

Perovskite Solar Cells



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固态钙钛矿太阳能电池最近才冒出来,但是光电转换效率已达到 20%。现在,一个非常简单溶液处理步骤可以让相邻的钙钛矿晶粒链接在一起,这种做法可以增加电池的稳定性,这点在未来的商业化开发中尤为重要。

钙钛矿太阳能电池毫无疑问是过去几年的重大科技进步之一。在一个标准太阳光 (100mW cm^{-2}) 照射下,最高被认证的光电转换效率已迅速飙升超过 20%。钙钛矿太阳能电池的高转换效率,简单器件制作过程和较低材料成本使得它比其它太阳能技术更具竞争优势。

固态钙钛矿太阳能电池的结构和工作原理非常简单。如图 1 所示,电子传输材料(ETM,如纳米结构 TiO_2) 被涂在导电基材上(如掺氟 SnO_2 透明导电玻璃),光活性的钙钛矿(典型如 $\text{CH}_3\text{NH}_3\text{PbI}_3$) 被旋涂在电子传输材料层上,另外一层空穴传输材料(HTM)被旋涂在钙钛矿膜层之上,最后一层金属层蒸镀加在上面用来做电极层。在光的照射下,钙钛矿膜层产生电子和空穴分离,电子通过电子传输层传到到导电基板,空穴通过空穴传输层传到到金属电极层。光激发产生的电子和空穴产生流动会产生电流(如图 1a)。

钙钛矿材料的本征特性,如吸收带很宽,快速电荷分离能力,较长的电子和空穴传输距离,和较长的激发态寿命使得钙钛矿成为非常有前途的固态太阳能电池材料,当然还有些问题阻碍它的广泛应用,特别是器件制作的重复性和使用稳定性。在最近 Nature Chemistry 文章里,瑞士化学家 Michael Gratzel 的研究小组做出了非常重要的一步,对改善器件制作的重复性和稳定性大有裨益(文献 1)。

自从 1991 年第一篇文章报道染料敏化电池(DSCs),即将分子染料用来敏化宽禁带半导体,人们付出巨大的努力寻找吸收光谱宽和摩尔消光系数高的分子染料。有机金属卤素钙钛矿在 2009 年首次被用做染料敏化电池在可见光区的光敏剂,当时是用 $\text{CH}_3\text{NH}_3\text{PbI}_3$,效率仅仅 3.8%。在 2011 年的时候,科学家将 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 做成量子点,用碘化物和三碘化物作为氧化还原对,在液体太阳能电池里将转换效率提高到 6.5%。最最实质的突破是在 2012 年, $\text{CH}_3\text{NH}_3\text{PbI}_3$ 被用作光敏材料用在全固态薄膜(亚微米级)介观太阳能电池上,效率达到 9.7%。几乎在同时,基于介观超结构有机金属卤素钙钛矿太阳能电池,在单质结构(single-junction)的器件中电池转换效率达到 10.9%。自从这两篇基石性的文章出现,钙钛矿材料一下子成为低成本高效率太阳能电池的希望。

在非常短暂的时间里,有关钙钛矿太阳能电池的各种激动人心的消息和进展纷至沓来,例如,一种用来制备固态介观钙钛矿太阳能电池的沉积方法,可以极大增加电池工作稳定性(功率转换效率 15.0%);一种用双源共蒸钙钛矿作为吸光层的平面异质结太阳能电池(功率转换效率 15.4%)。将介观和平面异质结结构的特点结合起来可以制备出非常均一和致密的钙钛矿膜层,从而可以显著的提高电池效率(功率转换效率 16.2%)。相应的,通过控制钙钛矿膜层的成膜过程和选择合适的材料可以在空气中使用溶液法在很低的温度下制备钙钛矿太阳能电池,平面异质结结构获得的最高效率在 19.3%。就在最近,甲基碘化铅钙钛矿里的 CH_3NH_3^+ 通过分子内交换变成了 $\text{HC}(\text{NH}_2)_2^+$,被认证的电池转换效率高达 20.1%。

虽说通过使用不同的材料和不同的技术钙钛矿太阳能电池的效率还有进一步的提升空间(理论值>30%),但是,钙钛矿太阳能电池目前所达到的效率已经让人们人们对它的实际应用充满幻想。然而,随着效率的提升,钙钛矿器件制备的重复性和长期稳定性必须得到解

