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Supporting Information for

Achieving high-performance planar perovskite solar cells with co-sputtered Co-doping NiO_x hole transport layers by efficient extraction and enhanced mobility

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Experimental Section

Substrates prepare and ETL deposition

FTO glasses used as transparent conductive substrates were ultrasonically cleaned by deterrent regent, deionized water, acetone and ethanol successively for 15 minutes and then dried by pressurized air flow. Electron selective TiO_2 films with different crystallinity were directly deposited on FTO glasses by a DC reactive magnetron sputtering system (Shenyang Tengao Vacuum Technology Co. Ltd., JSS-600) with a titanium target (99.99% purity) at room temperature. In our experiment, the angle between the target and the substrates was fixed at 37^{o} and the substrate rotation speed was 15 rpm during the deposition process. The base pressure of the deposition chamber was kept at $4 \varnothing 10^{-4}$ Pa and the work pressure was around 1.5 Pa. DC magnetron sputtering was conducted at a sputtering power range of 500 - 700 W and a fixed gas mixture flow atmosphere composed of 35 sccm Ar and 5 sccm O_2 . By adjusting the work pressure and sputtering power, distinctive films could be obtained with certain thicknesses. Prior to the deposition process, the Ti target was pre-sputtered for 10 min in order to eliminate the residual oxide layer.

Synthesis of CH_3NH_3I powder

Methylamine iodide (CH_3NH_3I) was synthesized and purified on the basis of a reported method. 30 mL methylamine (33%wt in ethanol, Sigma-Aldrich) were mixed with 28 mL hydroiodic acid (57% in water, Sigma-Aldrich) in a 250 mL round-bottomed flask at 0°C in ice bath and reacted for 2 h with stirring. The solvent was then removed with a rotary evaporator by heating the solution at 60 °C under reduced pressure, during which white powder precipitated. The product was washed with diethyl ether for three times, and then dissolved in ethanol, recrystallized with diethyl ether, and finally dried in a vacuum oven at 60 °C for 24 h.

Fabrication of perovskite solar cells

$CH_3NH_3PbI_3$ films around 300 nm were prepared with a reported method. Firstly, PbI_2 (Aladdin, 99.8%) and as-prepared CH_3NH_3I with a molar ratio of 1:1 were dissolved in anhydrous N, N-dimethylformamide (DMF, SCRC, 99.5%) and stirred at room temperature for 2 h to yield perovskite precursor solution. The solution was spin coated on the TiO_2 surface at 4000 rpm for 20 s, during which 500 μL chlorobenzene was dripped to the surface at 7 s. The as cast films were calcined on a hot plate (100 °C) for 30 min to remove residual solvent and crystallize the perovskite.

Thereafter, a hole-transporting layer was deposited onto the perovskite film by spin coating at 4000 rpm for 30 s. The solution recipe was 72.3 mg spiro-OMeTAD (Merk), 17.5 μL lithium-bis(trifluoromethanesulfonyl)imide (Li-TFSI, J&K scientific Ltd.) stock solution (520 mg/mL Li-TFSI in acetonitrile) and 28.5 μL 4-tert-butylpyridine (TBP, Sigma Aldrich) in 1 mL chlorobenzene (Sigma Aldrich). Finally, 120 nm-thick silver acting as the back contact was thermally evaporated on top of the hole transporting layer through a metal shadow mask, with an active area of 0.07 cm^2

Device characterization

Scanning electron microscopy (SEM) was conducted with a field emission scanning electron microscope (FEI, Magellan 400) to investigate the morphology and thickness of ETL. High resolution transmission electron microscopy (HRTEM, JEM2010, JEOL, Tokyo, Japan) was used to verify the crystalline existence of partly crystallized TiO_2 films. The surface roughness of the films was obtained by atomic force microscopy (AFM, SII Nano Technology Ltd., Nanonavi) in noncontact mode. The chemical composition and valence-band (VB) spectrum of the TiO_2 films were analyzed by X-ray photoelectron spectroscopy (XPS) with monochromated Al Kα radiation at a pass energy of 29.4 eV. X-ray diffraction (XRD) measurements were performed with a Ultima IV X-ray diffractometer using Cu Kα radiation under operation conditions of 40 kV and 40 mA, with a scanning speed of 5° per minute. The UV−vis transmittance spectra of TiO_2 films were recorded on UV-Vis spectrophotometer (HITACHI U-3010). Steady photoluminescence (PL) measurements were conducted at room temperature on a Horiba-Ltd. FluoroMax-4 device with an excitation wavelength of 457 nm. Time-resolved PL spectra were measured using a fluorescence lifetime spectrometer (Photo Technology International, Inc.). The PL lifetime of the $CH_3NH_3Pb_3I$ films on TiO_2/FTO glass substrates were calculated by fitting the experimental decay transient data with bi-exponential decay model. Current −voltage characteristics of solar cells were measured under simulated AM1.5G illumination of 100 mW/cm ^{2}. The light intensity was calibrated with a reference silicon solar cell (Oriel-91150). The J−V curves were respectively measured by applying an external voltage bias with a scan rate of 40 mV/s. Incident photon-to-current conversion efficiency (IPCE) was measured on a SM-250 system (Bunkoh-keiki, Japan). The intensity of monochromatic light was measured with a Si photodiode (S1337-1010BQ).

