**SOLAR CELLS**

**Stabilizing halide perovskite surfaces for solar cell operation with wide-bandgap lead oxysalts**

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We show that converting the surfaces of lead halide perovskite to water-insoluble lead (II) oxysalt through reaction with sulfate or phosphate ions can effectively stabilize the perovskite surface and bulk material. These capping lead oxysalt thin layers enhance the water resistance of the perovskite films by forming strong chemical bonds. The wide-bandgap lead oxysalt layers also reduce the defect density on the perovskite surfaces by passivating undercoordinated surface lead centers, which are defect-nucleating sites. Formation of the lead oxysalt layer increases the carrier recombination lifetime and boosts the efficiency of the solar cells to 21.1%. Encapsulated devices stabilized by the lead oxysalt layers maintain 96.8% of their initial efficiency after operation at maximum power point under simulated air mass (AM) 1.5 G irradiation for 1200 hours at 65°C.

The power conversion efficiency (PCE) of laboratory-scale metal halide organic perovskite solar cells (PSCs) has reached a certified value of 24.2%, exceeding those of cells that are based on cadmium telluride (CdTe) and copper indium gallium selenide (CIGS) (1). However, PSCs face long-term instability issues under realistic operation conditions, which remains a critical hurdle to be overcome before their commercialization (2–4). Lead halide perovskites generally suffer from instability under stimuli of heat, oxygen, moisture, light irradiation, and electric field (4–6). Tailoring the composition, crystallinity, and internal material strain have been shown to substantially improve the materials' intrinsic stability under different stimuli, but their instability from moisture and oxygen is still an outstanding issue to be solved (7–10).

Perovskite degradation is generally initialized from the defect sites at surfaces and grain boundaries, which are more reactive toward water and oxygen (11–15). Many organic molecules and polymers have been applied to chemically passivate the perovskite surface defects, and physical covering of some structural defects with hydrophobic organic materials can also enhance the stability of the perovskites (16–17). For example, Cs0.05FA0.81MA0.14PbI2.55Br0.45 (CsFAMA perovskite) was used in our study with a chemical composition of Cs0.0011FA0.00MA0.00PB25.46B0.06 (CsFAAMA perovskite, where MA is methylammonium and FA is formamidinium). The oxidic ions reacted with halide perovskite when perovskite films were dipped into (C8H17NH3)2SO4 and (C8H17NH3)3PO4 solutions for 30 to ~80 min followed by thermal annealing, according to the following chemical equations:

\[
\text{APbX}_3 + \text{SO}_4^{2-} \rightarrow \text{A}^+ + 3\text{X}^- + \text{PbSO}_4
\]  

\[
3\text{APbX}_3 + 2\text{PO}_4^{2-} \rightarrow 3\text{A}^+ + 9\text{X}^- + \text{Pb}_3\text{(PO}_4)_2
\]

where A = MA, FA, Cs, or a mixture thereof, and X = Br, I, or mixed halide ions. This reaction yielded stable white-colored PbSO4 and Pb3(P04)2 films, as shown in the photographs and verified with x-ray diffraction patterns in figs. S1 and S2.

Using the same method, a thin lead sulfate layer can be generated on the surface of the CsFAAMA perovskite films by reducing the reaction time. Because PbSO4 is electrically insulating, the reaction time and precursor concentration were carefully optimized to be 20 s and 4 mM,

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respectively, which yields a layer thickness of <5 nm that can maintain efficient charge transport (fig. S3). Perovskite films or devices with lead sulfate layers, hereafter referred to as lead sulfate samples, were obtained through octylammonium sulfate treatment if not specified otherwise.

Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images in figs. S4 and S5, A and B, show that the topography of the perovskite films was well maintained after the surface reaction, indicating a conformal coating of lead sulfate on the perovskites. Cross-sectional high-resolution transmission electron microscopy (HR-TEM) (fig. 1B) further revealed a uniform and compact lead sulfate layer that was closely stacked between the fullerene (C60) and perovskite films. The lead sulfate layer had a thickness of 3 to 4 nm, whereas the CsO layer was crystalline. We used scanning TEM characterization to verify the homogeneity of the sulfate layer on the top of perovskite films. We tested various perovskite/CsO interface regions (fig. S5C) and observed a thin but continuous lead sulfate layer both on the surface and at grain boundaries of the perovskite film, suggesting complete coverage of lead sulfate on the top surface of perovskite films.