决，这是这个技术规模化推广的前提。瑞士化学家 Michael Gratzel 和他的同事们最新发现，用两性磷酸胺化合物（butylphosphonic acid 4-ammonium chloride, 4-ABPACl）化学修饰一步法制备的钙钛矿（ $\text{CH}_3\text{NH}_3\text{PbI}_3$ ）晶粒界面可以提高转换效率，同时增加电池的稳定性。X 射线衍射（XRD）和扫描电镜（STEM）能量弥散 X 射线光谱分析（EDX）显示 4-ABPACl 起到链接钙钛矿晶粒的作用，原理上是化合物的端基（ $-\text{PO}(\text{OH})_2$ 和 $-\text{NH}_3^+$ ）与钙钛矿晶粒表面的碘离子形成氢键。这种两性磷酸胺化合物的引入有两个作用：一方面可以助力钙钛矿晶体在介孔层 TiO_2 骨架里的生长，还可以让钙钛矿膜层表面更平滑，这些都可以产生更均匀一致的钙钛矿膜层表面。

和常规的钙钛矿膜层器件相比，有 4-ABPACl 存在时一步法制备的钙钛矿电池在黑暗中可以忍受 85°C 的温度 350 小时。初步的稳定性研究表明，封装好的钙钛矿太阳能电池在 10mW cm^{-2} 紫外过滤的模拟太阳光照射下，温度 45°C 工作一周时间，转换效率还有 90%，相反，没有 4-ABPACl 的器件转换效率降到 70%。烷基磷酸胺基化合物的较链在 55% 的相对湿度条件下完成，器件的室内稳定性测试中也表现出非常正面的结果。

目前的发现使钙钛矿太阳能电池在实际应用中表现出更大的潜力。在器件的可重复性和稳定性方面还需要开发更新的技术来应对发热和湿度问题，当然高转换效率永远是最大驱动力。

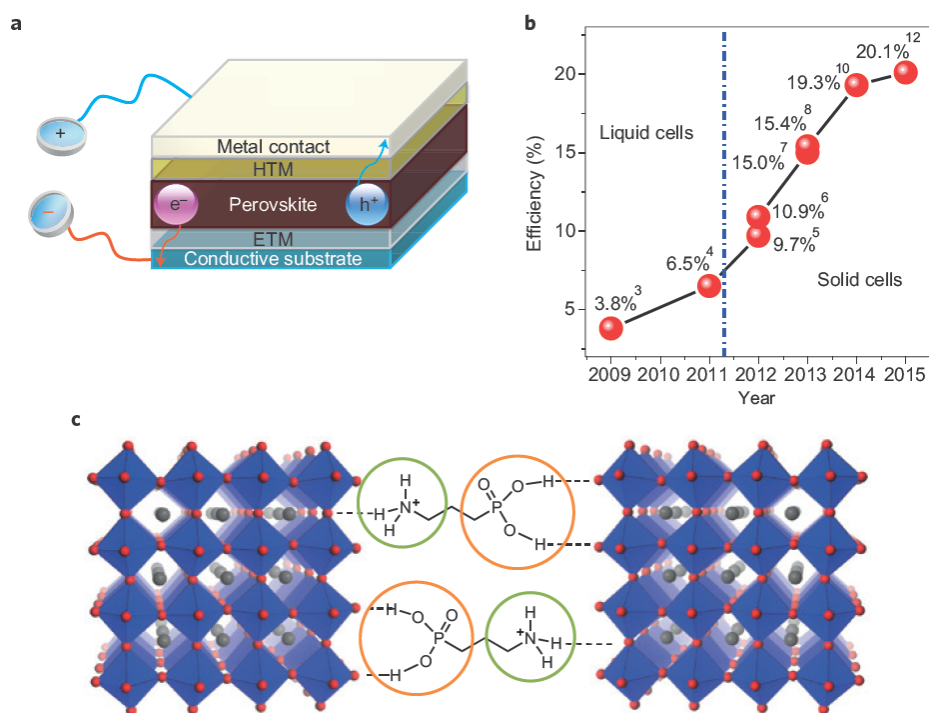


图 1 钙钛矿太阳能电池示意图。a. 钙钛矿太阳能电池结构和工作原理示意图，HTM 代表空穴传输层；ETM 代表电子传输层。b. 过去几年中有代表性的钙钛矿太阳能电池效率数据。c. 钙钛矿晶体互联示意图（红色圆球代表碘原子，蓝色八面体代表 PbI_6 ，灰色圆球代表 CH_3NH_3 ），烷基磷酸胺离子对钙钛矿晶粒的互联可以改善电池性能和增加稳定性。磷酸和胺基团分别用橘色和绿色圆圈表示。

