

成均国际太阳能论坛 聚焦钙钛矿太阳能电池

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2016年5月25至27日第五届成均国际太阳能论坛(SISF)在韩国首尔成均馆大学的六百年纪念礼堂举行。自2011年第一届SISF开始,新生代的光伏技术就一直是会议的讨论重点,这包括染料敏化电池和有机太阳能电池,然而2016年的SISF聚焦在钙钛矿太阳能电池。杰出的科学家们(两位大会报告和25位特邀报告)都是大热的钙钛矿太阳能电池研究方向的专家,会议讨论了钙钛矿太阳能电池最新进展和一些主要问题。

不断刷新纪录的高效率钙钛矿太阳能电池是2016年SISF上的热门话题之一。近期的报道已经证明钙钛矿材料组份优化可以提高电池的转换效率(PCE)。最早,当用溴的取代部分碘,可以显著改善器件的开路电压。近期的报导开始关注钙钛矿 ABX_3 结构中A离子的替换,其中 $A=CH_3NH_3$, $HC(NH_2)_2$ 或Cs, $B=Pb$ 或Sn, $X=I$ 或Br。大会的主讲Michael Grätzel(瑞士联邦理工学院)提出过基于三个正离子的钙钛矿体系。经认证的21%的转换效率是由甲胺基、甲咪基和 Cs^+ 三组分体系获得,实验室的PCE数据可以达到21.9%。来自EPFL的Anders Hagfeldt也提出引入Cs正离子来增强器件制作的可重复性及稳定性,并可以增大钙钛矿晶粒的尺寸。Sang Il Seok(韩国蔚山国立科技大学)近期获得了被国家可再生能源实验室认证PCE达到22.1%的器件(图2A),强调用溶剂工程和溶剂交换反应制作均匀钙钛矿膜层的重要性。Shuzi Hayase(日本九州工业大学)和Hiroshi Segawa(日本东京大学)指出钙钛矿和 TiO_2 之间界面的重要性,他们提出界面的陷阱可以被 $PbCl_2$ 所钝化。除了器件的制作过程之外,器件制作的前驱体也同样重要,Atsushi Wakamiya(日本东京大学)发展出了基于 $MAPbI_3$ -DMF晶粒体可即时使用的前驱体体系,并证明了PCE可高达19%。

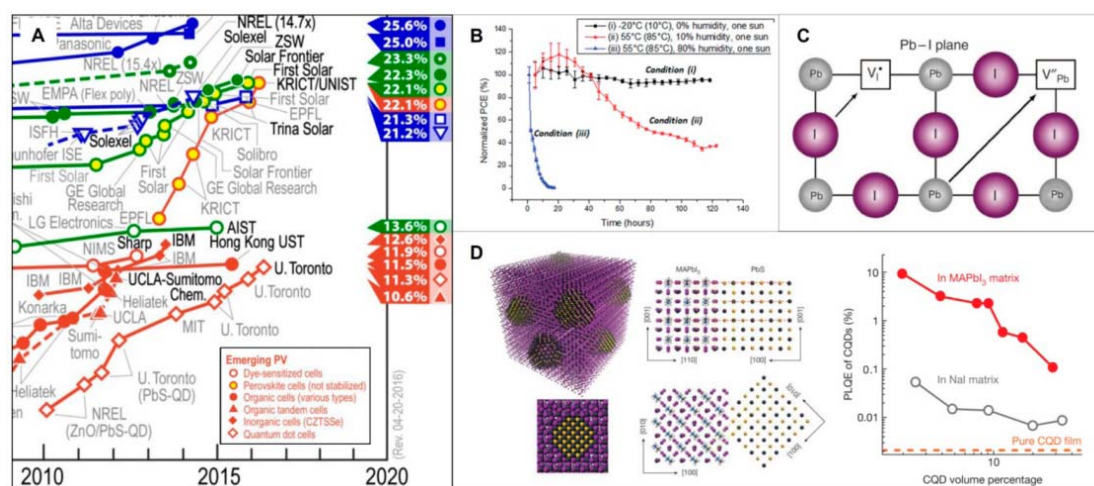
热、光和湿度对钙钛矿太阳能电池稳定性的影响是其能否商品化最有争议性的议题,这个问题在会上被数位特邀发言人所讨论。Yi-Bing Cheng(澳大利亚莫纳什大学)讨论了钙钛矿太阳能电池的热致衰减问题,他表示密封的钙钛矿膜层在没有紫外光照射时可以耐 $85^\circ C$ 的高温1000小时。然而,密封器件在 $85^\circ C$ 温度,当环境湿度为85%时会迅速衰减,这可以归因于水的渗入(图2B)。Seigo Ito(兵库县立大学)指出利用多孔碳电极可以显著增强钙钛矿太阳能电池的稳定性,这个可以归因于碳材料和钙钛矿之间强大的化学作用。另外,Mansoo Choi(首尔大学)做了一个很有趣的大会报告,他提出钙钛矿太阳能电池不可逆衰减是因为钙钛矿膜层和接触界面间受困的电荷。其他一些争议性的话题比如毒性、回收利用和大面积的工艺,这些问题站在产业化角度都是很重要,都被一些与会的代表提及。Tsutomu Miyasaka(桐荫横滨大学)讨论Pb的毒性和环境问题,他指出钙钛矿太阳能电池中 $\sim 0.32g$ 每平方米的铅含量比商用多晶硅太阳能电池焊锡膏

