

Supporting Information

Room-Temperature Solution-Processed Amorphous NbO_x as Electron Transport Layer in High-Efficiency Photovoltaics

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Experimental

Materials and Reagents: Fluorine-doped tin oxide (FTO, 7 Ω/sq) was purchased from Yingkou OPV tech New Energy Co. LTD. All the chemicals were used as received, including PbI₂ (99.9985%, Alfa Aesar), PbBr₂ (99.999%, Sigma Aldrich), CH₃NH₃I (MAI, Xi'an Polymer Light Technology Corp), CH(NH₂)₂I (FAI, Xi'an Polymer Light Technology Corp), Spiro-OMeTAD (99.7%, Lumtec Co., Taiwan). NbCl₅ (99.995%), Nb (C₂H₅O)₅ (ACS, 99.95%), Titanium(IV) isopropoxide (99.999%), 4-tert-butylpyridine (TBP, 96%), Bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI, 99.95%), and solvents of acetonitrile (99.9%), ethanol (99.8%), dimethylformamide (DMF, 99.8%), dimethylsulfoxide (DMSO, 99.9%), chlorobenzene (99.8%), and α, α, α-Trifluorotoluene (99%) were all purchased from Sigma Aldrich.

Electron transport layer preparation: To prepare NbO_x ETLs, 0.1 M Nb (C₂H₅O)₅ alcohol solution, 0.1 M NbCl₅ alcohol solution and 0.1 M Nb (C₂H₅O)₅ isopropanol solution were prepared by stirring for 2 h in the glove box (H₂O content lower than 0.01 ppm). The final solution was spin coated onto FTO substrates at 3000 r.p.m. for 30 s, and then UVO treatment or heated at 500 °C for 1 h to remove solvent in the air. As a contrast, TiO₂ ETL was prepared as reported. Finally, the ETL substrates were transferred immediately to the glove box for perovskite deposition.

Solar cell fabrication: FTO was patterned by etching with Zn powder and 4 M HCl, and then rinsed with cleaning fluid, deionized water, ethanol, acetone and isopropanol sequentially. The precursor solution of ETLs was spin coated on FTO in ambient air or in dry glove box, and then UVO treatment (BZS250GF-TC,

China) at room temperature or annealed at 500 °C for 1 h. TiO₂ ETL was prepared as reported. After depositing the ETL, the perovskite layer Cs_{0.05}[(FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}]_{0.95} was deposited by one-step spin coating method. Firstly, anhydrous mixture of DMF and DMSO (volume ratio is 4:1) containing FAI (1 M), PbI₂ (1.1 M), MABr (0.2 M) and PbBr₂ (0.2 M) was prepared firstly by stirring at 60 °C for 2 h. Then 1 M stock solution of CsI in DMSO was added to above solution (MA/FA perovskite) in the 5:95 ratios. Then, 80 μL solution was spread on the FTO/ETL substrate followed by a two-stage spin coating processes (1000 rpm for 10 s and 4000 rpm for 50 s). During the second spin coating stage, 330 μL of α, α, α-Trifluorotoluene were poured on the spinning substrate 30 s prior the end of the program. Finally, the substrates were annealed at 85 °C for 40 min. Precursor solution of hole transfer layer (HTM) was prepared by dissolving 72.3 mg of spiro-MeOTAD, 28.8 μL of 4-tert-butylpyridine, 17.5 μL of Li-TFSI/acetonitrile (520 mg mL⁻¹) in 1 ml of chlorobenzene. Then, HTM layer was deposited atop perovskite by spin coating at 3000 rpm for 30 s. Finally, a Ag back electrode was deposited by thermal evaporation under high vacuum (<10⁻³ Pa). The active area is 0.09 cm². All devices were fabricated in a glove box.

