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Supplementary Materials for

Redox mediator-modified self-assembled monolayer stabilizes buried

interface in efficient inverted Perovskite Solar Cells

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Methods

Materials

The materials used in this work have not undergone further purification and are primarily listed as follows: FTO glass substrate (Suzhou ShangYang); NiO_x nanoparticle powder (Shanghai Weizhu); Me-4PACz (TCI, >99.0%); Methylene Blue (Innochem, 98%); Pbl₂ (TCI, 99.999%); PbCl₂ (Alfa, 99.999%); DMF and DMSO (Sigma-Aldrich 99.9%); chlorobenzene (Sigma-Aldrich, 99.5%); isopropanol (Acros, 99.9%); FAI, MAI, MACI, CsI, PEACI, C₆₀, BCP (Xi'an Polymer Light Technology Corp).

Devic fabrication

For the fabrication of small-sized perovskite solar cells: FTO substrates were sequentially ultrasonically cleaned with a detergent, deionized water, ethanol, and again deionized water, each for 15 minutes. To fabricate the NiO_x layer, NiO_x nanoparticles were dissolved in deionized water at a concentration of 2 mg/mL, followed by spin coating at 4000 rpm for 30 s, and then annealed for 10 min. Subsequently, a Me-4PACz solution with a concentration of 0.35 mg/mL was spincoated onto the NiO_x layer at 4000 rpm for 30 s, followed by annealing for 10 min. For the oxide buffer layer, Methylene Blue (MB) was added to the SAM solution, with a mass ratio of MB to SAM of 1:4.5 (0.075 mg). For the perovskite film, a 1.5 M Cs_{0.05}FA_{0.85}MA_{0.1}PbI₃ solution was used, with a DMSO to DMF ratio of 1:4. Additionally, 10 mol% of MACI and 5 mol% of PbCl₂ were added. The solution was spin-coated at 1000 rpm for 10 s, followed by 5000 rpm for 40 s. During the last 5 s, 200 µL of CB was dripped, and the film was then annealed at 110°C for 20 min. Next, a passivation layer was spin-coated on the surface of the perovskite film using a 1 mg/mL PEACI solution, at 4000 rpm for 30 s, followed by annealing for 3 min. Finally, C60, BCP, and Ag were deposited by thermal evaporation with thicknesses of 15 nm, 7 nm, and 100 nm, respectively.

For the fabrication of 1 cm² perovskite solar cells: The FTO substrates were cleaned sequentially through ultrasonic treatment using a detergent, deionized water, ethanol, and a final rinse with deionized water, with each step lasting 15 minutes. To prepare the NiO_x layer, NiO_x nanoparticles were dispersed in deionized water at a concentration of 2 mg/mL, spin-coated at 5000 rpm for 30 s, and annealed for 10 minutes. A Me-4PACz solution (0.35 mg/mL) was then applied onto the NiO_x layer by spin coating at 5000 rpm for 30 s, followed by annealing for 10 minutes. For the oxide buffer layer, MB was mixed into the SAM solution, maintaining an MB-to-SAM mass ratio of 1:4.5 (0.075 mg). The perovskite film was prepared using a 1.5 M Cs0.05FA0.85MA0.1Pbl3 precursor solution, with a solvent ratio of DMSO to DMF set at 1:4. Additionally, 10 mol% MACl and 5 mol% PbCl₂ were added. The solution was spincoated in two steps: 1500 rpm for 10 s and 6000 rpm for 40 s, with 320 μ L of CB dripped during the final 5 s. The film was then annealed at 110°C for 20 minutes. A passivation layer was applied on the perovskite surface by spin-coating a 1 mg/mL PEACI solution at 5000 rpm for 30 s, followed by a 3-minute annealing step. Finally, C60, BCP, and Ag layers were thermally evaporated with thicknesses of 15 nm, 7 nm, and 100 nm, respectively.