中所含的铅量 ($43\text{g}/\text{m}^2$) 小很多。Alex K-Y. Jen展示用锡替代部分铅, Sang Il Seok教授无铅的 FASnI_3 钙钛矿电池转换效率只有4.8%。无铅的钙钛矿太阳能电池看上去很难。Hyun Suk Jung (韩国成均馆大学) 讨论了用极性非质子溶剂对透明氧化物 TiO_2 基板循环再利用问题, 失效的电池可以通过浸泡在二甲基甲酰胺 (DMF) 溶剂使基板重新利用, 效率不受影响。Hyun Suk Jung和Arie Zaban (以色列巴尔伊兰大学) 分别证明电喷雾和MAI蒸镀处理可以用于制备大面积器件。



在稳定性方面挑选合适的金属氧化物层是很重要的, 这个观点由Yang Yang团队提出 (美国加州大学洛杉矶分校)。

图一。特邀发言人 (海外: 24位, 国内: 3位) 以及与会者 (超过220名) 在第五届成均国际太阳能论坛 (SISF2016) 合影。



图二。(A) NREL电池研究最高的效率图表。(B) 密封的钙钛矿太阳能电池在三种不同的密封环境条件下的稳定性测试。经许可复制自参考文献2; 皇家化学学会版权保护2015。(C) 离子传输机制示意图包含常规的相邻位置之间的跃迁空缺。经许可复制参考文献3。自然出版集团版权保护2015。(D) 钙钛矿量子点外延生长和钙钛矿量子点在不同母体环境下荧光量子效率理论模型。经许可复制参考文献11; 自然出版集团版权保护2015。

另外一个引起大家广泛兴趣的问题是在金属卤化物钙钛矿光吸收动力学过程。有大量的报告都试图阐明钙钛矿太阳能电池中有机正离子、卤素阴离子和结构缺陷的作用, 这些动态过程对器件性能有相当大的影响。Filippo De Angelis

(意大利国家科研委员会)使用从头计算分子动力学模拟与第一性原理电子结构计算提出了在太阳能电池工作时有机正离子和离子/缺陷迁移所起的作用,他指出有机正离子在空间和时间上可能会局部地发生动态变化,这些都被认为是Rashba效应的结果,Rashba效应可以减少钙钛矿材料中载流子的复合。Anderw M. Rappe(美国宾夕法尼亚大学)指出Rashba自旋轨道提高了MAPbI₃中的载流子寿命。另一方面,David Cahen(以色列魏茨曼科学研究所)指出这种有机正离子对于高效率的钙钛矿太阳能电池并不是必不可少的,原因是基于MAPbBr₃和CsPbBr₃的钙钛矿太阳能电池也表现出类似的光电转换性能。Aron Walsh(英国巴斯大学)和Jingsong Huang(美国内布拉斯加大学林肯分校)就钙钛矿中离子迁移问题进行了更为重点的讨论。Aron Walsh通过第一性原理计算得出了碘离子移动的最低的活化能为0.58电子伏特,这一数值与Filippo De Angelis所得结果是一致的,图2c展示了离子迁移的原理。Jingsong Huang出示了MA正离子移动的实验证据,提出了MA正离子在PbI₂和MAPbI₃之间可逆性转换。Juan Bisquert(西班牙海梅一世大学)介绍了钙钛矿中离子的迁移和重新分配动力学,这产生了电容电流、接触势垒,电极选择性接触等问题。Prashant V. Kamat(美国圣母大学)和(美国国家可再生能源实验室)研究了钙钛矿中超快电荷转移动力学,这点对理解电荷转移行为至关重要。他们两位都对在不同激发强度下载流子复合的机制进行了讨论,还有, Jao Van de Lagemaat提到利用钙钛矿材料中热载流子具有极慢的冷却时间这一特点的可能性。

