Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Versatile Perovskite Solar Cell Encapsulation by Low-Temperature ALD-Al_2O_3 with Long-Term Stability Improvement

Supporting Information

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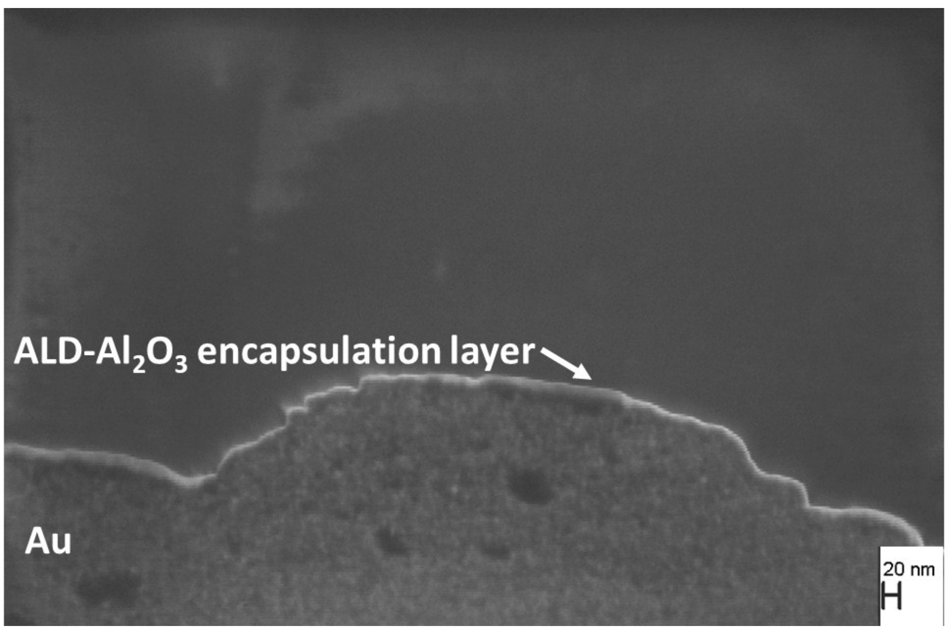

Figure S1. FIB-SEM observation of the ALD-Al_2O_3/Au interface after encapsulation process at 60 °C.

