

Universal Strategy with Structural and Chemical Crosslinking Interface for Efficient and Stable Perovskite Solar Cells

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A structural and chemical crosslinking interface is proposed here by adopting a bilayer tin dioxide (SnO_2) and incorporating methylenediammonium dichloride (MDACl_2) into the second layer.^[1] MDACl_2 can be dissolved by the perovskite precursor solution, so the structural crosslinking of the SnO_2 /perovskite interface is constructed. The incorporation of MDACl_2 enhanced the conductivity of the SnO_2 film and led to a greater presence of chloride ions at the SnO_2 /perovskite interface, and characterization confirmed the interaction between Cl^- and Sn^{4+} . Consequently, the open-circuit voltage (V_{oc}) and efficiency of the perovskite solar cells (PSCs) were increased. The target PSCs exhibited excellent stability, retaining 98% of their initial efficiencies after more than 6000 h of storage in dry air (~5% relative humidity) without encapsulation. After 1000 h of operation under one sun illumination, the device maintained 85.50% of the initial efficiency. Notably, this strategy enabled the achievement of 25% efficiency (reverse scan) with a low bandgap (1.53 eV) perovskite composition. These results are of great significance for the design and development of interfaces for efficient and stable PSCs.

Introduction

Perovskite solar cells have been developed rapidly due to the development of charge transport layers and perovskite films. In recent years, the introduction of tin dioxide (SnO_2) has greatly promoted the power conversion efficiency (PCE) of PSCs,^[2,3] and certified efficiency of 26.1% has been achieved for PSCs with single junction cells.^[4]

Generally, there are lots of undercoordinated halide ions and undercoordinated Pb^{2+} ions at the interfaces close to perovskite films and at the grain boundaries of perovskite, which lead to deep energy level traps and charge carrier recombination centers and deteriorate the photovoltaic performance of PSCs. To solve this problem, various materials, such as 4-imidazoleacetic acid hydrochloride (ImAchCl),^[5] rubidium fluoride,^[6] and biguanide hydrochloride (BGCl),^[7] have been introduced. They can act as a linker between SnO_2 and perovskite to assist the charge transfer and reduce interfacial defects, and passivate the iodine vacancies of perovskites at the interface by introducing excess halide ions. Also, some materials, such as 4-methylphenethylammonium chloride (4M-PEACl),^[8] cesium (Cs) and methylenediammonium (MDA) cations,^[9,10] are introduced into perovskite precursor solution to passivate defects at grain boundaries or regulate the strain relaxation of perovskite. Given the planar heterojunction structure of PSCs with SnO_2 , however, the limited contact area and the weak bonding at the SnO_2 /perovskite interface are not conducive to the extraction and transport of charge carriers. Therefore, new ideas and innovative work are needed for the interfaces of PSCs to enhance device performance and stability.

Results and discussion

Figure 1a shows the schematic of the fabrication process we proposed. Specifically, another SnO_2 layer mixed with MDACl_2 was spin-coated on Glass/ITO/ SnO_2 (ITO: indium tin oxide). Samples with SnO_2 / MDACl_2 are denoted as the target, while control samples adopt single-layer of SnO_2 . Conductive atomic-force microscopy (c-AFM) images were measured, with the structure of Glass/ITO/ SnO_2 . As shown in Figure 1b,c, the incorporation of MDACl_2 increased the average current from 1.91 nA to 2.57 nA, which should be conducive to the carrier transport in PSCs. Previous reports confirm that halogen ions, such as F^- , Cl^- and I^- , can interact with Sn^{4+} of tin dioxide,^[5-7,11] and may introduce additional free charge carriers and then improve the conductivity of SnO_2 . Figure 1d

shows the X-ray diffraction (XRD) patterns of SnO₂. Diffraction peaks at 26.4°, 33.7° and 51.3° have not been changed significantly. This is because the SnO₂ nanoparticles have been synthesized before the spin-coating, so MDACl₂ will not affect the crystallization process of SnO₂ nanoparticles. However, when SnO₂ colloidal dispersion was dried on quartz at 80 °C, the incorporation of MDACl₂ can affect its aggregation and growth behavior (the inset in Figure 1d). It indicates that there is interaction between them.