除太阳能光伏之外,钙钛矿材料卓越的光电性能还让它展示出了在各种领域被广泛运用的巨大潜力,例如光电探测器(可见光或X射线)、发光二极管(LEDs)、激光等。其中,Subodh Mhaisalkar(新加坡南洋理工大学)和Edward H. Sargent(加拿大多伦多大学)在2016年的第五届SISF会议上讲述LED器件中引入钙钛矿材料的话题。Subodh Mhaisalkar讨论了钙钛矿纳米粒子的合成,指出3D和2D的钙钛矿核-壳(core-shell)纳米粒子可以在改善稳定性(大于两个月)的基础上极大增强光致发光量子效率到92%。Edward H. Sargent通过控制钙钛矿层结构让电致发光电器件的外量子效率达到10%,他还提议在钙钛矿母体中掺杂量子点能让光致发光量子产率提高两个数量级(见图2D)。至于金属卤化物钙钛矿的本征光电性能,MAPbI₃被认为是MAX和PbX₂之间进行电荷转移的复合物,而不是半导体,这个观点由Chun-Sing Lee(香港城市大学)提出。然而,这个论点被激烈争论。

有机-无机杂化卤化物钙钛矿清晰的显示出其作为新生代光伏技术,也因为它杰出的光电性能吸引人们相当大的兴趣。尽管钙钛矿太阳能电池转换效率在短时间内实现了飞速的提高,但在对其工作原理还缺乏很好的理解,器件稳定性以及铅元素的毒性等方面仍存在许多问题。第五届成均国际太阳能论坛经过深入讨论对有些问题给出了部分的答案。然而,下一步的研究仍需要在其商业上的可行性,长期稳定性,无毒,和效率更高等等方面做出努力,这些将是下一届SISF讨论的话题。

A Sharp Focus on Perovskite Solar Cells at Sungkyun International Solar Forum (SISF)

The fifth Sungkyun International Solar Forum (SISF) was held at 600th Anniversary Hall, Sungkyunkwan University, Seoul, Korea, from May 25 to May 27 in 2016. Since the first SISF in 2011, next-generation photovoltaic technologies have been discussed, including dye-sensitized and organic solar cells. The focus of the SISF in 2016 shifted from dye-sensitized and organic photovoltaics to perovskite solar cells. Eminent scientists (2 plenary speakers and 25 invited speakers) working for researchers at the cutting edge of perovskite solar cells were invited to discuss state-of-the-art technologies and some critical issues to be addressed as well (Figure 1).

The record-breaking high efficiency of perovskite solar cells was still one of the hottest issues in SISF 2016. Recent reports have demonstrated that the compositional optimization of perovskites can improve the power conversion efficiency (PCE). Initially, partial substitution of iodide by bromide was actively investigated, in which improvement of open-circuit voltage was achieved. More recent reports started to focus on the A site of ABX_3 perovskite, where $A = CH_3NH_3, HC(NH_2)_2,$ or Cs, $B = Pb$ or Sn, and $X = I$ or Br. The plenary speaker, Micheal Grätzel (Ecole Polytechnique Federale de Lausanne (EPFL), Switzerland) presented a triple-cation-based perovskite system. A certified PCE of 21.0% was obtained by incorporating methylammonium (MA), formamidinium (FA), and Cs cations, while a laboratory PCE of 21.9% was demonstrated by using RbI. Anders Hagfeldt from EPFL presented the incorporation of Cs cations to enhance both the reproducibility and stability of the device and grain size as well. Sang Il Seok (Ulsan National Institute of Science and Technology (UNIST), Korea), who recently got a certified record PCE of 22.1% that was confirmed by the National Renewable Energy Laboratory (NREL) (Figure 2A),¹ emphasized the importance of the fabrication process for formation of a highly uniform perovskite layer using solvent engineering and exchange reactions. Shuzi Hayase (Kyushu Institute of Technology, Japan) and Hiroshi Segawa (The University of Tokyo, Japan) presented the importance of the interface between perovskite and TiO_2 , where surface traps can be passivated by $PbCl_2$. In addition to processing, the precursor is equally important. Atsushi Wakamiya (Kyoto University, Japan) developed a ready-to-use precursor chemical system based on $MAPbI_3$ -DMF crystals and demonstrated a PCE as high as over 19%.