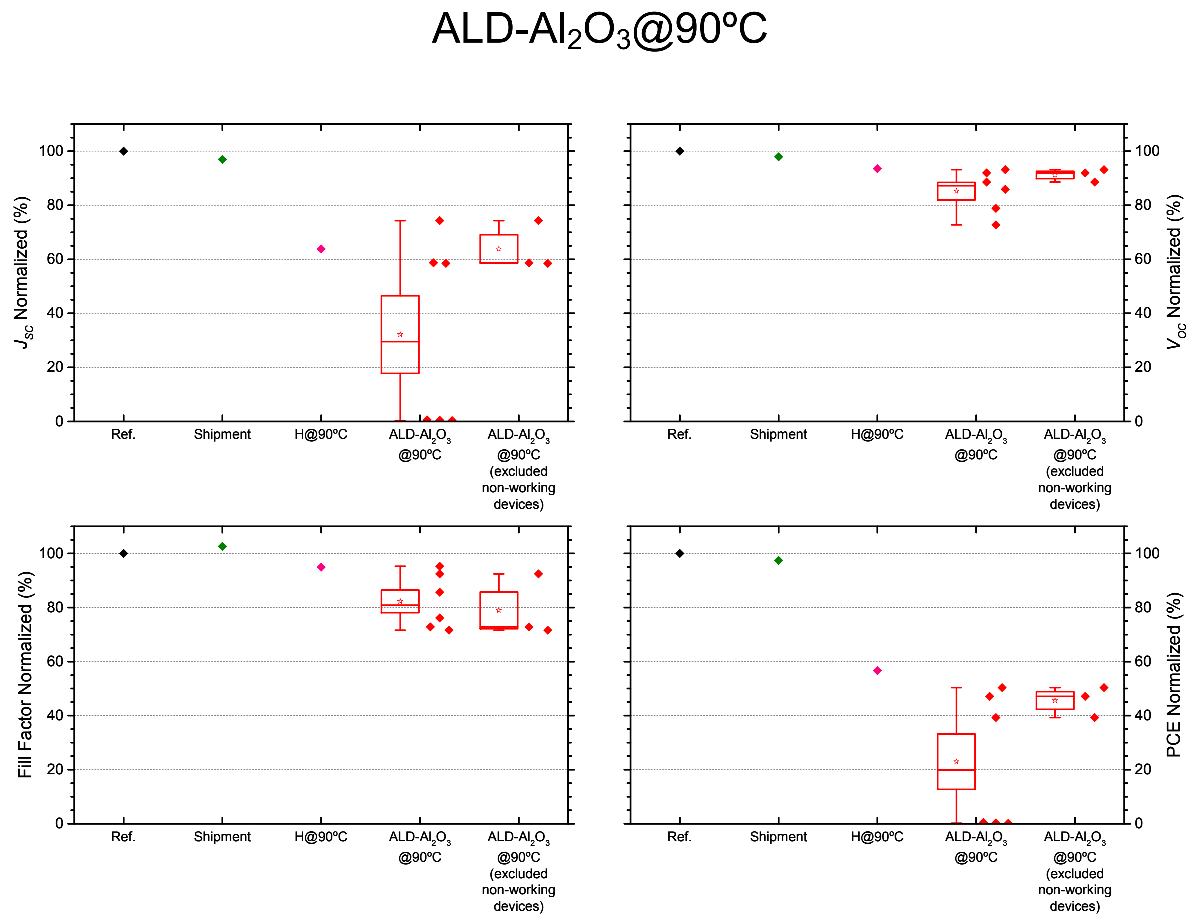

Figure S2. Summary of encapsulation process at 90 °C. Normalized evolution of photovoltaic properties (J_{SC}, V_{OC}, FF and PCE) for Ref, Shipment, H@90°C and ALD-Al_2O_3@90°C PSCs. In Box-whiskers, mean is represented by a star, while whiskers represent minimum and maximum values.

ALD-Al_2O_3@60 ºC

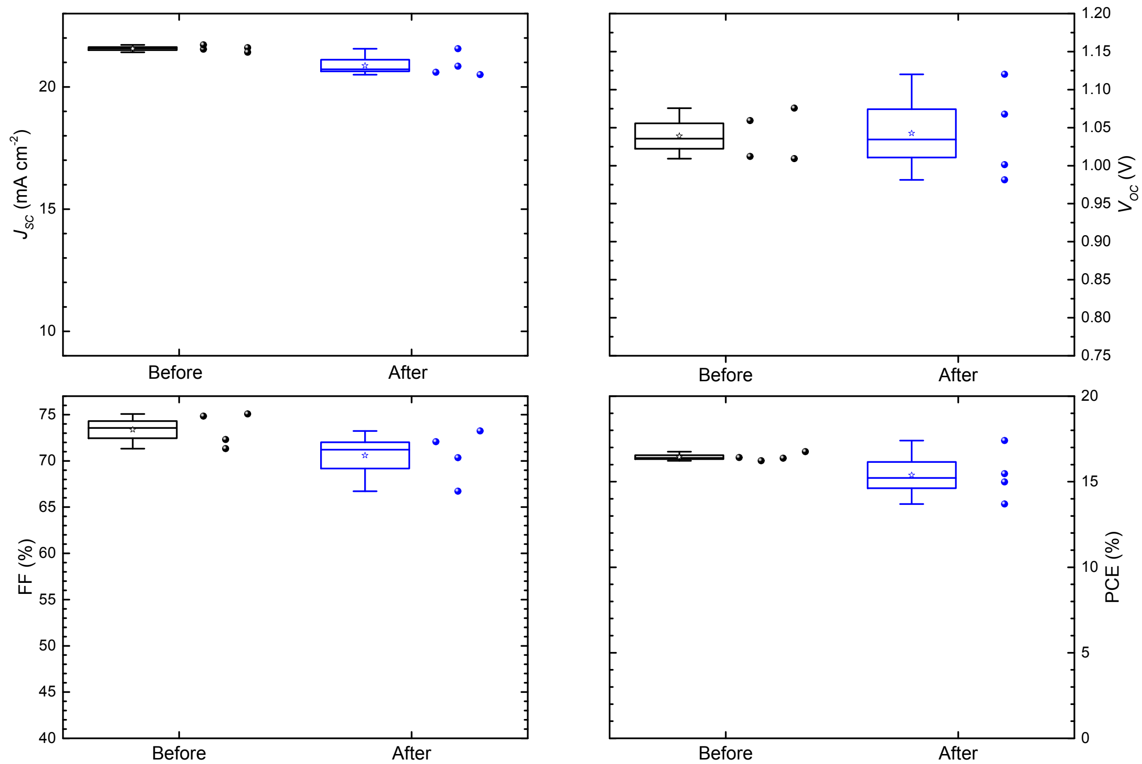

Figure S3. Box-whiskers statistical information of photovoltaic properties (J_{SC}, V_{OC}, FF and PCE) for Ref samples (black) and ALD-Al_2O_3@60ºC encapsulated ones (blue). Mean is represented as a star while minimum and maximum obtained values are limited by whiskers.