Fourier transform infrared (FT-IR) transmission spectra of CsFAMA perovskite powders before and after surface treatment were collected to probe the interactions of sulfate ions with the perovskite. The tetrahedral symmetric sulfate ions typically present one broad peak at ~1100 cm$^{-1}$ of the triply degenerate v3 band (19). The occurrence of v1 band (945 cm$^{-1}$) and split v3 bands (950 to ~1200 cm$^{-1}$) (Fig. 1C) suggests a distortion of the tetrahedral structure of sulfate ions and formation of strong ionic bonds between Pb$^{2+}$ and SO$_4^{2-}$ ions (20). The characteristic vibration peaks of the sulfate-treated sample were at the identical frequency (950 to ~1200 cm$^{-1}$) to those of pure PbSO$_4$ powder (fig. S6), which implies the similar IR vibration behavior of the surface layer on the perovskite surface.

We performed x-ray photoemission spectroscopy (XPS) measurements to further characterize the perovskite surface composition after surface treatment. The Pb 4f spectrum exhibited two contributions, 4f$_{7/2}$ and 4f$_{5/2}$ (Fig. 1D), located at 138.6 and 143.5 eV for the film without any treatment (control), respectively (21). The shift of the Pb peaks toward higher binding energies is evidence for the formation of stronger ionic bonding between Pb$^{2+}$ and SO$_4^{2-}$ ions (22). The S/Pb atom ratio was estimated to be 1.03 by the integrated area of corresponding peaks (Fig. 1E).

We performed first-principles density functional theory (DFT) computational analyses of the interaction between MAPbI$_3$ and PbSO$_4$ using a slab model of both materials and investigated the nature of their interface by means of ab initio Car-Parrinello Molecular Dynamics (CPMD). We initially considered a (001) MAI-terminated MAPbI$_3$ surface covered by eight PbSO$_4$ units arranged in a network similar to that of the perfect PbSO$_4$ crystal but matching the lattice of MAPbI$_3$. We evolved the system dynamics at 350 K for several picoseconds and observed the structural inter-

Fig. 1. Organohalide lead perovskite stabilized by a lead sulfate surface layer. (A) Schematic illustration of protection of perovskites through in situ formation of a lead sulfate top layer on the perovskite surface. (B) Cross-sectional HR-TEM image of the perovskite/lead sulfate/CsO interface. (C) FT-IR measurement of perovskite powder with or without the lead sulfate layer. (D and E) The XPS spectra of (D) Pb 4f and (E) S 2p for the perovskite films deposited on ITO glass.
mean $V_{OC}$ was 1.06 and 1.14 V for the control and sulfate-treated devices, respectively. Likewise, the mean PCE of the sulfate-treated devices reached 20.18 ± 0.56%. The enhanced $V_{OC}$ of the sulfate-treated devices, respectively. The lower charge trap density and longer carrier recombination lifetime of samples with lead sulfate top layers indicate that the reaction of sulfate and phosphate ions with defective perovskite surface reduces the surface defect density, in addition to the charge compensation effect of these ions. The wide-bandgap lead oxysalt layer should also contribute to the reduced surface charge recombination rate, similar to the passivation of silicon by oxides (26).

Fig. 2. Theoretical simulation. (A to F) Optimized geometries from the selected snapshots of the MAI-terminated + 8PbSO$_4$ CPMD simulation. The (A) initial geometry and the [(B) and (C)] optimized geometry after (B) 1.2 and (C) 3.6 ps are also shown. (D) The structure in which a MAI was exchanged with a PbSO$_4$ from geometry (C). (E) and (F) show optimized geometries of (E) MAI-terminated and (F) PbI$_2$-terminated interface with a PbSO$_4$ layer.