Characterization

To verify the valence band changes of surface elements in the NiO_x layer and perovskite film, X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB 250Xi) characterization was employed. To investigate the valence band structure and work function of the NiO_x/SAM hybrid hole transport layer surface, ultraviolet photoelectron spectroscopy (UPS, Thermo Fisher Scientific ESCALAB 250Xi) characterization was employed. The optical properties of the film were obtained using UV-vis spectrophotometer (UV-2600) and PL equipment (FLS 980). Kelvin probe force microscopy (KPFM, FMNanoview 1000) equipped with PPP-EFM-10 probes (n⁺-silicon, PtIr-coated, resonance frequency 45–115 kHz, force constant 5–9.5 N/m, tip height 10–15 μ m) was employed to assess the surface potential of the films. Conducting

atomic force microscopy (C-AFM, FMNanoview 1,000) were employed to assess the surface potential and measure the contact current of the films. To investigate the smoothness and distribution of SAM on the NiOx layer, Nano-FTIR (neaspec) technology was employed. Scanning electron microscopy (SEM, Hitachi S-4800) and X-ray diffraction (XRD, D8 Advance, Bruker) characterization were utilized to investigate the surface morphology and crystallinity of the perovskite films. Photoluminescence (PL) mapping was performed using a Nikon-ARsiMP-LSM-Kit-Legend Elite-USX laser confocal fluorescence lifetime imaging microscope, with excitation provided by a 405 nm wavelength laser. The carrier behavior of perovskite films was obtained by time-resolved photoluminescence and photoluminescence quantum efficiency (TRPL, FLS980). The carrier dynamics of the perovskite films were analyzed using time-resolved photoluminescence (TRPL) measurements performed with the FLS980 system. Cyclic voltammetry (CV) measurements were conducted at room temperature using a standard three-electrode setup. A glassy carbon electrode served as the working electrode, a platinum wire was used as the counter electrode, and an Ag/AgCl electrode acted as the reference. A 0.1 M KCl aqueous solution was selected as the supporting electrolyte, and the scan rate was maintained at 0.01 V s⁻¹.

The device performance was tested using a Keithley 2400 source meter at a scan rate of 0.06 V/s under simulated AM 1.5 G sunlight conditions, with a mask area of 0.08 cm². The external quantum efficiency and integrated current of the perovskite solar cells were measured using QE-R systems from Enli Tech. The operational stability of the devices was monitored under LED illumination (AM 1.5 G) at a temperature of $50 \pm 5^{\circ}$ C inside an N₂-filled glovebox. For the temperature cycling aging test, we utilized a temperature and humidity chamber (PL-80-2C, LAB COMPANION LTD), with each cycle ranging from 25°C to 85°C and back to 25°C, and a humidity level of 25%.

Density functional theory calculations

All density functional theory (DFT) calculations were carried out using the Vienna Ab initio Simulation Package (VASP) ^[1-2]. The exchange-correlation interactions were modeled with the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) framework ^[3-4]. To represent the core-valence electron interactions, the projected augmented wave (PAW) method was employed ^[5]. A plane-wave energy cutoff of 400 eV was utilized, and the Brillouin zone was sampled using a $2\times2\times1$ Monkhorst-Pack k-point grid. The structural optimization was completed for energy and force convergence set at 1.0×10^{-4} eV and 0.05 eV Å⁻¹, respectively.

The adsorption energy (E_{ads}) is defined as:

$$E_{ads} = E_{complex} - E_{slab} - E_{cluster}$$

where slab and cluster refer to the metal surface and adsorbate molecule, respectively.



Supplementary Fig. 1. Schematic diagram of the molecular structure of methylene blue.



Supplementary Fig. 2. Schematic diagram of a device structure comprising fluorinedoped tin oxide (FTO) /NiOx/SAM (SAM with MB)/Cs_{0.05}FA_{0.85}MA_{0.1}PbI₃ (MA is Methylamine)/phenethylammonium chloride PEACI/C60/bathocuproine (BCP)/Ag.



Supplementary Fig. 3. Efficiencies of PSCs with different MB concentrations.

