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A Victim of Halide Ion Segregation. How Light Soaking Affects Solar Cell Performance of Mixed Halide Lead Perovskites

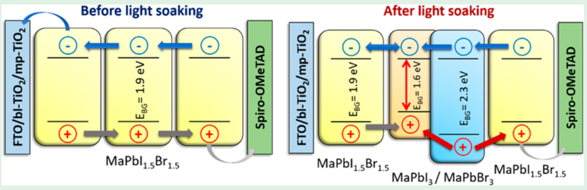
Gergely F. Samu,[†,§,∥] Csaba Janáky,[§,∥] and Prashant V. Kamat*[,†,‡]

[†]Radiation Laboratory and [‡]Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, United States

[§]Department of Physical Chemistry and Materials Science, University of Szeged, Rerrich Square 1, Szeged H-6720, Hungary

[∥]MTA-SZTE "Lendület" Photoelectrochemistry Research Group, Rerrich Square 1, Szeged H-6720, Hungary

Supporting Information



ABSTRACT: Photoinduced segregation in mixed halide perovskites has a direct influence on decreasing the solar cell efficiency as segregated I-rich domains serve as charge recombination centers. The changes in the external quantum efficiency mirror the spectral loss in the absorption; however, the time scale of the IPCE recovery in the dark is slower than the absorption recovery, showing the intricate nature of the photoinduced halide segregation and charge collection in solar cell devices.

The ability to tune the bandgap of mixed halide perovskites through halide composition is attractive to design solar cells with tailored response.[1−3] Halide ion migration in perovskite solar cells plays an important role in determining the overall photovoltaic performance.[4−7] Light soaking, for example, leads to migration of ions and vacancies toward the oxide interface, influencing the observed photovoltage.[8] Another property of the mixed halide lead perovskite is its ability to undergo phase segregation under continuous illumination.[4,9−13] For example, when methylammonium lead halide (Br/I, 1:1 ratio) is subjected to longer-term (>20 min) visible irradiation, it undergoes phase segregation to yield iodide-rich and bromide-rich domains (reaction 1)

$$n\mathrm{MAPbBr}_x\mathrm{I}_{3-x} + h\nu \rightarrow (n-2m)\mathrm{MAPbBr}_x\mathrm{I}_{3-x} + m\mathrm{MAPbBr}_{x-y}\mathrm{I}_{3-x+y} + m\mathrm{MAPbBr}_{x+y}\mathrm{I}_{3-x-y} \quad (1)$$

Upon stopping the illumination, the segregated phase is restored to the original mixed phase.[12−14] It was also found that the excitation intensity and duration of irradiation determine the dark recovery.[12,13] These intriguing behaviors of mixed halide perovskites have led us to probe halide ion segregation on the solar cell performance. The obvious question is, *What is the impact of longer-term light irradiation (or light soaking) on the performance of mixed halide perovskite cells?*

We prepared two sets of cells, one with a partial assembly excluding top gold contact and the other complete solar cell assembly using the same mixed halide perovskite deposition on a mesoporous TiO_2 film (see Scheme S1). The methylammonium lead halide films were cast using a stoichiometric composition with a Br/I ratio of 1:1. The partially assembled cell was used for absorption measurements. The absorption spectra recorded before and after 30 min of irradiation with visible light (100 mW/cm^2) are shown in Figure 1A. The decrease in absorbance at 620 nm suggests the diminution of the mixed halide phase. The concurrent increase in the absorption at shorter and longer wavelengths represents formation of bromide-rich and iodide-rich phases. To better visualize this process, the difference absorption spectra were recorded during the dark recovery (Figure 1B). In about 3 h, we saw almost complete recovery of the mixed halide phase. Details of the absorption changes and recovery can be found in our earlier studies.[12,13]

The next step was to evaluate the photovoltaic performance of fully assembled solar cells. The champion cell we tested for these measurements yields a power conversion efficiency of 4.4%, an open-circuit voltage of 1.04 V, a short circuit current of 6.4 mA/cm^2, and a fill factor of 66%. The cell was then subjected to visible light irradiation (100 mW/cm^2) for 30 min under open-circuit conditions. This allowed us to induce halide ion segregation through visible light excitation (identical to the conditions in Figure 1A). Upon evaluation of $J-V$ curves (Figure S1), we found a significant decrease in the solar cell performance with a V_{oc} of 0.91 V and J_{sc} of 4.2 mA/cm^2, resulting in a net photoconversion efficiency of 1.4%. This phenomenon was also observable for different cells irradiated for 15 and 30 min (as seen in Figure S2).

