Stability of 2D Perovskite Solar Cells

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Abstract

Solar energy is a renewable energy source more than capable of meeting the world's energy demand if properly harnessed. New thin film solar cell technologies such as organolead halide perovskite (OHP) solar cells have recently gained prominence for their rapidly increasing power conversion efficiency (PCE) and the possibility of low-cost scalable fabrication methods, such as screen printing and ink-jet printing. Unfortunately, these perovskites are typically unstable when exposed to either humidity or light, thus limiting their usefulness. One method to increase the stability of a common photovoltaic perovskite, methylammonium lead iodide (MAPI), is to create a layered 2D MAPI material by adding a bilayer of n-butylammonium spacer molecules to the crystal structure. The reason that this 2D structure is more stable, however, is not well understood. By using a variety of electrochemical and analytical techniques, we found that the improved stability in such materials is a result of a 2D perovskite specific degradation pathway that produces increasingly stable phases of the 2D perovskite, primarily at the exposed upper layer of the perovskite. These stable phases create a passivating layer and act to slow further degradation reactions. Using this knowledge, we tested a surface treatment designed to form 2D perovskite on the surface of a MAPI solar cell and showed that even a thin layer of 2D perovskite on MAPI can effectively delay device deterioration and preserve conversion efficiency. Furthermore, the choice of alkylammonium spacer can affect the stability of the solar cell when different electrode materials are used, providing a possible route to create stable solar cells using cheaper materials.

Background

With the rise of renewable energy, solar technology is an active area of research, potentially able to meet the world's energy needs if completely harnessed. Current commercial solar cells are made of silicon and are approaching the theoretical limit of 33.7% efficiency for a single material. To further improve on solar efficiency, different materials are currently being studied to be used in conjunction with silicon solar cells to improve photoconversion efficiency (PCE). Organolead halide perovskites are one of the most promising candidates for next-generation thin film solar cells. Most organolead halide perovskite devices are Pb-based and have reached PCEs greater than 25% in just 10 years, making them a promising alternative to silicon solar cells or as an extra photo-absorbing layer in solar cells.

Perovskites are any material which follows the general formula ABX_3, where A is typically a small organic cation with a 1+ charge, B is a metal cation with a 2+ charge, and X is a halide anion. However, perovskites tend to degrade when exposed to humid conditions, limiting their utility. While moisture driven degradation can be mitigated by encapsulating the perovskite solar devices, the fundamental chemical instability must be addressed in future devices to make them commercially viable.

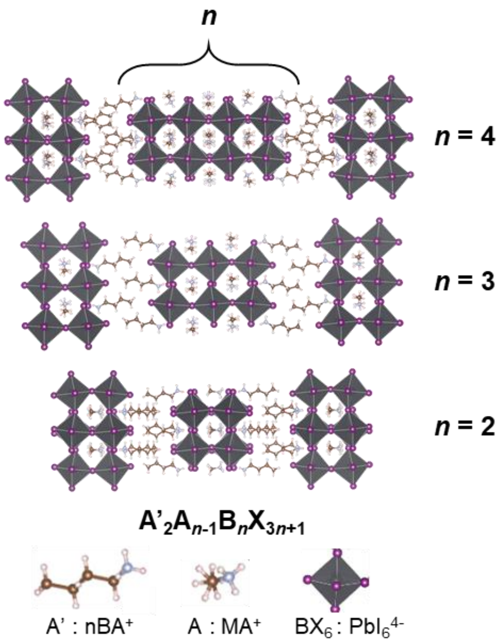

Figure 1: Crystal structures of Ruddlesden-Popper phase perovskites

In order to increase the stability of Pb-based perovskites, scientists have begun to explore 2D Ruddlesden-Popper phase perovskite material, which are perovskites with a bilayer of alkylammonium cation spacer molecules added to the crystal structure. This addition changes the general formula $APbX_3$ to $A'_2A_{n-1}Pb_nX_{3n+1}$, where n (n-value) is the number of PbI_6^{4-} composing the perovskite layer between each alkylammonium bilayer and A' is the newly introduced spacer organic cation (Figure 1). Due to quantum confinement, perovskites with different n-phases have different band gaps, allowing them to absorb and emit light at different wavelengths. Starting with one of the most common perovskites, methylammonium lead triiodide (MAPI), spacer molecules, such as n-butylammonium (nBA) and n-hexylammonium (nHA), can be added to form 2D Ruddlesden-Popper perovskites. These perovskites not as moisture sensitive as MAPI and can remain functional for longer. This improved stability has been attributed to the hydrophobicity of the larger alkyl spacer molecules, a 2D perovskite specific degradation pathway, and improved thermodynamic stability of the 2D perovskites. However, the exact mechanism has not been well understood.

