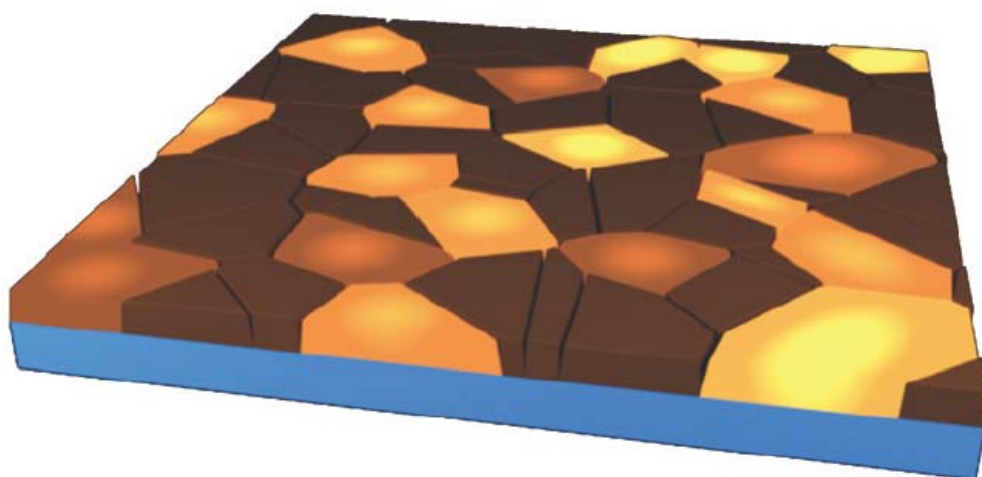


## 钙钛矿膜层亮暗斑块之谜 (作者: Udo Bach)

—钙钛矿电池研究从宏观到微观— (译者副标题)

最近一段时间有机无机杂化铅基卤素钙钛矿破天荒的成为光伏材料。新近的共聚焦荧光显微镜 (Confocal Fluorescence Microscopy) 研究更是给钙钛矿太阳能电池注入新的希望, 电池转换效率有望超过最新记录 20%。



图一: 涂在玻璃 (蓝色) 上发光的杂化有机无机铅基卤素钙钛矿膜层示意图。晶粒与晶粒之间的荧光效率变化十分明显 (颜色从黄色到棕色), 晶粒界面的荧光效率也很微弱。对这种现象的理解将可以提高钙钛矿太阳能电池的光电转换效率。

过去几十年溶液法处理半导体取得显著进步, 给人们提供了一种低成本制备电子器件的方法, 并被广泛应用在太阳能, 发光二极管 (LEDs) 和塑料电子学领域。尽管有明显的优势, 但是溶液法制备的器件性能无法与无机半导体器件媲美。以有机太阳能电池为例, 以低成本卷对卷方式生产的电池组件在转换效率上无法与传统的单晶和多晶硅电池组件抗衡。

但是, 有机无机杂化铅基卤素钙钛矿材料是乎要打破这一规律。这类材料最初是作为 LEDs 里的发光层和电化学太阳能电池里的吸光层来使用, 突破出现在 2012 年, 它被用在固态太阳能电池里作为吸光层。自那以后, 光电转换效率很快从 9.7% 飙升至现在的 20.1%, 从来没有任何的光伏技术有过这种情况。钙钛矿太阳能电池已经可以和当下表现最好的硅基和 GaAs 电池组件比拼。据《科学》杂志报道, 美国华盛顿大学的 David Ginger 和英国牛津大学的 Henry Snaith 和他们的同事研究了钙钛矿膜层的高分辨荧光特性, 很可能指出一种进一步提高电池转换效率的方法。

理想的光伏材料也一定是强发光材料, 眨眼看上去这有点矛盾的说法是 Schockley & Queisser 平衡原理的结果, 理想的光伏材料应该没有电子-空穴的再复合发光才对。这使得

在开路的情况下，辐射（或者发光）成为唯一释放能量的通道。相应的，具有强荧光特性的铅基卤素钙钛矿也具备卓越的光伏特性。

通过使用共聚焦荧光显微镜，美国华盛顿大学的 David Ginger，英国牛津大学的 Henry Snaith 和他们的同事可以研究旋涂制备的钙钛矿膜层（ $\text{CH}_3\text{NH}_3\text{PbI}_3$ ）的空间分辨荧光效率和寿命。这里共聚焦荧光显微镜测得的空间分辨荧光效率特别重要。测量的横向分辨率 348nm 要大于钙钛矿膜层的晶粒尺寸。这使得研究钙钛矿晶粒与晶粒间的光激发发光性能成为可能，也可以研究钙钛矿晶粒中间部位和接近晶粒边界部位的荧光情况。有几个发现出乎意料，毫无疑问将重塑钙钛矿电池研究的方向。