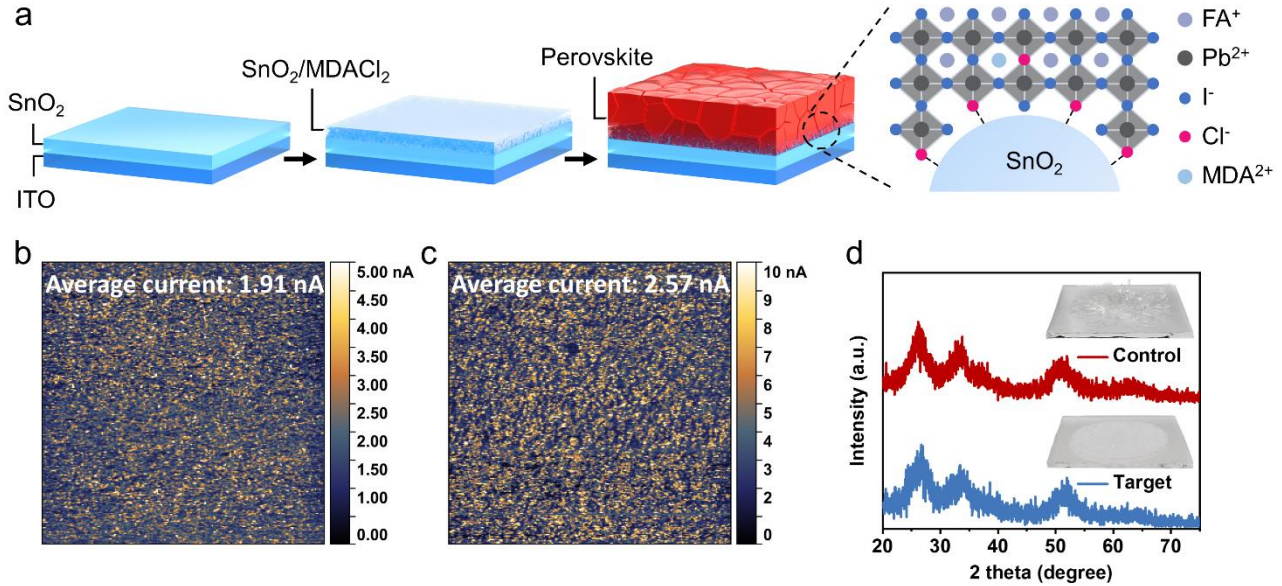


Figure 1. (a) Schematic of the fabrication process of target PSCs, and the schematic of structural and chemical crosslinking SnO₂/perovskite interface; c-AFM images (5 μm × 5 μm) of (b) control and (c) target SnO₂ films on Glass/ITO; (d) XRD patterns of control and target SnO₂ on silicon (The inset shows the photographs of SnO₂ dried on quartz at 80 °C).