Characterisations: The crystal structure was studied via X-ray diffraction (XRD, D/MAX-2400, Japan) analysis with Cu K α radiation (λ =0.1541 nm). The top view and cross section of the samples were investigated through field-emission scanning electron microscopy (SEM, SU8010, Hitachi, Japan). Component identifications were conducted through Energy dispersive X-ray spectroscopy (EDS, EMAX, HORIBA) and Attenuated total internal reflectance Fourier transform infrared spectroscopy (ATR-FTIR, EQUINOX55, Germany). Ultraviolet photoelectron spectroscopy (UPS) characterizations were performed by monochromatized HeI radiation at 21.2 eV. The current density-voltage (J - V) curves of PSCs were measured under simulated AM 1.5 illumination (100 mW cm⁻², Newport/94123A, USA) using a Keithley digital source meter (Keithley 2450, USA). All the devices were measured with a 50 ms delay after 10 mV voltage step, which is approximately equal to a scan rate of 0.2 V s⁻¹. Steady-state output of photocurrent, Linear sweep voltammetry curves and PCE were measured with Keithley 2450 digital source meter under a certain bias. The calculated values for shortcircuit photocurrent density (J_{sc}) from the incident photon-to-electron conversion efficiency (IPCE) spectra were based on data recorded by a setup, consist of a xenon light source, a monochromator, and a potentiostat. UV-Vis absorption and transmission spectrum were measured with UV-Vis spectrophotometer (HP-8453, USA). Tafel was measured with CHI 660C electrochemical workstation (Shanghai, China).

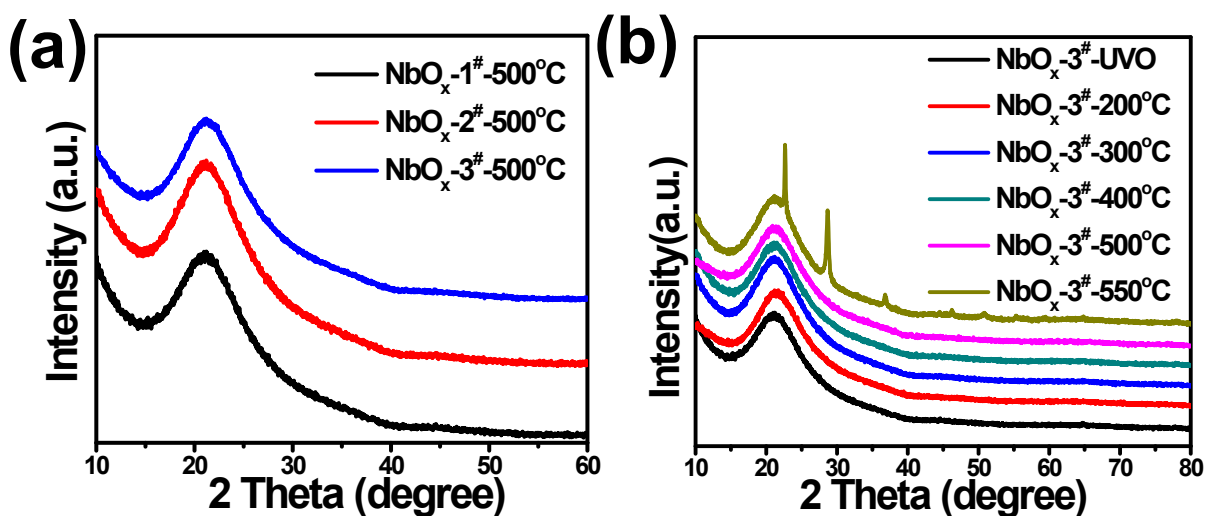


Fig. S1 (a) X-ray diffraction (XRD) patterns of the film prepared by spin coating of different precursor solution onto quartz glass substrate and heating at 500 °C. (b) XRD patterns of film prepared by spin coating of Nb (CH₃CH₂O)₅ alcohol solution onto quartz glass and heating at different temperature.