Thermal, photo-, and moisture stability are now the most critical issues for commercialization of perovskite solar cells, which was addressed by several invited speakers at SISF 2016. Yi-Bing Cheng (Monash University, Australia) discussed thermal degradation of perovskite solar cells. He showed that the encapsulated perovskite film itself is stable at 85 °C for 1000 h under UV-free light. However, the encapsulated device exposed at 85 °C with a relative humidity (RH) of 85% rapidly

degraded, which was ascribed to ingress of water (Figure 2B).² Seigo Ito (University of Hyogo, Japan) showed that utilization of a porous carbon electrode can significantly enhance the stability of perovskite solar cells, which was attributed to the strong chemical interaction between carbon materials and perovskite. Also, an interesting talk was delivered by Mansoo Choi (Seoul National University, Korea) as plenary speaker, where he presented evidence that irreversible degradation of perovskite solar cells resulted from trapped charges at the interfaces between the perovskite and selective contacts. Other critical issues such as toxicity, recycling, and large-area technologies, which is important from the commercialization point of view, were addressed by several invited speakers. Tsutomu Miyasaka (Toin University of Yokohama, Japan) discussed toxicity and environmental issues of Pb in perovskite solar cells. He argued that ~ 0.32 g/m² of Pb in a perovskite solar cell is much smaller than that used for soldering in commercial Si solar cells (43 g/m²). Alex K.-Y. Jen demonstrated partial substitution of Pb to Sn, while Prof. Sang Il Seok presented Pb-free $FASnI_3$ -based perovskite solar cells with a PCE of 4.8%. The Pb-free perovskite solar cell seems to still be a challenging issue. Hyun Suk Jung (Sungkyunkwan University, Korea) discussed recycling of TiO_2 -coated transparent conducting oxide substrates by the aid of a polar aprotic solvent. The dead cells can be reused by immersing them in dimethylformamide solvent by which the reused substrate showed the same photovoltaic performance. Hyun Suk Jung and Arie Zaban (Bar Ilan University, Israel) demonstrated electrospray coating technology and MAI vapor treatment, respectively, for large-area devices. Selection of an appropriate metal oxide layer is important in terms of stability, as mentioned by the Yang Yang (UCLA, USA) group.

Another issue attracting common interest was the underlying dynamic process in halide perovskite light absorbers. There have been a lot of reports trying to elucidate the role of organic cations, halide anions, and structural defects in perovskite solar cells, where their dynamic process has considerable effect on device performance.^{3–5} Filippo De Angelis (CNR-ISTM, Italy) presented the role of organic cation dynamics and ion/defect migration under solar cell operation using ab initio molecular dynamics simulations coupled with first-principles electronic structure calculations. He demonstrated that dynamic fluctuation of organic cations may occur locally in space and time, which was attributed to the origin of the Rashba effect responsible for the reduced charge carrier recombination in perovskite materials. Anderw M. Rappe (University of Pennsylvania, USA) pointed out the Rashba spin-orbit enhanced carrier lifetime in $MAPbI_3$. On the other hand,

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Figure 1. Photograph of invited speakers (overseas: 24; domestic: 3) and participants (more than 220) at the fifth Sungkyun International Solar Forum 2016 (SISF 2016).