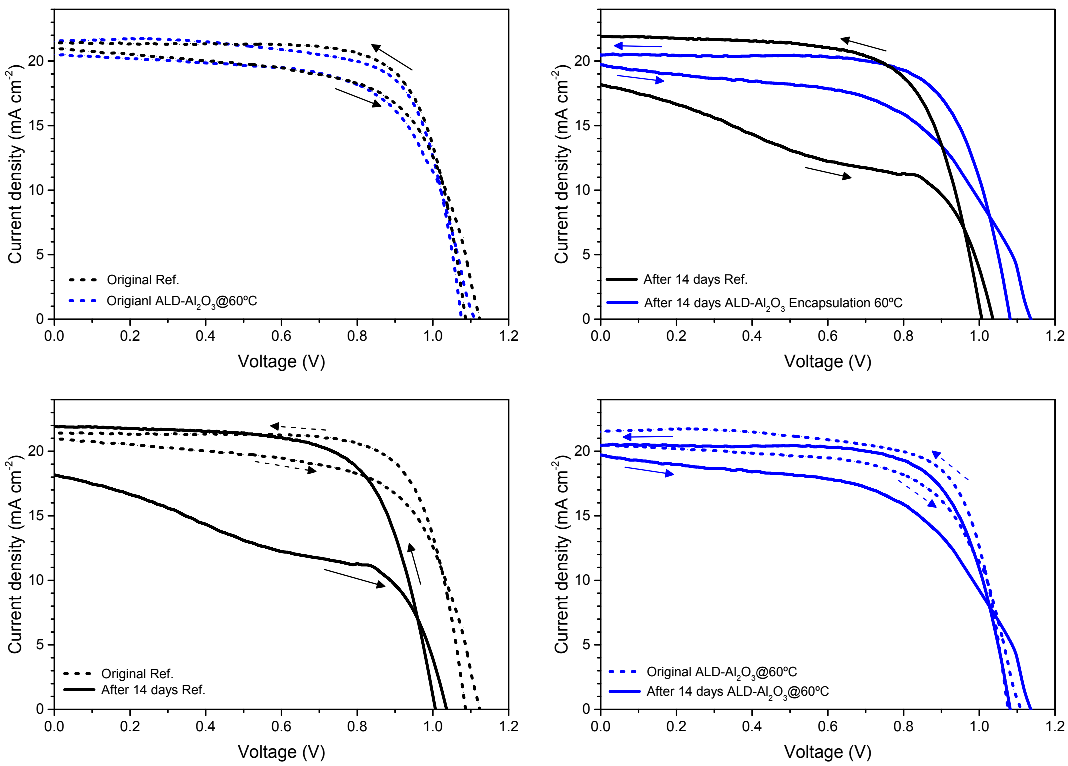

Figure S4. Evolution of hysteresis in Ref (black) and ALD-Al_2O_3@60°C (blue) before (dotted line) and after 14 days (~335h) aged (solid line). (Data regrouped differently from Figure 4e and 4f to facilitate the visualization).

XPS Measurements

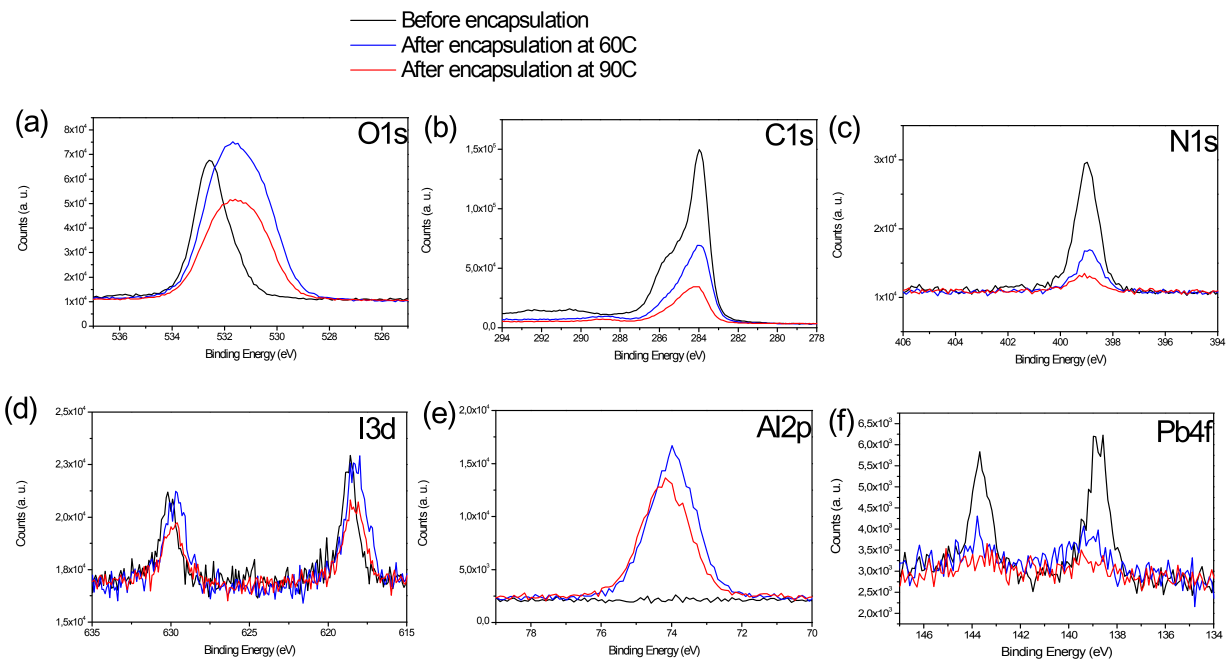

Figure S5. XPS high resolution spectra of the O1s (a), C1s(b),N1s (c), I3d (d) and Al2p (e) regions for non-encapsulated (black), ALD-Al_2O3@60°C encapsulated with a 2 nm of Al_2O_3 (blue) and ALD-Al_2O_3@90°C encapsulated with a 2 nm Al_2O_3 layer (red) in FTO/bl-TiO_2/mp-TiO_2/$MAPbI_3$ /Spiro-OMeTAD stacks. Despite the spiro-OMeTAD film exhibiting a thickness of 200 – 250 nm, Pb and I species are observed in the XPS scans which presumably originate from pinholes in the spiro-OMeTAD layer.

