

## Electronic Supplementary Information

### Inverted (p-i-n) Perovskite Solar Cells Using Low Temperature Processed TiO<sub>x</sub> Interlayer

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## Experimental Details

### a. NiO<sub>x</sub> Film Preparation

Nickel oxide was synthesized following the procedure described by Young, et al.<sup>1</sup> About 2 % (wt/wt) of NiO<sub>x</sub> powder was mixed with deionized water (DIW) (20 mg per 1 mL of DIW), and treated with ultrasound sonicator (UP50H, 50 Watt, frequency 30 kHz) for five to six round with each round for about five minutes to further crash the particles. In between each round the mixture was kept in an ultra-sonication bath to avoid aggregation of particles. The solution was then filtered with 0.45 μm pore size filter and spin-coated on ITO substrates.

### b. Synthesis of Organic Halides

To synthesize methyl ammonium iodide (MAI), methylamine was added in a round-bottom flask and immersed into an ice bath to keep the reaction temperature at 0 °C and equimolar amount of hydroiodic acid was added drop-by-drop with continuous stirring. The reaction mixture was left under stirring in the ice bath for 2 h. The solvent was then evaporated using a Rota vapor (BUCHI Rotavapor R-114 coupled with a BUCHI water bath B-480). The resulting crystals were re-dissolved in a small amount of ethanol and precipitated by adding diethyl ether and decanted. Washing with diethyl ether was repeated until clean white crystals were obtained. The crystals

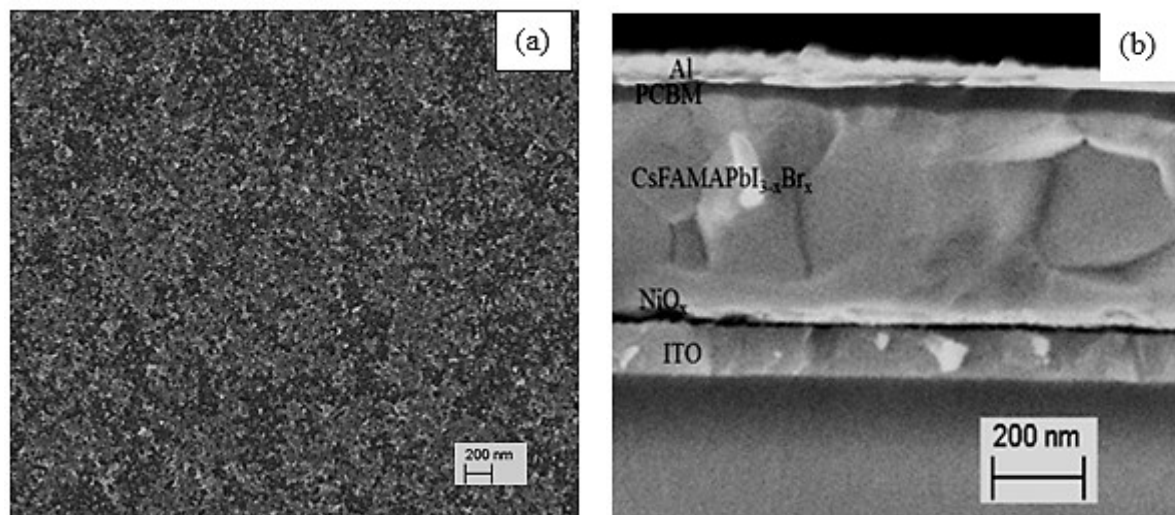
were then filtered with a Buchner funnel under vacuum and transferred to a round bottom flask followed by freeze drying. Finally the dried, white powder of MAI was transferred into a vial and kept in a nitrogen glove box. Formamidinium acetate salt (99 %) and Hydroiodic acid (HI, 57 wt % in H<sub>2</sub>O) in 1:1 mol ratio was used to synthesize formamidinium iodide (CH(NH<sub>2</sub>)<sub>2</sub>I) following the same synthesis procedure used for MAI. The same procedure was applied to synthesize methyl ammonium bromide (CH<sub>3</sub>NH<sub>3</sub>Br) using methyl amine and hydrobromic acid (HBr, ≥ 48 wt % in H<sub>2</sub>O) as a precursor materials.

### c. Synthesis TiO<sub>x</sub> Solution

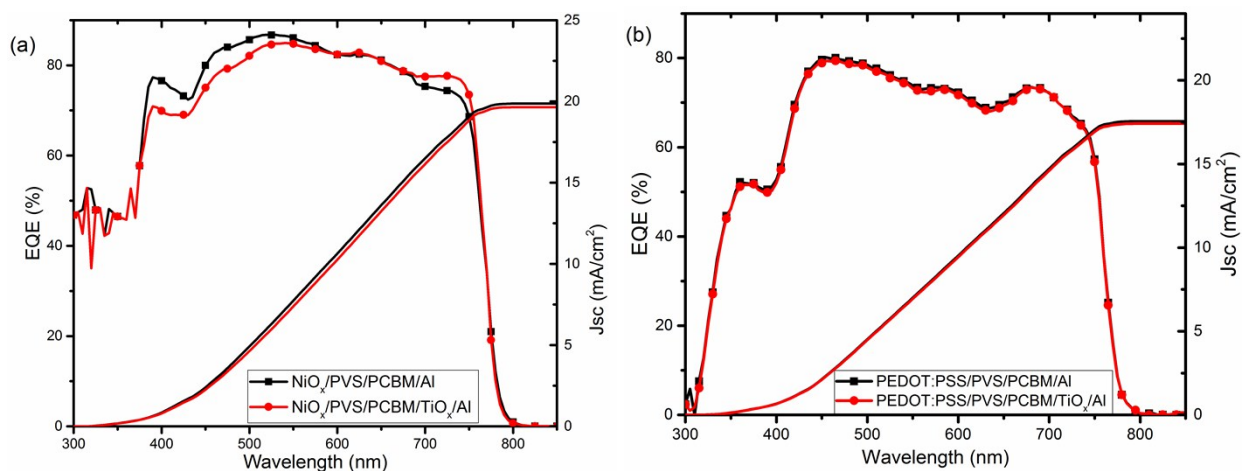
The sol-gel synthesis TiO<sub>x</sub> precursor solution was based on the procedure reported by S. H. Park et al.<sup>2</sup> A three-necked flask (100 mL) was used to mix the precursor material. It was first dried at about 120 °C with flowing dry nitrogen (N<sub>2</sub>) to remove any moisture. Then, a 2.5 mL of titanium (IV) isopropoxide (Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>), 10 mL of 2-methoxyethanol (CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OH) and 1 mL of ethanolamine (H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OH) were sequentially injected into the three-necked flask at room-temperature (RT).

