Impact of Surfaces on Photoinduced Halide Segregation in Mixed-Halide Perovskites

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ABSTRACT: Photoinduced halide segregation currently limits the perovskite chemistries available for use in high-bandgap semiconductors needed for tandem solar cells. Here, we study the impact of post-deposition surface modifications on photoinduced halide segregation in methylammonium lead mixed-halide perovskites. By coating a perovskite surface with the electron-donating ligand trioctylphosphine oxide (TOPO), we are able to both reduce nonradiative recombination and dramatically slow the onset of halide segregation in CH3NH3PbI2Br films. This result, coupled with the observation that the rate of halide segregation can be tuned by varying the selective contact, provides a direct link between surface modifications and photoinduced trap formation. On the basis of these observations, we discuss possible mechanisms for photoinduced halide segregation supported by drift-diffusion simulations. This work suggests that improved understanding and control of perovskite surfaces provides a pathway toward stable and high-performance wide-bandgap perovskites for the next generation of tandem solar cells.

Perovskite tandem solar cells have recently emerged as highly promising photovoltaic technologies. Unlike conventional solar cells, tandem cells use multiple semiconductors of varying bandgaps in a single photovoltaic device to absorb more of the solar spectrum and thereby increase power conversion efficiency (PCE).1–4 For monolithic perovskite–silicon tandems, the ideal perovskite bandgap is ~1.7 eV on top of 1.1 eV silicon.5 This optimized bandgap should allow for a theoretical PCE approaching 39%, well above the 25% PCE currently achieved by high-efficiency perovskite tandems.5,6 The ideal top-cell bandgap increases to ~1.8 eV if a second perovskite is used for the bottom subcell because the lowest bandgap currently achievable with perovskites is 1.19 eV,7,8 enabling a theoretical PCE near 38% from a potentially lower-cost tandem solar cell that can be manufactured at a large scale.5,9 However, while perovskites with ideal bandgaps are synthesizable via chemical substitution of bromide for iodide (i.e., CH3NH3Pb(I1−xBrx)3),10–12 this substitution makes them susceptible to halide segregation.13,14,15 This process of photoinduced halide segregation prevents the increase in bandgap from realizing a proportional increase in open-circuit voltage, ultimately limiting the benefits of bandgap-tunable, mixed-halide perovskites as top cells in tandems.15,16

Photoinduced halide segregation was first observed in CH3NH3Pb(I1−xBrx)3 compounds with bromine contents exceeding 20%. In these mixed-halide compounds, the photoluminescence (PL) was seen to shift to lower energies, centered at the emission energy of that in CH3NH3PbI3.11,17 This shift in PL is understood to coincide with demixing of the perovskite into iodide-rich and bromide-rich domains, which act as traps and increase the rate of recombination. This effect is also observed to be reversible if the samples rest in the dark.14,17 Further work has found that the rate and behavior of photoinduced halide segregation depends upon A site cation chemistry for ABX3 perovskites,11,18–20 can be expedited or suppressed by varying halogen to lead ratios,21,22 is morphology-dependent,23,24 is
driven by increasing injected carrier density in addition to photogenerated carriers, and appears dependent upon the carrier generation gradient.

To explain photoinduced halide segregation, specifically the reversibility and the 20% bromide threshold for methylammonium perovskites, several groups have developed thermodynamic models that predict the formation of a miscibility gap in the free-energy curve of the perovskite solid solution under illumination. These models point to the existence of either large polarons or a high density of free carriers under illumination as the thermodynamic driving force for demixing and allow for the observation that, when returned to the dark, the samples could return to a mixed equilibrium state. These models would suggest that photoinduced halide segregation is an intrinsic property of certain perovskite chemistries, largely independent of film morphology, and that avoiding it would require new perovskite compositions with, for instance, reduced electron–phonon coupling.

However, previously mentioned experimental observations appear to challenge these thermodynamic models by showing that the rate of halide segregation is impacted by tuning the precursor stoichiometry, film morphology, or generation profile, suggesting that our understanding of photoinduced halide segregation is either incorrect or incomplete. Recently, Barker et al. observed that photoinduced halide segregation can be suppressed not by varying chemistry but by instead varying the illumination profile incident on the perovskite film, linking heterogeneity in carrier generation to the halide segregation process and suggesting that photoinduced halide segregation arises from bromine preferentially moving away from illuminated areas in cubic perovskites. However, there remains insufficient data to link all of these observations with a complete model of photoinduced halide segregation. To intelligently select materials that are resistant to photoinduced halide segregation and therefore suitable for high-efficiency tandems, we must better understand the origin and nature of this photoinduced halide segregation. Here we present our observations that perovskite surfaces are an integral part of the progression of the halide segregation process. We show that by modifying surfaces to control carrier trapping we can substantially slow photoinduced halide segregation, and in doing so, we provide new insights into the mechanism of halide segregation in mixed-halide perovskites. Outside of the explanation set forth by Barker et al., prior models cannot straightforwardly explain how a surface modification would have such a large impact. We therefore present possible mechanisms of halide segregation, supported by drift-diffusion modeling, which are consistent with our experimental observations in the hopes of catalyzing further modeling and a deeper understanding of photoinduced halide segregation.