如果将共聚焦荧光显微镜和扫描电镜的测量结果关联，作者发现在同一膜层里不同的钙钛矿晶粒的光激发发光强度差异巨大，有 34% 的钙钛矿晶粒不发光或者发光很弱，发光晶粒的中心部位发光强度要强于晶粒的边沿部位。对时间分辨荧光光谱的研究发现发光晶粒的边沿部位的荧光寿命要短于晶粒中心部位的荧光寿命。进一步的研究还发现晶粒缺陷会加速电子和空穴复合。

过去，大家对晶粒界面在钙钛矿电池的运行中扮演什么角色是有争议的。有些研究预测钙钛矿晶粒越多电池效率越高，也有研究者建议晶粒界面的存在对电池是有好处。但是 David Ginger 和 Henry Snaith 的研究发现说明晶粒界面对钙钛矿电池效率的影响需要更仔细的评估。部分晶粒和晶粒界面的荧光非常弱更激起人们的希望--钙钛矿电池的转换效率还有巨大的改进空间。如果能将共聚焦荧光显微镜用来研究目前效率最高的钙钛矿器件，看看能否观察到钙钛矿晶粒之间荧光强度的巨大变化，如果这种现象是存在的，这将是鼓舞人心的证据，显著的器件效率改善是可以在不久的将来被实现。

在 David Ginger 和 Henry Snaith 的研究中，科学家还提到了另外两个可能改进钙钛矿器件性能重要的发现。首先是发现对钙钛矿膜层用吡啶蒸汽进行处理可以增强膜层的荧光性能，这一点对发光较暗的钙钛矿晶粒和晶粒界面更为明显，这可能意味着吡啶能有效钝化钙钛矿晶粒表面和晶粒界面的复合发光点。其次是共聚焦荧光显微镜和 X 射线能量色散谱仪结合发现钙钛矿膜层荧光强度比较强的晶粒氯的含量比较高，氯通常被加在钙钛矿旋涂液里以改善钙钛矿膜层的结晶过程，但是在最终的钙钛矿膜层里氯的含量非常少。希望将来能进一步的弄明白氯含量比较多的地方的化学本质和氯元素对激子复合的影响。

随着技术的逐步成熟，钙钛矿太阳能电池研究将更多依赖于对结构和性质关系的深入理解。David Ginger，Henry Snaith 和他们的同事开创性的工作，将高分辨荧光谱作为一种强有力的手段用来研究限制钙钛矿太阳能效率继续提升的钙钛矿膜层的缺陷或者不完美。受这一研究的鼓舞，其它的表面成像技术如近场扫描显微镜也许能提供更高的表面分辨率，让人们们对下一代薄膜太阳能电池有更多的了解。原理上，共聚焦荧光显微镜技术可以用在成型的钙钛矿太阳能电池上，特别是当外加电压接近器件开路电压（ $V_{oc}$ ）以阻断激子分离（电子和空穴分开）。他们的研究使荧光成像成为一种有力的工具可以用来揭示钙钛矿太阳能电池的衰减原理，这点本身就是未来研究的重点。

文献：

1. Nature Chemistry 7, 616, 2015
2. Science 348, 683, 2015

## PEROVSKITE SOLAR CELLS

## Brighter pieces of the puzzle

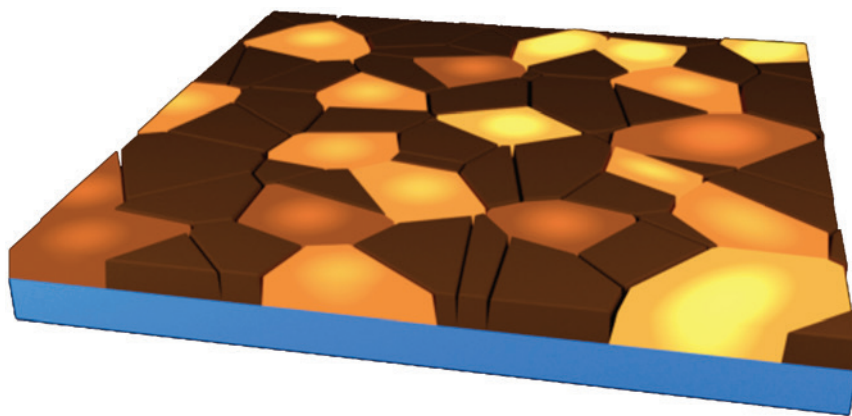
Hybrid organic–inorganic lead halide perovskites have recently emerged as ground-breaking photovoltaic materials. A recent confocal fluorescence microscopy study now raises hopes that perovskite solar cells can reach efficiencies beyond the recent record of 20%.

