Electronic Supporting Information (ESI) for

# Perovskite solar cells on metal substrate with high efficiency

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## Experimental

## Preparation of a CH<sub>3</sub>NH<sub>3</sub>I (MAI)

24 mL of methylamine (40% in methanol, TCI) and 10 mL of hydroiodic acid (57 wt% in water, Aldrich) are reacted in a 250 mL round bottomed flask at 0  $^{\circ}$ C and kept with stirring for

2 h. The suspension was carefully dried at 50  $^{\circ}$ C in rotary evaporator and the precipitate was obtained. The yellowish raw product of MAI was dissolved in ethanol, recrystallized with diethyl ether, and this procedure was repeated twice. After filtration, the final MAI was collected and dried at 60  $^{\circ}$ C in a vacuum oven for 24 h.

## Solar cell fabrication

F-doped SnO<sub>2</sub> (FTO) coated glass (Pilkington, TEC15) was sequentially washed with acetone, ethanol, isopropanol, and distilled water. Around 50-nm-thick dense layer of TiO<sub>2</sub> was deposited onto FTO substrate by spray pyrolysis on hotplate at 450 °C. The substrate was immersed in 40mM TiCl<sub>4</sub> aqueous solution for 30 min at 70 °C in oven and annealed 500 °C for 15 min in muffle furnace. Mesoporous TiO<sub>2</sub> (mp-TiO<sub>2</sub>) film of ~250nm were spin-coated onto the TiO<sub>2</sub> dense layer/FTO substrate, which was moved to muffle furnace and kept 30 min at 500 °C. 1 M CH<sub>3</sub>NH<sub>3</sub>Pbl<sub>3</sub> solution was prepared by mixing synthesized MAI powders with Pbl<sub>2</sub> (Aldrich) in the mixture solvent of *N*,*N*-dimethylformamide : *N*-Methyl-2-pyrrolidone (1:1, v/v). To deposite perovskite film, 100 µL of CH<sub>3</sub>NH<sub>3</sub>Pbl<sub>3</sub> solutions were then spun onto the mp-TiO<sub>2</sub>/dense TiO<sub>2</sub>/FTO substrate at 500 rpm for 5s, 5000 rpm for 20s and 100 mL of toluene in later spin-stage was quickly dropped onto the center of the substrate during spin coating. The obtained film was kept on hot plate at 100 °C for 1 h. Following the CH<sub>3</sub>NH<sub>3</sub>Pbl<sub>3</sub> film deposition, the hole transporting material (HTM) was coated at 3000 rpm for 30s. The solution of HTM was prepared by dissolving 72.3 mg spiro-MeOTAD, 17.5 µL lithium bis(trifluoromethylsulphonyl)imide/acetonitrile (500 mg mL<sup>-1</sup>), and 28.8 µL 4-tert-

butylpyridine in 1 mL chlorobenzene. Finally a silver as the cathode was deposited by thermal evaporation (Woosung HI-VAC) at 1 Å s-1 under vacuum pressure <  $10^{-6}$  Torr. The active area was fixed at 0.135 cm<sup>2</sup>. For perovskite solar cells on Ti substrate was also fabricated as follows. Ti foils (GoodFellow, 99.6 wt.% purity) were prepared in the form of ~15 × 15 × 0.127 mm<sup>3</sup>. Followed by washing Ti substrate using sonication in a bath with same solvents as FTO. Ti substrate was patterned by SiO<sub>2</sub> layer with a thickness of 200 nm was deposited using RF sputtering at deposition rate of 1.29 Å s<sup>-1</sup> with a RF power of 600 W and under 10 mTorr. Following procedures for perovskite, spiro-MeOTAD, and top cathode films are equal to FTO.

