

Suppressing Nickel Oxide/Perovskite Interface Redox Reaction and Defects for Highly Performed and Stable Inverted Perovskite Solar Cells

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The inorganic hole transport layer of nickel oxide (NiO_x) has shown highly efficient, low-cost, and scalable in perovskite photovoltaics. However, redox reactions at the interface between NiO_x and perovskites limit their commercialization. In this study, ABABr (4-(2-Aminoethyl) benzoic acid bromide) between the NiO_x and different perovskite layers to address the issues has been introduced. How the ABABr interacts with NiO_x and perovskites is experimentally and theoretically investigated. These results show that the ABABr molecule chemically reacts with the NiO_x via electrostatic attraction on one side, whereas on the other side, it forms a strong hydrogen bond via the NH_3^+ group with perovskites layers, thus directly diminishing the redox reaction between the NiO_x and perovskites layers and passivating the layer surfaces. Additionally, the ABABr interface modification leads to significant improvements in perovskite film morphology, crystallization, and band alignment. The perovskites solar cells (PSCs) based on an ABABr interface modification show power conversion efficiency (PCE) improvement by over 13% and maintain over 90% of its PCE after continuous operation at maximum power point for over 500 h. The work not only contributes to the development of novel interlayers for stable PSCs but also to the understanding of how to prevent interface redox reactions.

1. Introduction

Inverted PSCs with a p-i-n structure possess the advantages of low-temperature facile fabrication, low cost, and high stability compared to conventional PSCs.^[1–5] The commonly used hole

transport layer (HTL) including poly(3,4-ethylenedioxythiophene polystyrenesulfonate (PEDOT:PSS),^[6] poly(triarylamine) (PTAA),^[7,8] NiO_x ,^[9,10] CuO_x ,^[11] and CuSCN ^[12] are critical for high-performance devices, due to their advantages of excellent stability, high hole mobility and low cost.^[11] Among the inorganic HTL, NiO_x is one of the most effective inorganic p-type semiconductors for high-performance PSCs due to the advantages of suitable work function, high charge carrier mobility, easy synthesis process, low cost, and room temperature film formation.^[13–16] To further improve the electrical properties of NiO_x HTL and perovskite film quality on it, extensive research works including p-type doping and surface treatment have been conducted.^[15] For example, the dopants such as Cs,^[16] Cu,^[17,18] Li,^[19] Mg,^[20] Co,^[21] and Sr,^[22] Cr/CuGaO₂-CC composite,^[23] and doubled doping^[24] have been incorporated into the NiO_x to improve conductivity

and tune work function for better energy alignment. Besides, the post-surface modification by functional molecules, polymers, and inorganic salts improves the perovskite crystallinity, facilitates charge extraction, and inhibits surface recombination.^[25–28] For example, Ning's group observed the structural disorder resulting from the lattice mismatch of perovskites and NiO_x by molecular dynamic simulation.^[25] A secondary amine is introduced into the perovskites for better lattice match, thus reducing the interface disorder and defects density.^[29,30]

One of the challenges to further improving the performance of NiO_x -based inverted PSCs is the reactions between NiO_x and perovskites. McGehee et al. studied the redox reactions between NiO_x and perovskite by Ultraviolet photoelectron spectroscopy

(UPS) and X-ray photoelectron spectroscopy (XPS) characterizations. A simple method by incorporating excess A-site cations into the precursor solutions was demonstrated for preventing the formation of a $\text{PbI}_{2-x}\text{Br}_x$ layer.^[31] However, the excess A side cations cannot likely prevent the interface redox reaction because the NiO_x and perovskite chemical state at the bottom interface does not change. Hence, it is necessary to develop effective methods to suppress the interface reactions and improve the interface and thus device stability.

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In this work, the 4-(2-Aminoethyl) benzoic acid hydrobromide (ABABr) is proposed and introduced between a perovskite film and NiO_x HTL to defeat the redox reaction between the two layers through establishing chemical interactions and defects passivation. Our results indicate that NiO_x interface redox reactions are significantly diminished by the ABABr interlayer. We find that the ABABr molecule chemically reacts via electrostatic attraction on its one side with the NiO_x layer, while on its other, it formed hydrogen bonds via its NH_3^+ group with the perovskites layer, therefore diminishing the redox reaction between the NiO_x and perovskites layer and passivating the surfaces of both layers. Additionally, we investigate that the ABABr interface modification also results in improved perovskite crystallization, energy band alignment and thus improve device performance. PSCs with the ABABr interlayer modification on different perovskite including MA, FAcS, and FAMACs have been fabricated. Our results show that PCE improved over 13% as compared to the reference one and keep over 90% of its original PCEs over 500 hours of continuous operation at maximum power point (MPP) under one sun illumination. Our work not only contributes to highly performed and stable devices but also provides more insights on preventing interface redox reactions.