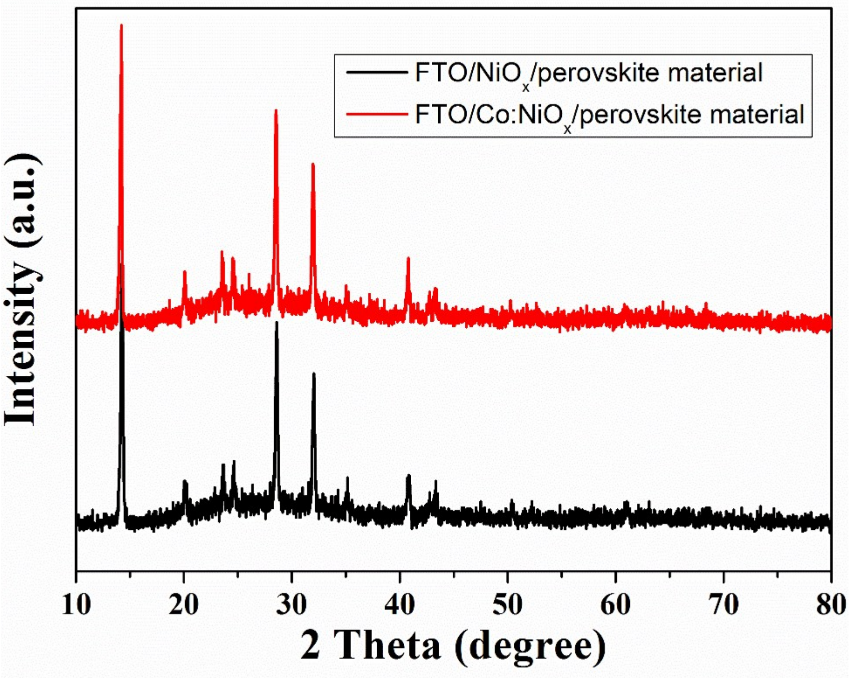

Fig. S1 The XRD patterns of perovskite absorber material ($CH_3NH_3PbI_3$) based on different hole transport layers.

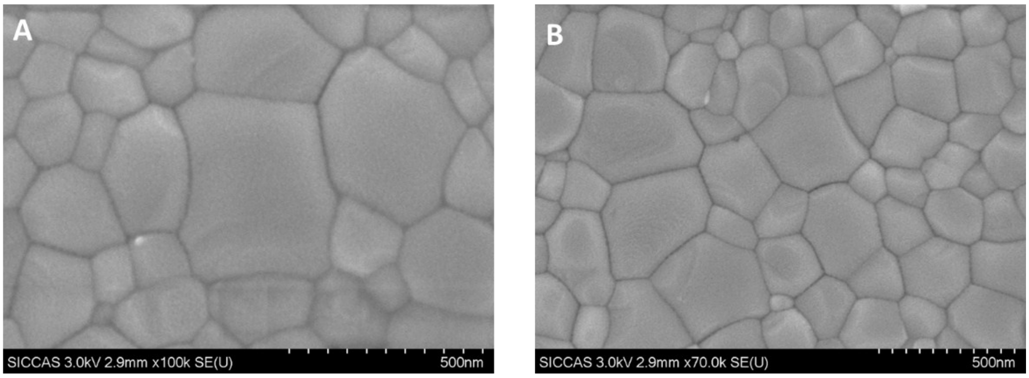

Fig. S2 Top view SEM images of perovskite absorber material ($CH_3NH_3PbI_3$) based on NiO_x (A) and Co:NiO_x (B) layers.