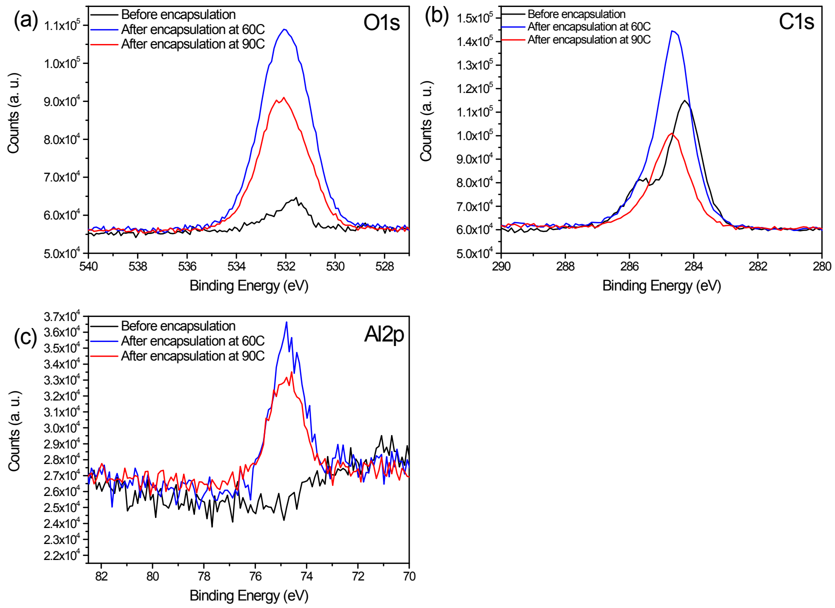

Figure S6. XPS high resolution spectra of the the O1s (a), C1s(b) and Al2p (c) regions for non-encapsulated (black), ALD-Al_2O3@60°C encapsulated with a 2 nm of Al_2O_3 (blue) and ALD-Al_2O_3@90ºC encapsulated with a 2 nm Al_2O_3 layer (red) in FTO/bl-TiO_2/mp-TiO_2/$MAPbI_3$ stacks

Table S1. XPS atomic percentages for FTO/bl-TiO_2/mp-TiO_2/$MAPbI_3$ /Spiro-OMeTAD stacks obtained from the C1s, N1s, O1s, Al2p, I3d and Pb4f high resolution spectra.

Atomic percentage	Without encapsulation	ALD-Al_2O_3@60°C (2 nm)	ALD-Al_2O_3@90°C (2 nm)
C	82.4	53.0	44.4
N	5.2	2.7	2.8
O	12.1	29.9	32.3
Al	0.0	14.1	20.2
I	0.2	0.2	0.2
Pb	0.1	0.1	0.1

Table S2. XPS atomic percentages for FTO/bl-TiO_2/mp-TiO_2/$MAPbI_3$ stacks obtained from the C1s, N1s, O1s, Al2p, I3d and Pb4f high resolution spectra.

Atomic percentage	Without encapsulation	ALD-Al_2O_3@60°C (2 nm)	ALD-Al_2O_3@90°C (2 nm)
C	53.3	52.0	48.4
N	10.1	3.6	2.9
O	3.9	21.9	26.6
Al	0.0	10.6	13.5
I	24.9	8.9	6.0
Pb	7.9	3.0	2.6