2. Results and Discussion

The interlayer fabrication method for ABABr is illustrated in Figure 1. The ABABr salt was prepared by reacting equimolar of ABA ((4-(2-Aminoethyl) benzoic acid) with HBr, (see details in the experimental section). Similar to our previous work^[9,10] first NiO_x layer was deposited. ABABr solution (2.5 mg mL⁻¹, 5 mg mL⁻¹, 7.5 mg mL⁻¹, 10 mg mL⁻¹ and 12.5 mg mL⁻¹) is deposited on top of NiO_x film, and

annealed at 100 °C for 10 min. The 3D perovskite film of $\text{Cs}_{0.05}(\text{MA}_{0.15}\text{FA}_{0.85})_{0.95}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ (CsFAMA) with excess PbI_2 was fabricated by one-step spin-coating anti-solvent assisted deposition method as described in details in the experimental section.

The NiO_x interface redox reaction with perovskite has been reported to cause challenging issues in destroying device stability.^[31,32] The reactions mainly involve



To inhibit redox reactions at the interface and improve interface stability a thin ABABr layer is introduced on top of NiO_x . A novel interaction between the home-synthesized ABABr molecule and NiO_x as well as between the ABABr molecule and perovskites is proposed, including the electrostatic attraction between the carboxylic acids of ABABr and NiO_x , and the formation of an ammonium bridge via hydrogen bond between NiO_x and perovskites, prohibiting NiO_x /perovskite surface reactions. Additionally, the amine can also enhance the stabilization of iodide ions and thus further protect NiO_x interfaces.

To confirm the improved interface stability from inherent redox reactions, we conduct XPS measurements of the as-deposited and aged NiO_x film, NiO_x /ABABr film, and studied the ion states of Ni. Figure S1, Supporting Information, illustrates the XPS sample preparation process. On two different substrates, e.g., ITO/ NiO_x (reference sample) and ITO/ NiO_x /ABABr the CsFAMA perovskites film was fabricated and then aged for one week under 1 Sun continuous illumination in the ambient environment. In the next step, the perovskite films are washed with DMF in order to expose the aged NiO_x film for XPS measurement. We determine the Ni^{3+} and Ni^{2+} ratio from the integrated area of each peak to compare the stability of NiO_x films, as shown in Figure 2a–d.

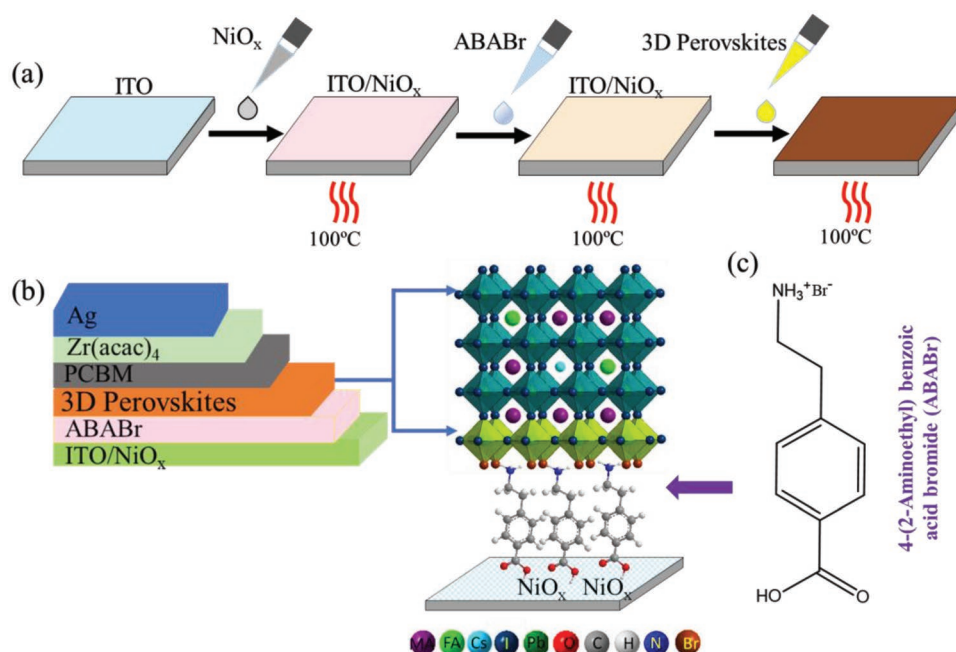


Figure 1. a) Procedure for the fabricating of ABABr interlayer. b) Schematic illustration of the 3D perovskites (CsFAMA) with ABABr interlayer and device architecture. c) Chemical structure of ABABr salt.

For the reference sample, the $\text{Ni}^{3+}:\text{Ni}^{2+}$ of the NiO_x film significantly change from 1.85 for the as-deposited sample to 1.31 for the aged sample. For the ABABr incorporated sample, the ratio of NiO_x film only slightly changes from 1.91 (as deposited) to 1.80 (aged). The results clearly show that much more Ni^{3+} ions are retained for the ABABr incorporated sample. Consequently, by the approach of inserting the ABABr interfacial layer, we considerably minimize the redox reactions and make the NiO_x interface more stable.