Udo Bach

**S**olution-processable semiconductors have seen a spectacular rise over the past decades, offering novel low-cost strategies for the fabrication of electronic devices such as solar cells, light-emitting diodes (LEDs) and plastic electronics. Despite their obvious advantages over wafer-based materials, their performances typically do not match those of their inorganic counterparts. Organic solar cells for example can be produced with low-cost roll-to-roll printing techniques, but their efficiencies cannot yet rival those of conventional single- or multi-crystalline silicon cells<sup>1</sup>.

Hybrid organic–inorganic lead halide perovskite materials have recently emerged as an exception to this rule. These solution-processed materials were initially reported as the emitter layers in LEDs<sup>2</sup> then as the absorber layer in electrochemical solar cells<sup>3,4</sup>. The first efficiency breakthrough came in 2012, with their application as an absorber material in solid-state solar cells<sup>5,6</sup>. Since then, their energy conversion efficiency has skyrocketed from 9.7% to 20.1% today<sup>7</sup>; no other photovoltaic technology has ever evolved at a comparable pace. The general properties of perovskite solar cells now rival even the best performing photovoltaic materials such as silicon and gallium arsenide. Writing in *Science*, David Ginger and co-workers now describe the high-resolution mapping of the fluorescence properties of perovskite films, which may point to ways to further improve their efficiencies<sup>8</sup>.

Ideal photovoltaic materials need to be highly luminescent. This correlation, which may at first sight seem counterintuitive, is a direct result of Shockley and Queisser's detailed balance principle: it arises from the fact that ideal solar cell materials completely lack non-radiative recombination. This leaves radiative emission as the only possible energy loss mechanism under open-circuit conditions. Accordingly, the high bulk luminescence of lead halide perovskite materials explains some of their remarkable photovoltaic properties<sup>9</sup>.



SOON HOCK NG

**Figure 1** | Schematic view of a luminescing hybrid organic–inorganic lead halide perovskite film on glass (shown in blue). A large grain-to-grain variation of relative fluorescence yields was observed (represented in blocks ranging from yellow to brown), as well as reduced luminescence at grain boundaries. Identifying the underlying quenching mechanisms should make it possible to further improve the efficiency of perovskite solar cells.

Using confocal fluorescence microscopy, Ginger and co-workers have now been able to spatially resolve the luminescence quantum yields, as well as the fluorescence lifetimes, in thin spin-coated  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite films on glass<sup>8</sup>. Here, the spatial resolution achieved with confocal fluorescence microscopy is critically important. The resulting lateral imaging resolution of 348 nm is comfortably higher than the actual average size of the perovskite grains that make up the absorber layer. This enabled the comparison of photoluminescence properties between grains, and also of luminescence close to and far from grain boundaries. Several of the findings are unexpected and will undoubtedly shape future directions in this strongly emerging research field.

By correlation of confocal fluorescence microscopy with scanning electron microscopy images, the photoluminescence intensity was found to vary strongly between different grains within the perovskite film, with up to 34% of the grains appearing dark (Fig. 1). Furthermore,

photoexcitation close to the centre of grains produced a stronger luminescence signal than photoexcitation in the vicinity of grain boundaries. Careful analysis of the time-resolved luminescence decay also revealed that fluorescence lifetimes are shorter in the vicinity of grain boundaries and in dark grains. Further study of the luminescence decay kinetics pointed towards accelerated trap-assisted charge recombination in these areas.

In the past there has been some controversy about the role of grain boundaries in the performance of perovskite solar cells. Some studies<sup>9</sup> predict performance increases for more crystalline perovskite layers while others suggest that the existence of grain boundaries even plays a beneficial role in perovskite solar cells<sup>10</sup>. The recent findings by Ginger and co-workers suggest that the influence of grain boundaries on device performance needs to be re-examined in more detail. The observation of significantly reduced luminescence in dark grains and at grain boundaries now sparks hopes that perovskite solar

cells still possess significant potential for improvement. It will be interesting to see confocal microscopy applied to today's highest performing perovskite films<sup>7</sup> to see whether a similar variation in luminescence behaviour can be observed. If it persists, then this can be seen as highly encouraging evidence that substantial efficiency improvements will be achievable in the future.

