

Electronic Supplementary Information

La₂O₃ Interface Modification of Mesoporous TiO₂ Nanostructures Enabling Highly Efficient Perovskite Solar Cells

Shoyebmohamad F. Shaikh, Hyeok-Chan Kwon, Wooseok Yang, Hyewon Hwang, Hongseuk Lee, Eunsong Lee, Sun Ihl Ma, and Jooho Moon*

Department of Materials Science and Engineering, Yonsei University
Seoul 120-749, Republic of Korea

*Corresponding author, e-mail: jmoon@yonsei.ac.kr, Tel.: +82-2-2123-2855, Fax: +82-2-312-5375.

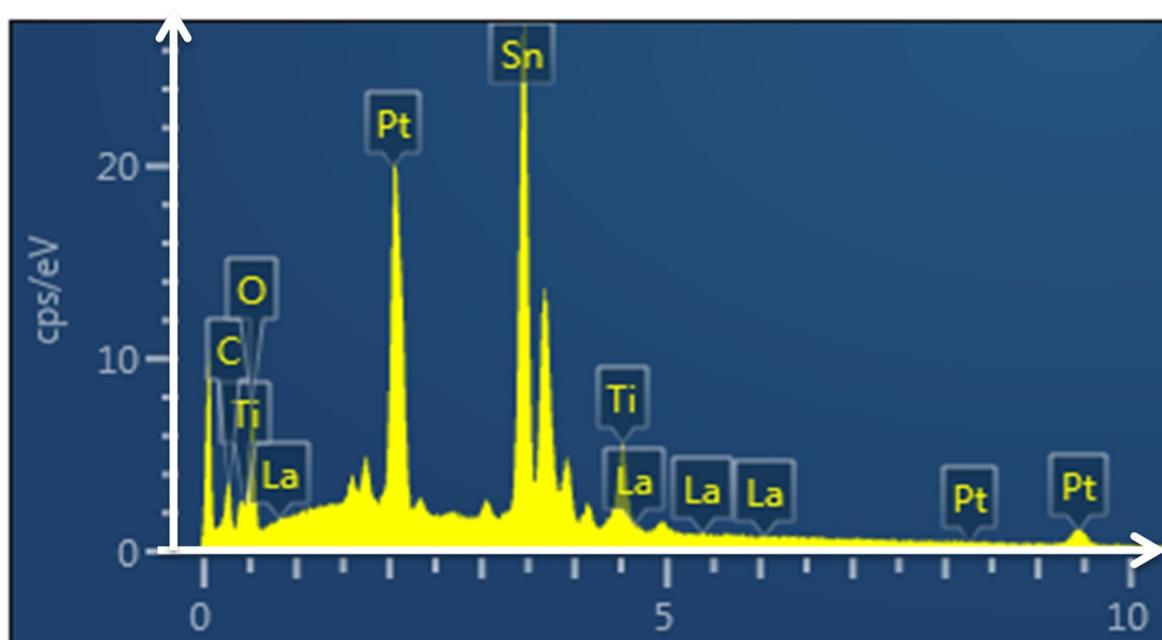


Fig. S1 EDX analysis of an FE-SEM image of mp-TiO₂-La₂O₃ ETL on an FTO substrate.

