Remnant PbI$_2$, an unforeseen necessity in high-efficiency hybrid perovskite-based solar cells? 

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Remnant PbI₂, an unforeseen necessity in high-efficiency hybrid perovskite-based solar cells?\(^a\)

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Perovskite-containing solar cells were fabricated in a two-step procedure in which PbI₂ is deposited via spin-coating and subsequently converted to the CH₃NH₃PbI₃ perovskite by dipping in a solution of CH₃NH₃I. By varying the dipping time from 5 s to 2 h, we observe that the device performance shows an unexpectedly remarkable trend. At dipping times below 15 min the current density and voltage of the device are enhanced from 10.1 mA/cm² and 933 mV (5 s) to 15.1 mA/cm² and 1036 mV (15 min). However, upon further conversion, the current density decreases to 9.7 mA/cm² and 846 mV after 2 h. Based on X-ray diffraction data, we determined that remnant PbI₂ is always present in these devices. Work function and dark current measurements showed that the remnant PbI₂ has a beneficial effect and acts as a blocking layer between the TiO₂ semiconductor and the perovskite itself reducing the probability of back electron transfer (charge recombination). Furthermore, we find that increased dipping time leads to an increase in the size of perovskite crystals at the perovskite-hole-transporting material interface. Overall, approximately 15 min dipping time (~2% unconverted PbI₂) is necessary for achieving optimal device efficiency.

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With the global growth in energy demand and with compelling climate-related environmental concerns, alternatives to the use of non-renewable and noxious fossil fuels are needed.\(^1\) One such alternative energy resource, and arguably the only legitimate long-term solution, is solar energy. Photovoltaic devices which are capable of converting the photon flux to electricity are one such device.\(^2\) Over the last 2 years, halide hybrid perovskite-based solar cells with high efficiency have engendered enormous interest in the photovoltaic community.\(^3,\)\(^4\) Among the perovskite choices, methylammonium lead iodide (MAPbI₃) has become the archetypal light absorber. Recently, however, Sn-based perovskites have been successfully implemented in functional solar cells.\(^5,\)\(^6\) MAPbI₃ is an attractive light absorber due to its extraordinary absorption coefficient of \(1.5 \times 10^4 \text{ cm}^{-1}\) at 550 nm;\(^7\) it would take roughly 1 \(\mu\)m of material to absorb 99% of the flux at 550 nm. Furthermore, with a band gap of 1.55 eV (800 nm), assuming an external quantum efficiency of 90%, a maximum current density of ca. 23 mA/cm² is attainable with MAPbI₃.

Recent reports have commented on the variability in device performance as a function of perovskite layer fabrication.\(^8\) In our laboratory, we too have observed that seemingly identical films

\(^a\)Invited for the Perovskite Solar Cells special topic.

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have markedly different device performance. For example, when our films of PbI₂ are exposed to MAI for several seconds (ca. 60 s), then a light brown colored film is obtained rather than the black color commonly observed for bulk MAPbI₃ (see Sec. S2 of the supplementary material for the optical band gap of bulk MAPbI₃). This brown color suggests only partial conversion to MAPbI₃ and yields solar cells exhibiting a $J_{sc}$ of 13.4 mA/cm² and a $V_{oc}$ of 960 mV; these values are significantly below the 21.3 mA/cm² and 1000 mV obtained by others. Under the hypothesis that fully converted films will achieve optimal light harvesting efficiency, we increased the conversion time from seconds to 2 h. Unexpectedly, the 2-h dipping device did not show an improved photovoltaic response ($J_{sc} = 9.7$ mA/cm², $V_{oc} = 846$ mV) even though conversion to MAPbI₃ appeared to be complete. With the only obvious difference between these two devices being the dipping time, we hypothesized that the degree of conversion of PbI₂ to the MAPbI₃ perovskite is an important parameter in obtaining optimal device performance. We thus set out to understand the correlation between the method of fabrication of the MAPbI₃ layer, the precise chemical compositions, and both the physical and photo-physical properties of the film. We report here that remnant PbI₂ is crucial in forming a barrier layer to electron interception/recombination leading to optimized $J_{sc}$ and $V_{oc}$ in these hybrid perovskite-based solar cells.

