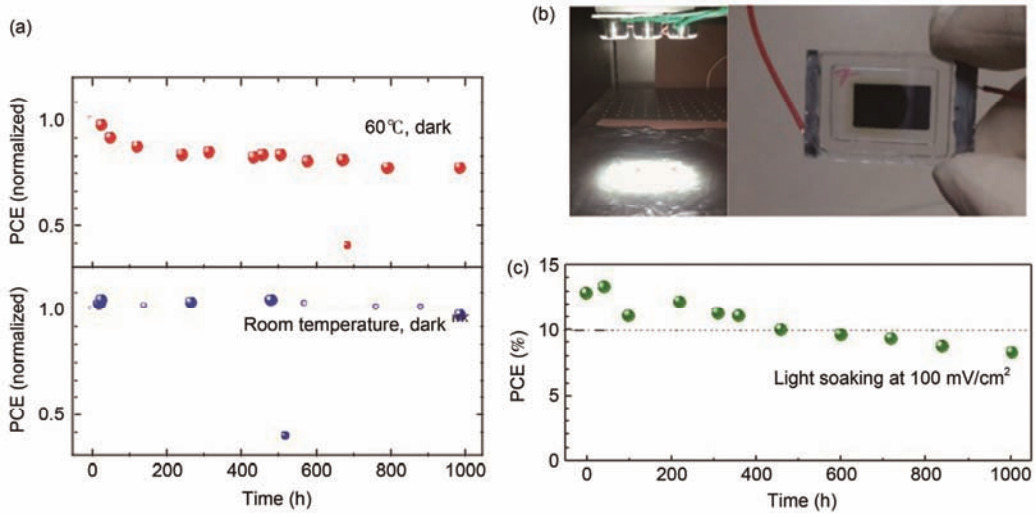

图 8 (网络版彩色)碳电极太阳能电池的稳定性表现. (a) 在暗态情况下的电池稳定性测试, 包括室温(蓝色)和 60℃(红色)两种状态; (b) 碳电极太阳能电池和光照稳定性测试的设备照片; (c) 100 mW/cm^{2}的光照下电池输出效率的衰减. Reprinted with permission from Ref. [111], Copyright © 2015 Elsevier

Figure 8 (Color online) Stability performance of the device. (a) Stability investigation on perovskite solar cells under different test conditions, including storing at room temperature in dark (blue), and storing at 60℃ in dark (red). (b) Light soaking test at 100 mW/cm^2 (with white light emitting diodes) and a photograph of the sealed device. (c) Evolution of PCE during the light soaking test (green). Reprinted with permission from Ref. [111], Copyright © 2015 Elsevier

究和改善的问题. 从器件不同结构部分的独立分析不仅能清晰地了解各个结构在钙钛矿太阳能电池衰减过程中所扮演的角色, 也能更有针对性地提出相应的解决方案.

对于钙钛矿吸光材料, 制备出来的晶粒大小与缺陷态密度会影响钙钛矿的稳定性, 水分、氧气与光照均会促进钙钛矿的分解过程, 即使在隔绝空气的情况下, 钙钛矿本身的热稳定性也较差, 在一定的温度下会自行分解. 同时钙钛矿也会存在晶体结构不稳定性的问题, 当钙钛矿由高光电性能的钙钛矿相转变为低光电性能的非钙钛矿相时会导致效率的急剧衰减; 对于空穴传输材料, 掺杂剂可能会导致钙钛矿结构的破坏与分解, 从而导致器件不稳定; 对于电子传输材料, 常用的TiO_2由于氧缺位与强电子提取能力会导致钙钛矿的分解以及电子传输效率的降低, 最终导致电池效率的衰减. 对于电极材料, 常用的银和铝由于扩散效应会与钙钛矿层接触形成卤化物, 不仅降低电极的导电能力还会破坏钙钛矿结构, 导致电池的衰减.

因此对于钙钛矿太阳能电池的稳定性问题, 今后的工作方向应主要包括: (1) 对于钙钛矿薄膜, 需要优化钙钛矿薄膜的制备方法以制备出大晶粒少缺陷的薄膜, 通过合适的封装隔绝空气中的水分和氧气对钙钛矿的影响, 研究对水分、氧气和温度不敏感

的钙钛矿材料, 保证钙钛矿薄膜在各种环境下的稳定性; (2) 对于空穴传输层, 需要研究无需使用TBP和Li-TFSI掺杂的有机空穴传输材料或者使用无机空穴传输材料从而减少钙钛矿晶体被破坏的可能; (3) 对于电子传输层, 在不影响电子传输效率的前提下尽量避免钙钛矿与二氧化钛的直接接触或者使用其他电子传输材料替代二氧化钛从而避免二氧化钛对钙钛矿的分解作用; (4) 对于电极材料, 通过避免钙钛矿与金属电极直接接触, 保证器件的稳定性, 或者使用全印刷碳电极为基础的介孔钙钛矿太阳能电池框架来提高器件的效率和稳定性.

通过对钙钛矿太阳能电池中各个结构的逐步优化, 相信在未来钙钛矿太阳能电池的稳定性能进一步提高, 为其在实际工程中的应用打下坚实的基础.

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Summary for “钙钛矿太阳能电池的稳定性”

The stability of perovskite solar cells

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Solar energy as a widespread clean energy is considered to be the key to solving future energy problems, solar cell technology is also evolving, of which perovskite solar cells because of its rapid growth efficiency gains wide attention. The great breakthroughs have been observed in organic-inorganic halide perovskite solar cells. However, the long-term stability due to decomposition and the toxicity of heavy metal lead have not been perfectly solved. Solving the stability problem will be the key to the future application of perovskite solar cells.

This review focuses the factors affecting the stability of perovskite solar cells from the perspective of perovskite solar cell structure, including perovskite materials, hole transport materials, electron transport materials, and electrodes. Through the analysis we found that for perovskite materials, grain size and defect density affect the stability of perovskite. The grain with large size will inhibit the defect state, improve the stability of the device. Moisture, oxygen and light will promote the decomposition process of perovskite, even in the case of isolated air. The thermal stability of perovskite is also poor and will be self-decomposition at a certain temperature. While perovskite will also have the problem of crystal structure instability, the perovskite may changes to the non-perovskite phase, which will result in a sharp attenuation of efficiency. The dopant in the hole transport material may cause destruction and decomposition of the perovskite structure. The titanium dioxide commonly used in electron transport materials can lead to the decomposition of perovskite and the reduction of electron transport efficiency due to oxygen vacancy and strong electron extraction. Silver and aluminum commonly used in electrode will be associated with the perovskite layer formation of halide, which may reduce the conductivity of the electrode and destroy the perovskite structure.

In order to solve the above problems, we propose that new preparation should be developed to get thin films with large grain size. The researchers also should find new perovskite material insensitive to moisture and oxygen, appropriate package to isolate the air from the water and oxygen. The inorganic perovskite materials with enhancing thermal stability of the perovskite film should be considered to improve the stability of perovskite solar cells. Developing organic hole transport materials that do not require additives or inorganic hole transport materials can reduce the possibility of perovskite crystals being destroyed by hole transport materials. Avoid direct contact between perovskite and titanium dioxide or use other electron transport materials instead of titanium dioxide to prevent the decomposition of perovskite. Furthermore, we recommend mesoscopic framework based on all inorganic metal oxides for organic-inorganic perovskite based photoelectric conversion devices.

solar cells, perovskite, stability

doi: 10.1360/N972017-00859