

## Electronic Supplementary Information

### Iodide/triiodide redox shuttle-based additives for high-performance perovskite solar cells by simultaneously passivating the cation and anion defects

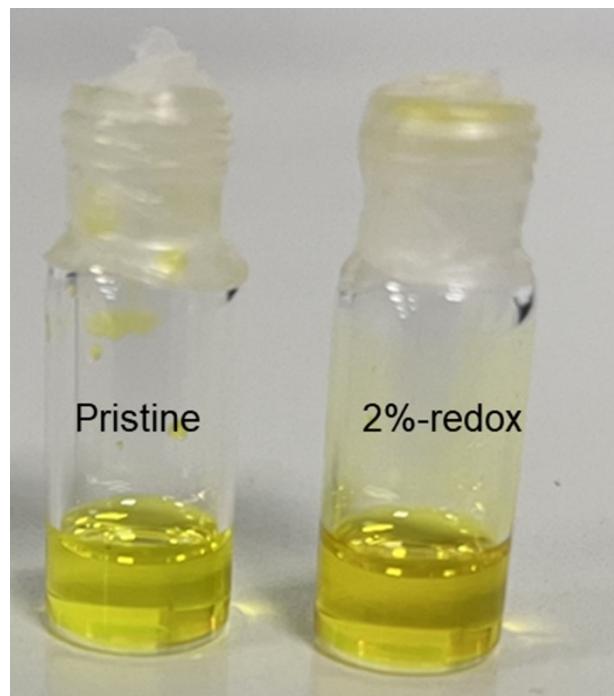
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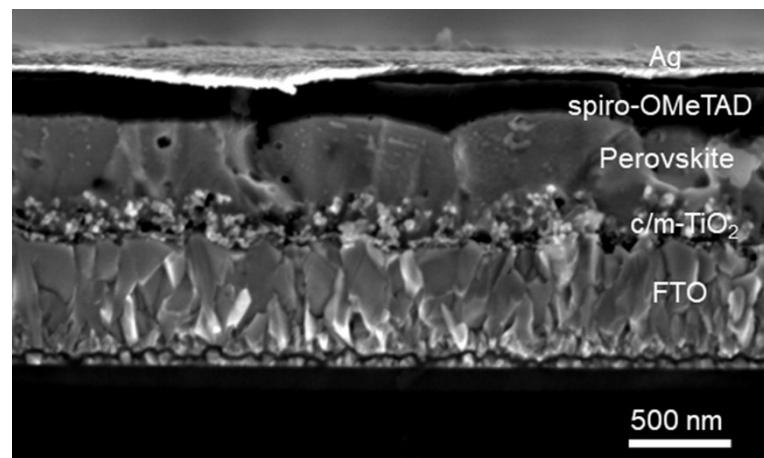
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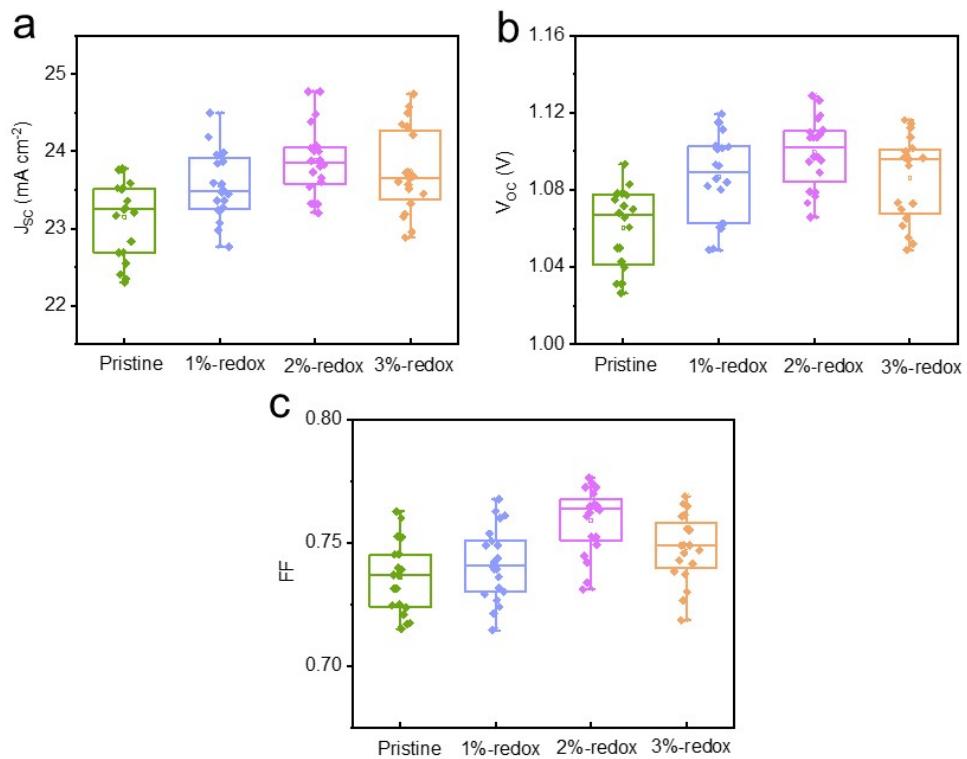
Email: Zongping Shao (shaozp@njtech.edu.cn)