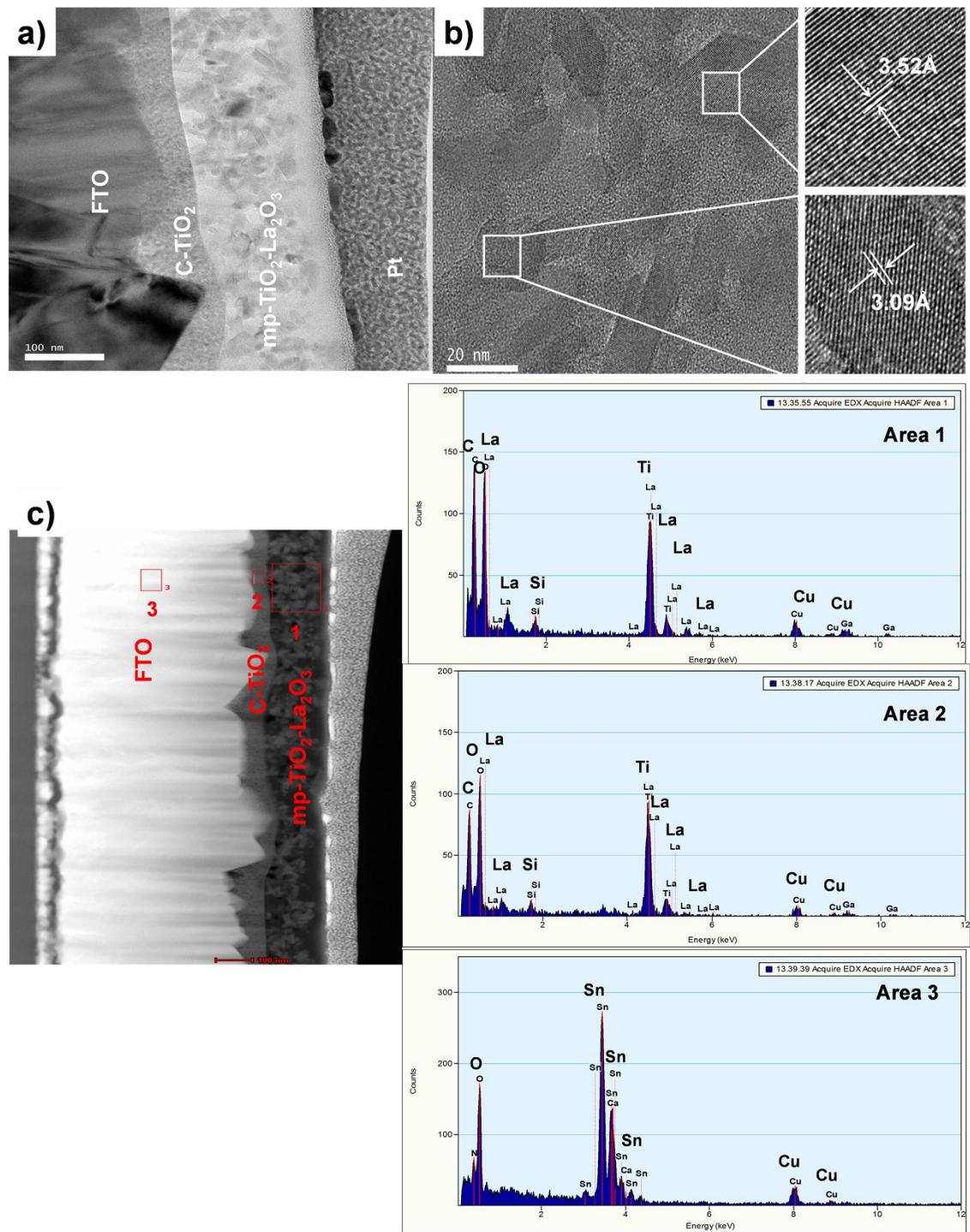


Fig. S2 a) A focused ion beam (FIB) cross-sectioned high resolution transmission electron microscopy (HRTEM) image of mp-TiO₂-La₂O₃, b) high-magnification TEM images of mp-TiO₂-La₂O₃ with *d*-spacing analyses (insets), and c) EDX analysis of FIB cross-sectioned interfaces of FTO/C-TiO₂/mp-TiO₂-La₂O₃ ETLs.