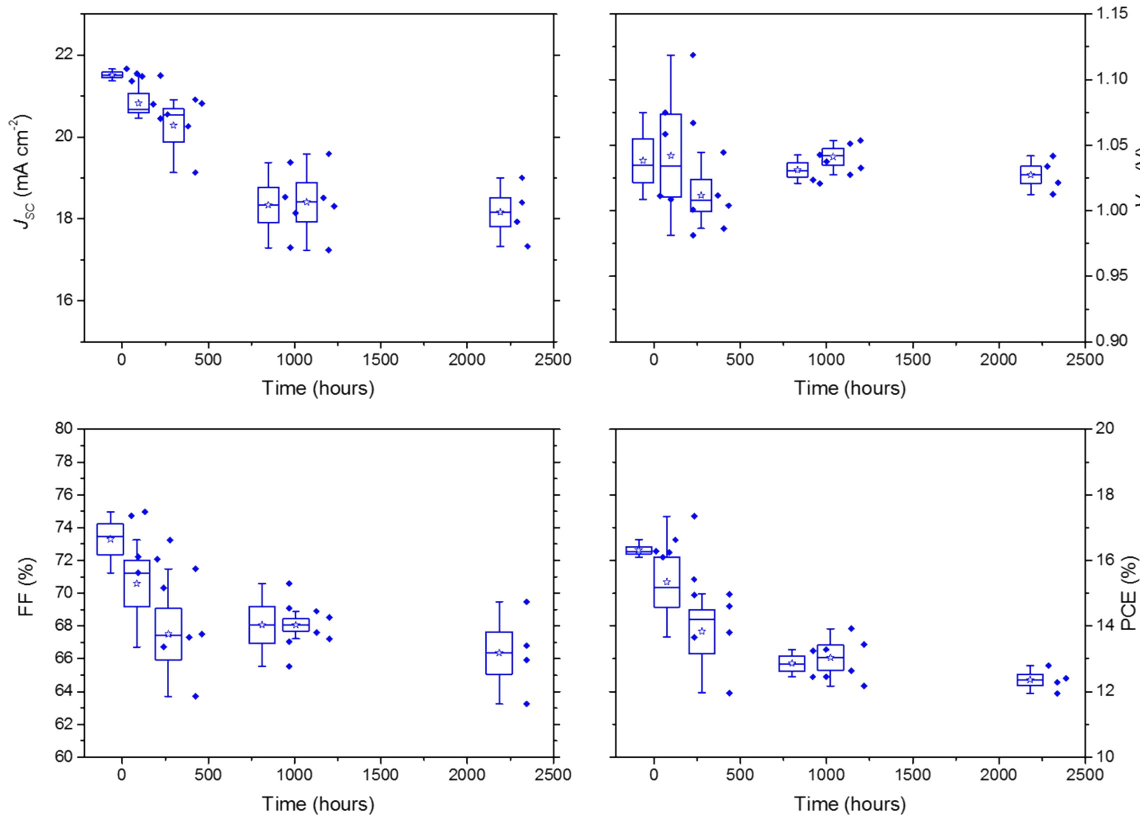

Figure S7. Statistical information of photovoltaic properties (J_{SC}, V_{OC}, FF and PCE) for the ALD-Al_2O_3@60°C encapsulated devices during stability test. Star denotes the mean value whereas the minimum and maximum values are represented by whiskers.

TRPL Model

$$PL\ (normalized) = y_0 + A_1 exp\left(-\frac{t}{t_1}\right) + A_2 exp\left(-\frac{t}{t_2}\right)$$

- Ref:

$$PL\ (normalized) = 0.00214 + 0.63278 exp\left(-\frac{t(ns)}{7.4402}\right) + 0.24939 exp\left(-\frac{t\ (ns)}{47.4442}\right)$$

$$\tau_1 = 5.1571,\ \tau_2 = 32.8858\ ;\ r^2 = 0.99714$$

- ALD-Al_2O_3@60ºC:

$$PL\ (normalized) = 0.00213 + 0.67181 exp\left(-\frac{t(ns)}{8.2015}\right) + 0.23255 exp\left(-\frac{t\ (ns)}{48.2685}\right)$$

$$\tau_1 = 5.6849,\ \tau_2 = 33.4572\ ,\ r^2 = 0.99782$$

Table S3. Summary of ALD solutions for stability improvement in PSC.