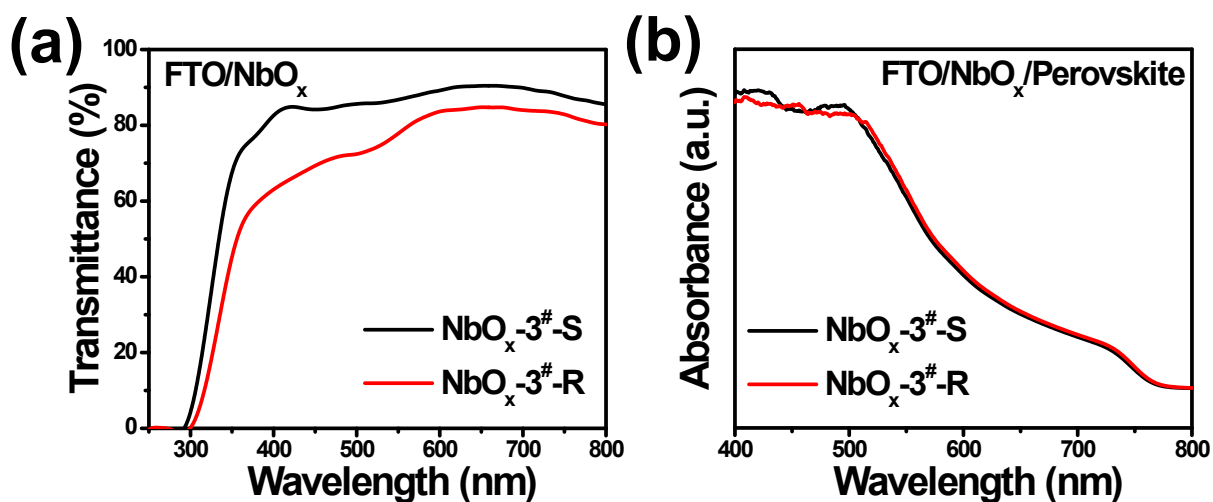


Fig. S2 (a) Transmittance spectra of the film prepared by spin coating of Nb (CH₃CH₂O)₅ alcohol solution under different relative humidity environment conditions; (b) UV-Vis absorption spectra of perovskite films on different NbO_x ETLs.

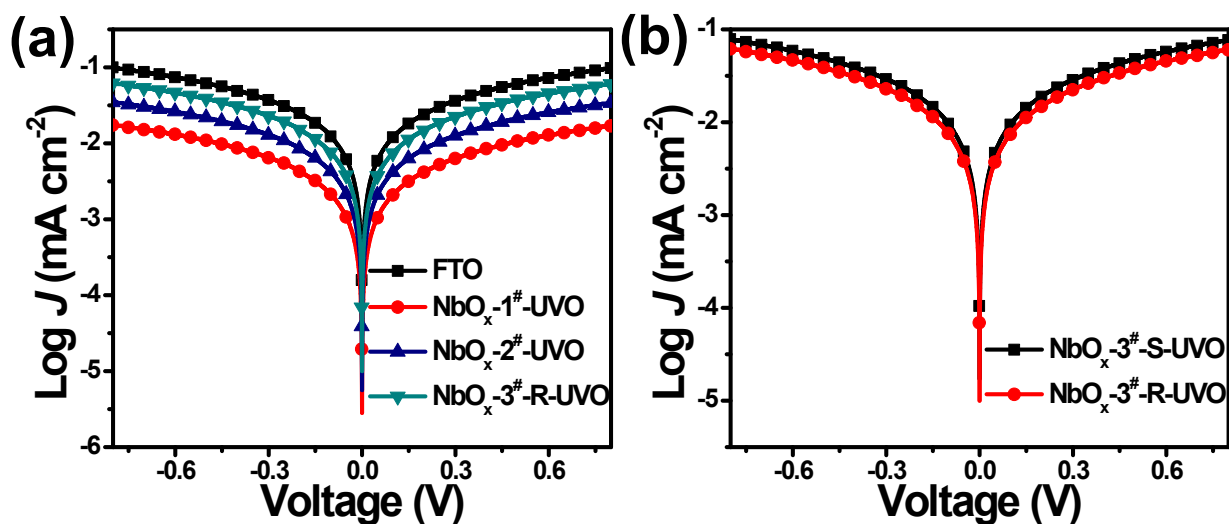


Fig. S3 Tafel plots of ETLs (structure: FTO/ETL/Ag).