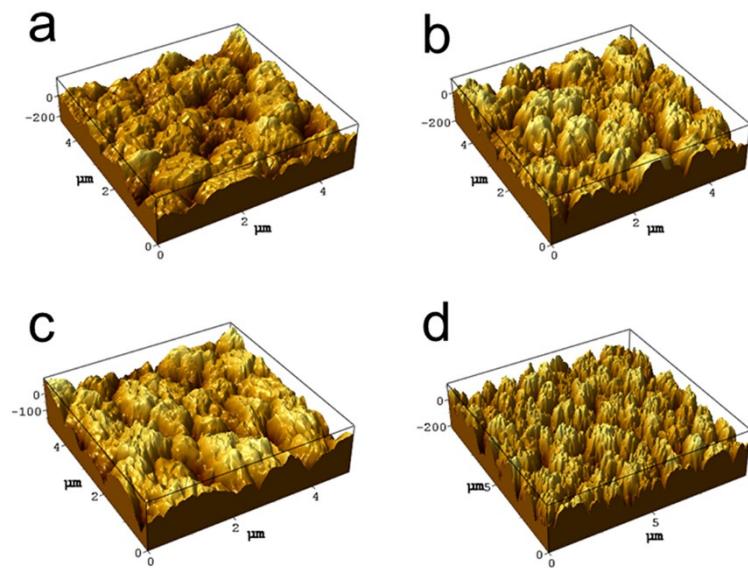
**Fig. S1** Digital photographs of perovskite precursor solutions without and with redox additive (2%).



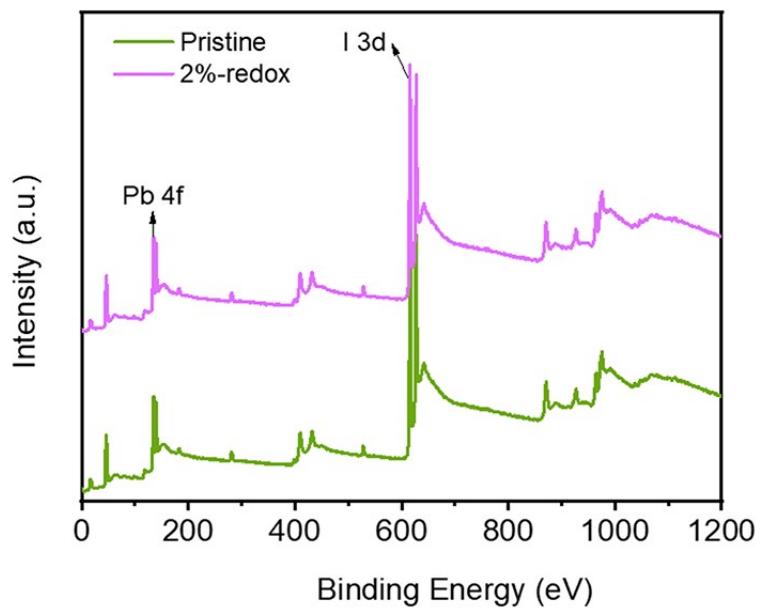
**Fig. S2** Cross-sectional SEM image of the 2%-redox additive modified PSC.



