铯能强化新生代太阳能电池

添加一点点金属就可能制备低廉，耐久的钙钛矿太阳能电池

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西安宝莱特光电科技有限公司（www.p-oled.cn）翻译整理

在全球都在寻求更好更廉价替代能源的关头，太阳能电池材料钙钛矿给世人光明的憧憬。钙钛矿电池转换效率的攀升速度没有其它的太阳能技术可以媲美，钙钛矿材料不但廉价而且容易制备，还可以像印刷报纸一样以卷对卷的方式制造，钙钛矿还可以作为叠层放置在大家熟知的硅太阳能板上提高其效率。但是钙钛矿电池很脆弱，湿气，空气，热，长时间在太阳下都可以使它失效。

现在，钙钛矿材料变得坚强起来。过去的几个月里，三个不同的研究小组在他们的报告中指出，在钙钛矿配方里加少许的铯可以极大提高器件的稳定性。当然，现在还不能说含铯的钙钛矿电池能忍受在屋顶常年的风吹日晒，但是，“这已经是一个突破”，瑞士联邦技术研究所的 Michael Gratzel 这样评价说，他是上述提到的三个小组里其中一个小组的负责人。

Tandem solar cells, such as this 10-centimeter disk, combine the benefits of perovskite and silicon.

钙钛矿在迅速的克服自身的缺点。第一次用钙钛矿制作太阳能电池是六年前，日本科学家得到的光电效率仅仅 3.8%，这个效率要远远低于硅基和其它商用的太阳能技术（Science 15 November 2013， p. 794）。但是就在上个月，在 MRS（Materials Research Society）的一个会议上，来自韩国的科学家出示了证据，他们可以将钙钛矿电池的效率做的与硅太阳能电池相媲美，钙钛矿电池的效率达到新的记录，21.7%，科学家变得越来越有信心，钙钛矿电池的转换也许不久会达到 30%，这样的效率目前只有昂贵的 GaAs 电池能做到。 英国牛津大学的物理学家 Henry Snaith 评价说：“原理上，我看不出有什么问题钙钛矿电池不能超越 GaAs 的转换效率。”

但是，和 GaAs 不同，钙钛矿材料非常便宜，它含有无机元素铅和碘，还含有非常简单

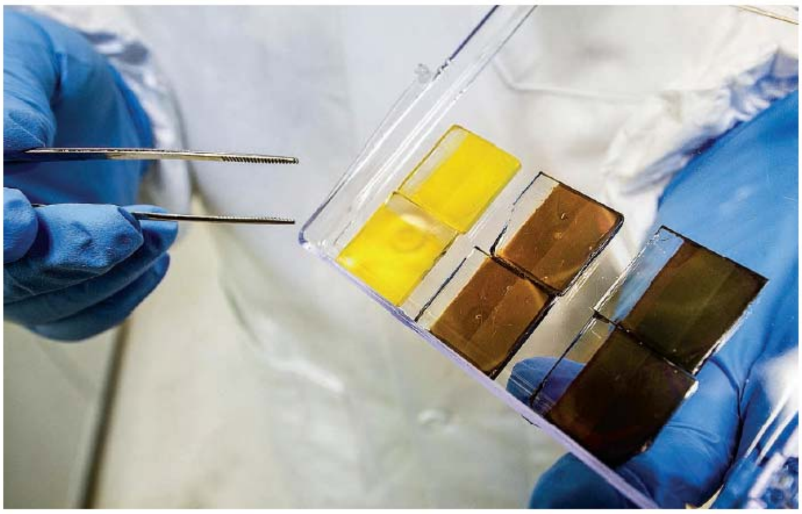
的甲胺基或者甲脒基，器件结构也是简单的层状结构。所有的合成和器件制作无需昂贵的高温设备和超净实验室，而其它的太阳能技术需要这些。“钙钛矿的这些特点真的非常卓越，”美国杜克大学的物理学家 David Mitzi 如此说。

