Supporting Information

Ultrathin Cu_2O as an efficient inorganic hole transporting material for perovskite solar cells

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HTM	Method	Device Structure	Work function [eV]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]	Ref.
CuSCN	Doctor blading	Mesoporous	5.3	1.02	19.70	62.0	12.4	1
CuSCN	Electrodeposition	Planar	—	1.0	21.9	75.8	16.6	2
CuI	Drop-casting	Mesoporous	5.2[a)]	0.55	17.80	62.0	6.0	3
NiO	Spin-coating	Planar	5.36	0.88	16.27	63.5	9.1	4
NiO	Spin-coating	Planar	5.4	0.92	12.43	68	7.8	5
NiO	Spin-coating	Planar	5.26	1.05	15.4	48	7.6	6
NiO	Spin-coating	Mesoporous	5.2 [a)]	1	14.65	64	9.44	7
NiO	Screen-printing	Mesoporous	5.1 [a)]	0.83	4.9	35	1.5	8
NiO	Electrodeposition	Planar	5.4 [a)]	0.786	14.2	65	7.26	9
NiOx	Sputter	Mesoporous	—	0.96	19.8	61	11.6	10
Cu (5 at%) doped NiO	Spin-coating	Planar	—	1.11	18.75	72	14.98	11
Cu_2O	Chemical reaction	Planar	5.2 [a)]	1.07	16.52	75.51	13.35	12
Cu_2O	Sputter	Planar	4.84	0.95	17.50	66.2	11.0	This work

Table S1. State of art researches on inorganic HTMs reported in perovskite solar cells.

[a)] Valence band value was provided instead of work function.

Table S2. The prices of commercial organic HTMs, in comparison with Cu_2O.

HTMs	Catalog #	Price (EUR)[a)]
Spiro-MeOTAD	792071-1G	331
PEDOT:PSS	483095-250G (1.3 wt%)	211.5
PTAA	702471-100MG	422
P3HT	445703-1G	565
Cu_2O	566284-5G	51.6

[a)] All data in this table is from Sigma-Aldrich website on 10/5/2015.

Table S3. Transient absorption characteristics of perovskite layers on different substrates.

Samples	τ_1		τ_2	
	Lifetime (ns)	Content (%)	Lifetime (ns)	Content (%)
PS/glass	5.51±0.3	77	22.83±2.87	23
PS/Cu_2O/glass	3.88±0.27	47	33.40±1.33	53
PS/PEDOT:PSS/glass	9.11±0.99	39	40.06±2.67	61

The kinetic spectrum was fitted according to the double exponential function:

$$y = y_0 + A_1 \exp\left(-\frac{t}{\tau 1}\right) + A_2 exp(-\frac{t}{\tau 2})$$

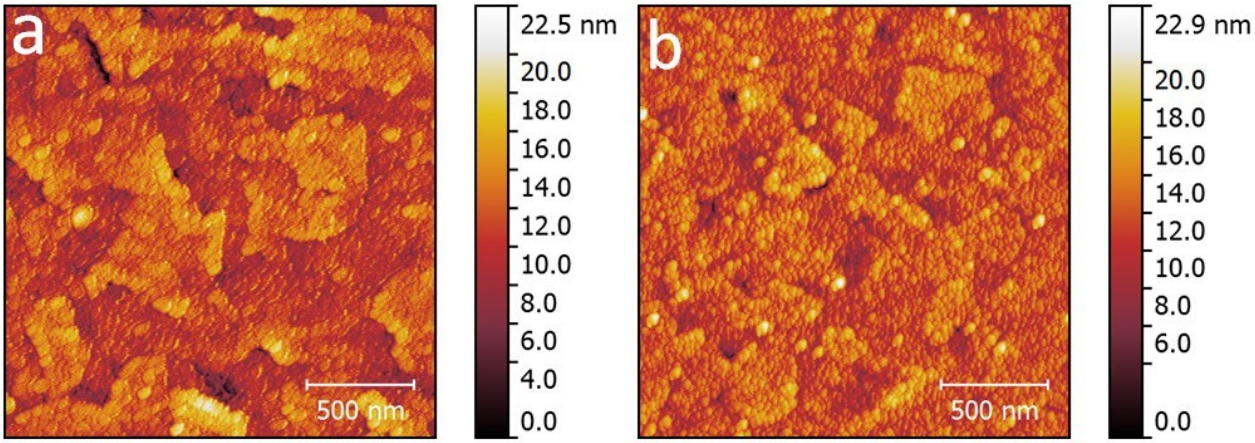

Figure S1. AFM image of a) ITO and b) 5 nm Cu_2O film covered ITO glass slide. The AFM indicates that the Cu_2O layer on ITO glass is uniform and the grain size is narrowly distributed. Average grain size: 40 nm.