Reference	Architecture	PSC Configuration			ALD Process			
		Perovskite Type	ESC	HSC	Material	Precursors	Temperature (ºC)	Thickness (nm)
Kim and Matinson (2015)[1]	Perovskite/ALD-Al_2O_3	$MAPbI_{3-x}Cl_x$	N/A	N/A	Al_2O_3	TMA/O_3 TMA/H_2O AIP/AA	100	[3-18]
Kim *et al.* (2016)[2]	ITO/NiO_x/Perovskite/ PCBM/ALD-TiO_2/Al/Au	$MAPbI_{3-x}Cl_x$	PCBM	NiO_x	a-TiO_2	TDMATi/H_2O	100	~10
Brinkmann *et al.* (2017)[3]	ITO/PEDOT/Perovskite/PCBM/AZO/SnO_x/Ag	$MAPbI_3$	PCBM	PEDOT	SnO_x	TDMASn/H_2O	80 (✓)	~20
Lee *et al.* (2016)[4]	FTO/bl-TiO_2/ALD-Al_2O_3/mp-TiO_2/Perovskite/PTAA/Au	$MAPbI_3$ (MA,FA)Pb(Br,I)$_3$	mp-TiO_2	PTAA	Al_2O_3	TMA/H_2O	120	~5
Koushik *et al.* (2017)[5]	ITO/c-TiO_2/Perovskite/ALD-Al_2O_3/Spiro-OMeTAD/Au	$MAPbI_{3-x}Cl_x$	c-TiO_2	Spiro-OMeTAD	Al_2O_3	TMA/H_2O	100	[0-2]
Kot *et al.* (2016)[6]	FTO/c-TiO_2/Perovskite/ALD-Al_2O_3/Spiro-OMeTAD/Ag	$MAPbI_3$	c-TiO_2	Spiro-OMeTAD	Al_2O_3	TMA/H_2O	Room Temperature (✓✓)	[0-7]
Dong *et al.* (2015)[7]	FTO/c-TiO_2/Perovskite/ ALD-Al_2O_3/Spiro-OMeTAD/Ag FTO/c-TiO_2/Perovskite/ Spiro-OMeTAD/ALD-Al_2O_3/Ag	$MAPbI_3$	c-TiO_2	Spiro-OMeTAD	Al_2O_3	TMA/O_3	70 (✓)	[0-0.3] [0-0.7]
Chang *et al.* (2015)[8]	ITO/PEDOT/Perovskite/ALD-ZnO/Ag NW/ALD-Al_2O_3/PET	$MAPbI_3$	ALD-ZnO	PEDOT	Al_2O_3	TMA/H_2O	100	50
Lee *et al.* (2017)[9]	FTO/bl-TiO_2/mp-TiO_2/Perovskite/Spiro-OMeTAD/Au/ALD-Al_2O_3	(MA,FA)Pb(Br,I)$_3$	mp-TiO_2	Spiro-OMeTAD	Al_2O_3	TMA/H_2O	90	~21.5
	FTO/bl-TiO_2/mp-TiO_2/Perovskite/Spiro-OMeTAD/Au/ALD-Al_2O_3			Spiro-OMeTAD			60 (✓)	~21.5
	FTO/bl-TiO_2/mp-TiO_2/Perovskite/PTAA/Au/ALD-Al_2O_3			PTAA			90	~21.5
	FTO/bl-TiO_2/mp-TiO_2/Perovskite/PTAA/Au/ALD-Al_2O_3			PTAA			60 (✓)	~21.5
	FTO/bl-TiO_2/mp-TiO_2/Perovskite/PTAA/Au/ (iCVD-pV3D3/ALD-Al_2O_3)x4			PTAA			60 (✓)	(250+21.5)x4
This work	FTO/bl-TiO_2/mp-TiO_2/Perovskite/Spiro-OMeTAD/Au/ALD-Al_2O_3	$MAPbI_3$	mp-TiO_2	Spiro-OMeTAD	Al_2O_3	TMA/H_2O	90 60 (✓)	~16 ~16

Legend. ESC: electron Selective Contact; HSC: Hole Selective Contact. ALD: Atomic Layer Deposition; iCVD: initiated Chemical Vapor Deposition; a-: amorphous; c-:compact; bl-:blocking; mp-:mesoporous. TMA: trimethylaluminium; AIP: aluminum triisopropoxide; AA: acetic acid; TDMATi: tetrakis(dimethylamido)titanium(IV); TDMASn: tetrakis(dimethylamino)tin(IV).
✓: yes, positive. ✗: no, negative. ?: Uncertain, doubtful. N/A: non-applicable. N.R.: not reported.

Table S3 (continuation). Summary of ALD solutions for stability improvement in PSC.