钙钛矿的吸光性能也非常出众，这导致钙钛矿太阳能电池可以非常薄，成本也就低很多。一般电池越薄效率越高，这是因为光照产生的电子不需要跑很远的距离就可以被电极捕获，也就避免了光生电流被晶体缺陷所淬灭的几率。

但是“如果没有稳定性，高效率是没有意义的，”英国牛津大学的物理学家 Giles Eperon 评价道，所以全球的科学家都在努力寻找更稳定的钙钛矿配方。科学家用锡，锑，铋，或者元素周期表里铅周围的元素试着取代铅，还用氯和溴试着取代碘，但是大多数这样的尝试都降低了器件的效率。

但是，有一个尝试用大一点的有机基团甲脒基（FA）取代甲胺基（MA）能提高效率。2015 年 6 月 12 日的 Science 报道说，韩国化学技术研究所的化学家 Sang Il Seok 领导的研究小组用甲脒碘基钙钛矿取得超过 20%的效率，同时，纯甲脒基钙钛矿和甲脒基和甲胺基混合钙钛矿都表现出比纯甲胺基钙钛矿要稳定一些的特性。当我们把甲胺基钙钛矿自手套箱里拿出来时，钙钛矿的降解非常迅速，膜层颜色从黑色变成黄色，这一变化意味着器件对光的吸收会减少。甲脒基和甲胺基混合钙钛矿也会降解，但明显要慢很多，降解速度可以用分钟来数，而不像甲胺基钙钛矿几乎是秒杀，Snaith 这样说。

现在，几个研究小组发现在他们的钙钛矿配方里加少许的铯可以帮助钙钛矿保持晶型和黑色的外观。韩国成均馆大学化学工程教授 Nam-Gyu Park 第一次提到这个方法。他们在 2015 年 10 月 21 日出版的 Advanced Energy Materials 上，介绍说他们将 10%的甲胺基用铯取代所制作的太阳能电池对湿度和太阳光的耐受力要“显著”好很多，尽管当时并没有给出具体的数字。


Perovskite solar cells reflect different colors depending on their composition; darker ones absorb more light.

这些电池的最高效率在 16.5%，有点比不过纯甲胺基钙钛矿电池。但是很快，在 2015 年 12 月 3 日的 Energy & Environment Science 杂志上，Gratzel 小组就发表文章，指出甲胺基，甲脒基和铯混合钙钛矿电池效率可以超过 21%，结果还被独立的第三方机构所认证。很明显，在制作更稳定和更高效钙钛矿电池时铯是个关键。Gratzel 继续指出：“我肯定这是这个领域应该走的方向。”

含铯的钙钛矿电池还可以很好的和硅太阳能电池结合，就在这周的 Science 杂志上

（Science 351, 151, 2016）Snaith 小组就报道了他们在这方面的进展，这里通常是将钙钛矿电池单元放在硅电池的上面。材料能吸收不同波长的光线，多余的能量被用来减弱电子和原子核之间作用力，这样电子就可以顺利穿越材料。硅的带隙是 1.1eV， 可以吸收光谱的红外区段，而典型的甲胺基钙钛矿带隙是 1.5eV，可以吸收更短波长，更蓝一点的光子。两种材料的结合，就可以覆盖更宽的太阳光波段，所以吸收更多，这一点在每种材料单独使用时都做不到。

要制作叠层高效的太阳能电池，科学家需要进一步加宽材料带隙宽度，这样能让更蓝的太阳光被电池吸收，Snaith 小组用溴将部分或者全部取代碘，但这一取代使电池对光和热的耐受性更进一步降低。

在他们目前的研究中，Snaith 小组将 17%的甲脒基用铯取代，制作的溴基钙钛矿电池可以经得住长时间的光照和温度，电池的效率在 17%，所产生钙钛矿有更宽的带隙（1.7eV），可以与硅太阳能电池匹配。研究者通过计算得出如果将这样的钙钛矿电池做在效率 19%的硅太阳能电池之上，叠层电池的整体效率可以达到 25%。Snaith 指出硅和钙钛矿的叠层太阳能电池效率最终将超过 30%。