文献 1: Nature Chemistry 7, 703, 2015

Weinstein, Meijer and colleagues designed a series of DBA compounds featuring a Pt(II) metal centre in a square-planar configuration, a common electron acceptor (naphthalene monoimide, NAP), and various electron donors that are derivatives of phenothiazine (PTZ; Fig. 1b). The donor and acceptor are attached to the metal centre via ethyne bridges ($-\text{C}\equiv\text{C}-$) in the *trans* configuration (Fig. 1b). The $\text{C}\equiv\text{C}$ stretching modes are 'frequency separated' from other modes in the complex and feature large extinction coefficients of about $2,000 \text{ M}^{-1} \text{ cm}^{-1}$. Moreover, the $\text{C}\equiv\text{C}$ stretch was shown to be coupled to the electronic transitions involving the metal centre. They found that exciting the $\text{C}\equiv\text{C}$ stretch suppresses the rate of formation of the charge-separated state, while the rate of formation of a triplet excited state (A^*) localized at NAP is enhanced, resulting in a strong decrease in the quantum yield of the charge separation (it was below the level of detection for one of the compounds). Moreover, the extent of the change in yield varies with the redox properties of the donor moiety. Note that not only are the experiments challenging, but there is also little predictive power for how strong the modulation will be.

The rate of an electron-transfer reaction depends on several factors, such as the energy barrier height, coupling strength, and the dynamics of passing over the barrier. All of these factors can potentially be affected by the excited vibrations at the bridge, and so to investigate the origin of the modulation, Weinstein, Meijer and co-workers performed calculations of the potential energy surface of the involved states along just a single $\text{C}\equiv\text{C}$ stretching coordinate. The calculations showed that the stretching motion affects the energy surface of the excited and charge-separated states in a significant way, indicating the propensity of the $\text{C}\equiv\text{C}$ mode to modulate the reaction outcome. However, the single-coordinate calculations are too simple to explain all the experimental observations⁵.

A schematic of a more general potential energy surface along two vibrational coordinates for reactants (for example, excited state) and products (for example, charge-separated state) is shown in Fig. 1c. One vibrational mode is not affected by the reaction and thus is not active for it, whereas another is affected strongly, providing the reaction coordinate. The conditions when a single vibrational mode represents the reaction coordinate, outlined in the graph,

could be considered a quite rare and special case. It is expected that a typical reaction-coordinate involves several vibrational modes, but characterization of multidimensional photoinduced electron transfer near multiple conical intersections, and deciphering the role specific vibrations play in competing reactions, is extremely difficult. Despite the challenges of the theoretical modelling, the molecular systems designed by Weinstein and co-workers show very efficient switching of the electron-transfer yield. Detailed understanding of the modulation mechanism in these and other DBA compounds⁶ will help in designing compounds with targeted state-specific electron-transfer properties. □

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References

1. Crim, F. F. *Proc. Natl Acad. Sci. USA* **105**, 12654–12661 (2008).
2. Skourtis, S. S., Waldeck, D. H. & Beratan, D. N. *J. Phys. Chem. B* **108**, 15511–15518 (2004).
3. Xiao, D., Skourtis, S. S., Rubtsov, I. V. & Beratan, D. N. *Nano Lett.* **9**, 1818–1823 (2009).
4. Lin, Z. *et al. J. Am. Chem. Soc.* **131**, 18060–18062 (2009).
5. Delor, M. *et al. Nature Chem.* **7**, 689–695 (2015).
6. Yue, Y. *et al. Dalton Trans.* **44**, 8609–8616 (2015).

PEROVSKITE SOLAR CELLS

Crystal crosslinking

Solid-state perovskite solar cells have recently emerged and have already reached efficiencies of 20%. Now, a simple solution-processing step that crosslinks neighbouring perovskite grain surfaces has been found to increase their stability, an important issue for future potential commercialization.

Licheng Sun

The emergence of perovskite solar cells undoubtedly represents one of the big scientific developments of the past few years. The highest certified solar-to-electrical power conversion efficiency of solid-state perovskite solar cells has rapidly risen to over 20% under 1 Sun (100 mW cm^{-2}) illumination. Their high efficiency, together with their easier preparation procedures and lower cost of components, has made perovskite solar cells very competitive over other types of solar cell.