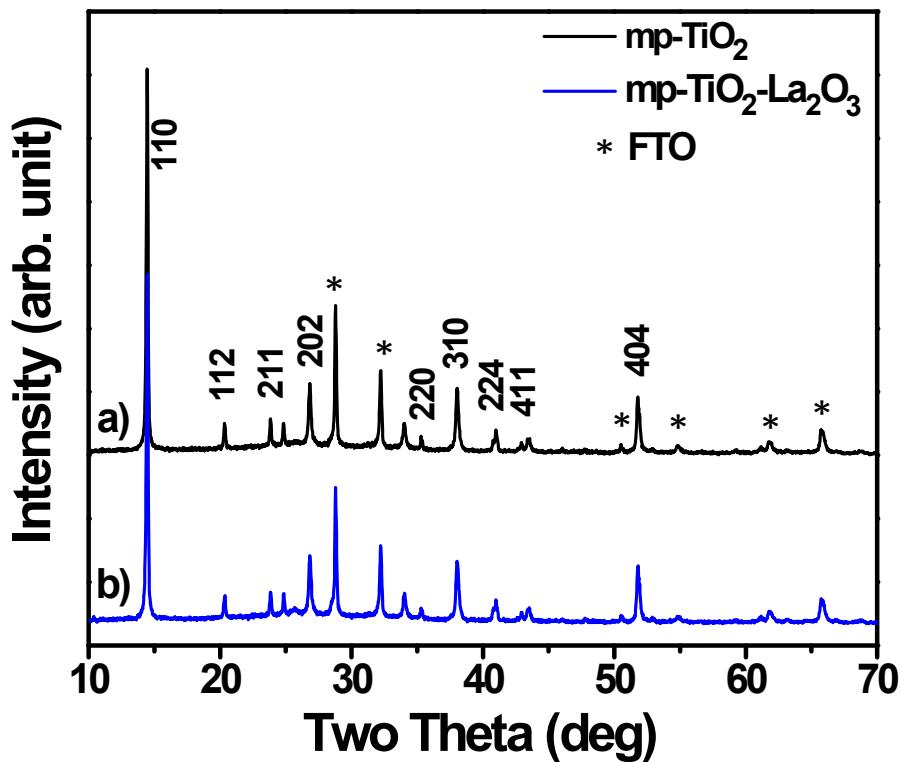


Fig. S3 XRD patterns of (a) mp-TiO₂/CH₃NH₃PbI₃ and (b) mp-TiO₂-La₂O₃/CH₃NH₃PbI₃. The asterisks (*) indicate FTO substrate peaks.

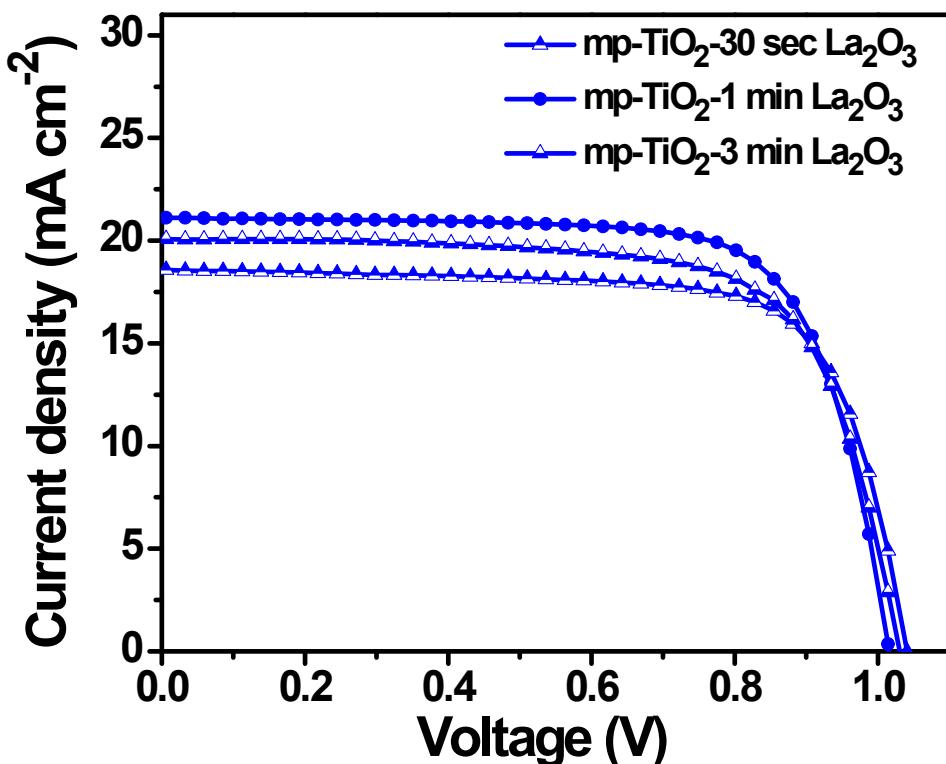


Fig. S4 J – V characteristics of an FTO/mp-TiO₂-La₂O₃/CH₃NH₃PbI₃/spiro-OMeTAD/gold device under illumination of simulated AM1.5G light (100 mW cm⁻²). The La₂O₃ interface modification layers were varied using different dip coating times of 30 s, 1 min, and 3 min. The scan rate was constant at 8.6 mV s⁻¹ for all the measurements.