In this work, we found evidence to support a 2D perovskite specific degradation pathway when the perovskites were exposed to moisture.[1] To do this, we used a variety of spectroscopic and electrochemical techniques to probe both perovskite films and solar devices. These techniques include photoluminescence (PL), time-of-flight secondary ion mass spectrometry (ToF-SIMS), and cyclic voltammetry (CV).

The three techniques (PL, ToF-SIMS, and CV) were used to understand the how the chemical composition of the perovskites changed as they degraded. Photoluminescence (PL) allowed us to determine how the amounts of each n-phase changed with time. This is possible because PL is essentially a fluorescence measurement, where light is shone onto a perovskite film and the fluorescence of the film is measured at different wavelengths. Since each n-phase has a different band gap, and therefore emits at a different wavelength, the intensity of the fluorescence can be used to determine how the amount of n-phase changes with time. However, PL is an inherently surface sensitive measurement, since light cannot penetrate all the way through the film.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) allows us to probe the interior of a perovskite device and quantifying chemical changes as they degrade. ToF-SIMS can probe the interior by digging into the surface using heavy Cs^+ atoms. After reaching the interior of the solar cell, we can probe the chemical composition of the inner layers using Bi_3^+ ions. By probing the interior of the solar cell, complementing the surface sensitive PL experiments, we can understand chemical information inside the perovskite solar cells.

Finally, cyclic voltammetry is an electrochemical technique that allows us to determine the photocurrent efficiency and verify that our solar cells are functioning as intended. It also serves as a metric for how well our solar cells are performing when we induce moisture driven degradation.

Results

The results of our experiments on MAPI and nBA-MAPI are described here, showing the improved stability of 2D perovskites. Further experimentation has shown that the choice of electrode and cation spacer can have a measurable impact on the performance of the perovskite solar cell.[2] The methods and any additional notes can be found in the papers by Wygnat et al.[1,2]

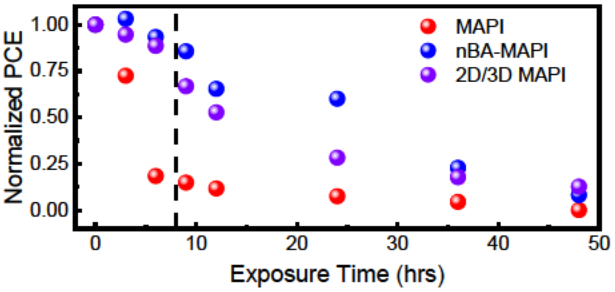

Figure 2: Normalized power conversion efficiency (PCE) of MAPI, nBA-MAPI, and 2D/3D MAPI devices following exposure to 78% RH over the course of 48 hours, showing the decrease in PCE for all devices as they degrade.

To investigate the improved stability of nBA-MAPI, we first constructed p-i-n solar device using PEDOT:PSS as the hole transport material and C_{60} as the electron transport material. In Figure 2, the normalized photoconversion efficiency (PCE) is shown, demonstrating how the efficiency of the nBA-MAPI devices is far more stable than the MAPI devices when exposed to 78% relative humidity over time. We then developed a surface treatment for the MAPI, creating a thin layer of nBA-MAPI on the top surface of the MAPI. This new perovskite structure is labeled 2D/3D MAPI since it consists of an upper 2D perovskite and a bulk 3D perovskite. Despite being primarily MAPI, the 2D/3D MAPI shows a stability profile more similar to that of 2D nBA-MAPI than regular MAPI (Figure 2). This suggests that the degradation not only occurs primarily at the surface of the perovskite, but it can also be inhibited by a thin layer of 2D perovskite. After a 9 hour degradation period, the nBA-MAPI device showed less than 20% reduction in PCE while the MAPI device showed a loss of about 80% efficiency. As a result, our characterization methods focused on this 9 hour degradation time as a point of comparison, highlighting any differences which may occur between perovskites.