We constructed perovskite-containing devices using a two-step deposition method according to a reported procedure with some modifications (see Sec. S1 of the supplementary material for the experimental details). MAPbI₃-containing photo-anodes were made by varying the dipping time of the PbI₂-coated photo-anode in MAI solution. In order to minimize the effects from unforeseen variables, care was taken to ensure that all films were prepared in an identical manner. The compositions of final MAPbI₃-containing films were monitored by X-ray diffraction (XRD). Independently of the dipping times, only the β-phase of the MAPbI₃ is formed (Figure 1). However, in addition to the β-phase, all films also showed the presence of unconverted PbI₂ (Figure 1, marked with *) which can be most easily observed via the (001) and (003) reflections at $2\theta = 12.56^\circ$ and $38.54^\circ$ respectively. As the dipping time is increased, the intensities of PbI₂ reflections decrease with a concomitant increase in the MAPbI₃ intensities. In addition to the decrease in peak intensities of PbI₂, the peak width increases as the dipping time increases indicating that the size of the PbI₂ crystallites is decreasing, as expected, and the converse is observed for the MAPbI₃ reflections. This observation suggests that the conversion process begins from the surface of the PbI₂ crystallites and proceeds toward the center where the crystallite domain size of the MAPbI₃ phase increases and that of PbI₂ diminishes. Interestingly, the remnant PbI₂ phase can be seen in the data of other reports, but has not been identified as a primary source of variability in cell performance.

Considering that the perovskite is the primary light absorber within the device, we wanted to further investigate how the optical absorption of the film changes with increasing dipping time.
FIG. 2. Absorption spectra of CH$_3$NH$_3$PbI$_3$ films as a function of unconverted PbI$_2$ phase fraction.

(Figure 2). The pure PbI$_2$ film shows a band gap of 2.40 eV, consistent with the yellow color of PbI$_2$. As the PbI$_2$ film is gradually converted to the perovskite, the band gap is progressively shifted toward 1.60 eV. The deviation of MAPbI$_3$'s band gap (1.60 eV) from that of the bulk MAPbI$_3$ material (1.55 eV) could be explained by quantum confinement effects related with the sizes of TiO$_2$ and MAPbI$_3$ crystallites and their interfacial interaction. Interestingly, we also noticed the presence of a second absorption in the light absorber layer, in which the gap gradually red shifts from 1.90 eV to 1.50 eV as the PbI$_2$ concentration is decreased from 9.5% to 0.3% (Figure 2—blue arrow).

Having established the chemical compositions and optical properties of the light absorber films, we proceeded to examine the photo-physical responses of the corresponding functional devices in order to determine how the remnant PbI$_2$ affects device performance. The pure PbI$_2$ based device remarkably achieved a 0.4% efficiency with a J$_{sc}$ of 2.1 mA/cm$^2$ and a V$_{oc}$ of 564 mV (Figure 3(a)). Upon progressive conversion of the PbI$_2$ layer to MAPbI$_3$, we observe two different regions (Figure 4, Table I). In the first region, the expected behavior is observed; as more PbI$_2$ is converted to MAPbI$_3$, the trend is toward higher photovoltaic efficiency, due both to J$_{sc}$ and V$_{oc}$, until 1.7% PbI$_2$ is reached. The increase in J$_{sc}$ is attributable, at least in part, to increasing absorption of light by the perovskite. We speculate that progressive elimination of PbI$_2$, present as a layer between TiO$_2$ and the perovskite, also leads to higher net yields for electron injection into TiO$_2$ and therefore, higher J values. For a sufficiently thick PbI$_2$ spacer layer, electron injection would occur in stepwise fashion, i.e., perovskite $\rightarrow$ PbI$_2$ $\rightarrow$ TiO$_2$. Finally, the photovoltage increase is attributable to

FIG. 3. (a) J-V curves and (b) EQE of CH$_3$NH$_3$PbI$_3$-based devices as a function of unconverted PbI$_2$ phase fraction.
FIG. 4. Summary of J-V data vs. PbI$_2$ concentration of CH$_3$NH$_3$PbI$_3$-based devices (Region 1: 0 to 15 min dipping time, Region 2: 15 min to 2 h dipping time).