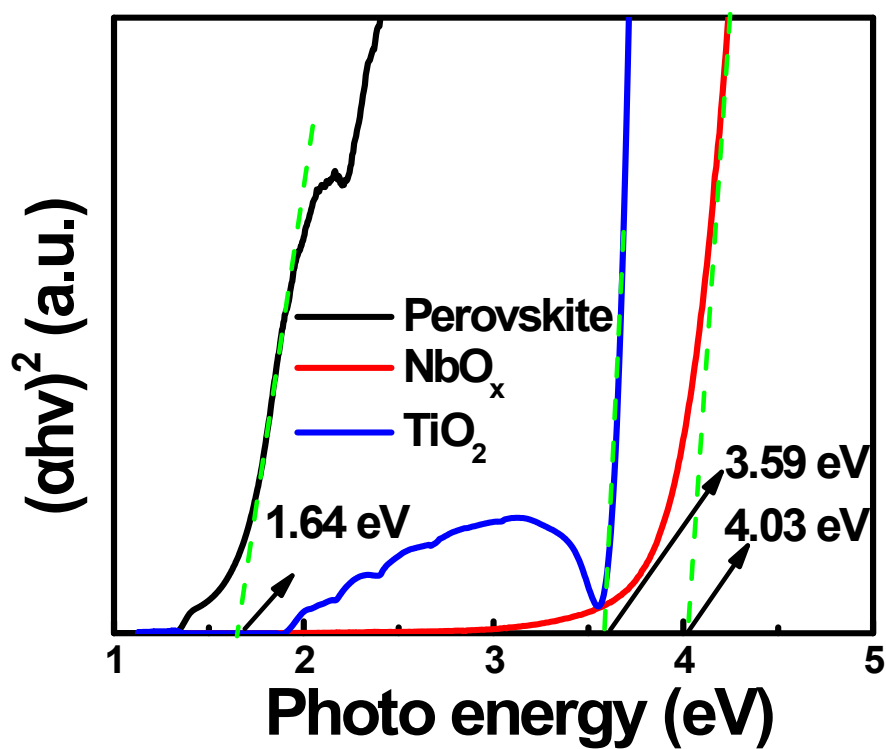


Fig. S4 The relationship of $(\alpha h\nu)^2$ vs energy for perovskite, NbO_x and TiO_2 , respectively. The bandgap of each material can be determined via linear extrapolation of the leading edges of the $(\alpha h\nu)^2$ curve to the base lines.