The structure and working principle of solid-state perovskite solar cells are quite straightforward. As shown in Fig. 1, an electron transport material (ETM, such as nanostructured TiO_2) is coated on a conductive substrate (fluorine-doped tin oxide glass for example), and a photoactive layer of perovskite (typically $\text{CH}_3\text{NH}_3\text{PbI}_3$)

is spin-coated on the ETM. Another layer of hole transport material (HTM) is then spin-coated on top of the perovskite, and a metal thin-film, which serves as the contact, is subsequently deposited. Under illumination with light, the perovskite material creates charge separation: electrons move to the conductive substrate through the ETM and holes move to the metal contact through the HTM. Those light-generated electrons and holes can then do the work and generate electricity through an external circuit (Fig. 1a).

The intrinsic properties of perovskites — such as their broad absorption spectrum, fast charge separation, long transport distance of holes and electrons, long lifetime of the charge-separated state — make them very promising materials for solid-state solar cells, yet some issues still need to be addressed before they can be widely used; in particular,

their reproducibility and long-term stability. As they describe in *Nature Chemistry*, the Grätzel group has now made an important step towards improving these two features¹.

Since the first report on dye-sensitized solar cells (DSCs) in 1991² — in which a molecular dye serves to sensitize a wide-bandgap semiconductor — a great deal of effort has been made to find dyes with a broader absorption spectrum and a higher molar extinction coefficient. Organometal halide perovskites were first used in 2009 as visible light sensitizers in liquid DSCs, with an efficiency of only 3.8% obtained with the perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ (ref. 3). A conversion efficiency of 6.5% was reported in 2011, also relying on $\text{CH}_3\text{NH}_3\text{PbI}_3$, this time as quantum dots, with iodide/triiodide as the redox couple in liquid solar cells⁴. A real breakthrough was achieved in 2012 with the use of $\text{CH}_3\text{NH}_3\text{PbI}_3$

for sensitization in an all-solid-state thin-film (submicrometre) mesoscopic solar cell, which showed an efficiency of 9.7% (ref. 5). Almost at the same time, efficient hybrid solar cells based on mesoporous super-structured organometal halide perovskites were also demonstrated that showed power conversion efficiencies up to 10.9% in a single-junction device⁶. Since the publication of these two studies as corner-stones, perovskite materials have been shown to hold great promise for low-cost, highly efficient solar cells.

Some exciting news and a variety of developments on perovskite solar cells came within a very short period of time — for example, a deposition method for the fabrication of solid-state mesoscopic solar cells, which greatly increased the performance reproducibility (power conversion efficiency of 15.0%, ref. 7), or a simple planar heterojunction solar cell incorporating dual-source vapour-deposited perovskite as the absorbing material (power conversion efficiency of 15.4%, ref. 8). The combination of these features of mesoscopic and planar structures led to extremely uniform and dense perovskite layers, and dramatically improved performances (power conversion efficiency of 16.2%, ref. 9). In turn, control of the formation of the perovskite layer and careful choices of other materials enabled the fabrication of perovskite solar cells in air and from solution at low temperatures, with the highest efficiency of ~19.3% in a planar geometry¹⁰.

Very recently, the methylammonium counter ion of $\text{CH}_3\text{NH}_3\text{PbI}_3$ was replaced with its formamidinium analogue through an intramolecular exchange process brought about a certified record efficiency of 20.1% for the resulting solar cell^{11,12}.

This present efficiency record already shows promise for practical applications, though there is still room for further improvement (theoretical values >30%) by changing the components and using different technologies. Yet, alongside efficiency improvements, reproducibility and long-term stability of the perovskite solar cells also need to be addressed to enable their widespread practical use. In their study, Michael Grätzel and co-workers have now found that using a bifunctional phosphonic acid–ammonium compound (butylphosphonic acid 4-ammonium chloride, 4-ABPACl) to chemically modify the grain surface of the perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) in a one-step spin-coating deposition process leads to more efficient and also more stable solar cells. Structural characterization by powder X-ray diffraction and mapping of the elemental distribution by EDX in STEM mode showed that the 4-ABPACl additives act as crosslinks between neighbouring grains (crystals) of