TABLE I. Photovoltaic performance of CH$_3$NH$_3$PbI$_3$-based devices as a function of unconverted PbI$_2$ fraction.

<table>
<thead>
<tr>
<th>Dipping time</th>
<th>PbI$_2$ concentration$^a$</th>
<th>J$_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>Fill factor (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 s</td>
<td>100%</td>
<td>2.1</td>
<td>0.564</td>
<td>32</td>
<td>0.4</td>
</tr>
<tr>
<td>5 s</td>
<td>9.5%</td>
<td>10.1</td>
<td>0.933</td>
<td>52</td>
<td>4.9</td>
</tr>
<tr>
<td>60 s</td>
<td>7.2%</td>
<td>13.4</td>
<td>0.960</td>
<td>52</td>
<td>6.7</td>
</tr>
<tr>
<td>2 min</td>
<td>5.3%</td>
<td>14.0</td>
<td>0.964</td>
<td>55</td>
<td>7.4</td>
</tr>
<tr>
<td>5 min</td>
<td>3.7%</td>
<td>14.7</td>
<td>0.995</td>
<td>57</td>
<td>8.3</td>
</tr>
<tr>
<td>15 min</td>
<td>1.7%</td>
<td>15.1</td>
<td>1.036</td>
<td>62</td>
<td>9.7</td>
</tr>
<tr>
<td>30 min</td>
<td>0.8%</td>
<td>13.6</td>
<td>0.968</td>
<td>64</td>
<td>8.5</td>
</tr>
<tr>
<td>1 h</td>
<td>0.4%</td>
<td>12.4</td>
<td>0.938</td>
<td>65</td>
<td>7.6</td>
</tr>
<tr>
<td>2 h</td>
<td>0.3%</td>
<td>9.7</td>
<td>0.846</td>
<td>68</td>
<td>5.5</td>
</tr>
</tbody>
</table>

$^a$Determined from the Rietveld analysis of X-ray diffraction data.

the positive shift in TiO$_2$’s quasi-Fermi level as the population of photo-injected electrons is higher with increased concentration of MAPbI$_3$.

The second region yields a notably different trend; surprisingly, below a concentration of 2% PbI$_2$, J$_{sc}$, $V_{oc}$, and ultimately $\eta$ decrease. Considering that the light-harvesting efficiency would increase when the remaining 2% PbI$_2$ is converted to MAPbI$_3$ (albeit to only a small degree), then the remnant PbI$_2$ must have some other role. We posit that remnant PbI$_2$ serves to inhibit detrimental electron-transfer processes (Figure 5). Two such processes are back electron transfer from TiO$_2$ to holes in the valence band of the perovskite (charge-recombination) or to the holes in the HOMO of the HTM (charge-interception). This retardation of electron interception/recombination observation is reminiscent of the behavior of atomic layer deposited Al$_2$O$_3$/ZrO$_2$ layers that have been employed in dye-sensitized solar cells.$^{15-18}$

It is conceivable that the conversion of PbI$_2$ to MAPbI$_3$ occurs from the solution interface toward the TiO$_2$/PbI$_2$ interface and thus would leave sandwiched between TiO$_2$ and MAPbI$_3$ a blocking layer of PbI$_2$ that inhibits charge-interception/recombination. For this hypothesis to be correct, it is crucial that the conduction-band-edge energy (E$_{cb}$) of the PbI$_2$ be higher than the E$_{cb}$ of the TiO$_2$.$^{19-21}$

The work function of PbI$_2$ was measured by ultraviolet photoelectron spectroscopy (UPS) and was observed to be at 6.35 eV vs. vacuum level, which is 0.9 eV lower than the valence-band-edge energy (E$_{vb}$) of MAPbI$_3$ (see Sec. S7 of the supplementary material$^{23}$ for the work function of PbI$_2$); the E$_{cb}$ (4.05 eV) was calculated by subtracting the work function from the band gap (2.30 eV).
FIG. 5. Model of charge-interception/recombination retardation by the unconverted PbI$_2$ layer in CH$_3$NH$_3$PbI$_3$-based solar cell.