In order to further understand the mechanism of suppression of ABABr, we experimentally and theoretically investigate its interactions with NiO_x and perovskites. We measure Fourier Transform Infrared (FTIR) spectroscopy to study the interaction between the NiO_x and ABABr. Figure 2e,f, shows

that the ABABr has the $\text{C}=\text{O}$ peak at 1706 cm^{-1} while pure NiO_x does not have a $\text{C}=\text{O}$ peak. On the other hand, after spin coating ABABr on top of NiO_x film, the $\text{C}=\text{O}$ peak shifts to 1724 cm^{-1} , an indication of the electrostatic interaction between NiO_x and COOH of ABABr. The ammonium group can interact with the perovskites via a hydrogen bond, which is widely discussed.^[33,34] We also conduct additional theoretical calculations to confirm our hypotheses and to better understand ABABr's interaction with NiO_x and perovskites. Figure 2f,g shows the theoretically calculated surface structure of $\text{NiO}_x/\text{ABABr}$ interface and perovskites/ABABr interface, whereas Figure 2h,i shows the corresponding differential charge density distributions, respectively. The calculated binding energy of Ni^{2+} from NiO and $-\text{COO}-$ from ABABr at

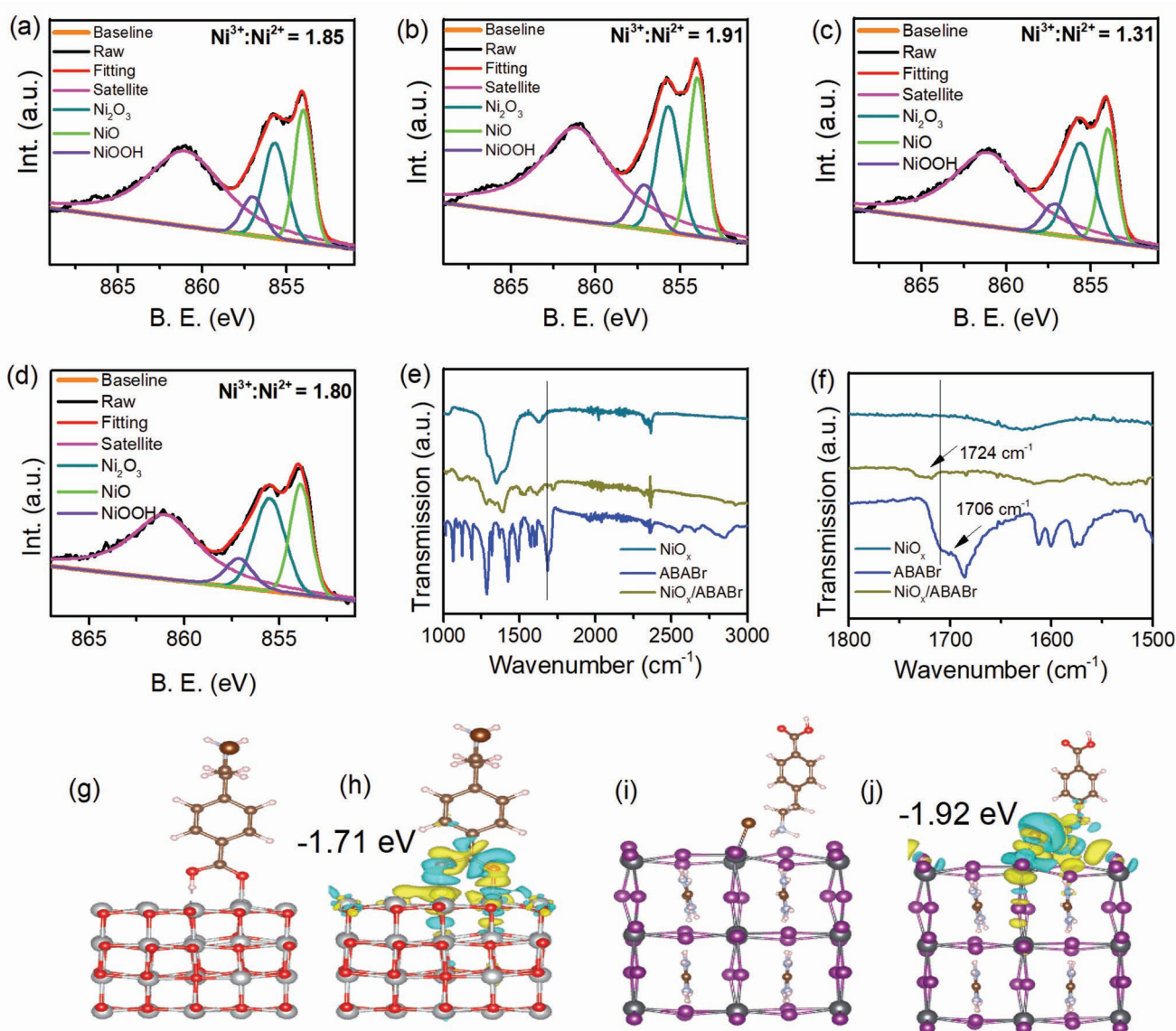


Figure 2. XPS spectra of ITO/NiO_x and $\text{ITO}/\text{NiO}_x/\text{ABABr}$ films a,b) as-deposited and c,d) aged. e,f) FTIR spectra of NiO_x , ABABr, and $\text{NiO}_x/\text{ABABr}$. The g) optimized surface structure and h) differential charge density distribution of the $\text{NiO}_x/\text{ABABr}$ interface. The i) optimized surface structure and j) differential charge density distribution of the perovskites/ABABr interface.

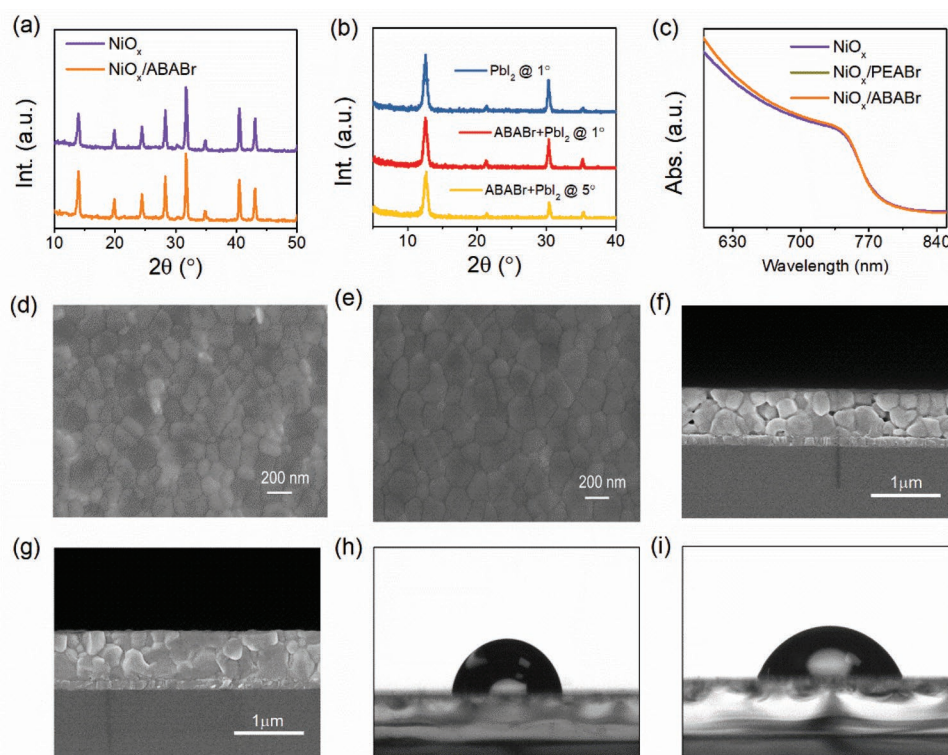


Figure 3. a) GIXRD spectra of perovskite on NiO_x and NiO_x/ABABr and b) PbI₂ on NiO_x and NiO_x/ABABr. c) The absorbance of perovskite films deposited on NiO_x and NiO_x/ABABr. Top view SEM images of perovskites deposited on d) NiO_x film and e) on NiO_x/ABABr. Cross-section SEM images of perovskite film deposited on f) NiO_x and g) on NiO_x/ABABr film. The contact angle of h) NiO_x film and i) NiO_x/ABABr film.