In their study, the researchers also described two major discoveries that could lead to better-engineered high-performance devices. Firstly they observed that post-deposition treatment of perovskite films with pyridine vapours enhanced the overall luminescence of the materials. This was especially true for dark grains and at grain boundaries — which points to a successful passivation of recombination centres at the perovskite/air interface, as well as at the grain boundaries. Secondly the combination of confocal luminescence microscopy with energy-dispersive X-ray spectroscopy (EDS) mapping showed that bright grains coincided with chloride rich areas. Chloride is added to the spin-coating

solution to improve the crystallization behaviour but generally only traces of it are observed in the final perovskite film<sup>11</sup>. Hopefully in the future it will be possible to further elucidate the chemical nature of the chloride-rich phases and their influence on charge recombination.

As the technology matures, progress in perovskite solar cell research will become more and more dependent on such comprehensive understanding of structure–property relationships. In this ground-breaking study, Ginger and co-workers were able to illustrate the important role of high-resolution luminescence mapping as a powerful tool to pinpoint imperfections within photovoltaic perovskite films that currently limit their performance. Inspired by this work, other imaging techniques such as near-field scanning microscopy could potentially provide substantially higher spatial resolutions and further insights into the *modus operandi* of next generation thin film solar cells. In principle there should be no barriers to applying this innovative confocal imaging technique to fully assembled perovskite solar cells,

in particular when external biases close to  $V_{OC}$  are applied to shut down charge separation processes. This would make luminescence imaging a powerful tool to reveal and battle degradation mechanisms in perovskite solar cells under prolonged operation, which in itself is a significant future task. □

*Udo Bach is in the Manufacturing Flagship of CSIRO, Clayton 3168 and the Department of Materials Science, and Engineering, Clayton 3800, Victoria, Australia.*

*e-mail: udo.bach@csiro.au*

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## SYNTHETIC BIOLOGY

# Six pack and stack

A pair of artificial DNA bases have now been shown to adopt an edge-to-edge geometry in DNA which is similar that found in Watson–Crick base pairing. Aptamers containing these bases have also been shown to bind more strongly to a target than those developed using only the four naturally occurring bases.

Cheulhee Jung and Andrew D. Ellington

The Watson–Crick base pairing of naturally occurring nucleotides has long been a subject of fascination amongst chemists, in that it represents one of only a few examples of extensive isosteric and isomorphic supramolecular chemistries<sup>1</sup>. It is not clear, however, whether any reliable genetic system would require these extensive isosteric and isomorphic properties as there have been few opportunities to examine whether the uniqueness of Watson–Crick base pairing is a result of chemical or biological rarity: that is, whether there are few such systems within the space of chemical compounds, or many such systems, all of which could have been equally successful if biology had happened to chance upon them. Two recent papers<sup>2,3</sup> published in the *Journal of the American Chemical Society*, now provide insights into whether other genetic alphabets may be equally pliable.

Steven A. Benner and co-workers have previously developed orthogonal, unnatural base pairs<sup>4</sup>, including 6-amino-5-nitro-2(1H)-pyridone (Z) and 2-aminoimidazo[1,2-a]-1,3,5-triazin-4(8H)-one (P) (Fig. 1a) — which combine with the four naturally occurring DNA bases to make a six-letter DNA system. DNA containing these Z and P unnatural bases can be amplified by polymerase chain reaction with high fidelity (99.8% per cycle)<sup>4</sup>. Millie M. Georgiadis and colleagues have now shown<sup>2</sup> that this is in part because the Z and P nucleotides form a relatively 'natural' stack, that is similar to that adopted by Watson–Crick pairs. This similarity is such that multiple unnatural base pairs can be incorporated adjacent to one another without disrupting the basic structure of DNA. This similarity also enables ZP-containing DNA to adopt canonical B

and A helical forms. Since the NO<sub>2</sub> group in the Z nucleobase can stack with the heterocyclic ring of an adjacent nucleobase, multiple adjacent Z–P nucleobase pairs seem to have a higher propensity to form A-DNA, which may enable facile B-to-A structural transitions that are sometimes required for protein interactions<sup>5</sup>.

Most importantly, though, the Z-nitro group imparts new properties to the major groove of DNA that can potentially be exploited for recognition by proteins. Furthermore, the sequence space available to the six-letter genetic alphabet is considerably larger than of the four-letter system. To create useful DNA molecules that take advantage of these properties a team led by Zhen Huang, Weihong Tan and Steven A. Benner adapted the six-letter genetic alphabet for *in vitro* evolution experiments<sup>3</sup>. Aptamers that could bind