We also recorded IPCE spectra at different times as the cell recovered in the dark (Figure 1C). The IPCE spectrum recorded immediately after 30 min of irradiation shows a nearly 50% drop

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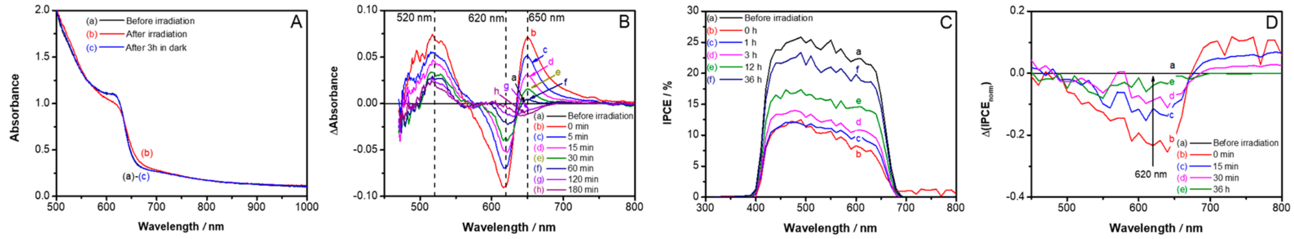

Figure 1. (A) Absorption spectra of a mixed halide perovskite film (a) before and (b) after irradiation for 30 min. (c) Dark recovery after 3 h. (B) Difference absorption spectra after 30 min of light soaking show dark recovery. (C) External quantum efficiency (IPCE) of a mixed halide perovskite solar cell (a) before light soaking and (b−f) during dark recovery following 30 min of light soaking. (A 420 nm cutoff filter was used for IPCE measurements, and residual dark currents were corrected for IPCE measurements). (D) Difference IPCE spectra showing the recovery of the solar cell response in the 600−700 nm region. (The spectra were normalized at 470 nm, and the IPCE was recorded before the continuous irradiation was used as the reference.)

in IPCE. The IPCE spectra were seen to recover slowly as we left the cell in the dark. Almost 90% of the recovery was seen in 36 h. This recovery time is notably longer than the recovery time scale we see in the absorption spectra (see Figure S3). The quick absorption recovery is indicative of the fact that the majority of the segregated phases have reversed back. However, the slower recovery in IPCE indicates that a few remaining charge carrier traps that are not captured through absorption changes are responsible for poor charge carrier extraction. This difference in the recovery time thus suggests the necessity of longer time to alleviate residual traps following light-induced halide ion segregation.

The drop in the IPCE response at longer wavelengths appears to be greater than that at shorter wavelengths. To obtain a closer look at this phenomenon, we recorded difference IPCE spectra at different recovery times following normalization (Figure 1D). The difference IPCE spectra recorded immediately after the 30 min irradiation of the solar cell shows depletion in the 550−680 nm region with a maximum at around 620 nm. This depletion in IPCE matches closely the decreased absorbance seen in the absorption spectrum after irradiation. This result confirms that the loss of contribution in the IPCE at longer wavelengths arises from the fraction of mixed halide that is lost in the segregation process. As we continue the recovery process in the dark, this depleted IPCE (500−670 nm) region recovers. This recovery of IPCE performance parallels the reversibility seen in the photoinduced segregation (see, for example, Figure 1A, B). It is important to note that the irradiated $MAPbI_3$ solar cells do not show such loss of IPCE response in the red region (see Figure S4).

The observed decrease in IPCE following 30 min of light soaking of mixed halide film arises from halide ion segregation and not from film degradation (both the absorption properties and IPCE recover almost completely when left in the dark). As noted in our previous study, the low-lying I-rich phase serves as a sink for photogenerated electrons and holes.[12] The gain in the IPCE at wavelengths greater than 700 nm is rather small and cannot account for the loss that we see in the 500−670 nm region. We attribute this discrepancy to the halide ion segregated domains within the film that block the flow of charge carriers. While the conduction bands of mixed halide and segregated phases are isoenergetic, the valence bands show an energy gradient causing the I-rich region to favor the hole accumulation (see the abstract graphic). The I-rich domains thus serve as recombination centers resulting in an eventual decrease in the IPCE and overall photoconversion efficiency.[10,12,15] As the mixed films recover in the dark, these recombination centers are removed and we see recovery of photovoltaic performance.

To summarize, the photoinduced segregation seen in mixed halide films makes the photovoltaic performance of perovskite solar cells less efficient as I-rich domains block the flow of charge carriers and promote charge carrier recombination. The dark reversibility is a silver lining here, and one should focus on speeding up the dark recovery time. Indeed, increased halide concentration is one way to speed up the dark recovery and minimize segregation effects.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.7b00589.

> Experimental methods including film preparation, solar cell fabrication, and related spectroscopic and photovoltaic measurements (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: pkamat@nd.edu. Twitter: @kamatlabND.

ORCID

Csaba Janáky: 0000-0001-5965-5173
Prashant V. Kamat: 0000-0002-2465-6819

Notes

The authors declare no competing financial interest.

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See the Supporting Information.

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