截止目前，30%的转换效率由 GaAs 所独有，这种电池非常昂贵，主要是在航天领域使用。如果含铯的钙钛矿能让高效率太阳能电池来到地球，捉摸不定的搅局者的美好日子就要来了。

SOLAR ENERGY

Cesium fortifies next-generation solar cells

A dash of the metal could hold the key to making cheap, durable perovskite photovoltaics

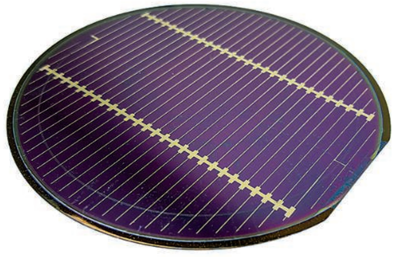
By **Robert F. Service**, *in Boston*

In a world looking for better, cheaper alternative energy, the solar cell materials called perovskites are a bright hope. Their efficiency at converting sunlight into electricity is climbing faster than that of any solar technology before them. They're cheap and easy to make, can be manufactured roll-to-roll like newsprint, and can even be layered atop conventional silicon solar cells to boost their output. But they are fragile stars: Moisture, air, heat, or even prolonged sunlight makes them fall apart.

Now, these materials are toughening up. Over the past few months, three separate teams have reported that adding a dash of cesium to their perovskite recipes produces efficient solar cells that are far more stable when exposed to the elements. It's still too early to say whether cesium-spiked perovskites will withstand years or decades on a rooftop. Even so, "this is really a breakthrough for the field," says Michael Graetzel, a chemist at the Swiss Federal Insitute of Technology in Lausanne, who leads one of the groups.

Perovskites are rapidly overcoming other shortcomings. The first perovskite-based solar cells, made 6 years ago by Japanese researchers, turned just 3.8% of the energy in sunlight into electricity, an efficiency well below that of silicon and other commercial technologies (*Science*, 15 November 2013, p. 794). But last month, at a meeting of the Materials Research Society here, researchers from South Korea reported evidence that their latest cells rival silicon, reaching a record 21.7% efficiency. Researchers are growing ever more hopeful that perovskite solar cells will soon approach 30% efficiency, rarefied territory now occupied only by costly gallium arsenide cells. "There seems to be no fundamental reason these materials won't achieve the efficiencies gallium arsenide has achieved," says Henry Snaith, a physicist at the University of Oxford in the United Kingdom.

Yet unlike gallium arsenide, perovskites are made from cheap components—typically including the inorganic elements lead and iodine, together with one of two simple organic compounds, methylammonium (MA) or formamidinium (FA)—in a layered crystalline arrangement. All the chemistry needed to make them can be done without the expensive high-temperature setups or clean room facilities needed for many other solar cell materials. "This is really quite remarkable for the perovskites," says David Mitzi, a physicist at Duke University in Durham, North Carolina.



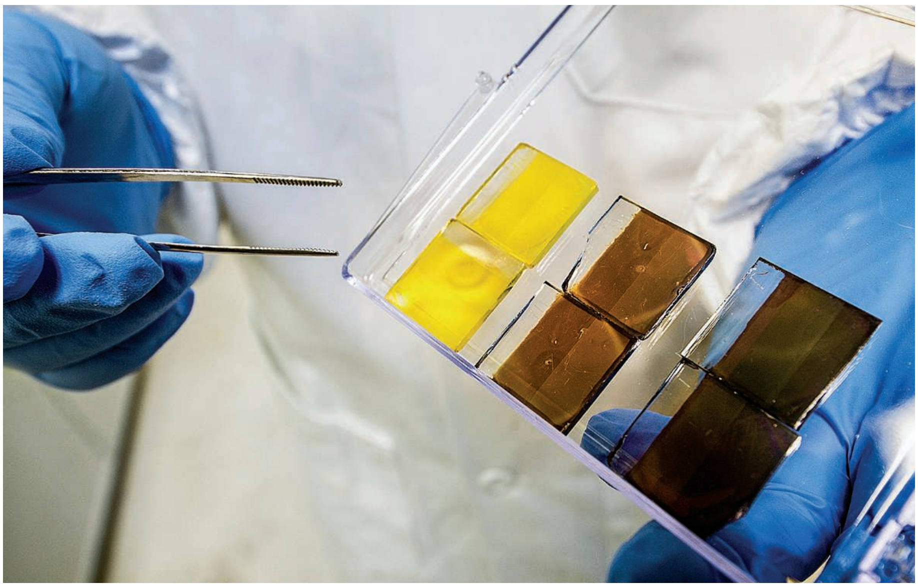
Tandem solar cells, such as this 10-centimeter disk, combine the benefits of perovskite and silicon.