Controlling and understanding perovskite surfaces has proved essential for increasing the efficiency and stability of perovskite solar cells. As evidence of the importance of controlling surfaces and surface defects, many researchers have focused on the development of surface treatments to reduce nonradiative recombination and increase photovoltaic performance of the pure iodide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$. Given the benefits of a subset of these treatments, namely, trioctylphosphine oxide (TOPO), iodopentafluorobenzene, and polystyrene, on the pure iodide perovskites, we were motivated to investigate the impacts of these surface treatments on the PL behavior of the mixed-halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Br}$.

Of the surface treatments explored, the Lewis base and ligand TOPO was observed to have the most significant impact on light-induced phase segregation in $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Br}$ (results of other surface treatments are given in SI Figure 1). In addition to TOPO, polystyrene was observed to slow the photoinduced shift in PL, albeit not as radically as the TOPO treatment (SI Figure 1). Both the TOPO and polystyrene are deposited as solutions with chlorobenzene, yet their impact on PL far exceeds that of the solvent (chlorobenzene) on its own (SI Figure 2), suggesting that the impact is due to the additives themselves. Figure 1 shows the impacts of a TOPO surface treatment on halide segregation. All samples were illuminated with 0.1 sun equivalent of 488 nm illumination such that the evolution in PL could be resolved in a period of seconds. Additionally, all samples were tested in a nitrogen-filled chamber with a fixed sample position and alignment, such that the PL intensity can be qualitatively compared between samples.

With no surface treatment, the standard photoinduced halide segregation process is observed (Figure 1a), with the formation of sub-bandgap emission over a period of seconds and a continued increase in the PL from smaller-bandgap

![Figure 1. Behavior of $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Br}$ with and without Lewis base treatment with TOPO as monitored by PL under 0.1 sun equivalent of 488 nm illumination through the top surface of a perovskite film over a 2 min time period (a) without and (b) with treatment and (c) after 10 min of continuous light exposure. The evolution of PL is highlighted with red arrows.](https://example.com/figure1.png)
domains over a 2 min time period. After 10 min, the signature of the wide bandgap cannot be detected (Figure 1c). Note that the evolution of the photoinduced halide effect is strongly dependent on the light intensity, as described elsewhere and shown in SI Figure 3.

However, when the same perovskite material is capped with TOPO (Figure 1b), not only is the initial PL intensity substantially increased, in line with previous reports, but the PL shift to lower energy appears halted within the same time window. After prolonged illumination, evidence of photoinduced halide segregation in the TOPO-treated samples is seen to emerge (Figure 1c); however, the rate of halide segregation as monitored by PL is substantially reduced with the TOPO treatment (SI Figure 4). This is additionally impressive given that the increased PL intensity of the TOPO sample suggests an increase in the steady-state perovskite carrier density, and increased carrier density has been previously linked to a faster rather than a slower shift in the PL. This suppressed rate of halide segregation with the use of TOPO is additionally observed at higher light intensities and with other perovskite compositions with higher bromide concentration (SI Figure 5). Finally, we confirm that beyond being an optical effect, this slowed PL shift reflects a delay in halide segregation by performing in situ X-ray diffraction (XRD) to monitor the cubic perovskite’s structure during illumination. XRD results for illuminated MAPbI$_3$Br$_2$ samples coated with TOPO show reduced structural distortion as compared to untreated controls (SI Figure 6). This lattice distortion, although not completely understood, has been previously linked to the formation of a lower-bandgap perovskite phase. It should be noted that a higher bromine content perovskite was selected for this experiment to better resolve the change in lattice structure under illumination.