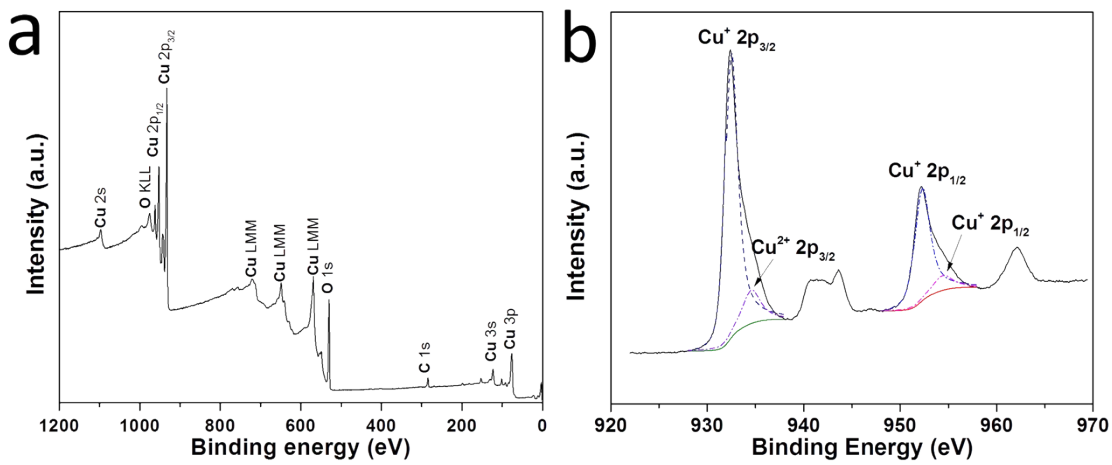

Figure S2. a) XPS survey spectrum and b) high resolution XPS spectrum of Cu 2p core level. From survey spectrum a), Cu, O, C elements are detected. The Cu $2p_{3/2}$ core peak (928 eV – 937 eV) is fitted using two components located at 932.4 eV and 934.6 eV, corresponding to Cu^{1+} and Cu^{2+} with the atomic percent of 86% and 14%, respectively.[13,14]

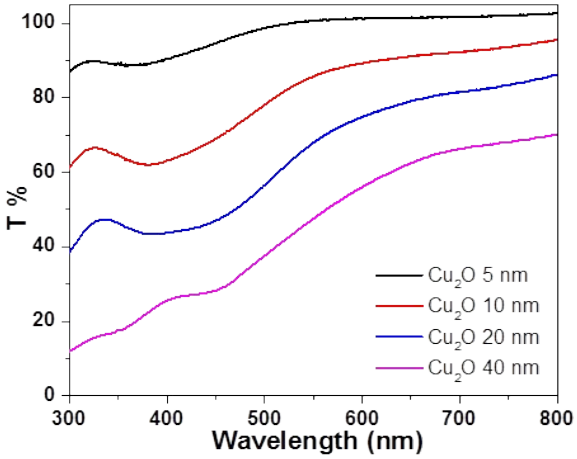

Figure S3. The transmittance spectra of Cu_2O layer with different thickness on ITO glass. The dependence of transmittance indicates that the Cu_2O layer has high absorption co-efficiency, which matches well with the data we presented in Figure 1 d). To confirm that most of incident light be absorbed by the perovskite layer, 5 nm thickness of Cu_2O layer was chosen to fabricate solar cells.

