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Surface Reconstruction of Halide Perovskites During Post-treatment

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**ABSTRACT:** Postfabrication surface treatment strategies have been instrumental to the stability and performance improvements of halide perovskite photovoltaics in recent years. However, a consensus understanding of the complex reconstruction processes occurring at the surface is still lacking. Here, we combined complementary surface-sensitive and depth-resolved techniques to investigate the mechanistic reconstruction of the perovskite surface at the microscale level. We observed a reconstruction toward a more PbI$_2$-rich top surface induced by the commonly used solvent isopropyl alcohol (IPA). We discuss several implications of this reconstruction on the surface thermodynamics and energetics. Particularly, our observations suggest that IPA assists in the adsorption process of organic ammonium salts to the surface to enhance their defect passivation effects.

The record performance of single-junction halide perovskite solar cells (PSCs) has now exceeded 25%. Important breakthroughs in defect passivation strategies have contributed to rapid performance improvements in recent years. However, achievable voltage losses are still short of the theoretical limit. More importantly, it has become apparent that the migration and redistribution of charged point defects by a potential gradient is known to underlie the operational instability of PSCs. This has motivated the development of surface passivation strategies by post-treatment of the perovskite surface. Significant instability of PSCs, by a potential gradient is known to underlie the operational instability of PSCs. This has motivated the development of surface passivation strategies by post-treatment of the perovskite surface. Significantly, IPA remains perhaps a crucial solvent for post-treatment, since the most common surface passivating agents, such as phenylethylammonium iodide (PEAI) and octylammonium iodide (OAI), are essentially insoluble in low-polarity solvents such as chloroform (CF) (Figure S1).

The control perovskite is based on an FAPbI$_3$ composition with 5 mol % of added MAPbBr$_3$. We monitored the photoluminescence (PL) of an as-fabricated perovskite film in situ with a 405 nm excitation wavelength (Figure 1a) in a nitrogen glovebox (<0.5 ppm of O$_2$/H$_2$O). The laser penetration depth was estimated to be 50 nm (Figure S2) and, therefore, was sensitive to any potential changes in the surface charge carrier recombination behavior. The PL intensity abruptly decreased with a broadening and redshifting of the PL peak upon dropping IPA (Figure 1b,c, Figure S3a). In general, this is indicative of increased nonradiative carrier recombination, which implies the generation of charge-trapping defect states. Time-resolved PL (Figure S3b) of the perovskite films further supports this, where the carrier lifetime...
decreased from 1021 to 793 ns for the control and treated films, respectively. The PL intensity is observed to gradually recover with time, possibly due to trap-filling by photo-generated carriers, as also seen in the control film without treatment (Figure S3c,d).

We further investigated the distribution and nature of the generated defects using positron annihilation spectroscopy (PAS). Positrons are implanted from the film surface and annihilate with electrons after trapping at negatively charged (or neutral) defects to emit two γ photons. The incident kinetic energy is controlled to vary the positron implantation depth (Figure 1d, Figure S4), from which the depth-resolved defect density of the film can be investigated. The treated film had a higher shape parameter within ∼40 nm from the film surface, implying the generation of negatively charged (or neutral) defects at the top surface region. We speculate that the formed defect is possibly an FA vacancy (VFA′), given the solubility of FAI in IPA.

The implied existence of VFA′ suggests that an iodine vacancy (VI) was likely generated concurrently, but PAS is unable to...
We therefore further probed the films with high-resolution X-ray photoelectron spectroscopy (XPS), with an estimated penetration depth 5–10 nm. The I:Pb ratio, calculated from the integrated areas of the Pb 4f doublet and I 3d peak (Figure 2a), was 2.45 for the control film and decreased to 2.04 for the treated film to approach that of stoichiometric PbI2. We note that the ultra-high-vacuum environment of the XPS instrument (∼10−7–10−8 Torr) may have accelerated the outgassing of the volatile halide,20,21 and therefore, only relative comparisons would be reliable. Closer inspection of the XPS spectra further showed that the Pb 4f5/2 (143.19 to 143.13 eV), Pb 4f7/2 (138.32 to 138.25 eV), and I 3d5/2 peak (Figure 2a), was 2.45 for the control film and decreased to 2.04 for the treated film to approach that of stoichiometric PbI2. We note that the ultra-high-vacuum environment of the XPS instrument (∼10−7–10−8 Torr) may have accelerated the outgassing of the volatile halide,20,21 and therefore, only relative comparisons would be reliable. Closer inspection of the XPS spectra further showed that the Pb 4f5/2 (143.19 to 143.13 eV), Pb 4f7/2 (138.32 to 138.25 eV), and I 3d5/2 (619.15 to 619.08 eV) characteristic peaks shifted to lower binding energies for the treated film when compared to the control, suggesting a change in the surface chemical environment. Together with the observed change in the I:Pb ratios, the shift direction and peak positions are consistent with the formation of PbI2 for the treated film.22 The existence of PbI2 was directly detected by grazing incidence X-ray diffraction (XRD) at an incident angle of ω = 0.2° (penetration depth ∼60 nm, see methods description in Supporting Information) (Figure 2c,d). Moreover, the PbI2:FAPbI3 peak intensity ratio was observed to decrease at an incident angle of ω = 1.0° (penetration depth ∼310 nm), suggesting that the PbI2 is located more toward the top perovskite region. Combining the experimental observations together, we thus propose the following reconstruction of the perovskite film surface during post-treatment, by a dissolution reaction process induced by IPA:

\[
\text{FAPbI}_3(s) \rightarrow \text{FAI(in IPA) + PbI}_2(s) + V^\ast_{FA} + V^\ast_1
\]