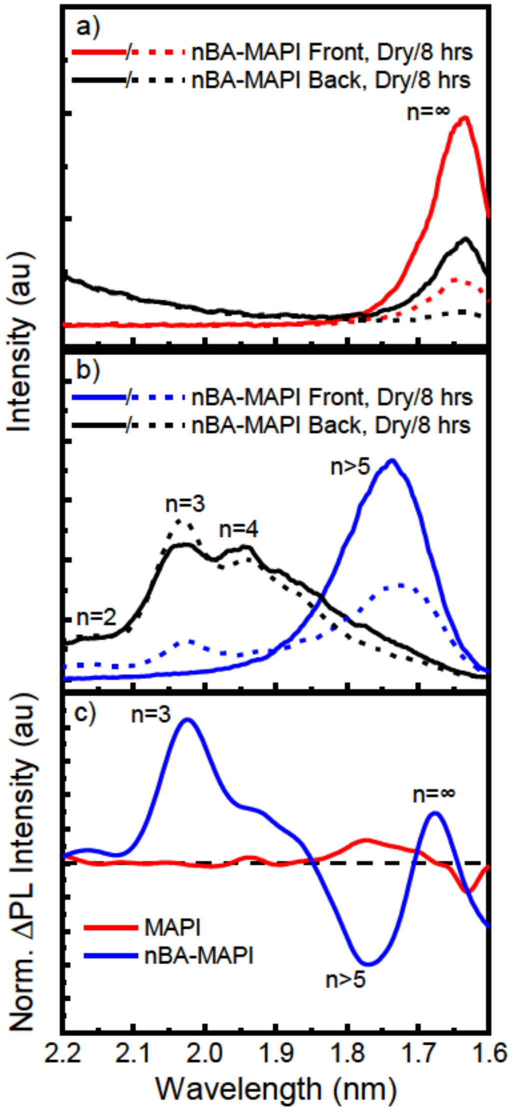

Figure 3: Photoluminescence spectra for the front and back of a) MAPI and b) nBA-MAPI films, before and after exposure to 78% relative humidity for 8 hours. c) Normalized difference plot for the front-side spectra for both films. nBA-MAPI shows the growth of $n = 3$ and ∞ peaks, as well as the loss of the $n > 5$ peak, while little change visible in the MAPI spectra.

To characterize the perovskites, we used photoluminescence (PL) spectroscopy to characterize the different n-phases present in the nBA-MAPI films. By measuring the PL of both the front and the back surface of perovskite films, we were able to understand how the perovskites change as they degrade (Figure 3). Specifically, both the MAPI and nBA-MAPI have single peaks on the front. MAPI has a single peak at 1.64 eV on both sides of the film, while nBA-MAPI has a "bulk" n>5 peak at 1.74 eV. The back of the nBA-MAPI however, has a variety of peaks at 2.04, 1.94, and 1.84 eV (n=3, 4, and 5 respectively). After the perovskite has been exposed the humidity, both the MAPI and nBA-MAPI exhibit a significant decrease in PL intensity on the front, indicative of crystallographic damage from humidity. However, the PL peaks on the back of the nBA-MAPI perovskite instead grows at higher energies. These peaks correspond to lower n = 2-4 phases, and the fact that they grow in intensity is in agreement with a stabilizing mechanism.[3] When the 2D/3D perovskites were characterized with PL, they exhibited a very similar spectra to that of the 3D MAPI, indicating that the thin layer of nBA-MAPI created on the surface did not affect the PL spectra significantly.

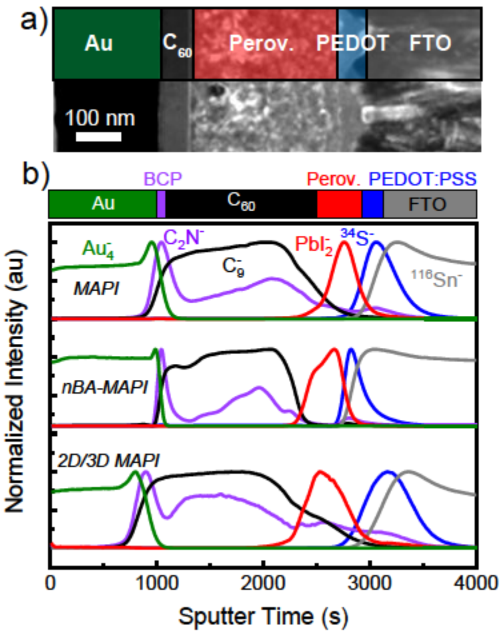

Figure 4: a) cross sectional tunneling electron microscope image of a typical nBA-MAPI device with layers labeled. b) Full negative-mode ToF-SIMS depth profiles for fresh MAPI (top), nBA-MAPI (middle) and 2D/3D MAPI (bottom) devices with characteristic species chosen to represent different layers and color-coded to the bar at top.