The $E_{cb}$ of PbI$_2$ is 0.26 eV higher than the $E_{cb}$ of TiO$_2$ and thus PbI$_2$ satisfies the conditions of a charge-recombination/interception barrier layer.

In order to probe the hypothesis that PbI$_2$ acts as a charge-interception barrier, dark current measurements, in which electrons flow from TiO$_2$ to the HOMO of the HTM, were made. Consistent with our hypothesis, Figure 6 illustrates that the onset of the dark current occurs at lower potentials as the PbI$_2$ concentration decreases. In the absence of other effects, the increasing dark current with increasing fraction of perovskite (and decreasing fraction of PbI$_2$) should result in progressively lower open-circuit photovoltages. Instead, the photocurrent density and the open-circuit photovoltage both increase, at least until to PbI$_2$ fraction reaches 1.7%. As discussed above, thinning of a PbI$_2$-based
sandwich layer should lead to higher net injection yields, but excessive thinning would diminish the effectiveness of PbI$_2$ as a barrier layer for back electron transfer reactions.

Given the surprising role of remnant PbI$_2$ in these devices, we further probed the two-step conversion process by using scanning-electron microscopy (SEM) (Figure 7). Two domains of lead-containing materials (PbI$_2$ and MAPbI$_3$) are present. The first domain is sited within the mesoporous TiO$_2$ network (area 1) while the second grows on top of the network (area 2). Area 2 initially contains 200 nm crystals. As the dipping time is increased, the crystals show marked changes in size and morphology. The formation of bigger perovskite crystals is likely the result of the thermodynamically driven Ostwald ripening process, i.e., smaller perovskite crystals dissolve and re-deposits onto larger perovskite crystals. The rate of charge-interception, as measured via dark current, is proportional to the contact area between the perovskite and the HTM. Thus, the eventual formation of large, high-aspect-ratio crystals, as shown in Figure 7, may well lead to increases in contact area and thereby contributes to the dark-current in Figure 6. Regardless, we found that the formation of large perovskite crystals greatly decreased our success rate in constructing high-functioning, non-shorting solar cells.

In summary, residual PbI$_2$ appears to play an important role in boosting overall efficiencies for CH$_3$NH$_3$PbI$_3$-containing photovoltaics. PbI$_2$’s role appears to be that of a TiO$_2$-supported blocking layer, thereby slowing rates of electron(TiO$_2$)/hole(perovskite) recombination, as well as decreasing rates of electron interception by the hole-transporting material. Optimal performance for energy conversion is observed when ca. 98% of the initially present PbI$_2$ has been converted to the perovskite. Conversion to this extent requires about 15 min. Pushing beyond 98% (and beyond 15 min of reaction time) diminishes cell performance and diminishes the success rate in constructing non-shorting cells. The latter problem is evidently a consequence of conversion of small and more-or-less uniformly packed perovskite crystallites to larger, poorly packed crystallites of varying shape and size. Finally, the essential, but previously unrecognized, role played by remnant PbI$_2$ provides an additional explanation for why cells prepared dissolving and then depositing pre-formed CH$_3$NH$_3$PbI$_3$ generally under-perform those prepared via the intermediacy of PbI$_2$.

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22 See supplementary material at http://dx.doi.org/10.1063/1.4895038 for experimental details, absorption spectrum of bulk CH$_3$NH$_3$PbI$_3$, fraction, size, absorption spectrum, work function of unconverted PbI$_2$, and average photovoltaic performance.