Supplementary Note S1: We added different amounts of MB into SAM solution, then characterized the efficiency of corresponding PSCs. When adding 0.075 mg MB into 1 mL SAM solution (0.35 mg/mL), corresponding to a molar ratio of 1:4.5, the PSCs reaches the maximum efficiency. Hence, we determined the optimal amounts of incorporated MB.



Supplementary Fig. 4. S 2p and P 2p spectra of the SAM with MB.



Supplementary Fig. 5. AFM images of the normal and target SAM. (a and b) The AFM images that are corresponding to the KPFM images shown in the main text. (c and d) The AFM images measured in another micro-region of normal and target SAM.



Supplementary Fig. 6. Schematic diagram of the testing mechanism of nano-FTIR.



Binding energy = -15.79 kcal/mol

Supplementary Fig. 7. DFT calculation of the interaction between MB and SAM.



Supplementary Fig. 8. Electrostatic potential of SAM.



Supplementary Fig. 9. Electrostatic potential of SAM with interacted MB.



Supplementary Fig. 10. Dynamic light scattering plots of SAM (Normal) and SAM with MB (Target).



Supplementary Fig. 11. Electrostatic potential of the methylene blue.



Supplementary Fig. 12. FTIR spectra of MB film and NiO_x/MB film.



Supplementary Fig. 13. Schematic diagram and operation images of a non-destructive method for uncovering the buried interface.



Supplementary Fig. 14. XPS spectra of the normal and target perovskite film (buried interface).



Supplementary Fig. 15. Efficiencies of PSCs with different MB concentrations in bulk perovskite film.



Supplementary Fig. 16. AFM image of the normal and target perovskite films.



Supplementary Fig. 17. GIWAXS images of the normal and target perovskite film.



Supplementary Fig. 18. Cross-sectional SEM images of perovskite films.



Supplementary Fig. 19. TPC and TPV decay curves of the normal and target devices.



Supplementary Fig. 20. Photograph of different NiO_x films.



Supplementary Fig. 21. Cyclic voltammetry curve of MB.



Supplementary Fig. 22. Pb 4f spectra of the normal and target (with MB) PbI_2 films.



Supplementary Fig. 23. Pb 4f spectra of the different PbI_2 films.



Supplementary Fig. 24. EIS spectra of Normal and Target PSCs measured in ambient air under dark conditions, with spectra collected over a frequency range of 0.1 Hz to 100 kHz.



Supplementary Fig. 25. Distribution histograms of the photovoltaic parameters of the 20 normal and target PSCs.



Supplementary Fig. 26. Peak ratio extracted from XRD spectra of the perovskite films.



Supplementary Fig. 27. The panel parameters of the thermal cycling aging test.

0.08 cm ²	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF (%)	PCE (%)		
Normal-R	25.46	1.174	81.54	24.37		
Normal-F	25.38	1.168	74.90	22.21		
Target-R	25.81	1.192	85.81	26.39		
Target-F	25.78	1.187	85.69	26.22		

Supplementary Table 1. The photovoltaic parameters for Normal and Target champion PSCs with an aperture area of 0.08 cm².

1 cm ²	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF (%)	PCE (%)
Normal-R	25.54	1.161	80.58	23.89
Normal-F	25.37	1.161	74.82	22.03
Target-R	25.64	1.182	82.12	24.89
Target-F	25.31	1.174	81.62	24.25
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Supplementary Table 2. The photovoltaic parameters for Target champion PSCs with an aperture area of 1 cm².

0.08 cm ²	J _{SC} (mA cm ⁻²)	V _{oc} (V)	FF (%)	PCE (%)
1	25.34	1.182	81.91	24.53
2	25.58	1.174	82.02	24.63
3	25.89	1.174	80.16	24.36
4	25.23	1.182	82.75	24.67
5	25.66	1.174	81.57	24.56
6	25.19	1.174	82.87	24.50
7	25.51	1.187	79.66	24.12
8	25.16	1.187	81.04	24.20
9	25.73	1.174	80.13	24.20
10	25.54	1.182	79.82	24.10
10	25.54	1.182	79.82	24.10

Supplementary Table 3. The photovoltaic parameters for 10 Target PSCs with an aperture area of 1cm².

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