Given the exceptional behavior of the TOPO surface treatment, it is important to consider how it impacts the perovskite. Previous reports on similar Lewis base ligands suggest that they are capable of donating electrons to the surface of the perovskite and leave the bulk of the perovskite largely unaffected. In line with these previous reports, X-ray photoelectron spectroscopy (XPS) of perovskite films capped with TOPO shows a substantial presence of phosphorus at the surface of the perovskite, which is quickly reduced below instrument detection limits after removal of the film’s surface by sputtering (SI Figure 7). Additionally, XPS provides insights into the impact of TOPO treatment on the energetics of the perovskite surface. Employing techniques previously described, the relative binding energies of elements unique to the perovskite with and without the electron-donating TOPO surface treatment can be compared to explore variations in surface vacuum level alignment. Figure 2a,b highlights the binding energy for lead and iodide peaks for perovskite samples with and without TOPO normalized to a surface carbon peak at 285 eV (SI Figure 8).

In these results, a consistent shift to lower binding energy is observed for photoemitted electrons from the perovskite layer.
when coated in TOPO. This apparent lower binding energy implies an increase in kinetic energy for emitted electrons from TOPO samples with respect to the neat films, suggesting the TOPO induces a surface dipole that points away from the perovskite surface and accelerates electrons as they pass through this layer. A similar effect is observed by monitoring photoemitted electrons from photoemission spectroscopy in air, where an increase in the kinetic energy of emitted electrons from TOPO-coated films shifts the observed takeoff in photoemitted electrons to lower energy (SI Figure 9). We attribute this observed surface dipole to the electron-donating nature of TOPO: the ligand may donate electrons to passivate some surface defect on the perovskite, thereby giving the TOPO a net positive charge, and in doing so will create a surface dipole that shifts the vacuum level to lower energy by as much as 500 meV (as estimated by the shift in peak binding energy observed in XPS). The result is a perovskite surface that will accumulate electrons and repel positive charge, as shown schematically in Figure 2c. Our data suggest that this variation in surface energetics with TOPO treatment results in decreased nonradiative recombination and increased photo-stability, manifesting in increased PL intensity and slowed photoinduced halide segregation.

To further understand how surface treatments modulate photoinduced halide segregation, we prepared heterojunction samples with varying selective contacts and measured the PL evolution. As can be seen in Figure 3a, with the introduction of either the hole-transport layer (HTL) poly(triaryl amine) (PTAA) or the electron-selective contact (ETL) C60, the initial PL is greatly quenched. However, this PL quenching and associated reduction in steady-state carrier density does not in and of itself prevent photoinduced halide segregation. The PL of the light-soaked heterojunction samples is shown in Figure 3b. After 10 min of illumination, the PL of the HTL capped perovskite is largely unaffected, while the perovskite capped with the ETL has substantial PL from a lower-bandgap phase.

The suppression of photoinduced halide segregation with the addition of a HTL shows a trend similar to that of the perovskite samples treated with TOPO. While the HTL can accept holes, it cannot efficiently accept electrons. As such, and given the highly quenched PL under illumination conditions, we expect holes to be efficiently transferred to the HTL, leaving electrons in the perovskite and preventing the accumulation of positive charge within the perovskite. Such an effect could result in an electronic landscape that is similar to the TOPO/perovskite interface. This further reinforces our observation that photoinduced halide segregation is greatly impacted by variations in perovskite surfaces and provides guidance for how surface treatments may be developed to suppress photoinduced halide segregation in operational solar cells. Given the observed variation in PL evolution between the PTAA and C60 heterojunction samples observed in Figure 3, constructing perovskite solar cells in a p-i-n architecture could allow for the deposition of a Lewis base treatment to suppress photoinduced halide segregation after perovskite deposition and before the addition of an ETL.

Overall, our experimental observations link changes in the perovskite surface and surface energetics to changes in photoinduced halide segregation, a process that up to now has been largely believed to be an intrinsic property of some perovskite compositions, only addressable by changes in perovskite chemistry. In light of our results, we now propose a general model to explain how surface treatments that result in reduced nonradiative recombination or charge accumulation may inhibit halide segregation. In short, we suggest that carrier trapping at surface states induces electric fields that impact the movement or accumulation of ionic defects and that this movement could drive local variations in chemistry that result in photoinduced trapping. We should note that this model does not preclude thermodynamic stabilization of an iodide-rich perovskite phase under illumination but perhaps suggests a mechanism by which these stable domains begin to form.

