Optimization of the Ag/PCBM interface by a rhodamine interlayer to enhance the efficiency and stability of perovskite solar cells

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The hole transporting layer was grown from the stable NiOx dispersion. As shown in Fig. S1 by AFM, a pinhole free layer was obtained with 20 nm thick and a 3.5 nm average surface roughness.

Fig. S1. Morphologic and profile of the NiOx layer on ITO.

Fig. S2. Cyclic voltammetry of Rhodamine 101. The measurement was performed using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) in dichloromethane as electrolyte, platinum wire as counter electrode, Ag/AgCl sat electrode as reference and glassy carbon as working electrode.
**HOMO-LUMO calculation**

The HOMO-LUMO calculation of Rhodamine is summarized in Table S1. A 2.11 eV estimated bandgap was obtained from the cyclic voltammetry ($E_g = \text{LUMO-HOMO}$). This value agrees with the reported optical band gap.[1]

**Table S1.** Electric parameters calculated from the cyclic voltammetry.

<table>
<thead>
<tr>
<th></th>
<th>HOMO</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{ox}$ vs. $E(\text{Ag/AgCl}_{\text{sat}})$ V</td>
<td>$E_{ox}$ vs. NHE</td>
<td>$E_{red}$ vs. $E(\text{Ag/AgCl}_{\text{sat}})$ V</td>
</tr>
<tr>
<td></td>
<td>$(E_{ox} \text{ vs. } E(\text{Ag/AgCl}_{\text{sat}}) + 0.207)$ V</td>
<td>$(E_{red} \text{ vs. } E(\text{Ag/AgCl}_{\text{sat}}) + 0.207)$ V</td>
</tr>
<tr>
<td>1.04</td>
<td>1.211</td>
<td>-5.611</td>
</tr>
<tr>
<td>-1.10</td>
<td>-0.893</td>
<td>-3.501</td>
</tr>
</tbody>
</table>

**Kelvin Probe Force Microscopy (KPFM) measurements of the Silver Electrode**

The effect of the Rhodamine interlayer on the $W_F$ of silver was investigated by KPFM. First, the surface potential (SP) of the reference sample (100 nm film of silver on glass) was measured. Then, the SP of silver films with a Rhodamine layer atop or beneath was measured. The increase in the surface potential was calculated as $\Delta SP (\text{mV}) = SP_{\text{sample}} - SP_{\text{reference}}$ and the values are reported in Table S2. The increase in the SP indicate that the $W_F$ of silver is lowered [2]. The decrease in the $W_F$ is shown in Table S2 calculated from the formula $\Delta W_F (\text{eV}) = W_{F_{\text{sample}}} - W_{F_{\text{reference}}}$. These results are in agreement with KPFM measurements of the $W_F$ of Au/Rhodamine layers which show that Rhodamine produce an increase in the $W_F$ of Au films indicating a decrease in the $W_F$ of gold [2]. Finally, the $W_F$ of the silver electrode was measured for complete perovskite solar cell (PSC) devices with or without Rhodamine layer. The $W_F$ of silver in the device with Rhodamine changed by -0.18 eV (from -4.5 to -4.3 eV) whereas it is almost identical to the reference sample for the cell without Rhodamine layer.

**Table S2.** Modification in the surface potential (SP) and the $W_F$ of the Silver electrode from KPFM measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta SP (\text{mV})$</th>
<th>$\Delta W_F (\text{eV})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass/Ag (Reference)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Glass/Ag/Rhodamine</td>
<td>413</td>
<td>-0.43</td>
</tr>
<tr>
<td>Glass/Rhodamine/Ag</td>
<td>307</td>
<td>-0.30</td>
</tr>
<tr>
<td>Glass/ITO/NiOx/Perovskite/PC70BM/Ag</td>
<td>26</td>
<td>-0.04</td>
</tr>
<tr>
<td>Glass/ITO/NiOx/Perovskite/PC70BM/Rhodamine/Ag</td>
<td>152</td>
<td>-0.18</td>
</tr>
</tbody>
</table>