In order to further characterize the perovskite films in greater detail, we used ToF-SIMS to understand the chemical stability within a full perovskite solar cell. This is significant because it allows the interfaces between the electron transport material and perovskite to be studied. Once full depth profiles of the perovskite solar cells had been collected, fresh and degraded ToF-SIMS profiles could be compared and analyzed. It is important to note that the x-axis of the profiles (sputtering time) depends on both the material and thickness, so it cannot be directly used as measure of depth in the solar devices. For example, cross sectional tunneling electron microscope images of the solar device show C_{60} as one of the thinner layers (Figure 4a). The C_{60} layer in the ToF-SIMS however, consists of one of the thickest layers at sputter times from about 700-2000 seconds (Figure 4b). Since each only negative ions are detected, each layer has a characteristic ion which is indicative of that layer, Au_4^- for Au, C_2N^- for BCP, C_9^- for C_{60}, PbI_2 for the perovskite, $^{34}S^-$ for PEDOT:PSS, and $^{116}Sn^-$ for FTO. Focusing on the top C_{60}/Perovskite interface, the perovskite is most susceptible to damage because that is where the hydration of the perovskite is most prominent. When the MAPI device is exposed to humidity for 9 hours, the PbI_2^- peak grows a shoulder and a new C_2N^- peak appears as a result of the degradation (Figure 6a). However, when nBA-MAPI and the surface treated 2D/3D MAPI is exposed to humidity, there is no appearance of the degradation peaks, indicating that the perovskites did not interact with the water at the C_{60}/Perovskite interface (Figure 6b, c). This taken together with the improved electrochemical stability of the nBA-MAPI perovskites and 2D/3D MAPI is strong evidence for a correlation between chemical and electronic stability of perovskites.

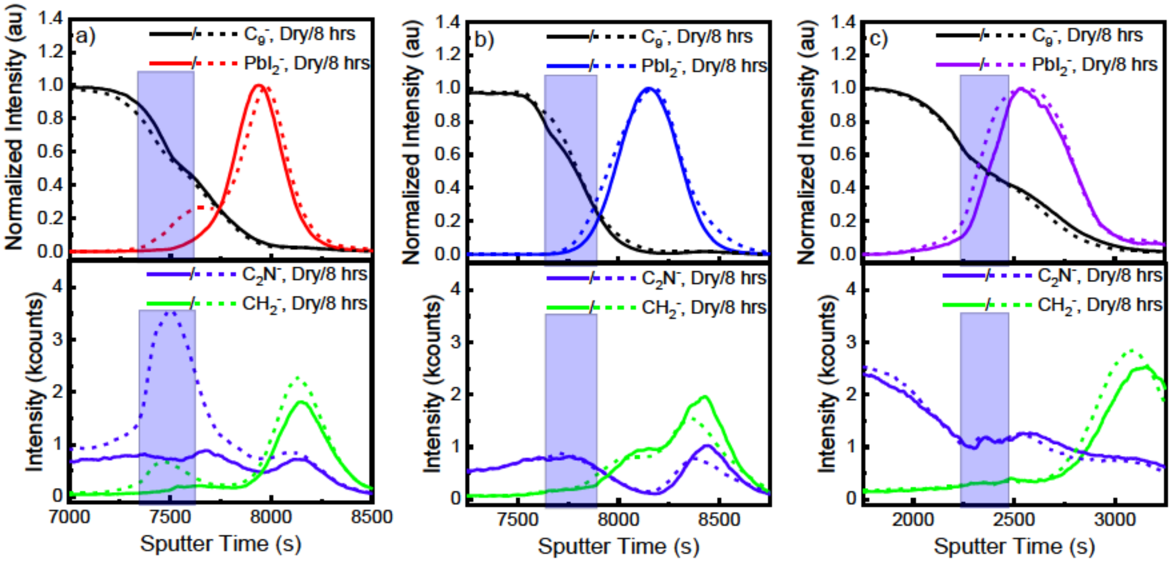

Figure 5: Negative-mode ToF-SIMS depth profiles of (a) MAPI, (b), nBA-MAPI, and (c) 2D/3D MAPI devices, before and after exposure to humidity, near the C$_{60}$/perovskite interface; the blue box represents the hydration region in each device. The top profiles show the changes to the C$_{60}$ (C$_9^-$) and perovskite (PbI$_2^-$) with exposure; nBA-MAPI and 2D/3D MAPI show little change, while MAPI shows the formation of a new peak in the hydration region. The bottom profiles show changes to N- and H-containing organic species (C$_2$N$^-$ and CH$_2^-$, respectively). A clear peak in both ions is visible at 7500 s, within the hydration region, in (a), while neither nBA-MAPI nor 2D/3D MAPI show any increase in these species. Such species are indicative of the formation of degraded hydrated MAPI species.