the NiO_x/ABABr interface is -1.71 eV and the binding energy of Pb from perovskites and ammonium from ABABr at perovskites/ABABr interface is -1.92 eV, indicating the strong interactions between NiO_x/ABABr/perovskites interface, which is in accordance with the experiment result. The results indicate the electrostatic attraction between ABABr and NiO_x and hydrogen bond between NH₃⁺ groups and perovskites layers.

We also note that the ABABr interlayer significantly improves the crystallinity of perovskite films. The grazing incidence X-ray diffraction (GIXRD) is conducted to study the film crystallinity. According to the GIXRD spectra shown in Figure 3a, the (001) peak at 14.0° is improved quantitatively, indicating improved crystallinity. The optical properties of the perovskite films deposited on NiO_x and NiO_x/ABABr are studied by measuring their absorbance (Figure 3c). We find that ABABr treatment increases the absorption of perovskite films, which is may be due to improved crystallinity on NiO_x.

The top view and cross-section view scanning electron microscope (SEM) of perovskite film on the top of NiO_x and NiO_x/ABABr are presented in Figure 3d–g. It can be seen that the crystal grain size of perovskites is significantly increased from 150 nm for the reference sample to over 200 nm for the target on the top of NiO_x/ABABr. Additionally, the perovskite grains became much more compact and enlarge without any pinholes. These results suggest that ABABr incorporation not only passivates NiO_x surface, but also increases the grain size, passivates perovskites grain boundaries,

reducing trap states at the interface, and thus facilitating carrier extraction by forming a closely contacted interfaces.^[35,36] Therefore, the ABABr on NiO_x is also good for high-quality perovskite films.