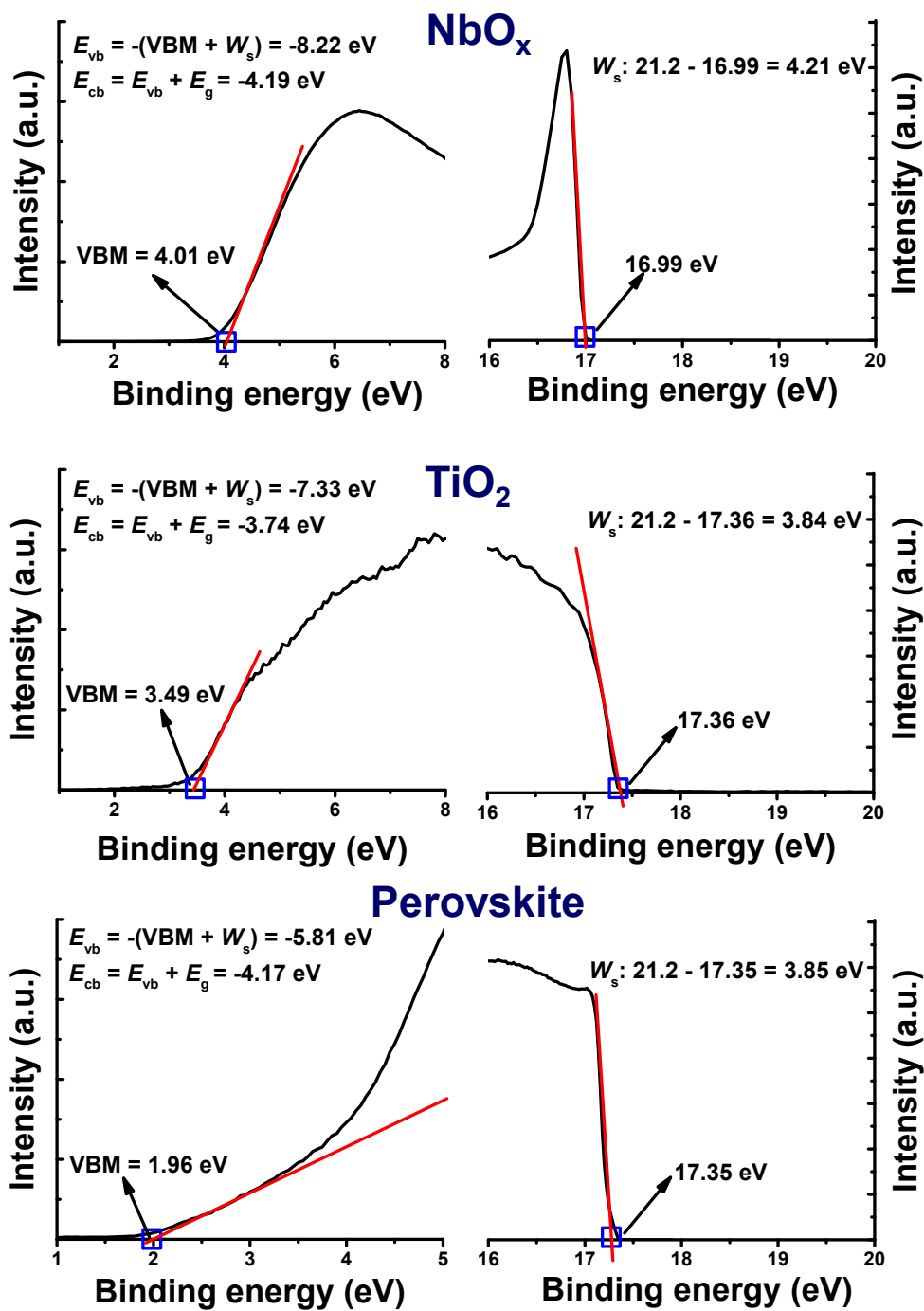


Fig. S5 Zoom of the ultraviolet photoelectron spectrometer (UPS) absorption spectra and calculation details of work function (W_s), valence band (E_{vb}) and conduction band (E_{cb}); horizontal value of the intercept of the left part, as indicated by the red line, corresponds to VBM; W_s equals to 21.2 eV minus the horizontal value of the intercept of the right part, as indicated by the red line.

