

PEROVSKITE SOLAR CELLS

Switchable photovoltaics

The migration of ions under the effect of an external electric field locally modifies the doping of organometal halide perovskite films. This is used to reversibly switch the photocurrent direction in very simple photovoltaic architectures.

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In high-performing p–n junction solar cells based on semiconductors such as silicon, copper indium gallium selenide or gallium arsenide, the distribution of p- and n-type dopants in the active area of the devices — and consequently the direction of the internal electric field — is usually determined at the fabrication stage. The photogenerated current can thus flow between the electric contacts of the solar cell only in one direction. Writing in *Nature Materials*, Xiao and collaborators now show that organometal halide perovskite solar cells are an exception to this rule; in fact, they demonstrate that the distribution of dopants in the perovskite layer can be modified after device fabrication, by applying an external electric field between the two terminals. This leads to a field-switchable photovoltaic effect with very high photocurrent¹.

Unprecedentedly rapid progress has been made in perovskite photovoltaic technology

in the past few years^{2,3}. As a result, solar cells with a certified power conversion efficiency of 20.1%⁴ and a laboratory cell surpassing 19%⁵ have been demonstrated in 2014. Organic–inorganic perovskites are characterized by a balanced electron- and hole-transport behaviour that has not been observed in other semiconductors used in photovoltaics^{6,7}. Such uniqueness makes perovskites suitable for several planar thin-film solar-cell configurations including p–n junctions, p–i–n junctions and Schottky junctions.

In an effort to further investigate charge transport in these materials, Xiao and colleagues observed a switchable photovoltaic effect in a simple solar-cell architecture, in which a layer of methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$ or MAPbI_3) was sandwiched between a bottom contact of indium tin oxide/poly(3,4-ethylenedioxythiophene):

poly(4-styrenesulphonate) (ITO/PEDOT:PSS) and a gold top electrode (Fig. 1a). The initial application of an external voltage to the gold contact (positive poling) or to the PEDOT:PSS contact (negative poling) was able to change the direction of the current generated by this vertical device under exposure to light (Fig. 1b). This phenomenon was also demonstrated using other organolead trihalide perovskite materials, such as $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$, $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$, and different top electrodes including nickel, gallium and platinum. A similar reversibility has been recently reported in photovoltaic devices based on ferroelectric BaFeO_3 materials^{8,9}. There, however, the switchable photocurrent was in the microampere range, four orders of magnitude lower than that measured by Xiao *et al.* in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells. In their vertical structure, the short-circuit current density was switched between 18.6 and -20.1 mA cm^{-2} and the open-circuit voltage between 0.42 and -0.73 V . Interestingly, these values are in the same range as those observed in more complex architectures that use additional electron- or hole-accepting layers. The results indicate that most of the photogenerated excitons dissociated to free charges directly in the perovskite layer, and that both electrodes had comparable efficiency in collecting electrons and holes.

Xiao *et al.* also attempted to observe this photovoltaic effect in a laterally structured device (Fig. 1c), in which two identical gold electrodes contacted a perovskite thin film. In view of the symmetric configuration adopted for the electrodes, no internal electric field was created in the device in the absence of poling, and no photovoltaic effect was observed. After the application of an external voltage, however, a short-circuit current density of $\pm 0.075 \text{ mA cm}^{-2}$ and an open-circuit voltage of $\pm 0.5 \text{ V}$ were measured from the device under 0.25 sun illumination. Importantly, the photovoltage was almost unaffected by changes in the spacing between the electrodes; this suggests that the observed behaviour has little correlation with the ferroelectric photovoltaic effect reported in BaFeO_3 , which instead depends on the amount of active material placed between the electric contacts.