Perovskites are also exceptionally good at absorbing photons. As a result, cells can be made very thin, which further lowers costs. A thinner cell can also be more efficient, because electrons energized by sunlight are less likely to get hung up on imperfections in its crystalline lattice as they travel to an electrode, which feeds them to an external circuit.

Yet "high efficiency is meaningless if the cells aren't stable," says Giles Eperon, a physicist at Oxford. So researchers around the globe are searching for more stable perovskite recipes. They've swapped out lead for tin, antimony, and bismuth: other metals nearby in the periodic table. And they've replaced iodine with bromine and chlorine. Most such changes reduce the materials' efficiency.

But one change—replacing MA with FA, a slightly larger organic molecule—actually increases it. In the 12 June 2015 issue of *Science*, for example, Sang Il Seok, a chemist at the Korea Research Institute of Chemical Technology in Daejeon, South Korea, and his colleagues reported achieving more than 20% efficiency with FA-lead iodide perovskite solar cells. Cells with FA alone or a mixture of FA and MA also appear to be somewhat more stable than pure MA-lead iodide cells. When MA cells are taken out of a protective glove box, they degrade almost immediately, turning from black to yellow—a change that shows they are absorbing a narrower band of visible light. Mixed FA-MA materials also degrade, but more slowly: in minutes rather than seconds, Snaith says.

Now, several groups have found that adding cesium to their recipe seems to further stabilize the other components and helps the mixture retain its perovskite structure and black appearance. Nam-Gyu Park, a chemical engineer at Sungkyunkwan University, Suwon, in South Korea, first described the approach. In a 21 October 2015 online paper in *Advanced Energy Materials*, he and colleagues reported that replacing 10% of the MA with cesium yielded



Perovskite solar cells reflect different colors depending on their composition; darker ones absorb more light.

PHOTOS: (TOP TO BOTTOM) OXFORD PV; © LEN COLLECTION/ALAMY STOCK PHOTO solar cells that held up "significantly" better to humidity and sunlight, although they did not give specific numbers.

These cells had a top efficiency of 16.5%, a step behind the best MA-only cells. But progress has continued. In a paper published online 3 December 2015 in *Energy & Environmental Science*, Graetzel and colleagues reported perovskite cells with a mix of MA, FA, and cesium that had an efficiency of just over 21%, a result verified by an independent lab. It seems clear that cesium is a key to making cells more stable and powerful. "I'm sure this is where the field is going to go," Graetzel says.

Cesium-containing perovskites can also be coaxed to work well with silicon cells, as Snaith and colleagues report online this week in *Science*. Such combinations typically layer a perovskite cell on top of a silicon cell. The materials absorb different wavelengths of light, because they have different band gaps—the amount of extra energy they must absorb to shake electrons loose from their atoms so they travel through the material. Silicon, with a band gap of 1.1 electron volts (eV), is good at absorbing photons on the red end of the visible spectrum. Typical MA-based perovskites have a bandgap of 1.5 eV and thus absorb slightly shorter, or bluer, photons. Combining the two materials captures more of the solar spectrum—and thus more energy—than either could harvest alone.

To make tandem cells perform better, researchers want to widen their net by pushing the band gap of perovskites higher so they will absorb even bluer light. Groups led by Snaith and others have done that by replacing some or all of the iodine with bromine. But the changes made the cells more vulnerable to heat and light.