(mean $V_{OC}$ was 1.06 and 1.14 V for the control and sulfate-treated devices, respectively. Likewise, the mean PCE of the sulfate-treated devices reached 20.18 ± 0.56%. The enhanced $V_{OC}$ and PCE as well as hysteresis-free behavior of the sulfate-treated devices together indicate the surface charge traps were passivated by the lead sulfate top layer.

To quantify how much cation passivates the perovskite surface, we fabricated solar cells with different cations and anions, and detailed statistical analysis on the device parameters are summarized in table S3. Octylammonium iodide treatment increased the mean $V_{OC}$ of the cells from 1.06 to 1.08 V, implying that there is a small but distinct contribution from alkylammonium cations to the passivation of perovskite surface. However, when anions were changed by replacing octylammonium iodide with octylammonium sulfate, the mean $V_{OC}$ of the cells increased from 1.08 to 1.14 V. Moreover, a high mean $V_{OC}$ of 1.13 V could be maintained if methylammonium sulfate was used instead of long-chain alkylammonium cations, implying that sulfate anions dominated in surface passivation. We infer that the perovskite films are mostly covered by the lead sulfate layer after treatment because of the preferential reaction between Pb cations and sulfate anions, as indicated by the results of DFT simulations, so octylammonium cations have less interaction with the perovskite surface. We further demonstrated the universality of this synthetic strategy of using phosphate ions to form a Pb$_3$(PO$_4$)$_2$ surface layer and examined the device performance. One solar cell device based on phosphated CsFAMA perovskite exhibited a $J_{SC}$ of 22.54 mA cm$^{-2}$, $V_{OC}$ of 1.14 V, and FF of 0.813, yielding a PCE of 20.87% without hysteresis (fig. S10 and table S4).

Trap density of states (tDOS) of the control and sulfate-treated devices was measured with thermal admittance spectroscopy. A device with sulfate top layers had a lower tDOS almost over the whole trap depth region (Fig. 3D). The density of shallower trap states (0.25 to 0.42 eV) of the sulfate-treated device was only about 10% of the control device. Our previous characterizations have revealed that the shallow traps mainly locate at the grain boundaries (23). Thus, sulfate ions can effectively reach the grain boundaries during the treatment and passivate them, subsequently increasing the device $V_{OC}$.

The time-resolved photoluminescence (TRPL) spectra of the control CsFAMA perovskite film show a biexponential decay with a fast and a slow component (Fig. 3E). The surface layer mainly affected the fast PL decay process. The fast-component of the recombination process from the control and sulfate-treated films were fitted to be 3.2 and 24.7 ns, respectively, which is consistent with the enhanced steady-state PL results (Fig. 3F). The enhanced PL intensity and PL decay lifetime illustrate that the nonradiative recombination of photo-generated carriers in perovskite films is reduced by the formation of lead sulfate surface layers (24, 25).

Devices were then irradiated under AM 1.5 G simulated illumination, and weak laser pulses (337 nm, 4 ns) were used to modulate $V_{OC}$ to measure the decay of transient photovoltage signals. As seen in Fig. 3G and fig. S11, the charge-recombination lifetime under 1 Sun illumination was increased from 0.27 μs for the control device to 0.58 and 0.47 μs for sulfate- and phosphate-treated devices, respectively. The lower charge trap density and longer carrier recombination lifetime of samples with lead sulfate top layers indicate that the reaction of sulfate and phosphate ions with defective perovskite surface reduces the surface defect density, in addition to the charge compensation effect of these ions. The wide-bandgap lead oxysalt layer should also contribute to the reduced surface charge recombination rate, similar to the passivation of silicon by oxides (26).