**Influence of the Rhodamine layer on the photovoltaic parameters**

The effect of Rhodamine on the photovoltaic parameters of the pin solar cell with the configuration ITO/NiOx/CH$_3$NH$_3$PbI$_3$/ETL/Ag is presented in Figures S3 and S4. The electron transport layer (ETL) was comprised of PC$_{60}$BM, PC$_{70}$BM, PC$_{70}$BM/Rhodamine, or PC$_{60}$BM/Rhodamine. Figure S3 shows that the addition of the Rhodamine layer cause a decrease in the series resistance (Rs) for the devices with PC$_{60}$BM or PC$_{70}$BM as ETL. The device with the PC$_{70}$BM/Rhodamine bilayer presented the lowest Rs. Then, an optimization study of the thickness of the Rhodamine layer was carried out for PSCs with the configuration ITO/NiOx/CH$_3$NH$_3$PbI$_3$/PC$_{70}$BM/Rhodamine/Ag. The PCE, Jsc and Rs of a batch of 16 devices fabricated with Rhodamine layers of thickness ranging from 0 to 50 nm is shown in Fig. S4. For this study, Rhodamine was dissolved in isopropyl alcohol (IPA) at concentrations of 0, 0.5, 2, 4, and 6 mg/mL IPA and spin casted at 4000 rpm yielding films of 0, 2, 8, 16, and 50 nm, respectively. The thickness of the layer derived from the 0.5
mg/mL solution was out of the limit of detection of our profilometer. We estimated the layer thickness to be about 2 nm from the curve of concentration vs. thickness. For the devices, the optimal thickness of the Rhodamine layer is 2 nm since it yields the highest Jsc, the lowest Rs and consequently the highest PCE.

**Figure S3.** Series resistance (Rs) of PSCs with different electron transport layers.

The photovoltaic response of the fabricated ITO/NiO\textsubscript{x}/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/PC\textsubscript{70}BM/Rh/Ag based devices is presented in Fig. S5. A champion 16.6 % power conversion efficiency was achieved. As shown in Fig. S5a, devices showed null hysteresis even at a fast 400 mV/s sweeping voltage during the measurement. The EQE (Fig. S5b) exhibited an almost flat response along the absorption band of the perovskite resulting in an integrated 20.89 mA/cm\textsuperscript{2} short-circuit current density and a stabilized power output (SPO) reaching 16.62 % as shown in Fig. S5c.

**Figure S4.** Dependence of the PCE, J\textsubscript{sc} and R\textsubscript{s} on the thickness of the Rhodamine layer.

**Figure S5.** Photovoltaic performance of the champion device of ITO/NiO\textsubscript{x}/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/PC\textsubscript{70}BM/Rh/Ag.
Fig. S5. Photovoltaic parameters of the ITO/NiO$_x$/CH$_3$NH$_3$PbI$_3$/PC$_{70}$BM/Rh/Ag based devices. (a) J-V curve of the champion device reaching a PCE of 16.6% and null hysteresis. (b) External quantum efficiency and integrated $J_{sc}$. (c) Steady state current and PCE as a function of time showing a stabilized power output of 16.62%.

Fig. S6a shows the XRD diffractogram of the complete devices taken at different times, evidencing the formation of degradation byproducts, such as CH$_3$NH$_3$PbI$_3$.H$_2$O, PbI$_2$ and AgI. The peak assignation corresponded to the reflection peaks of perovskite (110), (200), (220), (211), (202) and (310) at 14.1°, 20°, 23.4°, 24°, 27.5 and 31.8°, respectively. [3] The silver electrode presented reflection of the (111) plane at 38.1°, while the AgI and PbI$_2$ at 39.2° and 12.6° corresponding to the (111) and (004) plane, respectively. Finally, the CH$_3$NH$_3$PbI$_3$.H$_2$O perovskite was observed at 8.6° and 10.7°.[4] In order to show a clearer peak assignation, Fig. S6b shows the zoom image of XRD diffractogram for the samples after 30 days.

Fig. S6. XRD spectra of the complete devices showing degradation byproducts. (a) XRD for all samples measured at 0, 10 and 30 days. (b) Zoom image of the XRD diffractogram for devices after 30 days.
Fig. S7. (a-c) Topography and (d-f) surface potential maps of (a, d) perovskite layer on NiOx, (b, e) PC$_{60}$BM layer on perovskite and (c, f) PC$_{60}$BM / Rhodamine bilayer on perovskite.

Fig. S8. Grain size (black squares) and roughness (blue circles) of perovskite (PVKT), PC$_{70}$BM and PC$_{70}$BM/Rhodamine (Rh) surfaces.

Fig. S9 shows the surface potential profiles of the PC$_{70}$BM, and PC$_{70}$BM/Rhodamine grown on perovskite.
**Notes and references**