Furthermore, we also measured the water contact angle of NiO_x and NiO_x/ABABr films (Figure 3h,i). The reduced contact angle can release the surface tension and help the precursor spread evenly for crystal grain formation. Also, the reduced water contact angle indicates the possible bonding between ABABr and NiO_x. It should be noted that we spin-coat PbI₂ on the ABABr film and then measured its GIXRD to see if any 2D perovskite phase is formed. The result from Figure 3b shows that there is no new peak in comparison with the pure PbI₂. Even after changing the GIXRD incidence angle from 1.0° to 0.5° to reduce the penetration depth, there is still no new 2D peak. In light of this, whether there will be a 2D phase remains an open question.^[37,38]

In addition, the alignment of the energy bands between the light absorber and charge transport layer plays a crucial role in the extraction/transfer of photoinduced carriers. Therefore, ultraviolet photoelectron spectroscopy (UPS) is performed to assess the energy levels of perovskites film fabricated on NiO_x and NiO_x/ABABr (Figure S3, Supporting Information). It can be seen from Figure 4a, that after ABABr modification, the HOMO levels of perovskites become deeper, which provide more driving force for hole injection to the hole transport material (HTM) and this in turn leads to the highest V_{oc} for devices.^[39–42] Their LUMO levels were calculated according to

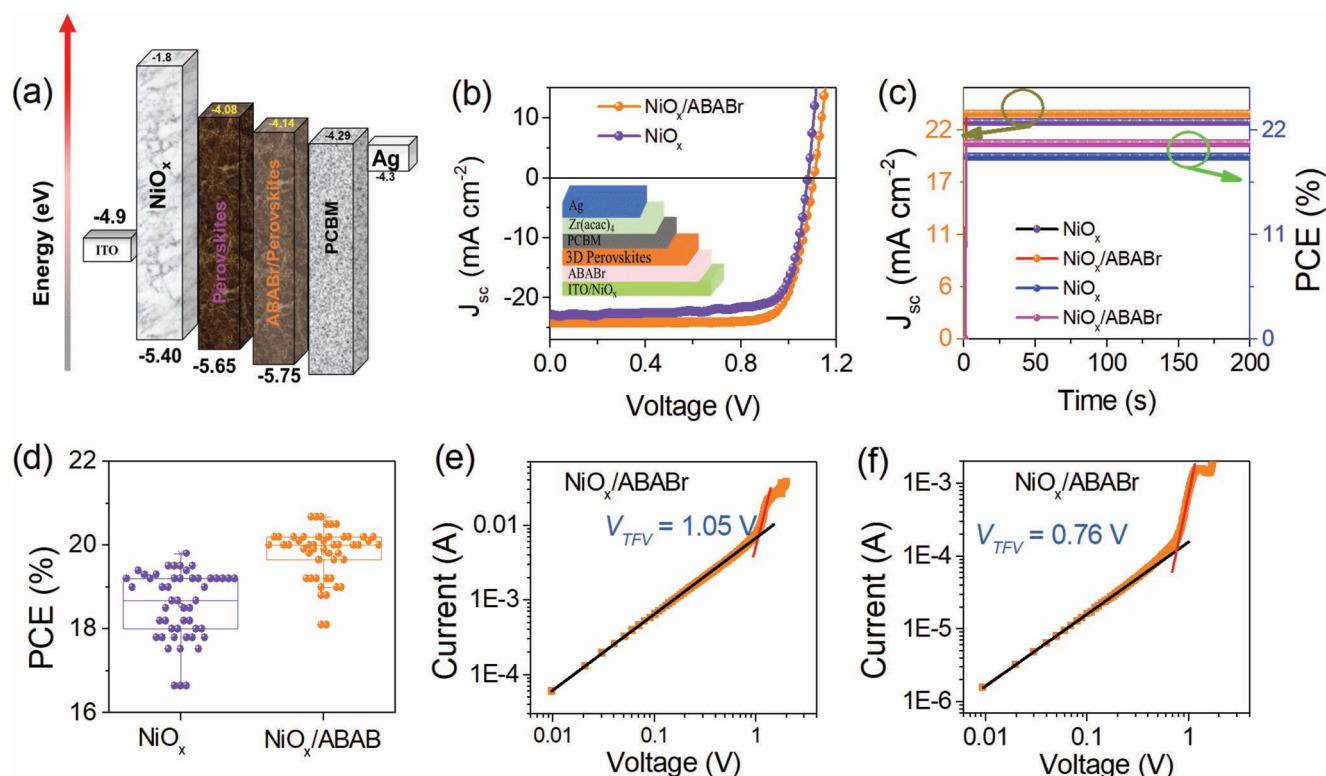


Figure 4. a) Energy level diagram. b) J - V curves of CsFAMA-based perovskite device deposited on NiO_x and $\text{NiO}_x/\text{ABABr}$. The inset shows the device structure fabricated in this work. c) Stabilized PCE and J_{sc} of ABABr treated and untreated devices. d) Statistical PCE distributions of 50 devices with and without ABABr treated. SCLC curve of perovskite devices deposited on e) NiO_x and f) $\text{NiO}_x/\text{ABABr}$.