In their current study, Snaith's team replaced 17% of the FA with cesium. The resulting bromine-based perovskites could withstand exposure to prolonged light and high temperatures. The cells were also 17% efficient, and they had the wider band gap needed to work well with silicon. The researchers calculate that by layering the material atop a 19% efficient silicon cell, they could create a tandem cell with an efficiency of 25%. Snaith says silicon-perovskite tandems eventually ought to exceed 30% efficiencies.

So far, numbers like that have been the sole territory of gallium arsenide cells—devices so expensive they are used primarily in space, where it's worth paying a premium for higher efficiency. If cesium-spiked perovskites can bring high-efficiency solar cells down to Earth, the temperamental challengers' brightest days may still lie ahead. ■

ENVIRONMENTAL SCIENCE

Conservation researchers get a new roost in Cambridge

Renovated building aims to foster alliances

By **Erik Stokstad** *in Cambridge, U.K.*

Conservation and cement often don't mix. But a concrete, 1960s-era Brutalist office building here is set to become home to one of the largest concentrations of conservation scientists in the world. Five hundred researchers, conservation practitioners, and support staff are now settling into the freshly refurbished David Attenborough Building, renamed after the prominent naturalist and television host. The building is the new hub of the Cambridge Conservation Initiative (CCI), an effort to expand collaborations between the University of Cambridge, its Museum of Zoology, and the many conservation groups here.

David Attenborough visited the conservation hub when it was named for him last year.

"The scale of the ambition and vision is really remarkable," says biologist Georgina Mace of University College London, who has advised CCI but is not involved in the center. Academics will find new opportunities to apply their research, planners predict, while conservation groups will get help addressing key problems. "This building will become a flagship for conservation," predicts Peter Crane, Dean of the Yale School of Forestry & Environmental Studies.

Cambridge has long been a conservation hotbed. Organizations with nearby headquarters, the Royal Society for the Protection of Birds and the British Trust for Ornithology, were joined over the years by others including BirdLife International, the United Nations Environment Programme's World Conservation Monitoring Centre (WCMC), and the International Union for Conservation of Nature's Global Species Programme. In 2007, nine groups and the university founded CCI to strengthen ties, and have raised some £2 million for pilot projects.

Several years ago, CCI saw an opportunity to deepen such alliances after the university's mathematics and metallurgy departments left their aging downtown home: a three-story, turreted concrete fortress. CCI helped the university raise nearly one-third of the £58 million spent on the renovation, which included adding a green roof and an atrium with a 12-meter-tall wall of plants. Architects worked to avoid isolated offices, instead creating long sight lines and numerous common rooms. "I see this as an experiment," says Mike Rands, CCI's director. He notes that a team of social scientists is studying how the building affects interactions between the academics and the conservation advocates.

The offices will be occupied by up to 150 people from university departments, including zoology, plant sciences, law, and business, along with an estimated 350 from conservation organizations. Smaller groups are moving in all of their employees, whereas larger ones will rotate in staffers. "There is an incredible buzz about the place," says Matt Walpole, WCMC's director of partnerships and development.

Fostering collaboration between academics and conservation advocates will likely bring benefits, but it also has hazards, says Josh Tewksbury, a conservation biologist with the University of Colorado, Boulder, who is not involved in the project. "For a university, there's always a brand risk to the credibility of science by bringing in advocacy organizations," he says. Those groups, meanwhile, risk being distracted by basic research not relevant to their missions.

But Rands believes that by harnessing "the Cambridge brand" for conservation research, the hub will become a go-to resource for government, business, and philanthropy leaders. In November, for instance, the president of Madagascar paid a 3-hour visit. "We'll see more of this happening," Walpole predicts.

In the meantime, the new space is having a psychological impact on its occupants. "It is an impressive statement of intent," says conservation scientist Andrew Balmford of the University of Cambridge. "Everyone feels an inch taller." ■

PHOTO: CCI