The precursor solution was stirred for 60 min at room temperature under N<sub>2</sub> atmosphere and then heated for 60 min at 80 °C (using a silicon oil bath), followed by heating at 120 °C for 60 min with continuous stirring to distilled off low boiling solvent. The solution was then transformed into a low-density gel with dark-wine color. The mixture was cooled to room temperature and isopropyl alcohol (IPA, 5 mL) was added to prepare TiO<sub>x</sub> sol-gel precursor solution. The TiO<sub>x</sub> sol-gel precursor was further diluted in IPA with 1:150 (v/v) ratio to be used in the device.

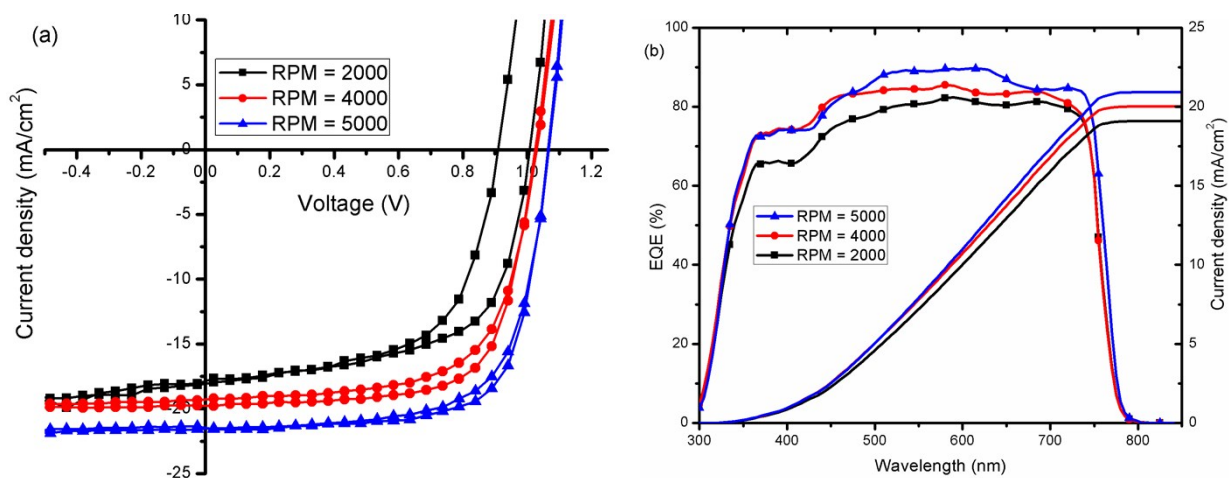
## Result



**Figure S1.** (a) Topographic SEM image of  $\text{NiO}_x$  nanoparticles on ITO-coated glass substrate, and (b) cross-section SEM image of mixed-halide mixed-cation PSCs without  $\text{TiO}_x$  interlayer (PCBM/Al structure).



**Figure S2.** External quantum efficiency (EQE) of inverted PSCs with, (a)  $\text{NiO}_x$  HTL, and (b) PEDOT:PSS HTL with and without  $\text{TiO}_x$  interlayer on top of PCBM and the corresponding current density calculated from the EQE data.



**Figure S3.** (a) J-V curves, and (b) external quantum efficiency (EQE) as well as the calculated current density from the EQE data of PSCs with different thickness of TiO<sub>x</sub> interlayer processed at various spin-coating speeds (i.e. 2000, 4000 and 5000 revolutions-per-minute (RPM) yielding TiO<sub>x</sub> films thickness of about 35 to 40, 15 to 20 and 10 to 15 nm, respectively).

**Table S1.** Fitting parameters of the equivalent circuits for the characteristic EIS response of PSCs with TiO<sub>x</sub> interlayer (PCBM/TiO<sub>x</sub>/Al) and control devices (PCBM/Al).

Device structure	R <sub>s</sub> (Ω)	R <sub>internal</sub> (Ω)	CPE1		R <sub>surface</sub> (Ω)	CPE2	
			T1	P1		T2	P2
PCBM/Al	20	189	2.5×10 <sup>7</sup>	0.925	23	0.04	0.85
PCBM/TiO <sub>x</sub> /Al	22	38.5	2.0×10 <sup>7</sup>	0.9	16	0.06	0.85

## Reference

- 1 X. Yin, P. Chen, M. Que, Y. Xing, W. Que, Ch. Niu, J. Shao, *ACS Nano*, 2016, 10, 3630-3636.
- 2 S. H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee, A. J. Heeger, *Nat. Photonics*, 2009, 3, 297-303.