HOMO levels and bandgaps obtained from onsets of UV-Vis absorptions spectra. The LUMO of perovskites films fabricated on $\text{NiO}_x/\text{ABABr}$ match better with the electron transport layer (ETL) than that on NiO_x alone, which is beneficial for electron extraction and transport.^[38,43,44]

The PSCs devices with a structure of ITO/NiO_x (with or without ABABr)/perovskites/PCBM/ $\text{Zr}(\text{acac})_4$ /Ag are fabricated (Figure 4b inset). The J - V curve is shown in Figure 4b and the characteristic device performance parameters are summarized in Table S1, Supporting Information. The J_{sc} , V_{oc} , and FF for triple-cations CsFAMA perovskite composition are increase from 22.80 mA cm^{-2} , 1.081 V , and 77.5% to 24.17 mA cm^{-2} , 1.106 V , and 79.52% , respectively. Resultingly, the PCE is improved from 19.21% to 21.27% . We also fabricate CsFA-based devices with an MA-free perovskite composition to confirm the general function of ABAB treatment. The corresponding J - V curve and characteristic parameters are shown in Figure S2 and Table S1, Supporting Information, respectively. The MA-free perovskite device also shows an improvement in J_{sc} , V_{oc} , and FF, achieving a high PCE from 17.35% to 18.75% . Therefore, we believe that our method is effective for both triple cations and MA-free perovskite compositions.

We have also studied the trap state density of the devices based on NiO_x and $\text{NiO}_x/\text{ABABr}$. We fabricate hole-only devices with a structure of ITO/NiO_x (with/without ABABr)/perovskite/PTAA/Ag, and measure the J - V curve under dark, as shown in Figure 4e,f. Based on the space charge limited current (SCLC) method, the fitted red line with a slope of $n = 1$ represents the ohmic region, and the fitted green line

represents a trap-filled limited region ($n > 2$). The defects density (n_t) can be calculated by

$$n_t = 2\epsilon_r\epsilon_0 V_{TFL} / (eL) \quad (2)$$

where L is the thickness of perovskite film, ϵ_0 is the vacuum permittivity, ϵ_r is the relative dielectric constant of perovskite, and V_{TFL} is trap-filled limit voltage. By applying the ABABr modification to NiO_x , the V_{TFL} is reduced from 1.05 V to 0.76 V , implying reduced electronic disorder in a film due to a decrease in the density of trap states, in good agreement with improved crystallinity and a substantial improvement in the device's performance.

We tested device operational stability over time with and without ABABr interface modifications, under 1 sun illumination at maximum power point tracking. From Figure 5a, it is evident that the ABABr interface modification contribute significantly to the operational stability of devices. After 500 h of continuous operation, we found that ABABr-treated devices retained over 90% of their original PCE. By contrast, devices not treated with ABABr retain only 50% of their original PCE.

Regarding device stability, we have also studied the change of the PSCs with time from the analysis of the J - V curves. The J - V curves of CsFAMA perovskite devices deposited on NiO_x and $\text{NiO}_x/\text{ABABr}$ under continuous illumination in an ambient environment after 0, 72 h, and 168 h without encapsulation are shown in Figure 5b,c. The J - V curves of the control device show significant series resistance and rapidly decreasing J_{sc} , which indicate that charge extraction is seriously hindered.