We now discuss some possible implications of this inferred surface reconstruction. Ultraviolet photoelectron spectroscopy (UPS), with a penetration depth 2–5 nm, was used to investigate any band structure changes at the surface. The Fermi level was observed to downshift from −4.68 eV for the control film to −4.77 eV for the film treated with IPA (Figure 2b), indicating a more p-doped surface for the latter relative to the bare perovskite surface. The overall band structure of the treated surface further downshifted relative to the vacuum level due to the deeper valence band maximum (inset of Figure 2b), consistent with a relatively more FAI deficient surface.23 This possibly creates a beneficial band bending going from the perovskite bulk to the surface contacting a hole-transporting material (Figure S5a). The surface PbI2 for the treated film might also contribute to interfacial passivation.24 In reality, however, we observed that the treated device performance was inferior to the control with a more pronounced current–voltage hysteresis (Figure S5b,c), likely due to the generated vacancy defects, given that defect migration (due to the bias potential) is known to underlie the hysteretic behavior.5

First-principles density functional theory (DFT) calculations were performed on slabs based on the deduced reconstruction to compare their thermodynamics and energetics. We note that, realistically, the perovskite surface is expected to be a complex amalgamation of exposed atoms, local atomic pairing/ reorientation, and defects.25 However, simplified slab models are necessarily required to reduce computational complexity. Nevertheless, relative comparisons can be made on the basis of the predicted results. Experimental investigations have observed that the pristine perovskite surface (without treatment) is terminated mostly by organic halides.26,27 This is also supported by computational results.28 Our results imply that IPA reconstructs the surface toward a relatively more PbI2-rich surface. Therefore, we chose the two extreme cases of
complete FAI termination (Figure 3a) and PbI$_2$ termination (Figure 3b) to model the pristine (control) and reconstructed (treated) surfaces, respectively, again noting that the slabs are used to predict relative trends.

The predicted bandgap decreased while the ionization energy increased for the PbI$_2$ termination surface (Figure 3c), matching the in situ PL and UPS observations. The surface energy more than doubled for the PbI$_2$ termination surface, indicating that the surface became more thermodynamically unstable with treatment. This likely contributed to the observed aggravated instability of the treated films (Figure S6). The generated defects might additionally lower the FAPbI$_3$ cubic-to-hexagonal phase transformation activation energy barrier to also accelerate the degradation. Given the increased surface energy, we postulated that ammonium salts may preferentially adsorb onto the treated surface. We further calculated the formation enthalpy to attach either OAI or PEAI to the surfaces (Figure 3d). The adsorption enthalpies for both were significantly more negative on the PbI$_2$ termination surface, for OAI, −0.78 versus −1.88 eV (141% increase), and −0.9 versus −3.75 eV for PEAI (317% increase), suggesting that the surface reconstruction plays a vital role in the passivation process.

The theoretical calculations imply that ammonium salts are thermodynamically more favored to adsorb onto the treated surface. We investigated this with a modified 2-step surface post-treatment process (Figure S7). Initially treating a perovskite film with pure IPA before subsequently depositing octylammonium bromide (OABr) in CF (at the same concentration) further improved the device performance (Figure 3e). The champion device surface treated with the modified 2-step approach reached a power conversion efficiency of 22.9% in reverse bias (Figure 3e) with negligible current–voltage hysteresis, relative to the 22.4% of the conventionally treated device. The improved performance was attributed to increases in the device open-circuit voltage (1.129 to 1.146 V) and fill factor (79.1% to 79.6%); this is indicative of an enhanced defect passivation effect with the modified 2-step treatment. Therefore, the observations support the theoretical predictions that IPA assists in the adsorption process of ammonium salts to the surface and thus the passivation of defects. The surface is first reconstructed by removing FAI to expose the undercoordinated Pb$^{2+}$ (i.e., $V^*_P$) for the ammonium groups to bond with via electrostatic Coulombic interactions and/or hydrogen bonding.

We speculated that the PL evolution as OAI or PEAI (in IPA) is deposited on the surface may be related to their adsorption enthalpies. Further measurements show that although both treatments led to instantaneous PL enhancements immediately upon deposition (Figure 3fg, Figure S8), the PL intensity subsequently decayed ~10 s after deposition for the OAI treated film. With the PbI$_2$ termination surface, the computed adsorption enthalpies imply a significantly weaker interaction of OAI (relative to PEAI) with the perovskite surface, which may possibly be correlated with the differing PL dynamics. On the other hand, the adsorption enthalpies are negligibly different when calculated using the FAI termination surface, which may be challenging to reconcile with the experimental observations. We also monitored the recombination dynamics with further in situ PL measurements during annealing (Figure 59a,b). A rapid initial exponential decay in PL intensity was observed for both films due to increased phonon scattering at elevated temperatures. However, only the OAI treated film counteracted the initial drop to eventually increase its PL intensity due to the activated defect passivation effect. The evolution and emission characteristics of the wide bandgap phases notably differ between the OAI and PEAI treated films and will be the subject of future investigations (Figure 59c–e).

In summary, we observed a reconstruction of the perovskite top surface induced by IPA, which is ubiquitously used as the solvent for surface treatment with organic ammonium salts. We discussed several implications of this reconstruction on the perovskite surface energetics and thermodynamics. Importantly, given the profound differences between the reconstructed surface and the perovskite bulk/pristine surface, these results will guide further experimental and theoretical investigations of the perovskite surface and surface passivation strategies.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c00757. Materials and methods, photographs of ammonium salts in CF, PL penetration depth estimation, in situ and time-resolved PL spectra of the perovskite films, PAS profiles of the perovskite films, device energy alignment and performance, humidity stability testing on the perovskite films, modified surface treatment process, in situ PL of films undergoing surface treatment, and in situ PL of films undergoing postannealing (PDF).

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Notes
The authors declare no competing financial interest.

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