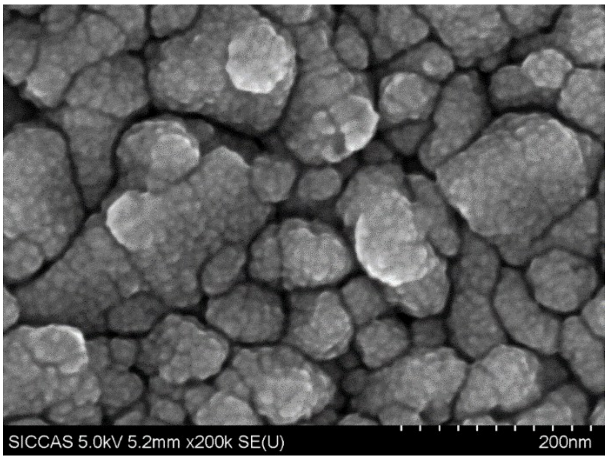

Fig. S3 Top view SEM image of NiO_x layer.

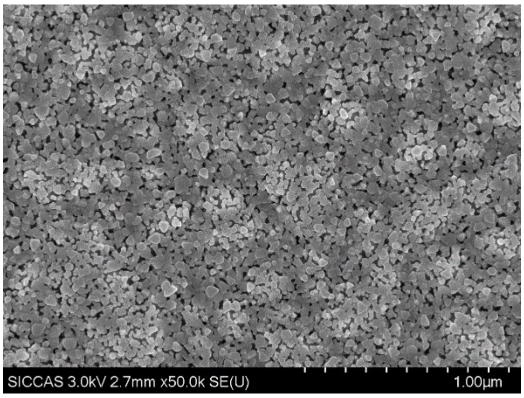

Fig. S4 Top view SEM image of NiO_x on FTO substrate via solution processed method

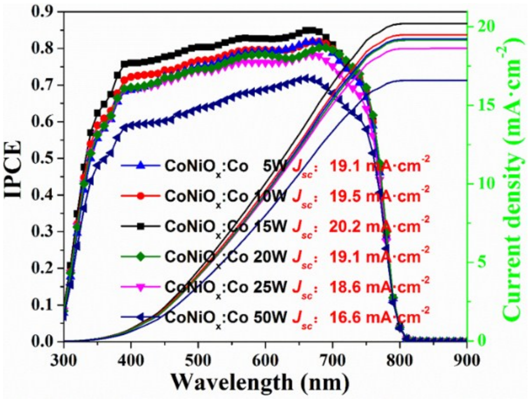

Fig. S5 Incident photon-to-current conversion efficiency (IPCE) spectra and the corresponding integration photocurrent of the device based on Co:NiO$_x$ HTLs as doping power was 5W, 10W, 15W, 20W, 25W and 50W, respectively.

Table S1 The photovoltaic parameters of the PSCs based on NiO_x HTLs with different sputtering time.

Devices	**V_{oc} (V)**	**J_{sc} (mA cm^{-2})**	**FF (%)**	**PCE (%)**
1 min	1.012	16.49	49.27	8.22
2 min	1.008	18.80	54.76	9.60
3 min	1.028	16.46	51.33	8.69
4 min	0.964	14.44	49.92	6.94

Table S2 The photovoltaic parameters of the PSCs based on Co:NiO$_x$ HTLs with different doping power loaded on Cu target.

Devices	**V_{oc} (V)**	**J_{sc} (mA cm^{-2})**	**FF (%)**	**PCE (%)**
5 W	1.008	18.76	58.08	9.63
10 W	1.012	19.38	61.08	11.12
15 W	1.010	20.02	63.35	12.63
20 W	1.011	18.88	61.44	10.52
25 W	1.009	17.97	58.92	9.86
50 W	1.006	15.32	50.06	6.89

Table S3 The contents of elements in Co:NiO_x film based on Si substrate.

Element	**Line Type**	**Apparent Concentration**	**k Ratio**	**Wt %**	**Wt % Sigma**	**Atomic %**
O	K series	0.5	0.00169	10.25	0.21	19.79
Si	K series	2.51	0.01991	57.58	0.45	63.3
Ni	K series	1.2	0.01198	31.66	0.49	16.65
Co	K series	0.02	0.00019	0.51	0.19	0.27
Total:				100		100