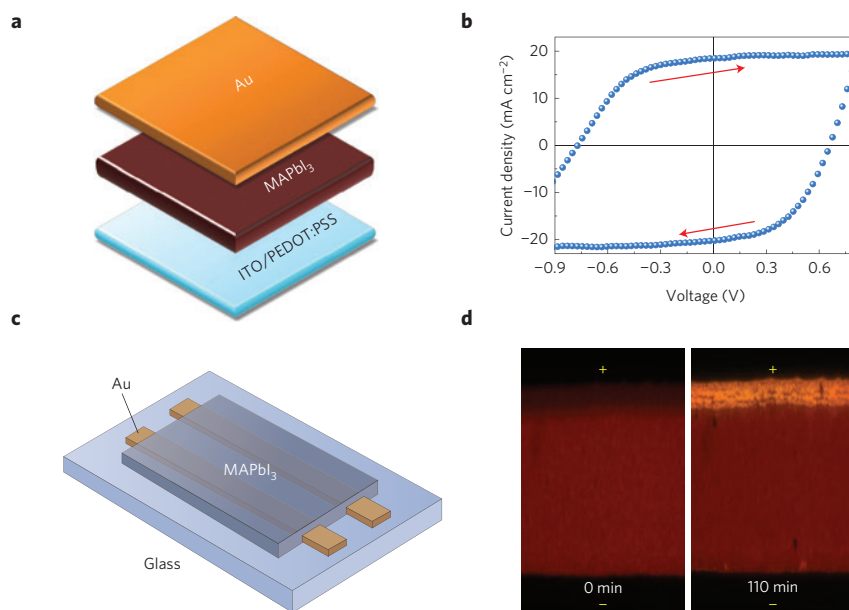



Figure 1 | Perovskite solar cells with vertical or lateral structure, and their field-switchable photovoltaic effects. **a**, Vertical-structure device with methylammonium lead iodide (MAPbI_3) perovskite sandwiched between layers of poly(3,4-ethylenedioxythiophene):poly(4-styrenesulphonate) (PEDOT:PSS) and gold. **b**, Current–voltage curves for the vertical structure. The photocurrent switches depending on the initial biasing conditions of the device. The arrows show the voltage scanning direction. **c**, Lateral-structure device with MAPbI_3 deposited on Au strips. **d**, Optical images of the lateral-structure device before (left) and after (right) about 2 hours of the poling process. The transparency of the perovskite material near the anode side changes as a result of ion drift. Figure reproduced from ref. 1, 2015 Nature Publishing Group.

To understand the mechanism behind the field-switchable photovoltaic effect in organolead halide perovskites, the researchers investigated the role of ion drift. Methylammonium (CH_3NH_3^+) or Pb^{2+} cations and I^- anions can migrate following the direction of an applied electric field or in opposition to it, according to their sign, and create vacancies in the perovskite structure. The accumulation of ions and vacancies close to the electrodes induces doping in these regions, and as a consequence a p–i–n junction is formed in the initially neutral layer. A reversed applied voltage can flip the p–i–n structure to n–i–p by moving the ions or ion vacancies in the opposite direction. Kelvin probe force microscopy experiments were conducted to measure the work function of the perovskite close to the gold electrode in the vertical structure after positive and negative poling, and confirmed the proposed doping mechanism. Field-driven ion drift was also monitored in the lateral-structure device by optical microscopy (Fig. 1d). The dark red perovskite near the anode side turned transparent after poling for 2 hours, and the composition of

the transparent area was different from the stoichiometric perovskite, as a result of ion migration from the anode.

The possibility of locally modifying the doping of organolead halide perovskite films by means of the reported poling process offers several advantages. As shown in this work, a simple solar cell composed of a perovskite film without electron- and hole-transporting layers could provide an efficient photovoltaic effect because the p–i–n structure created by means of this self-doping mechanism can effectively transport the photogenerated charges towards the electrodes. The researchers have also demonstrated that multiple lateral photovoltaic structures can be connected in series, and they achieved an open-circuit voltage as high as 47 V by connecting 125 cells together. Although the photocurrent generated in the latter structures is lower than that typically obtained with these materials, significant improvements are expected by decreasing the interelectrode spacing down to a size comparable to or lower than the diffusion length of electrons and holes in perovskite. This might lead to

the realization of efficient solar cells with extremely high photovoltage that do not require the use of transparent electrodes based on materials in short supply, such as indium. Moreover, the demonstration of reversible photocurrent switching may allow the realization of electrically and optically readable memristors based on organic–inorganic perovskites. 

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