Table S1 Summary of photovoltaic performance metrics of the champion devices fabricated by varying the dip coating times

ETL	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
mp-TiO ₂ -30 s La ₂ O ₃	18.63	1.00	67.01	12.53
mp-TiO ₂ -1 min La ₂ O ₃	20.84	1.01	74.64	15.81
mp-TiO ₂ -3 min La ₂ O ₃	20.36	1.01	70.64	14.55

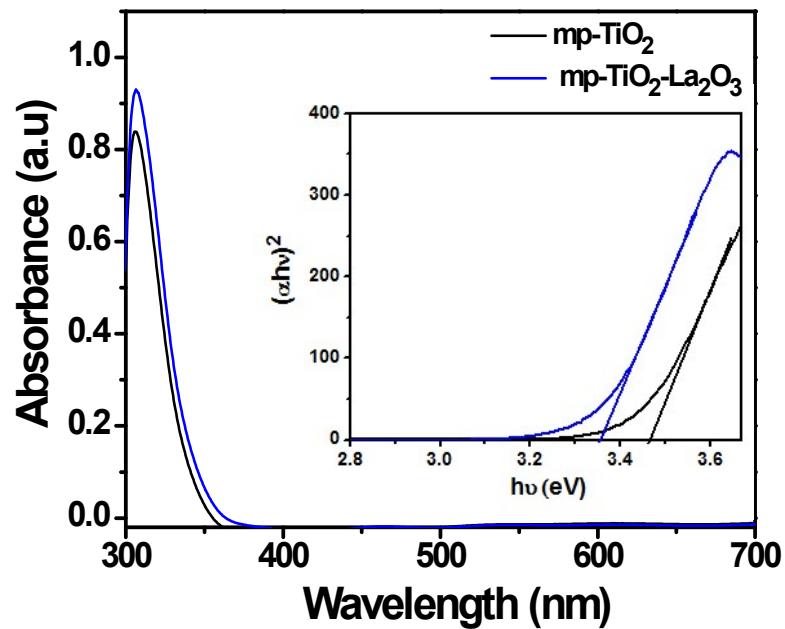


Fig. S5 UV-vis absorbance spectra of mp-TiO₂ and mp-TiO₂-La₂O₃ ETLs before depositing CH₃NH₃PbI₃. The inset Tauc plot shows the band gap positions of the mp-TiO₂ and mp-TiO₂-La₂O₃ ETLs.

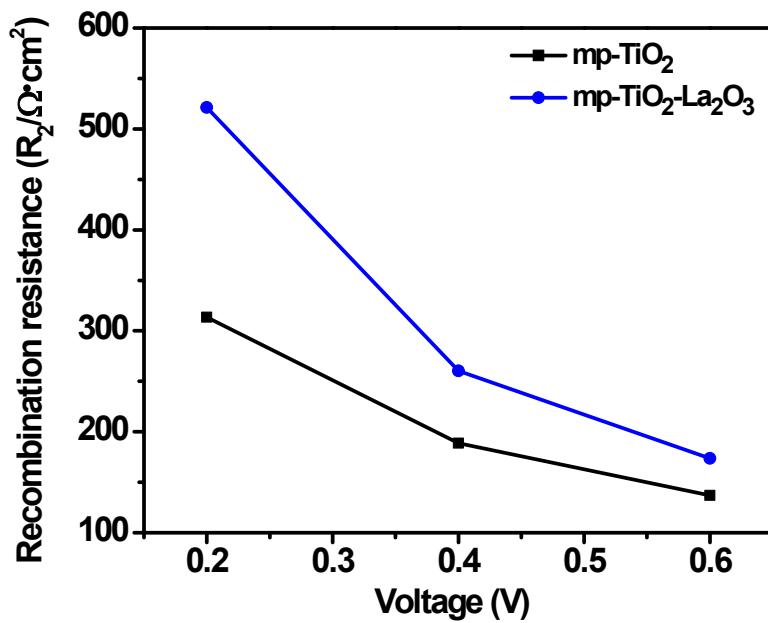


Fig. S6 Recombination resistances of both mp-TiO₂ ETL- and mp-TiO₂-La₂O₃ ETL-based devices obtained at different bias potentials under illumination of 100 mW cm⁻² AM 1.5.