Reference	Architecture	Procedure Characteristics			
		Applied to PSC?	Protective coating/Passivation layer/Real Encapsulation coating	Directly grown over PSC?	Remarks
Kim and Matinson (2015)[1]	Perovskite/ALD-Al_2O_3	✗	Protective coating	N/A, No PSC fabrication	First time used a non-hydrolytic ALD route in PSC. No PSC fabrication.
		✗	Protective coating	N/A, No PSC fabrication	
		✗	Protective coating	N/A, No PSC fabrication	
Kim *et al.* (2016)[2]	ITO/NiO_x/Perovskite/ PCBM/ALD-TiO_2/Al/Au	✓	Electron Extraction Layer + Protective coating	✗. Metal contact grown afterwards	No genuine encapsulation. Relatively high temperature (100ºC) to be applied elsewhere. Low efficiency (<9%).
Brinkmann *et al.* (2017)[3]	ITO/PEDOT/Perovskite/ PCBM/AZO/SnO_x/Ag	✓	Electron Extraction Layer + Protective coating	✗. Metal contact grown afterwards	No genuine encapsulation. Low efficiency (<13%).
Lee *et al.* (2016)[4]	FTO/bl-TiO_2/ALD-Al_2O_3/ mp-TiO_2/Perovskite/PTAA/Au	✓	Passivation layer	✗. Perovskite, HSC and metal contact grown afterwards	No genuine encapsulation. ALD-Al_2O_3 passivation at *n*-type side. ALD-Al_2O_3 deposition before perovskite and HSC. High temperature (120ºC) to be applied elsewhere. ALD-Al_2O_3 film heated at 500ºC together with mp-TiO_2.
		✓	Passivation layer	✗. Perovskite, HSC and metal contact grown afterwards.	
Koushik *et al.* (2017)[5]	ITO/c-TiO_2/Perovskite/ ALD-Al_2O_3/Spiro-OMeTAD/Au	✓	Passivation layer	✗. Spiro-OMeTAD and metal contact grown afterwards	No genuine encapsulation. ALD-Al_2O_3 passivation at p-type side. ALD-Al_2O_3 deposition before Spiro-OMeTAD. Relatively high temperature (100ºC) to be applied elsewhere.
Kot *et al.* (2016)[6]	FTO/c-TiO_2/Perovskite/ ALD-Al_2O_3/Spiro-OMeTAD/Ag	✓	Passivation layer	✗. Spiro-OMeTAD and metal contact grown afterwards	No genuine encapsulation. ALD-Al_2O_3 passivation at p-type side. ALD-Al_2O_3 deposition before Spiro-OMeTAD. Low efficiency (<13%).
Dong *et al.* (2015)[7]	FTO/c-TiO_2/Perovskite/ ALD-Al_2O_3/Spiro-OMeTAD/Ag	✓	Passivation layer	✗. Spiro-OMeTAD and metal contact grown afterwards	No genuine encapsulation. ALD-Al_2O_3 passivation at *p*-type side. ALD-Al_2O_3 deposition before Spiro-OMeTAD. Rapid degradation of PV properties while ALD process (very fast damage).
	FTO/c-TiO_2/Perovskite/ Spiro-OMeTAD/ALD-Al_2O_3/Ag	✓	Protective coating	✗. Metal contact grown afterwards	No genuine encapsulation. Rapid degradation of PV properties while ALD process (fast damage).
Chang *et al.* (2015)[8]	ITO/PEDOT/Perovskite/ ALD-ZnO/Ag NW/ALD-Al_2O_3/PET	✓	Real encapsulation	✗. ALD-Al_2O_3 deposited onto PET and glued over the PSC.	Genuine encapsulation, but not directly coted onto PSC. Encapsulation effect coming from ALD-Al_2O_3 and PET film difficult to decouple. Relatively high temperature (100ºC) to be applied elsewhere. Low efficiency <11%, but semitransparent PSC.
Lee *et al.* (2017)[9]	FTO/bl-TiO_2/mp-TiO_2/Perovskite/ Spiro-OMeTAD/Au/ALD-Al_2O_3	✓	Real encapsulation	✓	Genuine encapsulation. Relatively high temperature (90ºC) to be applied elsewhere. Extra stability given by more stable perovskite more than encapsulation.
	FTO/bl-TiO_2/mp-TiO_2/Perovskite/ Spiro-OMeTAD/Au/ALD-Al_2O_3	✓	Real encapsulation	✓	Genuine encapsulation. Extra stability given by more stable perovskite more than encapsulation.
	FTO/bl-TiO_2/mp-TiO_2/Perovskite/ PTAA/Au/ALD-Al_2O_3	✓	Real encapsulation	✓	Genuine encapsulation. Relatively high temperature (90ºC) to be applied elsewhere. Thermal/moisture resistance given by PTAA more stable perovskite more than encapsulation.
	FTO/bl-TiO_2/mp-TiO_2/Perovskite/ PTAA/Au/ALD-Al_2O_3	✓	Real encapsulation	✓	Genuine encapsulation. Thermal/moisture resistance given by PTAA more stable perovskite more than encapsulation.
	FTO/bl-TiO_2/mp-TiO_2/Perovskite/ PTAA/Au/ (iCVD-pV3D3/ALD-Al_2O_3)x4	✓	Real encapsulation	✓	Genuine encapsulation. Thermal/moisture resistance given by PTAA more stable perovskite more than encapsulation. Unusual and complex and solution mixing techniques and materials.
This work	FTO/bl-TiO_2/mp-TiO_2/Perovskite/ Spiro-OMeTAD/Au/ALD-Al_2O_3	✓	Real encapsulation	✓	Genuine encapsulation. Relatively high temperature (90ºC) to be applied elsewhere.
		✓	Real encapsulation	✓	Genuine encapsulation.

Legend. ALD: Atomic Layer Deposition; a-: amorphous; c-:compact; bl-:blocking; mp-:mesoporous. ✓: yes, positive. ✗: no, negative. ?: Uncertain, doubtful. N/A: non-applicable. N.R.: not reported.

Table S3 (continuation). Summary of ALD solutions for stability improvement in PSC.