#### Characterization and measurement

The transmittance spectra of each substrate was measured on UV/Vis/NIR spectroscopy (Cary 5000, Agilent). Sheet resistance of various Ag films was measured by hole effect measurement system (HMS-5500, Ecopia). As-prepared sample of XRD patterns were recorded with a Bruker D8 Advance, equipped with Cu Ka radiation. The samples were scanned from 5° to  $60^{\circ}$  (scanning step 1° min<sup>-1</sup>). Surface morphology was observed by field emission-scanning electron micro-scopy (FE-SEM, Nano230, FEI). The photovoltaic properties of the fabricated perovskite solar cells were investigated using solar simulator (AM 1.5 G, 100 mW cm<sup>-2</sup>, Sol3A, class AAA, Oriel) as a light source with the calibrated light intensity to 1 sun using a reference Si solar cell (PV Measurements, Inc.). Photocurrent density-voltage (J-V) curves of the photovoltaics were measured with reverse scan (from open-circuit to short-circuit under the forward bias voltage) at scan rate of 100 mV s<sup>-1</sup>. Especially as shown Fig. S5 and Table S2, both at forward (from short-circuit to open-circuit under the forward bias voltage) and reverse direction with negligible hysteresis were conducted at scan rate of 10 mV s<sup>-1</sup>. The photovoltaic parameters were obtained from J-Vcurve. The incident photon-to-current efficiency (IPCE) spectra were measured by PV measurement (PV Measurements, Inc., QEX7 series). The cross sectional image were obtained by focused ion beam (Helios 450HP, FEI). Bending test was measured in devices as a function of the number of bending cycles in outward directions at a bending radius of ~6 mm.



Fig. S1 Optical image of perovskite solar cells using UTMF (12nm of Ag film) as semitransparent top electrode on Ti substrate



Fig. S2 SEM image of perovskite deposited on TiO<sub>2</sub>/Ti substrate



Fig. S3 XRD spectra for  $CH_3NH_3PbI_3/mp-TiO_2/FTO$  substrate.



Lsec: 29.7 0 Cnts 0.000 keV Det: Octane Plus Det







In general, the conductivity of the thin metal films is strongly dependent on the quality of the films which is composed of roughness, grain size, and film continuity.<sup>1</sup> It is well known silver prefer 3D island growth,<sup>2</sup> and morphology changes are observed at the different thickness of Ag films in Fig. S6. This formation of inhomogeneous islands may seem leading the poor quality, which result in poor conductivity than theory values.

Table S1. Photovoltaic parameters of perovskite solar cells on glass substrate using 12nm of Ag film as semitransparent top electrode with front and back illumination. For back illumination, added Ti substrate at the rear of glass side and without Titanium substrate as the back scatter. (with reverse scan at scan rate of 100 mV s<sup>-1</sup>)

		$V_{ m oc}$ / V	J <sub>sc</sub> / mA cm <sup>-2</sup>	FF (%)	PCE (%)
Front Illumination		0.948	14.8	0.593	8.32
Back Illumination	Without Ti	0.934	9.2	0.645	5.54
	With Ti	0.936	9.8	0.646	5.93



Fig. S5 *I-V* curves of perovskite solar cells using UTMF (12nm of Ag film) on Ti substrate with reverse and forward scan with scan rate of 10 mV s<sup>-1</sup>.

Table S2 Average photovoltaic parameters in batch of sixteen devices on Ti substrate using 12nm of Ag film as semitransparent top electrode with reverse and Forward scan under AM 1.5 G illumination (scan rate of 10 mV s<sup>-1</sup>).

Ag thickness (12nm)	V <sub>oc</sub> / V	J <sub>sc</sub> / mA cm <sup>-2</sup>	FF (%)	PCE (%)
Forward Scan	0.868 ± 0.022 (0.908)	7.22 ± 1.18 (8.9)	66.32 ± 2.15 (69.4)	4.22 ± 0.58 (5.60)
Reverse Scan	0.875 ± 0.025 (0.915)	7.24 ± 1.21 (8.9)	68.25 ± 1.82 (70.3)	4.36 ± 0.75 (5.72)



Fig. S6 SEM images with different thickness of Ag film (a) 8nm (b) 12nm (c) 16nm (d) 20nm

The investigation of surface morphology for various Ag films were conducted by SEM as shown Fig. S6. The comparison represents that the more continuous film with increasing film thickness.

#### Reference

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