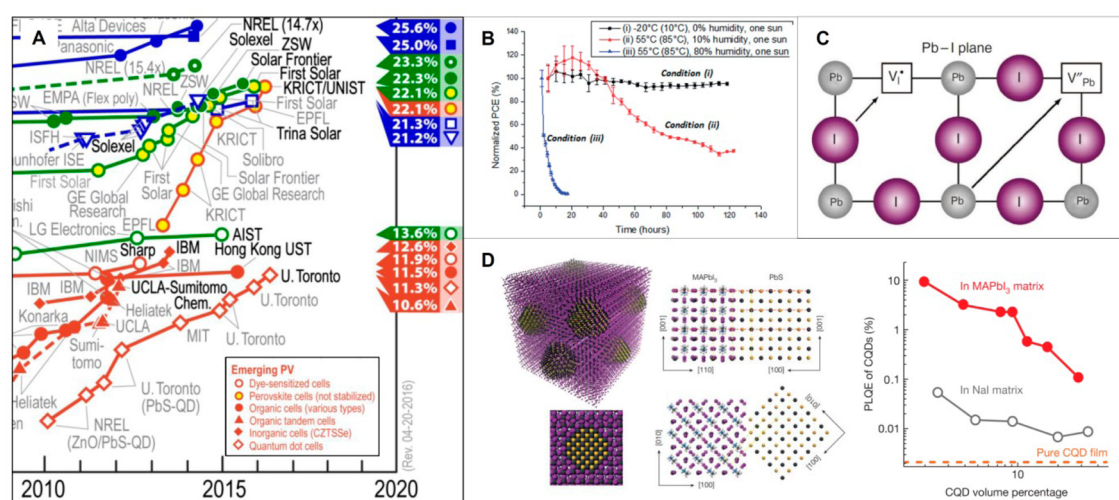


Figure 2. (A) NREL best research cell efficiency chart. (B) Stability testing of sealed perovskite solar cells sealed under three different environmental conditions. Reproduced with permission from ref 2; Copyright 2015, Royal Society of Chemistry. (C) Schematic illustration of the ionic transport mechanisms involving conventional vacancy hopping between neighboring positions. Reproduced with permission from ref 3; Copyright 2015, Nature Publishing Group. (D) Theoretical model of perovskite epitaxial growth on colloidal quantum dots and photoluminescence quantum yield of colloidal quantum dots in different matrixes. Reproduced with permission from ref 11; Copyright 2015, Nature Publishing Group.

David Cahen (Weizmann Institute, Israel) showed that such an organic cation may not be essential for an efficient perovskite solar cell by suggesting similar photovoltaic performance of perovskite solar cells based on MAPbBr_3 and CsPbBr_3 . The ion migration issue in perovskites was more intensively discussed by Aron Walsh (University of Bath, U.K.) and Jinsong Huang (University of Nebraska Lincoln, USA). Aron Walsh suggested a lowest activation energy (0.58 eV) for Γ^- movement from first-principles calculation, which was in agreement with the results obtained by Filippo De Angelis. The mechanism for ion migration is shown in Figure 2C.³ Jinsong Huang presented experimental evidence of moving the MA cation, which renders reversible conversion between PbI_2 and MAPbI_3 . Juan Bisquert (Universitat Jaume I, Spain) introduced dynamics effects closely related to the migration and redistribution of ions in perovskites, leading to capacitive current, modification of the contact barrier, and reaction with selective contact. Ultrafast charge carrier dynamics, which are essential for understanding of charge-transfer behavior, were dealt with by Prashant V. Kamat (University of Notre Dame, USA) and Jao van de Lagemaat (NREL, USA). Both of them discussed the

mechanism of charge carrier recombination under different excitation intensity, where Jao van de Lagemaat mentioned additionally the possibility of using a hot carrier based upon its extremely slow cooling time in perovskite materials.

Apart from photovoltaics, on the basis of their unprecedented excellent optoelectronic properties, perovskite materials have shown great potential to be used in a variety of optoelectronics including photodetectors (visible or X-ray), light-emitting diodes (LEDs), and lasing.^{6–11} Among them, LED devices incorporating perovskite materials were dealt with by Subodh Mhaisalkar (Nanyang Technological University, Singapore) and Edward H. Sargent (University of Toronto, Canada) at the fifth SISF in 2016. Subodh Mhaisalkar discussed the synthesis of perovskite nanoparticles and showed that 3D and 2D perovskite core–shell nanoparticles greatly enhanced the photoluminescence quantum yield (PLQY) up to 92% with improved stability (>2 months). Edward H. Sargent achieved an external quantum efficiency (EQE) of $\sim 10\%$ from an electroluminescence device by controlling the dimensionality of the perovskite layer. He also proposed that incorporation of colloidal quantum dots in a perovskite matrix can enhance the

PLQY by more than 2 orders of magnitude (see Figure 2D). Regarding the intrinsic optoelectronic property of halide perovskites, MAPbI₃ was proposed to be the charge-transfer complex between MAX and PbX₂, instead of a semiconductor, by Chun-Sing Lee (City University of Hong Kong, Hong Kong). However, this was hotly debated.

Organic–inorganic halide perovskites definitely shed light on next-generation photovoltaics and attract considerable interest due to their superb optoelectronic properties. Although sharp growth in photovoltaic performance of perovskite solar cells was achieved in a very short time,¹² there are still many questions in terms of the operation mechanism for better understanding and stability and the underlying lead toxicity. We have discussed in depth and addressed in part answers to the questions from the fifth SISF. Nevertheless, further studies are inevitably required to provide robust solutions for commercially viable, long-term stable, nontoxic, and high-efficiency perovskite solar cells, which will be hopefully discussed at the next SISF.

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Notes

The authors declare no competing financial interest.

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