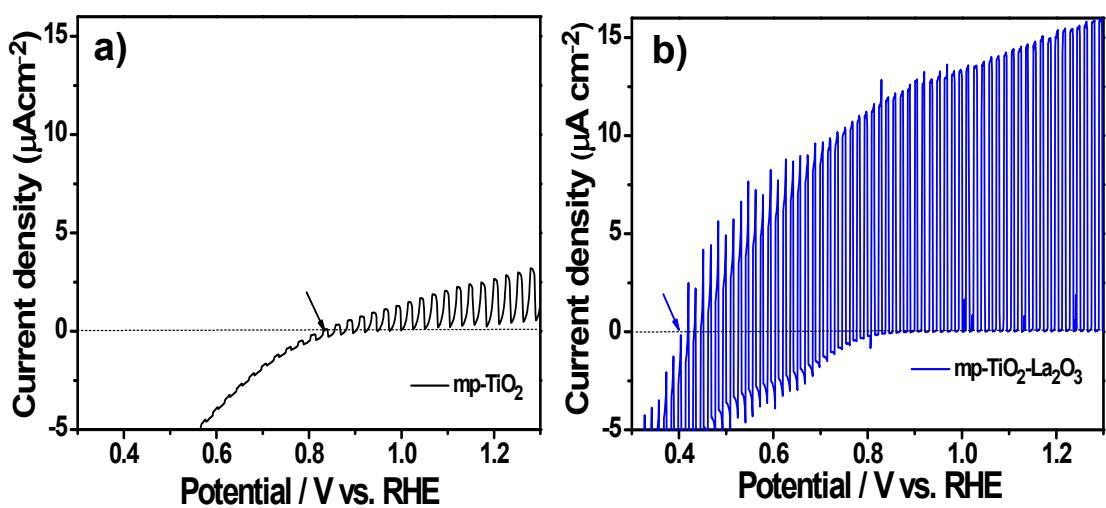


Fig. S7 Photocurrent-potential curve measured in a 0.5 M aqueous Na_2SO_4 solution under illumination of simulated AM1.5 light. The measurement was performed using the three-electrode configuration with a Ag/AgCl electrode as the reference electrode, Pt mesh as the counter electrode, and either (a) FTO/mp-TiO₂ or (b) FTO/mp-TiO₂-La₂O₃ as the working electrode in a 0.5 M aqueous Na_2SO_4 solution.

