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

John Ciro,^a Santiago Mesa,^a Jose Ignacio Uribe,^{a,b} Mario Alejandro Mejía-Escobar,^a Daniel Ramirez,^a Juan Felipe Montoya,^a Rafael Betancur,^a Hyun-Seok Yoo,^c Nam-Gyu Park^{c,†} and Franklin Jaramillo^{a,†}

^a Centro de Investigación, Innovación y Desarrollo de Materiales – CIDEMAT, Facultad de Ingeniería, Universidad de Antioquia UdeA, Calle 70 No. 52-21, Medellín. Colombia.

^b Grupo de Estado Sólido, Instituto de Física, Universidad de Antioquia UdeA, Calle 70 No. 52-21, Medellín, Colombia.

^c School of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Korea.

[†] Corresponding Authors F.J. <u>franklin.jaramillo@udea.edu.co, N-Y.P. npark@skku.edu</u>



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

The hole transporting layer was grown from the stable NiO_x 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. 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 (Eg = LUMO-HOMO). This value agrees with the reported optical band gap.[1]

номо			
E _{ox} vs. E(Ag/AgCl _{sat.}) V	E _{ox} vs. NHE	HOMO = - (E _{ox} vs. NHE + 4.4) eV	
	(E _{ox} vs. E(Ag/AgCl _{sat.}) + 0.207) V		
1.04	1.211	-5.611	
LUMO			
E _{Red} vs. E(Ag/AgCl _{sat.}) V	E _{ox} vs. NHE	LUMO = - (E _{Red} vs. NHE + 4.4) eV	
	(E _{Red} vs. E(Ag/AgCl _{sat.}) + 0.207) V		
-1.10	-0.893	-3.501	

 Table S1. Electric parameters calculated from the cyclic voltammetry.

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 Δ SP (mV)=SP_{sample}-SP_{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 Δ W_F (eV)= W_{Fsample}-W_{Freference}. 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 SP 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.

Sample	ΔSP (mV)	ΔW _F (eV)
Glass/Ag (Reference)	0	0
Glass/Ag/Rhodamine	413	-0.43
Glass/Rhodamine/Ag	307	-0.30
Glass/ITO/NiOx/Perovskite/PC70BM/Ag	26	-0.04
Glass/ITO/NiOx/Perovskite/PC70BM/Rhodamine/Ag	152	-0.18

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 $ITO/NiO_x/CH_3NH_3PbI_3/ETL/Ag$ is presented in Figures S3 and S4. The electron transport layer (ETL) was comprised of $PC_{60}BM$, $PC_{70}BM$, $PC_{$

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.



Figure S4. Dependence of the PCE, J_{sc} and R_s on the thickness of the Rhodamine layer.

The photovoltaic response of the fabricated $ITO/NiO_x/CH_3NH_3PbI_3/PC_{70}BM/Rh/Ag$ 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/cm² short-circuit current density and a stabilized power output (SPO) reaching 16.62 % as shown in Fig. S5c.



Fig. S5. Photovoltaic parameters of the ITO/NiO_x/CH₃NH₃PbI₃/PC₇₀BM/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 difractogram of the complete devices taken at different times, evidencing the formation of degradation byproducts, such as $CH_3NH_3PbI_3.H_2O$, PbI_2 and Agl. 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 Agl and PbI₂ at 39.2° and 12.6° corresponding to the (111) and (004) plane, respectively. Finally, the $CH_3NH_3PbI_3.H_2O$ 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), PC₇₀BM and PC₇₀BM/Rhodamine (Rh) surfaces.

Fig. S9 shows the surface potential profiles of the PC₇₀BM, and PC₇₀BM/Rhodamine grown on perovskite.



Fig. S9. Surface potential profiles of a) PC₇₀BM and b) PC₇₀BM/Rhodamine (Rh) bilayer.

Figure S10 show the photoluminescence (PL) spectra of samples with the configuration Glass/perovskite, Glass/perovskite/PCBM and Glass/PCBM/Rhodamine. We found no effect of the Rhodamine on the quenching or the PL intensity of the peak corresponding to the emission of perovskite



Fig S10. Photoluminescence spectra of Perovskite samples on glass with or without ETL layers.

Notes and references

- A. Synak, P. Bojarski, B. Grobelna, L. Ku, A. Lewkowicz, Determination of Local Dye Concentration in Hybrid Porous Silica Thin Films, (2013).
- K. Sun, B. Zhao, V. Murugesan, A. Kumar, K. Zeng, J. Subbiah, et al., High-performance polymer solar cells with a conjugated zwitterion by solution processing or thermal deposition as the electron-collection interlayer, J. Mater. Chem.,. 22 (2012) 24155–24165. doi:10.1039/C2JM35221D.
- [3] M.V.L. and Y.Q. Shenghao Wang, Luis K. Ono, Matthew R. Leyden, Yuichi Kato, Sonia R. Raga, Smooth perovskite thin films and efficient perovskite solar cells prepared by the hybrid deposition method, (2015). doi:10.1039/C5TA03593G.
- [4] A.M.A. Leguy, Y. Hu, M. Campoy-Quiles, M.I. Alonso, O.J. Weber, P. Azarhoosh, et al., Reversible Hydration of CH₃ NH₃ Pbl₃ in Films, Single Crystals, and Solar Cells, Chem. Mater. 27 (2015) 3397–3407. doi:10.1021/acs.chemmater.5b00660.