Figure 4 presents this model, showing how surfaces impact halide segregation under illumination and how this effect may be suppressed by a surface treatment such as TOPO. Using a
drift-diffusion model (full details presented in the SI), we investigate the impacts of carrier trapping on halide redistribution. Figure 4a shows the initial condition of the system, right after the light as been switched on (i.e., before any trapping process or ion migration occurs). We assume that mobile halide vacancies are uniformly distributed and are charge-compensated by immobile ions or other ionized point defects. In addition, we consider a density of surface traps with a capture cross section that favors electron trapping at the top surface of an intrinsic perovskite. These assumptions are consistent with previous reports of likely trap states in $\text{CH}_3\text{NH}_3\text{PbI}_3$ and the predicted intrinsic nature of these perovskites. Before trapping occurs, we consider the effective charge of these traps to be neutral, which could either be due to the charge of the defect state itself or due to the existence of a defect pair of compensating charges at the surface.

Trapping of electrons (Figure 4b) induces the formation of an electric field pointing toward the surface of the film. To shield the trap-induced field, halide vacancies migrate toward and accumulate near the surface states, leaving a depletion region populated by immobile anions (Figure 4c). Given that for lead halide perovskites, the concentration of vacancies is predicted to far exceed that of free carriers within the tested illumination conditions, and halide vacancies (as opposed to holes) will preferentially accumulate at the perovskite surface. In the case of the Lewis base TOPO, the molecular dipole opposes this trap-induced field, and fewer holes and vacancies accumulate at the surface as a result (Figure 4d). We suggest that it is the redistribution of ions in response to carrier trapping that drives photoinduced halide segregation and that treatment such as TOPO slows this process by reducing the driving electric field.

In order for this redistribution of ions to precipitate halide segregation, this movement must impact bromide and iodide differently. While the details of ionic conductivity in mixed perovskites remains an open area of study, work on single-halide perovskites suggests that such an effect is possible. For one, defect calculations suggest a lower activation energy for the formation of bromide vacancies with respect to iodide vacancies. As such, in a mixed-halide perovskite, the drift of positively charged vacancies toward the perovskite surface is likely to be equivalent to a preferred drift of bromide away from the surface, and the accumulation of halogen vacancies should therefore result in the formation of an iodide-rich phase. Second, Kim et al. have recently described the photoinduced formation of iodide vacancies, where free holes oxidize iodide otherwise in the perovskite lattice. If iodide is easier to oxidize than bromide in the mixed-halide perovskite, illumination should preferentially increase the formation of iodide vacancies and consequently the conductivity of iodide, again resulting in a local change to the perovskite chemistry.

In the model outlined above, the driving force for halide segregation increases with the number of trapped electrons. Consequently, any treatment or chemical variation that changes either the concentration or the energy of surface trap states would impact the evolution of photoinduced halide segregation and could explain experimental observations linking morphology and chemical variation to the rate of photoinduced halide segregation. This is consistent with our observation that in order to slow photoinduced halide segregation one can either reduce the number of surface defect states (as with TOPO) or prevent the accumulation of positive charges at the interface (as with TOPO and PTAA). Both strategies would negate an electric field that drives halogen vacancy accumulation toward the surface.

Additionally, such a trapping mechanism could also be consistent with the observation that photoinduced halide movement in $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Br}_{3-x}$ perovskites leads to a 20% bromide phase. Changing the halogen ratio in mixed halide perovskites is experimentally observed to change the ionization potential and bandgap of the materials and is theoretically predicted to change the defect formation energies and trap depths. If the band structure for $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Br}_{3-x}$ is such that at ~20% bromide the prevailing surface trap is no longer energetically stable or is no longer a deep trap, we would predict the driving force for photoinduced halide segregation to be negated. Such a mechanism could also explain why Cs compounds, which have been observed to have a deeper valence band than their methylammonium counterparts, appear more stable to photoinduced halide segregation up to higher bromine contents.

Our results definitively show that perovskite surfaces are an integral part of the halide segregation process and that any model that seeks to fully explain photoinduced halide segregation must take surfaces into consideration. Through post-deposition treatments of perovskites, we were able to slow down the formation of lower-bandgap iodide-rich domains in mixed-halide perovskite. These results suggest that carrier trapping and charge accumulation at perovskite surfaces are principle drivers of photoinduced halide segregation, and efficiently passivating and treating surfaces is a pathway toward stabilized wide-bandgap perovskites. While the surface treatments presented here only slowed photoinduced halide segregation, it is possible that deeper understanding will allow for complete suppression of photoinduced halide segregation by surface passivation, and materials previously thought unusable for photovoltaic applications might be candidates for high-efficiency perovskite tandems.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.8b01562.

Experimental and modeling methods and additional characterization of the impacts of surface treatment on mixed-halide perovskites including additional PL data of mixed-halide perovskites with alternative light intensities and surface treatments, in situ X-ray diffraction data, additional X-ray photoelectron spectroscopy data, and photoemission spectroscopy data (PDF).

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Notes
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