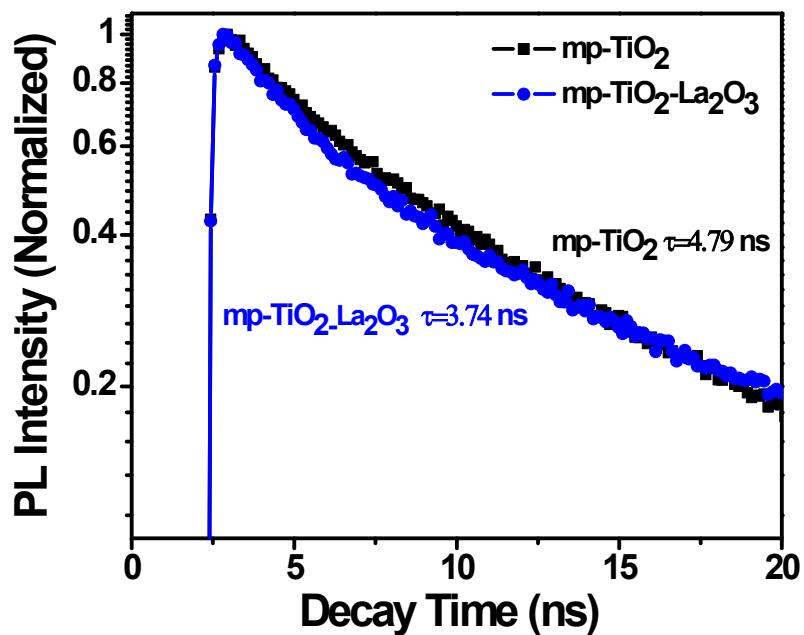


Fig. S8 Time-resolved PL spectra of both ETL samples on a glass substrate including glass/mp-TiO₂/CH₃NH₃PbI₃ and glass/mp-TiO₂-La₂O₃/CH₃NH₃PbI₃.

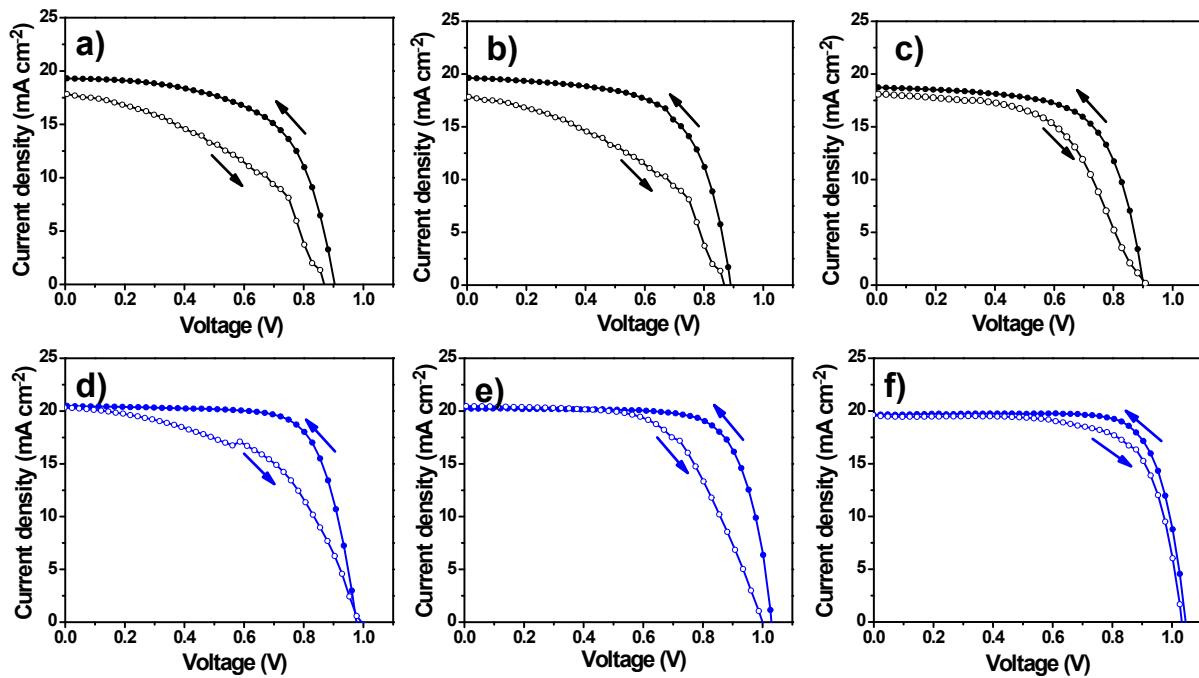


Fig. S9 J – V characteristics of forward and reverse scans for both FTO/mp-TiO₂/CH₃NH₃PbI₃/spiro-OMeTAD/Au and FTO/mp-TiO₂-La₂O₃/CH₃NH₃PbI₃/spiro-OMeTAD/Au devices under illumination of simulated AM1.5G light (100 mW cm^{-2}) at different scan rates of (a, d) 520, (b, e) 52, and (c, f) 8.6 mV s^{-1} .