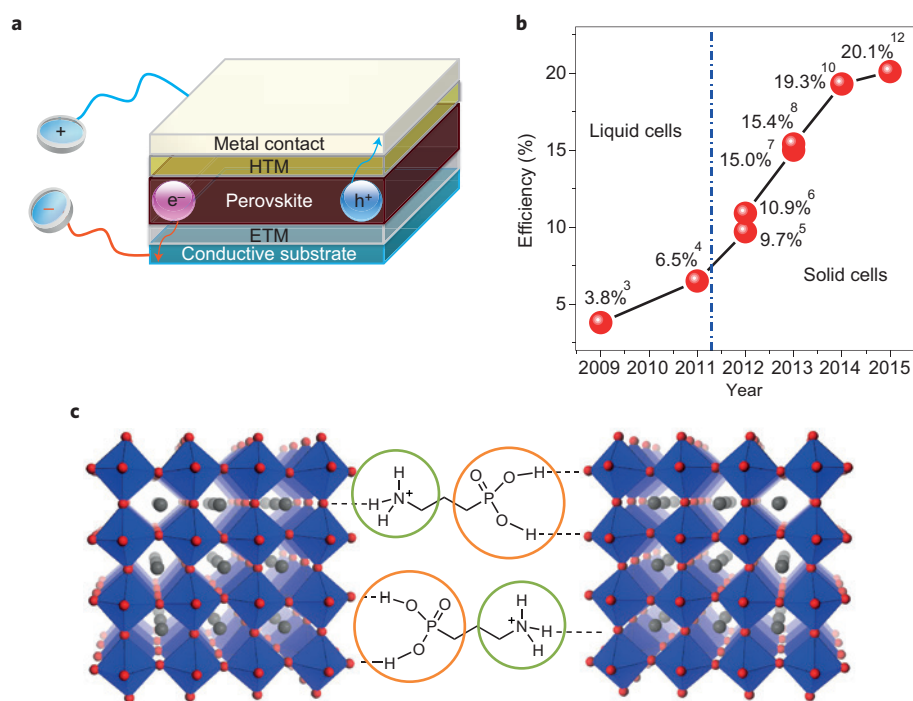


Figure 1 | Schematic representation of perovskite solar cells. **a**, A representative illustration of the general structure and working principle of perovskite solar cells. HTM: hole transport material; ETM: electron transport material. **b**, Some representative efficiencies of perovskite solar cells reported in the past few years with related references. **c**, Crystal crosslinking of perovskite grains (colour code: red spheres, I; blue octahedra, PbI_6 ; grey spheres, CH_3NH_3) by alkyolphosphonic acid ammonium cations for the improvement of performance and stability of solar cells¹. The phosphonic acid and ammonium moieties are circled in orange and green, respectively. Original figure by Bo Xu at KTH.

the perovskite material, through hydrogen bonding between the compound's terminal groups ($-\text{PO}(\text{OH})_2$ and $-\text{NH}_3^+$) and the iodide ions of the perovskite surface. The presence of the additives has two effects: it facilitates the growth of perovskite crystals within the mesoporous TiO_2 scaffold (Fig. 1c), and also creates a smooth, capping coating over the perovskite layer that makes for a more uniform surface.

In comparison to the solar cells prepared with pristine $\text{CH}_3\text{NH}_3\text{PbI}_3$, those prepared using the one-step solution deposition of the perovskite in the presence 4-ABPACl can tolerate exposure to a high temperature of 85 °C for 350 hours in the dark. Preliminary stability investigation of the encapsulated perovskite solar cell by continuously illuminating the devices under 10 mW cm^{-2} UV-filtered simulated sun light at 45 °C for one week showed 90% retention of the initial performance, whereas the control devices without the treatments of 4-ABPACl retained only 70% of the initial performance under the same ageing conditions. Indoor stability tests in which the crosslinking of ammonium alkyolphosphonic acid was carried out in ambient conditions at 55% relative humidity also showed very positive results.

The present findings show great potential for the practical applications of perovskite solar cells. Further work on the development of new technologies for yet higher reproducibility and stability against heat and humidity is still needed, while higher efficiency is always a big driving force for the whole field. □

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References

- Li, X. *et al.* *Nature Chem.* **7**, 703–711 (2015).
- O'Regan, B. & Grätzel, M. *Nature* **353**, 737–740 (1991).
- Miyasaka, T. *et al.* *J. Am. Chem. Soc.* **131**, 6050–6051 (2009).
- Park, N.-G. *et al.* *Nanoscale* **3**, 4088–4093 (2011).
- Park, N.-G. *et al.* *Sci. Rep.* **2**, 591 (2012).
- Miyasaka, T. *et al.* *Science* **338**, 643–646 (2012).
- Grätzel, M. *et al.* *Nature* **499**, 316–319 (2013).
- Snath, H. J. *et al.* *Nature* **501**, 395–398 (2013).
- Seok, S. I. *et al.* *Nature Mater.* **13**, 897–903 (2014).
- Yang, Y. *et al.* *Science* **345**, 542–546 (2014).
- Seok, S. I. *et al.* *Nature* **517**, 476–480 (2015).
- Seok, S. I. *et al.* *Science* **348**, 1234–1237 (2015).

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