R-functionalized benzylphosphonic acid SAMs for improved efficiency in inverted triple cation lead perovskite solar cells

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Introduction
Inverted (p-i-n) lead perovskite solar cells have reached power conversion efficiency (PCE) levels >18% in comparison to conventional (n-i-p) perovskite solar cells with PCEs >22% [1-3]. In order to improve the PCEs of the solar cells with inverted architecture, they are currently being investigated intensively. Among the different ideas and concepts, self-assembled monolayers (SAMs) have shown promise [3]. In this study, we investigate the influence of functionalized benzylphosphonic acid SAMs (R-BPA SAMs) in a glass/ITO/NIO/R-BPA SAM/perovskite/PbO2/MgO solar cell setup, in which nickel oxide [4] (NiO) is used as a hole transport material and [6,6]-Phenyl C61 butyric acid methyl ester (PC61BM) is used as an electron transport material. We use a cesium (Cs+), formamidinium (FA+), and methylammonium (MA+) based triple cation perovskite as absorber layer. Benzylphosphonic acid molecules, for the modification of the NiO+ layer, were investigated including five different functional groups such as 4-bromo-(Br-), 4-fluoro- (F-), 4-nitro- (NO2-), 4-amino- (NH2-), and 4-methoxy- (HOCO-).

Characterization and results

Table 1: The table enlists the PCE, open circuit voltage (VOC), short circuit current density (JSC), and fill factor (FF) for the solar cells represented in Figure 4.

<table>
<thead>
<tr>
<th>Reference (w/o SAM)</th>
<th>PCE (%)</th>
<th>VOC (V)</th>
<th>JSC (mA cm-2)</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-BPA SAM</td>
<td>16.5</td>
<td>0.957</td>
<td>24.4</td>
<td>0.71</td>
</tr>
<tr>
<td>F-BPA SAM</td>
<td>13.4</td>
<td>1.087</td>
<td>22.5</td>
<td>0.54</td>
</tr>
<tr>
<td>NH4-BPA SAM</td>
<td>13.8</td>
<td>0.987</td>
<td>21.2</td>
<td>0.67</td>
</tr>
<tr>
<td>OCH3-BPA SAM</td>
<td>13.9</td>
<td>1.007</td>
<td>20.3</td>
<td>0.68</td>
</tr>
<tr>
<td>OCH2-BPA SAM</td>
<td>14.3</td>
<td>0.987</td>
<td>23.4</td>
<td>0.62</td>
</tr>
<tr>
<td>BPA SAM</td>
<td>12.2</td>
<td>1.047</td>
<td>22.4</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Figure 2: (A) Ultraviolet visible spectra, and (B) X-ray diffraction (XRD) patterns for glass/ITO/NIO/R-BPA SAM/perovskite substrate. (8 represents unreacted cubic lead iodide (PbI2) impurities.)

In this work, we investigated the effect of R-BPA SAMs on Cs0.9(FA0.85MA0.15)Br0.95(PbI3Br0.7) based inverted solar cells. The absorption spectra of the perovskite films prepared on the modified NiOx films (see Figure 2A) do not reveal a change in the absorption onset of the perovskite layers. The slight difference in the absorption spectra in the lower wavelength region might stem from a slight variation in layer thickness. The X-ray diffraction patterns in Figure 2(B) show that the perovskite films crystallize in a cubic crystal structure and no significant changes in the full width half maximum of the peaks of the perovskite thin film due to the R-BPA SAMs are observed. The SEM (top view) images show similar grain sizes and a narrower size distribution for NO2-BPA SAM and OCH3-BPA SAM as compared to the reference (w/o SAM) and other R-BPA SAMs as shown in Figure 3(A-F) and Figure 5(A) respectively. Figure 5(B-C) represent the contact angle measurement images for glass/NIOx (12.8°) and glass/NIOx/Br-BPA SAM (71.9°) using water. This indicates the presence of the Br-BPA molecules, which change the surface properties of the NiOx layers. The J-V curves of the perovskite solar cells and the corresponding performance parameters (PCE, VOC, JSC, and FF) are presented in Figure 4 and Table 1, respectively. Upon introduction of the (4-bromobenzyl)phosphonic acid Br-BPA SAM, improvements in JSC, VOC and FF were observed. Thereby the overall performance of the solar cells increased from 11.90±0.06% (reference, average of 10 devices) to 13.65±0.31% for the Br-BPA SAM modified NiOx hole transport layers. The champion cell with Br-BPA SAM showed a PCE of 16.5% and with the introduction of a F-BPA SAM we observed a VOC of 1.087 V.

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References