Table S2 Photovoltaic parameters of both FTO/mp-TiO₂/CH₃NH₃PbI₃/spiro-OMeTAD/Au and FTO/mp-TiO₂-La₂O₃/CH₃NH₃PbI₃/spiro-OMeTAD/Au devices shown in Fig. S9 (a-f) as a function of scan rate and scan direction

Scan rate (mV s^{-1})	ETLs	Scan direction	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
520	mp-TiO ₂	Reverse	19.28	0.90	60.44	10.53
		Forward	18.20	0.88	39.45	6.53
	mp-TiO ₂ -La ₂ O ₃	Reverse	20.48	1.00	73.19	15.02
		Forward	20.33	1.04	52.25	10.55
52	mp-TiO ₂	Reverse	19.63	0.89	63.42	11.08
		Forward	17.88	0.86	44.32	6.83
	mp-TiO ₂ -La ₂ O ₃	Reverse	20.21	0.99	74.52	15.48
		Forward	20.44	1.02	59.68	11.87
8.7	mp-TiO ₂	Reverse	18.73	0.90	65.73	11.10
		Forward	17.70	0.87	57.83	8.98
	mp-TiO ₂ -La ₂ O ₃	Reverse	19.65	1.03	77.44	15.81
		Forward	19.63	1.01	70.56	14.38

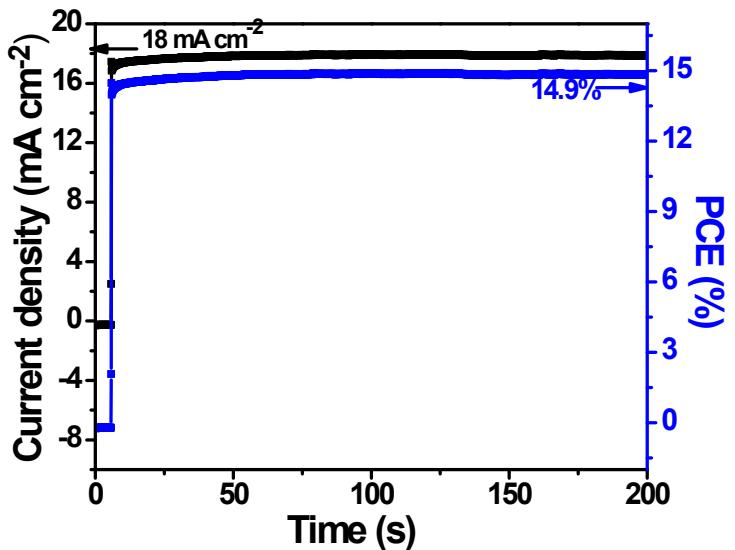


Fig. S10 Stabilized photocurrent density (black) and PCE (blue) measured at the maximum power voltage of 0.83 V for 200 s.

Table S3 Comparative study of interface modifications on TiO_2 ETLs for perovskite solar cell applications

ETL Type and Material	Chemicals/Method	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)	Approximate enhancement in PEC (%)	Reference
mp- TiO_2	Cesium carbonate/ Spin coating	19.8	0.97	62.0	11.9	23	[7]
mp- $\text{TiO}_2\text{-Cs}_2\text{CO}_3$		21.3	1.03	65.0	14.2		
C- TiO_2	Polyoxyethylene/ Spin coating	17.9	1.00	66.0	11.8	20	[10]
C- $\text{TiO}_2\text{-PEO}$		20.7	1.02	65.0	13.8		
C- TiO_2	Cesium bromide/ Spin coating	18.7	0.99	69.0	13.1	32	[15]
C- $\text{TiO}_2\text{-CsBr}$		20.7	1.06	75.0	16.3		
mp- TiO_2	Magnesium methoxide/ Spin coating	20.11	0.85	67.1	11.4	13	[19]
mp- $\text{TiO}_2\text{-MgO}$		20.02	0.89	71.2	12.7		
mp- TiO_2	Aluminum tri-sec-butoxide/ Dip coating	17.6	0.87	67.9	10.4	23	[20]
mp- $\text{TiO}_2\text{-Al}_2\text{O}_3$		20.1	0.96	66.1	12.7		
mp- TiO_2	Lanthanum (III) nitrate/ Dip coating	18.73	0.90	65.73	11.10	46	Present Work
mp- $\text{TiO}_2\text{-La}_2\text{O}_3$		20.84	1.01	74.64	15.81		