We performed long-term stability tests of encapsulated CsFAMA perovskite devices under a plasma lamp with light intensity equivalent to AM 1.5 G (fig. S12), without ultraviolet filter in air (relative humidity ~60 ± 10%). All devices were loaded with a resistance so that they worked at MPP at the beginning of the tests. The J-V curves were automatically recorded with a reverse scan rate of 0.1 V s$^{-1}$ every 6 hours. We frequently checked the stabilized efficiency during the test and did not find obvious differences between the stabilized efficiency and that from J-V scanning. Most importantly, instead of monitoring device stability at a reduced temperature of 20 to 25°C that may cause the overestimation of solar cell
stability, we conducted the stability testing at real operation temperature and used a light source with a substantial ultraviolet component. The temperature of the devices under illumination was measured to be ~65°C, which is typical of the thermal heating effect of light. For the devices with the lead sulfate layer, the PCE slightly improved during the first 120 hours of testing and then degraded linearly with both reduced Jsc and FF over time. After 1200 hours of testing, the efficiency slowly dropped to 96.8% of the initial value. This CsFAMA perovskite device is one of the most stable reported when tested at MPP conditions (table S5).

In ambient conditions, hydration and oxidation of perovskites are among main paths for the degradation of perovskite films (23, 27). We studied the water resistance of perovskites with lead sulfate surface layers on MAPbI3 single crystals. MAPbI3 crystals were treated with the sulfate precursor solution followed by thermal annealing at 100°C for 10 min (supplementary materials). When dipped in water, the control MAPbI3 crystal without any treatment quickly turned yellow within 10 s because of the fast decomposition of MAPbI3 with water, forming PbI2 or other hydrates, whereas the sample with a sulfate layer remained black after dipping in water for >60 s (Fig. 4A and movie S1). The much later appearance of yellow PbI2 from perovskite single crystals showed that the lead sulfate top layer was compact enough to slow down the permeation of water into perovskite.

We tested the water resistivity of the lead sulfate layer by dripping water on top of the devices with and without sulfate treatment. A device with the lead sulfate layer remained black for 3 min after dripping water, whereas the control device quickly decomposed to yellow-colored PbI2 (fig. S13). We also tested the protection effect of lead sulfate layer on polycrystalline films that had the same stacking structure of the devices but without metal electrodes. The perovskite film with lead sulfate layer was sandwiched between PTAA and phenyl C61 butyric acid methyl ester (PCBM) layers. We recorded the

![Fig. 3. Photovoltaic performance, passivation effects, and long-term stability studies of sulfate-treated devices. (A) J-V curves of the champion sulfate-treated device measured in both reverse (blue) and forward (red) scanning directions. (B) Steady-state measurement of the photocurrent (orange) and PCE (blue) of the champion device with a lead sulfate layer held at MPP voltage of 0.99 V. (C) J-V curves of perovskite solar cells based on perovskite films treated with different precursor solution. (D) TDOS obtained through thermal admittance spectroscopy for the devices with (blue) or without (orange) lead sulfate top layers. The vertical dashed lines define trap bands with different trap energy depths: shallow trap states (band 1, 0.35 to 0.40 eV) and deep trap states (band 2 and band 3, >0.4 eV). (E) Steady-state PL and (F) time-resolved PL of the perovskite films with and without lead sulfate layers. (G) TPV decay curves of the photovoltaic devices with and without lead sulfate surface layers. (H) Stability test of encapsulated solar cell devices based on control (blue) and sulfate-treated (red) CsFAMA perovskite active layers.](http://science.sciencemag.org)
Ammonium cations have also been reported to enhance the stability of perovskites (28). We tested another set of perovskite thin films in air under illumination without any charge transport layers to study which species—specifically, ammonium or sulfate ions—play the dominating role in stabilizing perovskite films. The CsFAMA perovskite film treated with octylammonium iodide fully bleached after testing for 4 days, only slightly preventing the decomposition of the perovskite film as compared with the control sample without any treatment (fig. S15), but perovskite films with sulfate treatment remained black after 4 days. About 56 and 64% of the films' absorbance at 740 nm remained for films treated with methylammonium sulfate and octylammonium or sulfate ions, respectively, after 4 days. About 56 and 64% of the films were observed for the single crystals (Fig. 4, E to F). We thus conclude that ion migration is much easier at extended defects such as film surface and grain boundaries (31). We expect that the stabilization was mainly derived from sulfate rather than ammonium ions.