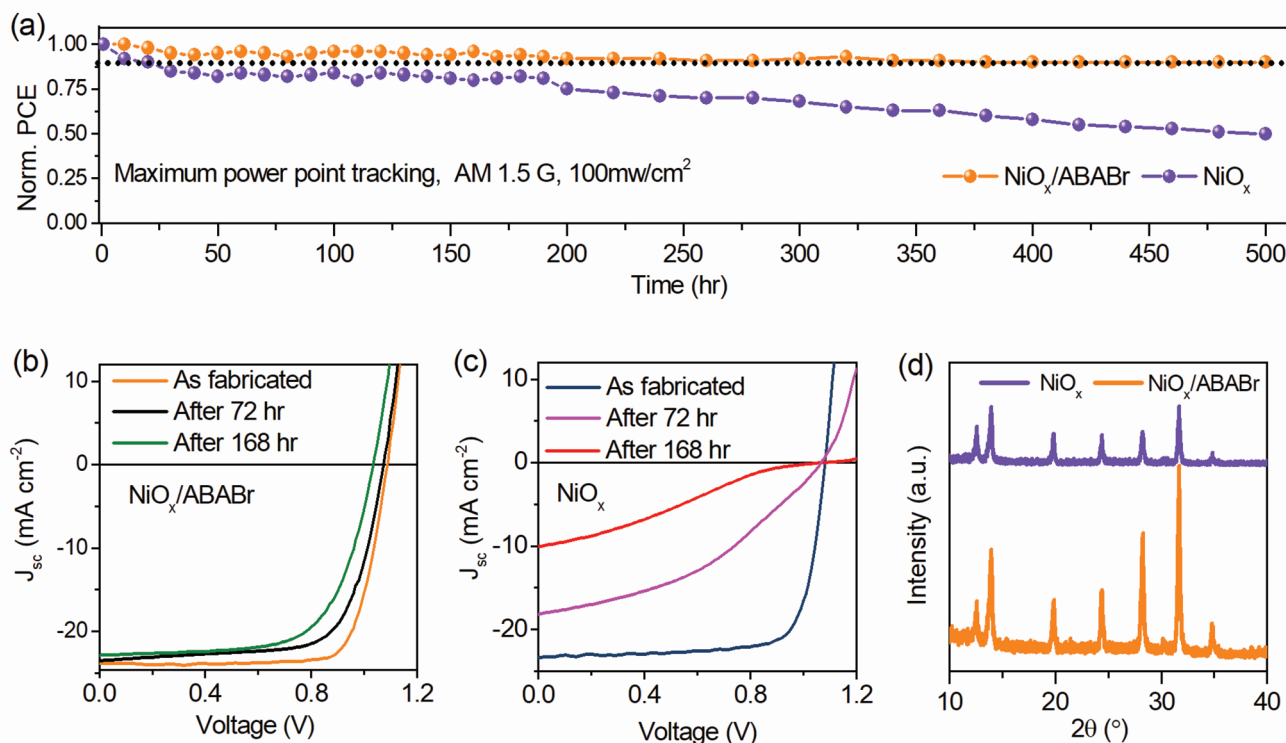


Figure 5. a) MPP tracking to compare the stability of ABABr treated device with the untreated device. J - V curves of CsFAMA perovskite device deposited on b) NiO_x/ABABr and c) NiO_x under continuous illumination after 0, 72, and 168 h. d) XRD patterns of perovskite films under continuous illumination after 168 h.

However, after ABABr modification, the PCE and J_{sc} degradation are reduced, with the “S” shape disappearing after continuous illumination, showing that ABABr-modified devices have effective charge extraction. Therefore, the ABABr modification layer is effective in improving perovskite film and device stability by inhibiting interface redox reactions.

Figure 5d shows that the XRD of the perovskite films under continuous illumination after 168 h is used to further confirm the film stability. In order to determine the degradation level, we calculated the ratio between the (001) peak at 13.97° and the PbI₂ peak at 12.61°. The ratio for degraded perovskite film on NiO_x is 1.58, while for the perovskite film on NiO_x/ABABr is 2.38, indicating an improvement in interface stability after ABABr modification.

3. Conclusion

In summary, we develop a novel interlayer of ABABr to overcome redox reactions at NiO_x surfaces. XRD, SEM, and UPS measurements have also revealed improved crystallinity in perovskites as well as improved energy level alignment. By utilizing ABABr as an interface layer, we demonstrate that this strategy is applicable to multiple types of NiO_x and different perovskite layers. We find that, on one side, the ABABr molecule forms electrostatic attraction with the NiO_x layer, and on the other side, it forms hydrogen bonds via the NH₃⁺ group with the perovskites layer, thus diminishing the redox reaction in the NiO_x and perovskites

layer and protecting both of them. With the incorporation of ABABr to the interface, PSCs reach PCE of 21.27%. In addition, the device stability is significantly improved after suppressing the redox reaction at the interface between NiO_x and perovskites with ABABr and maintains over 90% of the original PCE after 500 hr continuous operation at maximum power under 1 sun illumination. This work provides a new pathway for improving the performance and stability of NiO_x-based PSCs.

4. Experimental Section

Materials: Lead (II) iodide (PbI₂, 99%), Lead (II) bromide (PbBr₂, 99%) and Cesium iodide (CsI) were purchased from TCI. Methylammonium bromide (MABr), formamidine iodide (FAI) were purchased from Dyesol. Dimethyl sulfoxide (DMSO, extra dry, 99%), *N,N*-Dimethylformamide (DMF, extra dry, 99%), isopropyl alcohol (IPA), Chlorobenzene (CB, extra dry, 99.8%) were purchased from Acros. PCBM was purchased from Solarmer Energy, Inc. 4-(2-Aminoethyl) benzoic acid (ABA, 97%), HBr (48% wt in H₂O), and Zirconium (IV) acetylacetonate (ZrAcac, 98%) were purchased from Sigma-Aldrich. NiO_x nanoparticles inks were prepared according to the previous reports.^[9,10]

ABABr Salt Synthesis: Regarding ABABr, is synthesized similarly to the previous report. Simply 5 mmol 4-(2- aminoethyl) benzoic acid was added into 10 mL deionized water, then 0.68 mL HBr aqueous solution was added dropwise. After stirring for 2 h at 0 °C, the precipitate was obtained by rotary evaporation, washed several times with ethanol and ether, and finally dried in an oven at 60 °C for 12 h to obtain ABABr powder.