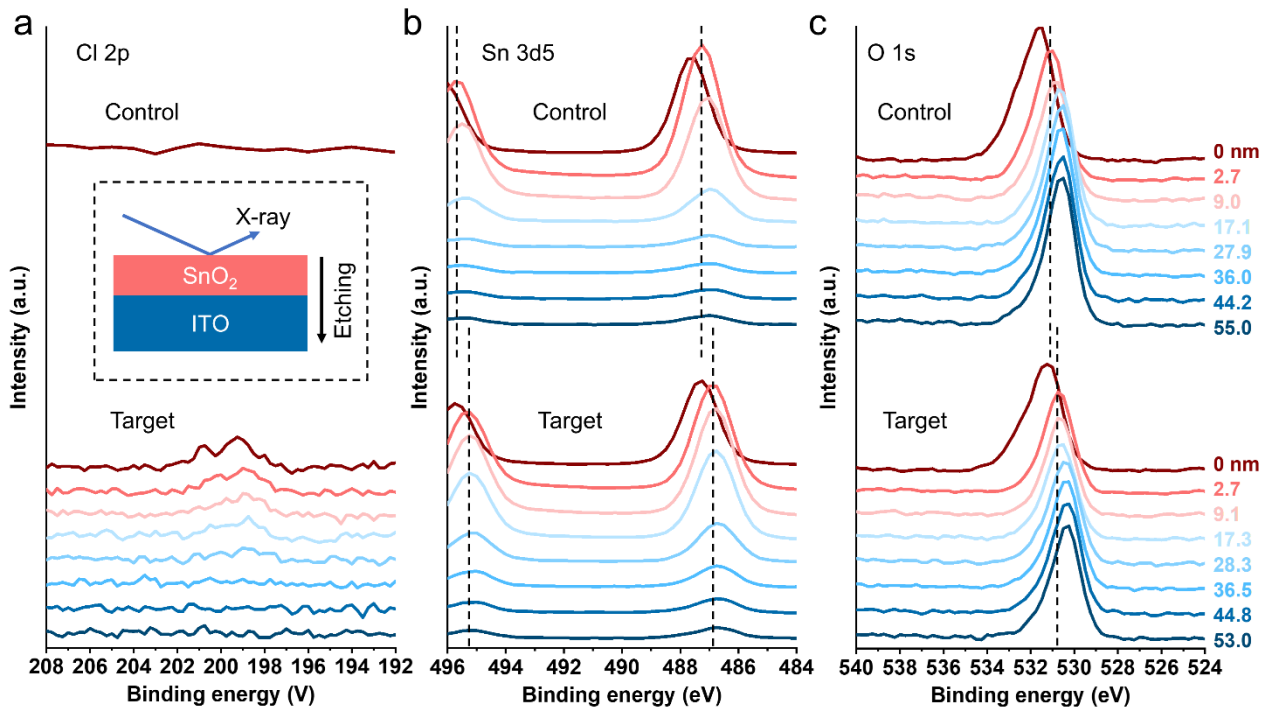


Figure 2. Depth-dependent XPS spectra of (a) Cl 2p, (b) Sn 3d5 and (c) O 1s in control and target Glass/ITO/SnO₂ samples.

Figure 2a-c shows the X-ray photoelectron spectroscopy (XPS) spectra of Cl 2p, Sn 3d5 and O 1s at different depths in control and target samples. There is no signal of Cl in the control sample, while an obvious signal of Cl 2p can be observed in the target sample (Figure 2a). When the etching depth reaches 36.5 nm, the chloride signal is obviously weakened, which approximately corresponds to the ITO/SnO₂ interface. When it comes to the XPS spectra of Sn and O elements (Figure 2b,c), the peak location on the surface layer is obviously different from that after etching for a period of time. It is because the surface is contaminated by CO₂, O₂, H₂O, etc. from air. Thus, the signal change after 15 s of etching (corresponding to etching depth of 2.7 nm) is mainly analyzed to avoid spurious signals. Sn 3d5 has a lower binding energy in the target sample, compared with the control sample (Figure 2b). Oxygen signal also shows a similar phenomenon, but the shift is much smaller (Figure 2c). Previous reports confirm that halogen ions, including F⁻, Cl⁻ and I⁻, can bond with tin ions due to their strong electronegativity.^[5-7,11] Given the results above, it is reasonable to speculate that the Cl⁻ ion in MDACl₂ interacts with the Sn⁴⁺ in tin dioxide, resulting in the obvious shift of the peak position of Sn elements.