Mass transport of ions is another critical issue that limits the stability of the encapsulated perovskite devices. Ion migration is significantly enhanced under illumination (29), which may change the composition and morphology of perovskite films by forming pinholes in addition to causing the degradation of charge transport layers and electrodes (30). We also showed that ion migration is much easier at extended defects such as film surface and grain boundaries (31). We expect that the formation of a layer of lead oxysalt with strong ionic chemical bonding should stabilize the perovskite surface and suppress the ion migration through it. We measured with temperature-dependent electrical conductivity the activation energy \( \frac{\Delta E}{k_B T} \) for ion migration of perovskite films. Lateral structure devices were fabricated by means of thermal evaporation of two Au electrodes on PTAA/perovskite/PCBM films. The activation energy can be extracted from the Nernst-Einstein relation: \( \sigma(T) = \sigma_0 \exp(-E_a/k_B T) \), where \( k_B \) is the Boltzmann constant, \( \sigma_0 \) is a constant, and \( T \) is temperature. The applied electric field was fixed at 0.4 V/μm, which was near the operational electric field in solar cell devices. For the CsFAMA perovskite films, ionic conductivity began to dominate the total conductivity, with an \( E_a \) of 0.288 eV when the temperature was increased to 314 K in the dark (Fig. 4C). When illuminated at 0.1 sunlight intensity, the transition temperature was reduced to 273 K, accompanied with a lower \( E_a \) of 0.104 eV. This observation agrees well with our previous results that light would facilitate the ion migration (29).

For the sulfate-treated perovskite film, we did not observe such a transition from electronic to ionic conductivity when the temperature was increased to 330 K both in the dark and under illumination (Fig. 4D). A constant slope was obtained with an \( E_a \) of 0.036 eV, which we ascribed to electronic conduction. We also measured \( E_a \) of individual MAPbI_3 single crystals to isolate the influence of untreated grain boundaries in polycrystalline films, which act as the main channel for ion migration (31). Similar phenomena were observed for the single crystals (Fig. 4, E to F). We thus conclude that ion migration is efficiently suppressed by the lead sulfate top layer on the surface of perovskite, possibly because surface defects such as vacancies were immobilized by the strongly bonded lead sulfate layer, which also explains the restrained morphological variation of perovskite films with the presence of the lead sulfate layer (fig. S16).

Generally, ion migration through grain boundaries is much slower than at the surface, so the exclusion of ion migration at a film surface should also indicate the absence of ion migration through sulfated grain boundaries.

REFERENCES AND NOTES
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Author contributions: J.H. conceived the idea and supervised the research of this work. S.Y. and S.C. fabricated and characterized the perovskite films and solar cells. E.M. and F.D.A. did the theoretical simulation. Y.F. conducted the temperature-dependent conductivity measurement. Y.Z. and X.X. carried out the PL and TRPL characterizations. Z.Y. and J.Z. did the encapsulation and stability tests of perovskite devices. C.W. and Y.G. conducted the XPS tests. J.H., S.Y., and S.C. wrote the manuscript, and all the authors reviewed the manuscript.

Competing interests: J.H. and S.Y. are inventors on U.S. patent application (62/798,671) submitted by the University of Nebraska–Lincoln and University of North Carolina at Chapel Hill that covers conversion of halide perovskite surfaces to insoluble, wide-bandgap lead oxysalts for enhanced solar cell stability.

Data and materials availability: All data are available in the manuscript or the supplementary materials.

SUPPLEMENTARY MATERIALS

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Materials and Methods

Figs. S1 to S16

Tables S1 to S5

References (32, 33)

Movie S1

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Stability through oxysalts
The stability of organic-inorganic perovskite solar cells is limited by degradation from oxygen and water. Yang et al. show that in situ reaction of perovskites with sulfate or phosphate ions can create thin, strongly bonded lead oxysalt layers that protect defect sites. This layer also boosts charge carrier lifetimes that lead to a power conversion efficiency of more than 20%. Encapsulated devices maintained about 97% of this efficiency with simulated solar irradiation for nearly 2 months at a realistic operation temperature of 65°C.
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