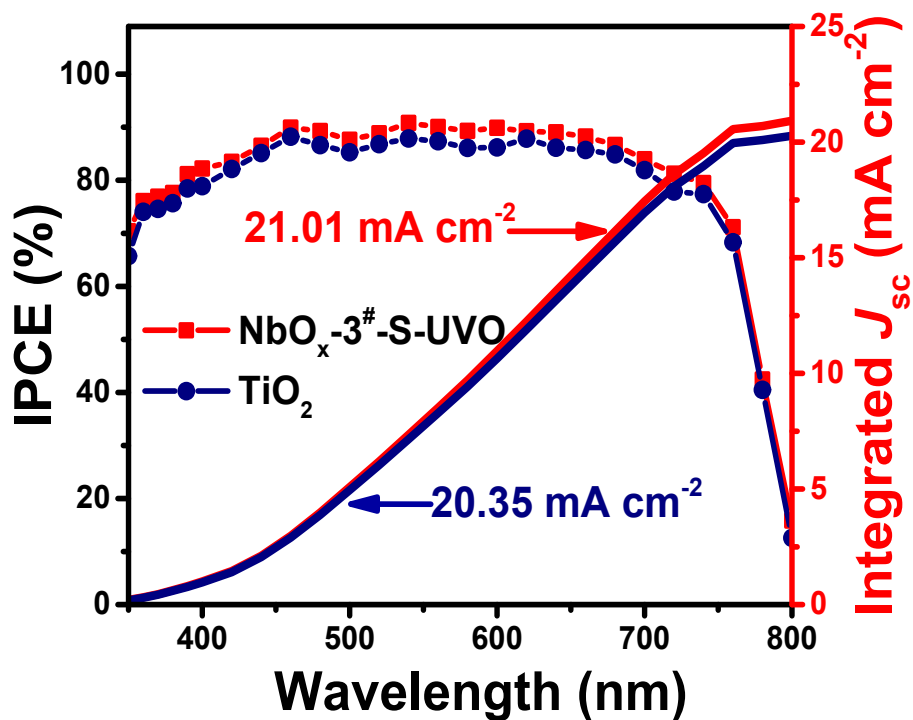


Fig. S6 IPCE spectra and integrated current density of the PSCs based on different ETLs.

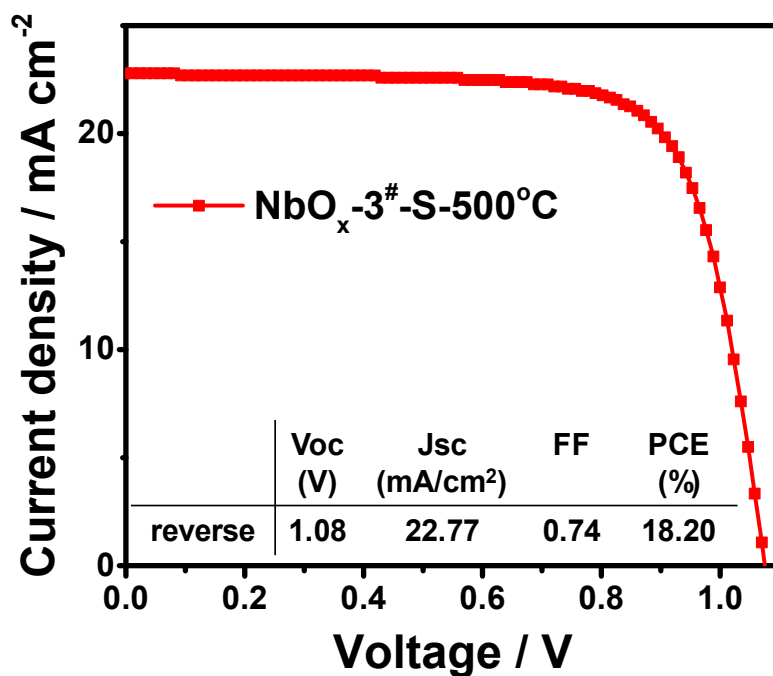


Fig. S7 $J-V$ curve and performance parameter (reverse scan) of the PSC based on $\text{NbO}_x\text{-3}^\#\text{-S-500}^\circ\text{C}$ ETLs.