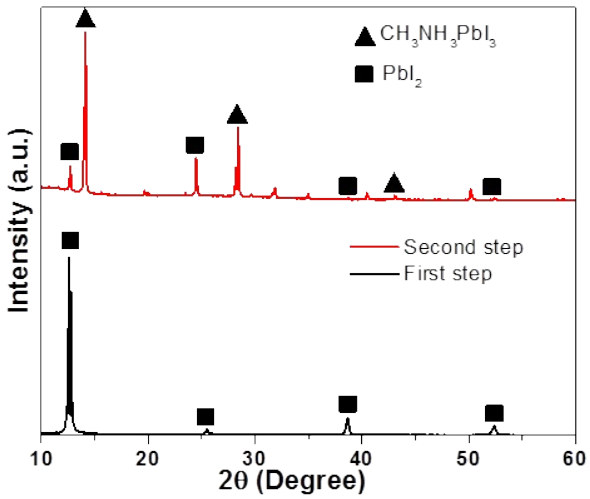

Figure S4. XRD of PbI_2 and perovskite prepared by the two-step process. The XRD spectra indicate that besides $CH_3NH_3PbI_3$, there is still some PbI_2 left after dipping into CH_3NH_3I solution for 30 s. This spectrum is consistent with previous report that the CH_3NH_3I insertion hardly proceeds beyond the surface of thin PbI_2 films, and that the complete transformation of the crystal structure requires several hours and the perovskite dissolves in the CH_3NH_3I solution, hampering the transformation.[15] However, the incomplete conversion seemed to work as we still got high efficiencies with the same method utilized in some references.[16, 17] The reason is the passivation effect of PbI_2, which acts as a blocking layer between Cu_2O and the perovskite itself, reducing the probability of back electron transfer (charge recombination).[18]

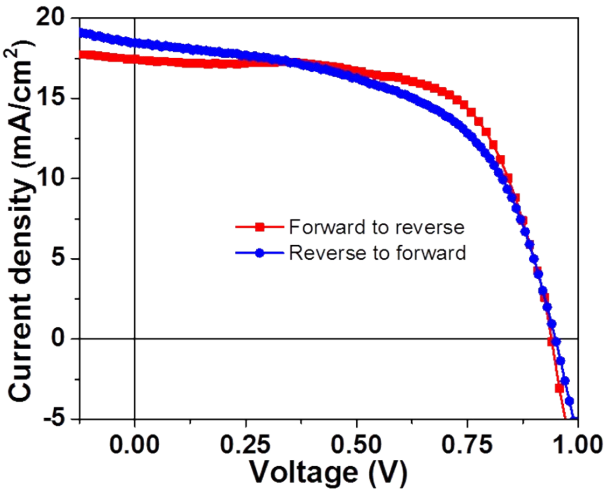

Figure S5. Hysteresis of $CH_3NH_3PbI_3$ perovskite solar cells using 5 nm Cu_2O as HTM.

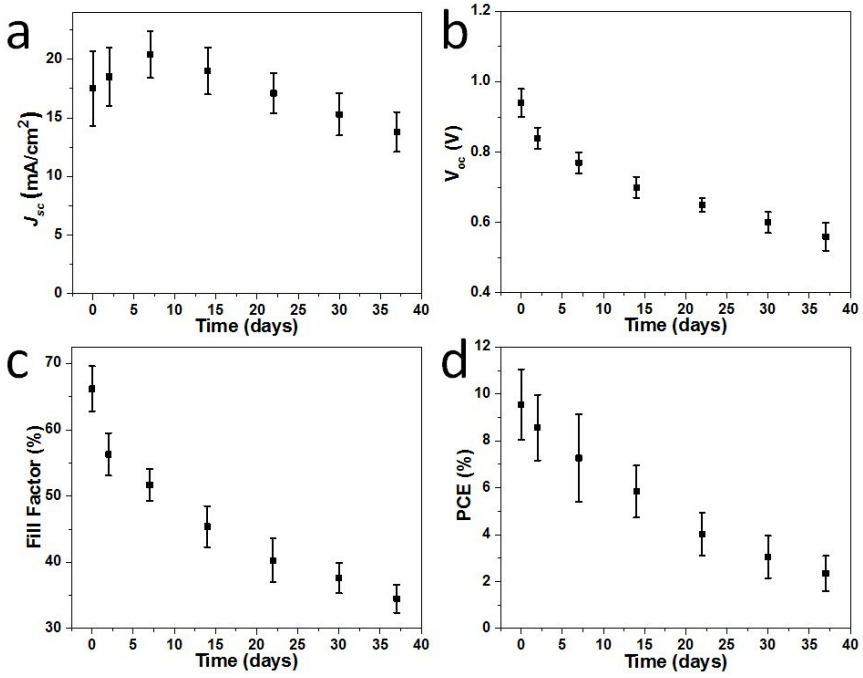

Figure S6. Stability of $CH_3NH_3PbI_3$ perovskite solar cell with 5 nm Cu_2O layer as HTM. The decrease of solar cells PCE is mainly attributed to the decrease of V_{oc} and FF, which is most probably caused by the oxidation of Ag electrode and the Cu_2O layer due to the penetration of oxygen.