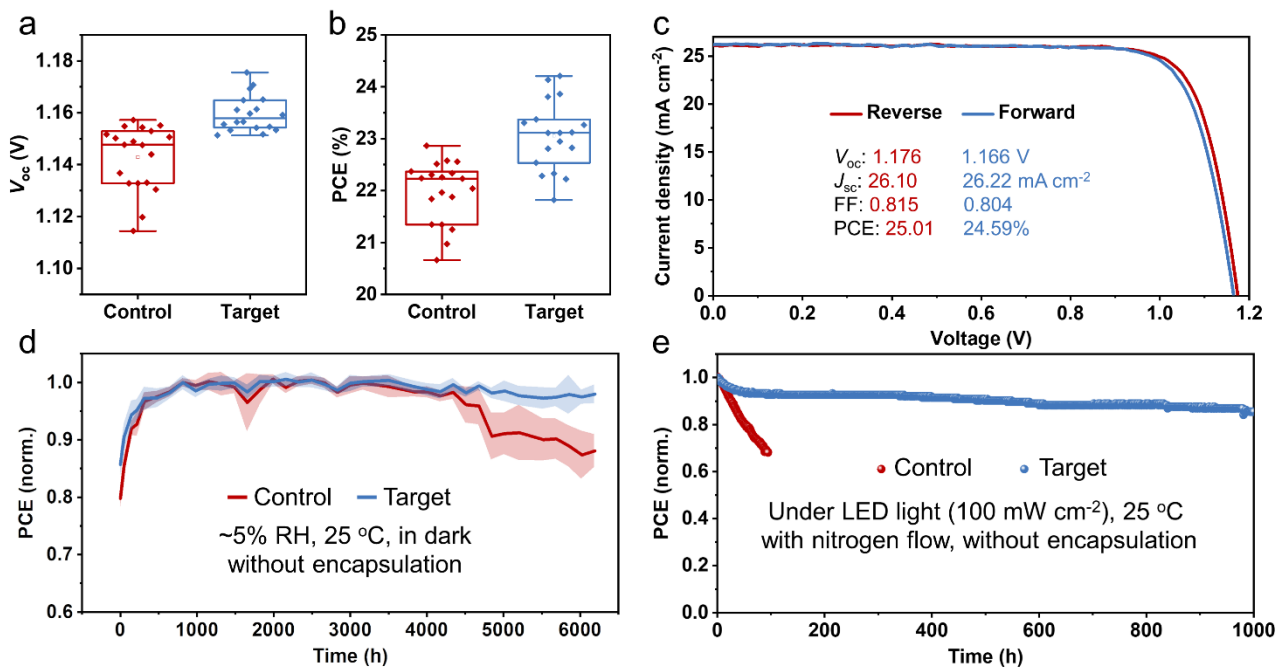


Figure 3. (a) V_{oc} , (b) PCE statistics of control and target PSCs; (c) $J-V$ curves of target PSCs with low bandgap (1.53 eV) perovskite; (d) long-term stability of the unencapsulated PSCs (5 cells for each condition) stored in dry air; (e) operational stability of the unencapsulated PSCs under LED light.

Based on the structure of Glass/ITO/SnO₂/Perovskite/Spiro-OMeTAD/Au, PSCs with and without SnO₂/MDACl₂ layers were fabricated, and statistical results of device performance are shown in Figure 3a,b. It is apparent that target PSCs show higher V_{oc} , leading to increased efficiencies. In contrast, short-circuit current density (J_{sc}) shows negligible difference between control and target cells. Low bandgap (1.53 eV) perovskite was also used to further improve the device performance and confirm whether the strategy is still applicable to other compositions of perovskite. As shown in Figure 3c, the champion cell with SnO₂/MDACl₂ layer presented the efficiency of 25.01% (reverse scan), and showed negligible hysteresis.

The long-term stability of the PSCs with slightly large bandgap (1.56 eV) perovskite is shown in Figure 3d. Target cells showed the average efficiency of 22.78% after storage of 6192 h in dry air (relative humidity of ~5% and ~25 °C), corresponding to 98% of the highest value. As shown in

Figure 3e, the target cell presented promising operational stability, retaining 85.50% of the initial PCE after 1000 h of illumination of white light-emitting diode (LED) light (100 mA cm^{-2}). We speculate that the improved stability is attributed to the reduced interfacial defects and stronger interaction between chloride ions and lead ions, which reinforces the interface between perovskite and SnO_2 . These results suggest that the structural and chemical crosslinking interface not only improves device performance but also enhances their stability.

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