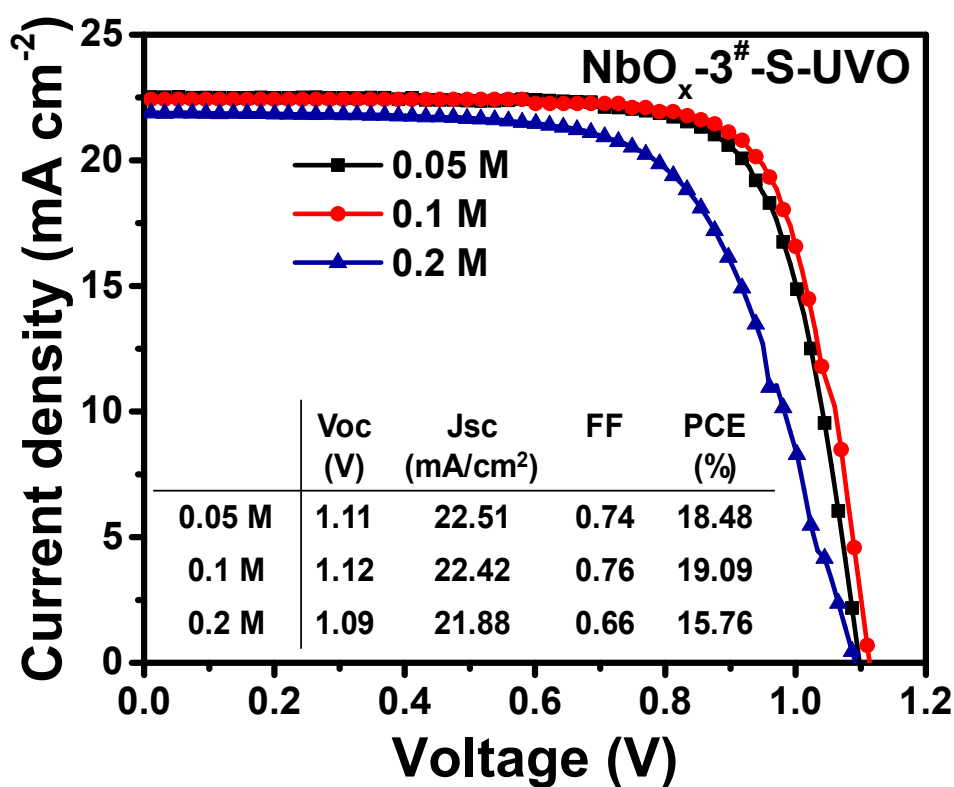


Fig. S8 J - V curve and performance parameter (reverse scan) of the PSC based on ETLs of different thickness.