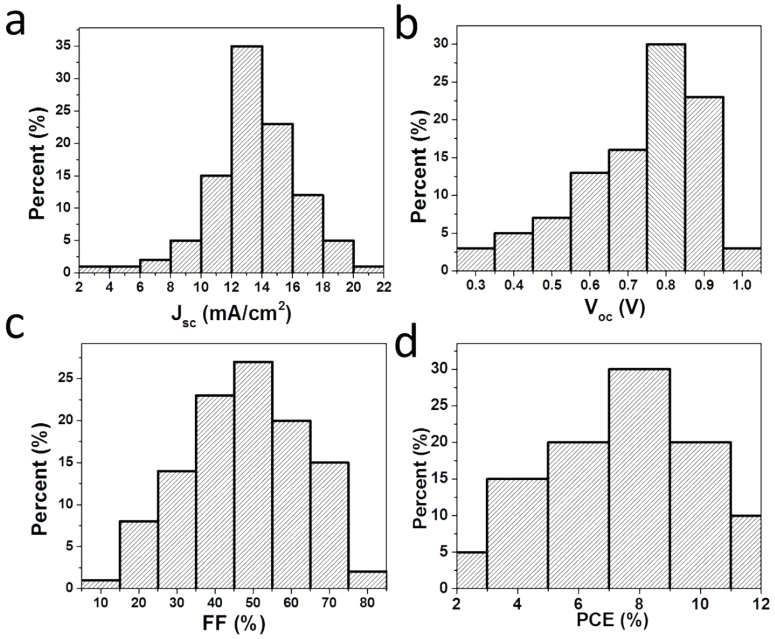

Figure S7. The statistical histogram plots of J_{sc}, V_{oc}, FF and PCE for perovskite solar cells based on 5 nm Cu_2O HTM.

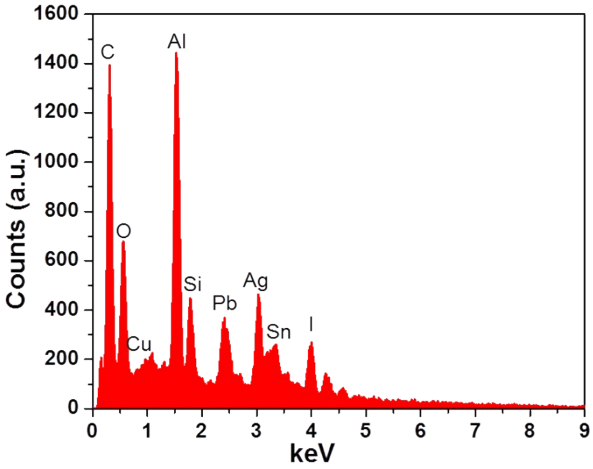

Figure S8. The EDAX spectrum of ITO/Cu_2O/$CH_3NH_3PbI_3$ solar cells.

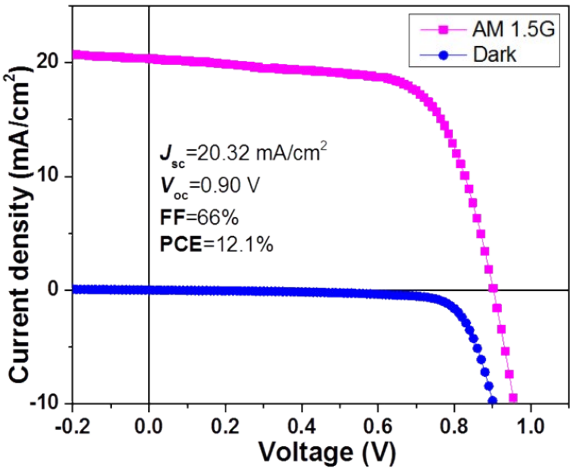

Figure S9. The I-V performance of solar cells based on glass/ITO/PEDOT:PSS substrate.

References

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