Device Fabrication: Cs_{0.05}(MA_{0.15}FA_{0.85})_{0.95}Pb(I_{0.85}Br_{0.15}) and Cs_{0.1}FA_{0.9}PbI₃ perovskite precursors were dissolved in the mixed solvent of DMF and DMSO with a volume ratio of 8:2. The precursors were

then filtered by a 0.2 μm PTFE syringe filter before use. Patterned ITO-coated glasses were washed with detergent, deionized water, acetone, and ethanol with ultra-sonication 15 min each and dried by a nitrogen gas flow. Then the ITO glasses were treated by ultraviolet ozone for 20 min. Next, 50 μL NiO_x (20 mg mL^{-1} in deionized water) was spin-coated on ITO glass at 2500 rpm for 50 s. The ABABr in IPA with different concentrations is deposited on the NiO_x film at 3000 rpm for 40 s and then annealed at 100 $^\circ\text{C}$ for 10 min. After transferring substrates with NiO_x film into the nitrogen-filled glovebox, the mixed perovskite precursor was spin-coated on top of the NiO_x layer at 1000 rpm for 6 s and 4000 rpm for 30 s, and 150 μL of chlorobenzene was dropped onto the spinning samples at the 20 s of the second step to form a brown film. Then the film was annealed at 100 $^\circ\text{C}$ for 60 min. Next, 20 mg mL^{-1} PC61BM in chlorobenzene was spin-coated on the perovskite surface at 2000 rpm for 40 s, followed by spin-coating zirconium (IV) acetylacetonate ($\text{Zr}(\text{acac})_4$) (2 mg mL^{-1} in isopropanol) at 4000 rpm for the 40 s. Finally, the 120 nm Ag electrode was thermally evaporated on top of the device under a vacuum of 2×10^{-6} Torr in the high-vacuum deposition system with a device area of 0.0725 cm^2 .

Measurements and Characterizations: Simulated AM 1.5 sunlight was generated by an Abet Class AAB AM 1.5G solar simulator. The light intensity (100 mW cm^{-2}) was calibrated by an ISO 17025- certified KG3-filtered silicon reference cell. The J - V curve was recorded by a Keithley 2635 source meter. UV-vis absorption spectra were obtained from a UV-vis spectrometer (Perkin Elmer Lambda 750). The continuous light illumination stability characterization was measured with Keithley 2635 with white LED as the light source. Scanning electron microscope images were recorded by a Hitachi S4800 FEG Scanning Electron Microscope. GIXRD measurements were performed by Bruker D8. X-ray photoemission spectroscopies were performed with a Kratos AXIS UltraDLD ultrahigh vacuum (UHV) surface analysis system. XPS measurements were performed to characterize the elemental constituents using a monochromatic Al $K\alpha$ X-ray gun (1486.6 eV) with a total instrumental energy resolution of 500 meV.

Computational Method: The theoretical calculation by the Vienna ab initio Simulation Package (VASP) code was conducted.^[45,46] To calculate the exchange-correlation functional of electrons, the Perdew-Burke-Ernzerh (PBE) functional of the generalized gradient approximation (GGA) was adopted.^[47,48] The perovskite surface slab model with a vacuum layer of 20 Å was assembled dependent on the cubic-phased $2 \times 2 \times 2$ supercells. The NiO surface slab model with a vacuum layer of 20 Å was assembled based on the cubic-phased $2 \times 2 \times 2$ supercells. A cutoff energy of 400 eV for the plane wave expansion was utilized. The energy convergence of 1.0×10^{-5} eV and the Γ -centered k -point mesh of $2 \times 2 \times 1$ were adopted, and the force on all atoms was less than 0.05 eV Å $^{-1}$. The binding energy (E_b) is defined as

$$E_b = E_{\text{total}} - E_{\text{PVK}} - E_{\text{molecule}} \quad (3)$$

where E_{total} is the total energy of the slab after the perovskite-molecule interactions, E_{PVK} and E_{molecule} are the energy of the perovskites and the molecules before interaction, respectively. The difference charge density distribution is defined as $\Delta\rho = \rho_{\text{total}} - \rho_{\text{PVK}} - \rho_{\text{molecule}}$, where ρ_{total} is the total charge density of the slab after the perovskite-molecule interactions, ρ_{PVK} and ρ_{molecule} are the charge densities of the perovskites and the molecules before interactions, respectively.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

4-(2-Aminoethyl) benzoic acid bromide, interface modifications, NiO_x redox reaction, stability

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