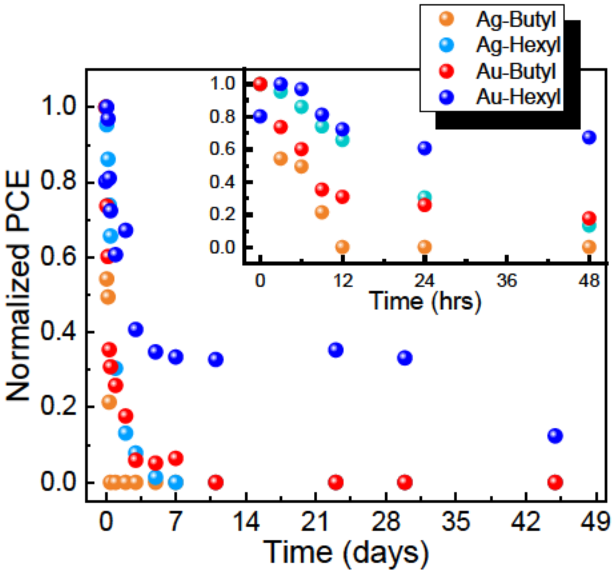

Figure 6 Normalized PCE of butyl- and hexyl-MAPI devices fabricated using both Ag, and Au electrodes, exposed to 78%RH. All devices except for the Au-hexyl devices showed complete degradation within two weeks. The inset shows the rate of PCE loss over the first two days.

In addition to the work focusing on the degradation of 2D perovskites, the effect of alkylammonium spacer molecule on electrode stability was studied. In particular, n-butylammonium (nBA) and n-hexylammonium (nHA) were used as spacer molecules in a 2D perovskite structure. Then, either gold or silver electrodes were used in the solar cell. Electrochemical stability tests revealed that nHA resulted in a far more stable solar device, even when Ag was used as the electrode material (Figure 6). In fact, the Ag-butyl devices completely failed by 12 hours of exposure while the Au-butyl devices retained about 50% of their initial efficiencies. The hexyl devices on the other hand, were much more stable, retaining at least 70% of their initial efficiencies. The Au-hexyl devices performed the best, maintaining a significant portion of their efficiency for over 40 days.

Discussion

Taking all of the electrochemical, photoluminescence, and ToF-SIMS data, we found that the 2D perovskites (nBA-MAPI) was more stable than the general 3D perovskite and improve the stability of a 3D perovskite if even a thin layer of 2D perovskite was formed on the top surface of a 3D perovskite. There are a few hypotheses that explain the improved stability of 2D perovskites, and this data supports a degradation pathway-based hypothesis. In this degradation pathway specific to 2D perovskites, the perovskite can decrease its n-value by one. An example for n=4 nBA-MAPI degrading into n=3 nBA-MAPI is as follows.

$$(nBA)_2MA_3Pb_4I_{13}\ (n=4) \xrightarrow{H_2O} (nBA)_2MA_2Pb_3I_{10}\ (n=3) + MAPbI_3\ (n=\infty)$$

This degradation pathway not only allows the perovskite to still function as a photoactive material, since they still have perovskite properties. These lower n-value perovskites have also been shown to possibly be more thermodynamically stable than their higher n-value counterparts.[4] This pathway and improved stability is supported by our photoluminescence experiments and our electrochemical stability tests (Figure 2 and 3).

The ToF-SIMS experiments sheds further light on the degradation process of these perovskites, indicating that important degradation processes occur at the upper C_{60}/perovskite interface. These degradation processes likely do not occur uniformly, otherwise they would inhibit electron transfer (Figure 7). Since the degradation processes initially occur on the upper surface, a treatment was developed to create a thin layer of 2D perovskite on top of a primarily 3D perovskite. This 2D/3D perovskite was significantly more stable than the 3D perovskite and could provide a simple method to improve the stability of 3D perovskites.