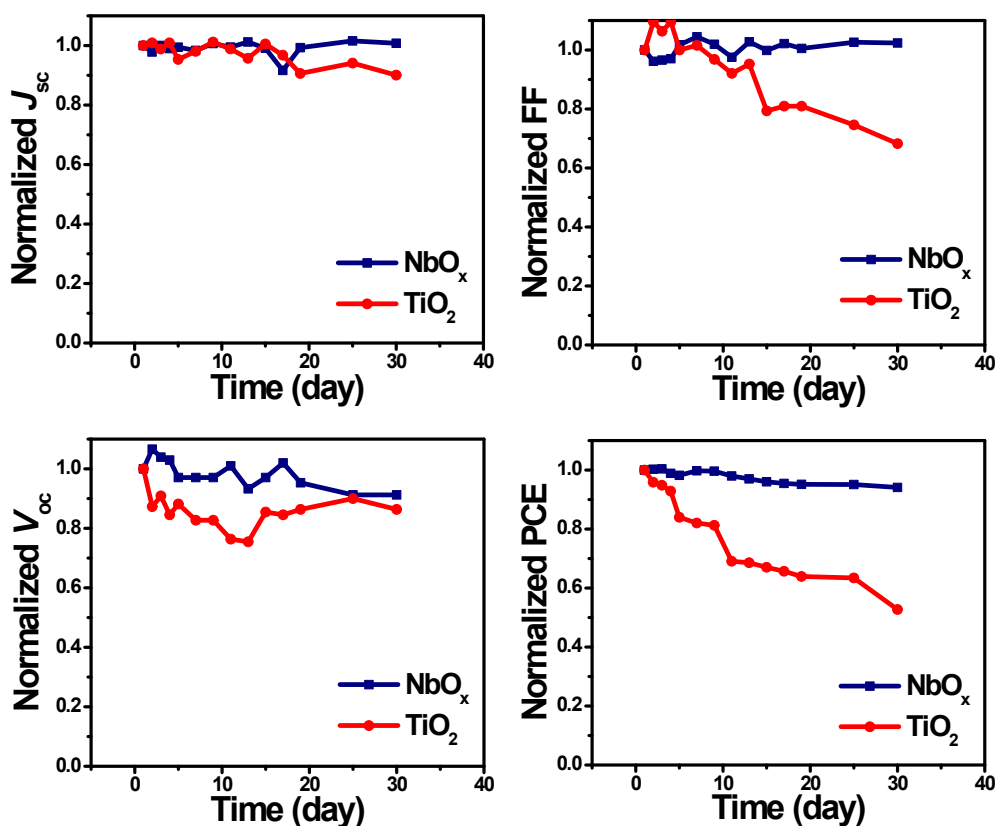


Fig. S9 Stability test of two PSCs based on NbO_x -ETL and TiO_2 -ETL, respectively, the devices were stored in a desiccator in dark after J - V measurement in the ambient air (ca. 20% RH, 25 °C).

Table S1 Several works on amorphous ETLs that were used in PSCs developed so far.

| ETL | Oxide Deposition Technique | Processing Temperature [°C] | Perovskite Composition | PCE (%) | Ref. |
|------------------|----------------------------|-----------------------------|---|------------|------|
| NbO _x | Spin Coating | 500 | CH ₃ NH ₃ PbI _{3-x} Cl _x | 8.8±1.15 | 17 |
| NbO _x | E-beam evaporation | RT ^{c)} | MA _{2/6} FA _{4/6} Pb(Br _{1/6} I _{5/6}) ₃ | 18.59 | 16 |
| NbO _x | Sputtering | RT | CH ₃ NH ₃ PbI ₃ | 17.1 | 15 |
| SnO _x | Spin Coating | 140 | CH ₃ NH ₃ PbI ₃ | 12.93 | 29 |
| SnO _x | PEALD ^{a)} | 100 | CH ₃ NH ₃ PbI ₃ | 17.16 | 30 |
| SnO _x | CBD ^{b)} | 55 | CH ₃ NH ₃ PbI ₃ | 14.8 | 31 |
| SnO _x | Spin Coating | 100 | CH ₃ NH ₃ PbI _{3-x} Cl _x | 14.36 | 32 |
| SnO _x | E-beam evaporation | RT | Cs ₂ (MA _{0.17} FA _{0.83}) ₉₅ Pb(I _{0.83} Br _{0.17}) ₃ | 12.21 | 27 |
| SnO _x | Spin Coating | 180 | (FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} | 15.8 | 33 |
| SnO _x | PEALD | 100 | MA _{0.7} FA _{0.3} PbI ₃ | 18.36 | 34 |
| TiO _x | CBD | 250 | CH ₃ NH ₃ PbI ₃ | 3.82 | 21 |
| TiO _x | Sputtering | RT | CH ₃ NH ₃ PbI _{3-x} Cl _x | 16.08 | 19 |
| TiO _x | Spin Coating | 150 | CH ₃ NH ₃ PbI _{3-x} Cl _x | 16.2 | 22 |
| TiO _x | Spin Coating | 150 | CH ₃ NH ₃ PbI _{3-x} Cl _x | 16.4 | 23 |
| TiO _x | E-beam evaporation | RT | CH ₃ NH ₃ PbI ₃ | 14.70±0.54 | 20 |
| TiO _x | CBD | 80 | CH ₃ NH ₃ PbI ₃ | 5.10 | 24 |
| TiO _x | Spin Coating | 100 | CH ₃ NH ₃ PbI ₃ | 14.67 | 25 |
| TiO _x | Spin Coating | RT | CH ₃ NH ₃ PbI ₃ | 14.3 | 26 |
| WO _x | Spin Coating | 150 | CH ₃ NH ₃ PbI ₃ | 8.99±0.41 | 13 |
| WO _x | Spin Coating | 150 | CH ₃ NH ₃ PbI ₃ | 13.10 | 12 |
| WO _x | Spin Coating | 120 | CH ₃ NH ₃ PbI ₃ | 15.65 | 14 |

a) PEALD: Plasma-Enhanced Atomic Layer Deposition; b) CBD: Chemical Bath Deposition; c) RT: Room Temperature.