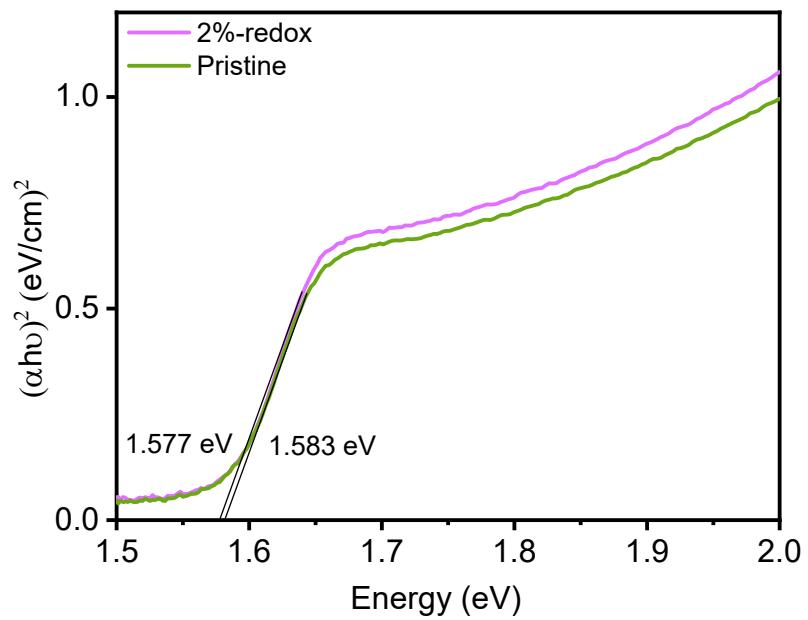
**Fig. S3** The parameter distributions of 20 cells without and with different amounts of redox additive: (a)  $J_{sc}$ , (b)  $V_{oc}$  and (c) FF.



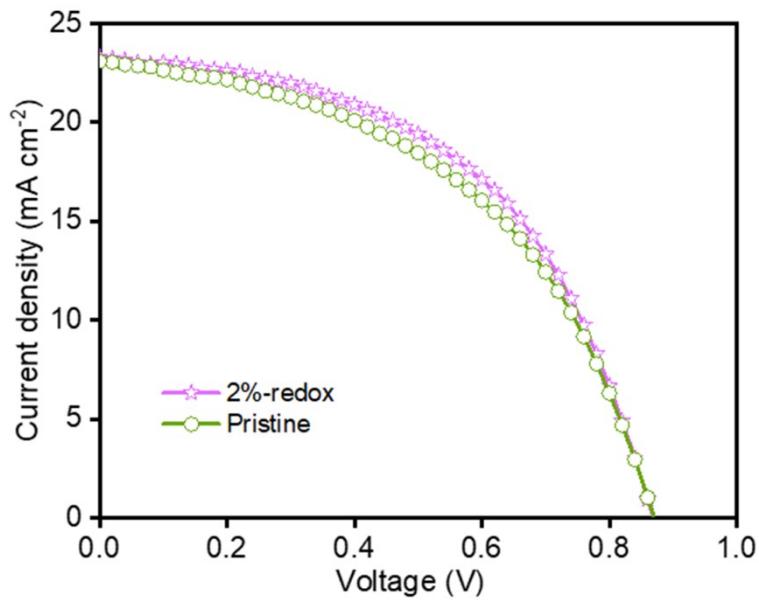
**Fig. S4** 3D-AFM models of (a) pristine, (b) 1%-redox, (c) 2%-redox and (d) 3%-redox films.



**Fig. S5** XPS survey spectra of the pristine and 2%-redox films.



**Fig. S6** Tauc plots of the pristine and 2%-redox films.



**Fig. S7**  $J$ - $V$  curves of carbon electrode-based pristine and 2%-redox cells.

**Table S1** Photovoltaic parameters of  $\text{MAPbI}_3$ -based PSCs without and with different amounts of redox additive.

Perovskite	$J_{sc}$ (mA cm $^{-2}$ )	$V_{oc}$ (V)	FF	PCE (%)
Pristine	22.8	1.08	0.744	18.2
1%-redox	23.1	1.09	0.763	19.2
2%-redox	23.8	1.11	0.770	20.4
3%-redox	24.2	1.09	0.747	19.7

**Table S2** Dynamic decay time parameters from TRPL measurements of the pristine and 2%-redox films deposited on the glass.

Perovskite	$\tau_1$ (ns)	$\tau_1$ ratio (%)	$\tau_2$ (ns)	$\tau_2$ ratio (%)	average $\tau$ (ns)
Pristine	3.04	9.78	54.04	90.22	49.0
2%-redox	0.67	5.98	72.26	94.12	68.0

**Table S3** Photovoltaic parameters of carbon-based HTL-free  $\text{MAPbI}_3$  and 2%-redox cells.

Perovskite	$J_{\text{sc}}$ (mA cm $^{-2}$ )	$V_{\text{oc}}$ (V)	FF	PCE (%)
Pristine	23.1	0.87	0.479	9.60
2%-redox	23.2	0.87	0.508	10.3