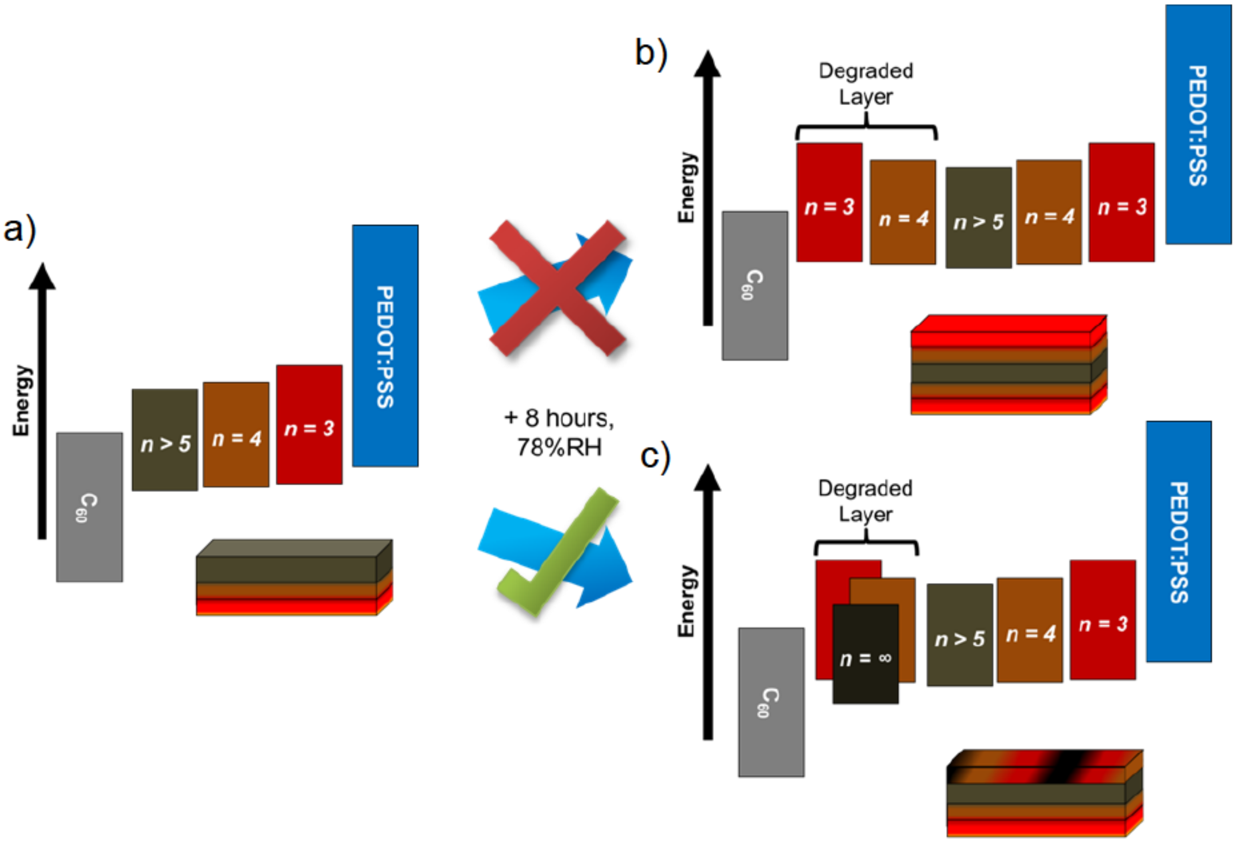

Figure 7: a) Possible band schematic for a fresh nBA-MAPI device, shown below, as determined by PL spectroscopy. The $n > 5$ layer is at the film surface, closest to the C_{60}, while lower n phases rest atop the PEDOT:PSS layer; this allows for both hole and electron transport from the perovskite to the device. b) Proposed band schematic and device cross section assuming disproportionation creates conformal low-n layers from the C_{60} interface downward toward the bulk. These layers would inhibit electron transfer to the C_{60}, and therefore is not expected to occur. c) Proposed band schematic and device cross section assuming disproportionation creates a well-mixed layer of low-n and MAPI layers at the surface. The presence of the MAPI would allow electrons to be transferred from the bulk nBA-MAPI to the C_{60}, even with the presence of the low-n nBA-MAPI.

In addition to learning about perovskite degradation, we found that hexylammonium based 2D perovskites were more stable than butylammonium based perovskites, even when inexpensive Ag electrodes were used. This additional stability of the hexylammonium spacer could be a result of increased hydrophobicity and decreased anion diffusion, both of which allow the hexylammonium based perovskite to be more stable when Ag and Au electrodes are used. These results indicate that 2D perovskites with different spacers could one day not only improve the stability of perovskite solar cells, but also allow for cheaper electrical contacts such as Ag and Cu.

References

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