Reference	Architecture	Applicability	Encapsulation	
		Universally applicable?	Normalized ΔPCE	Encapsulation Stability carried out?
Kim and Matinson (2015)[1]	Perovskite/ALD-Al_2O_3	✗	N/A	N/A
		✗	N/A	N/A
		✗	N/A	N/A
Kim *et al.* (2016)[2]	ITO/NiO_x/Perovskite/ PCBM/ALD-TiO_2/Al/Au	✗	N/A. No genuine encapsulation method	N/A. No genuine encapsulation method
Brinkmann *et al.* (2017)[3]	ITO/PEDOT/Perovskite/PCBM/AZO/SnO_x/Ag	✗	N/A. No genuine encapsulation method	N/A. No genuine encapsulation method
Lee *et al.* (2016)[4]	FTO/bl-TiO_2/ALD-Al_2O_3/mp-TiO_2/Perovskite/PTAA/Au	✗	N/A. No genuine encapsulation method	N/A. No genuine encapsulation method
		✗	N/A. No genuine encapsulation method	N/A. No genuine encapsulation method
Koushik *et al.* (2017)[5]	ITO/c-TiO_2/Perovskite/ALD-Al_2O_3/Spiro-OMeTAD/Au	✗	N/A. No genuine encapsulation method	N/A. No genuine encapsulation method
Kot *et al.* (2016)[6]	FTO/c-TiO_2/Perovskite/ALD-Al_2O_3/Spiro-OMeTAD/Ag	✗	N/A. No genuine encapsulation method	N/A. No genuine encapsulation method
Dong *et al.* (2015)[7]	FTO/c-TiO_2/Perovskite/ ALD-Al_2O_3/Spiro-OMeTAD/Ag	✗	N/A. No genuine encapsulation method	N/A. No genuine encapsulation method
	FTO/c-TiO_2/Perovskite/ Spiro-OMeTAD/ALD-Al_2O_3/Ag	?	N/A. No genuine encapsulation method	N/A. No genuine encapsulation method
Chang *et al.* (2015)[8]	ITO/PEDOT/Perovskite/ALD-ZnO/Ag NW/ALD-Al_2O_3/PET	✗	N/A and N.R. Encapsulation was not made growing a layer onto the solar cell, so losses N.R.	✓. Stability improved.
Lee *et al.* (2017)[9]	FTO/bl-TiO_2/mp-TiO_2/Perovskite/Spiro-OMeTAD/Au/ALD-Al_2O_3	✗	~ -95% (✗✗✗)	N.R.
	FTO/bl-TiO_2/mp-TiO_2/Perovskite/Spiro-OMeTAD/Au/ALD-Al_2O_3	✗	~ -70% (✗✗)	N.R.
	FTO/bl-TiO_2/mp-TiO_2/Perovskite/PTAA/Au/ALD-Al_2O_3	✗	~ -40% (✗)	N.R.
	FTO/bl-TiO_2/mp-TiO_2/Perovskite/PTAA/Au/ALD-Al_2O_3	✗	~ -10% (?)	N.R.
	FTO/bl-TiO_2/mp-TiO_2/Perovskite/PTAA/Au/ (iCVD-pV3D3/ALD-Al_2O_3)x4	✗	~ -1.4% (✓)	✓. Stability improved.
This work	FTO/bl-TiO_2/mp-TiO_2/Perovskite/Spiro-OMeTAD/Au/ALD-Al_2O_3	✓	~ -76.8% (✗✗)	✗. Not stable enough
		✓	~ -6.4% (✓)	✓. Stability improved.

Legend. ALD: Atomic Layer Deposition; a-: amorphous; c-:compact; bl-:blocking; mp-:mesoporous. ✓: yes, positive. ✗: no, negative. ?: Uncertain, doubtful. N/A: non-applicable. N.R.: not reported.

References

1 I. S. Kim and A. B. F. Martinson, *J. Mater. Chem. A*, 2015, **3**, 20092–20096.

2 I. S. Kim, D. H. Cao, D. B. Buchholz, J. D. Emery, O. K. Farha, J. T. Hupp, M. G. Kanatzidis and A. B. F. Martinson, *Nano Lett.*, 2016, **16**, 7786–7790.

3 K. O. Brinkmann, J. Zhao, N. Pourdavoud, T. Becker, T. Hu, S. Olthof, K. Meerholz, L. Hoffmann, T. Gahlmann, R. Heiderhoff, M. F. Oszajca, N. A. Luechinger, D. Rogalla, Y. Chen, B. Cheng and T. Riedl, *Nat. Commun.*, 2017, **8**, 13938.

4 Y. H. Lee, J. Luo, M. K. Son, P. Gao, K. T. Cho, J. Seo, S. M. Zakeeruddin, M. Grätzel and M. K. Nazeeruddin, *Adv. Mater.*, 2016, **28**, 3966–3972.

5 D. Koushik, W. J. H. Verhees, Y. Kuang, S. Veenstra, D. Zhang, M. A. Verheijen, M. Creatore and R. E. I. Schropp, *Energy Environ. Sci.*, 2017, **10**, 91–100.

6 M. Kot, C. Das, Z. Wang, K. Henkel, Z. Rouissi, K. Wojciechowski, H. J. Snaith and D. Schmeisser, *ChemSusChem*, 2016, **9**, 3401–3406.

7 X. Dong, X. Fang, M. Lv, B. Lin, S. Zhang, J. Ding and N. Yuan, *J. Mater. Chem. A*, 2015, **3**, 5360–5367.

8 C. Y. Chang, K. T. Lee, W. K. Huang, H. Y. Siao and Y. C. Chang, *Chem. Mater.*, 2015, **27**, 5122–5130.

9 Y. Il Lee, N. J. Jeon, B. J. Kim, H. Shim, T. Y. Yang, S. Il Seok, J. Seo and S. G. Im, *Adv. Energy Mater.*, 2017, 1701928.