

Supplementary Material

Facilitating Charge Transfer and Band Alignment in Perovskite Solar Cells via Interfacial Regulation with Nb₂CT_x MXene Oxidized Derivative

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Experimental Section

Materials

Nb₂AlC was sourced from Jilin 11 Technology Co., Ltd. Tetramethylammonium hydroxide (TMAOH 25% in water) was obtained from Alfa Aesar. Aladdin supplied 99% ascorbic acid (C₆H₈O₆) and 49 wt % HF. *N,N*-dimethylformamide (DMF, 99.9%) Titanium (IV) isopropoxide, dimethyl sulfoxide (DMSO, 99.9%), chlorobenzene (CB, 99.8%), Isopropyl alcohol (IPA, 99.9%, ultra-dry) and 4-*tert*-butylpyridine (TBP, 96%) were purchased from Sigma Aldrich. Lead iodide (PbI₂), Lead bromide (PbBr₂), Formamidinium iodide (FAI), Methylammonium bromide (MABr), Cesium iodide (CsI), F-PEAI and Lithium bis (trifluoromethane sulphonyl) imide (Li-TFSI, 99.5%) were purchased from Xi'an Polymer Light Technology Corp. SnO₂ hydrocolloid, ITO glass substrates and Spiro-OMeTAD (99.8%) were purchased from Advanced Election Technology Co.

Preparation of Multi-Layer Nb₂CT_x MXene

Multi-layer Nb₂CT_x MXene was fabricated from Nb₂AlC MAX phase by etching the aluminum layer. Typically, 3g of Nb₂AlC powder was added into 55 mL HF solution (49% wt%) and treated under continuously stirring for 72 h at 55 °C. Afterwards, the resulting mixture was centrifuged using deionized water at 8000 rpm multiple times until the pH reached 6. Finally, the multi-layer Nb₂CT_x MXene was obtained by drying the mixture under vacuum at 60 °C for 12 hours.

Delamination of Few-Layer Nb₂CT_x MXene

Few-layer Nb₂CT_x MXene was exfoliated from multi-layer product above. 2 g multi-

layer Nb₂CT_x MXene powder was put into a Teflon-lined stainless-steel autoclave with 20 mL deionized water, 40 mL undiluted tetramethylammonium hydroxide (25% TMAOH), 1.0 g ascorbic acid and delaminated at 140 °C for 24 h. The product was then centrifuged at 8000 rpm to separate from excess impurities. Subsequently, deionized water was added to the product and sonicated for 60 min to further exfoliate the MXene. Finally, colloidal solution of the few-layer Nb₂CT_x was obtained via centrifuging the nanosheets at 3500 rpm for 1 h.

Device Fabrication

ITO substrates were cleaned stepwise with detergent, deionized water, acetone, and ethanol, each for 30 min. After drying, the substrates were treated with UV-ozone for 20 min. SnO₂ hydrocolloid was spin-coated on ITO substrate at 4000 rpm for 40 s, followed by annealing at 150 °C for 30 min on the hot plate. For the fabrication of Nb₂CT_x derived layer, the Nb₂CT_x colloid was firstly diluted to 4 mg mL⁻¹ with deionized water. Then the aged colloid was spin-coated onto the UV-ozone treated ITO/SnO₂ substrate at 2000 rpm for 30 s, followed by annealing at 200 °C for 30 min. After that, the samples were transferred to a glovebox full of nitrogen. The perovskite precursor was prepared by mixing 1.4 M FAPbI₃ and MAPbBr₃ solution dissolved in DMF: DMSO (4:1 volume ratio) in a volume ratio of 19:1, while the FAPbI₃ and MAPbBr₃ were both contained 9% PbI₂, PbBr₂ excess in sequence. Then, 1.5 M CsI in DMSO was prepared and mixed with the precursor solution described above in a volume ratio of 1:24. Besides, 15 mol% MACl was added to the precursor solution to obtain the final triple-cation perovskite precursor. 80 μL of the perovskite precursor

were spin coated onto the ETL substrates at 4000 rpm for 40 s, while 200 μL mixed antisolvent with chlorobenzene and isopropanol in a volume ratio of 9:1 containing 0.5 mM F-PEAI was injected onto the film at 7 s before the end of spinning process. Then the perovskite film was obtained after annealing on the hot plate at 100 $^{\circ}\text{C}$ for 60 min. For the HTL, a solution of 80 mg Spiro-OMeTAD in 1 mL of chlorobenzene was prepared and spin-coated onto the perovskite layer at 4000 rpm for 30 s. In this solution, 35.5 μL of a Li-TFSI acetonitrile solution with a concentration of 260 mg mL^{-1} and 35 μL of tBP were added. Finally, the Ag electrode was prepared by thermal evaporation on top of the Spiro-OMeTAD layer.

Characterizations

The scanning electron microscopy (SEM) images of Nb_2CT_x MXene relevant materials and devices were measured by JSM-7900F (JEOL). transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded by JEM-2200FS (JEOL). X-Ray diffraction (XRD) measurements were obtained on Bruker D8 X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature. UV-vis absorption spectra were monitored by a Hitachi U4150 spectrophotometer over the wavelength range of 200-800 nm. UV-Ozone treatment was used by a BZS250GF-TS UV-ozone cleaner. Atomic force microscopy (AFM) images were obtained with Bruker Dimension Icon. Steady-state photoluminescence (PL) was monitored on Shimadzu RF-5301PC spectrophotometer, while time-resolved PL (TRPL) spectra were carried out by a PL spectrometer (Edinburgh Instruments, FLS 920) with the excitation wavelength at 475 nm. Electrochemical impedance

spectroscopy (EIS) measurement was obtained by a VSP multi-channel potentiostat-galvanostatic system (Biologic, France). Ultraviolet photoelectron spectroscopy (UPS) results were recorded by ThermoFisher ESCALAB 250Xi ($h\nu = 21.22$ eV). The J - V curves were carried out using a Keithley 2400 source meter measurement system under AM 1.5G. The EQE results were measured by CrowntechQTest Station 1000AD (SOFN INSTRUMENTS CO., LTD).

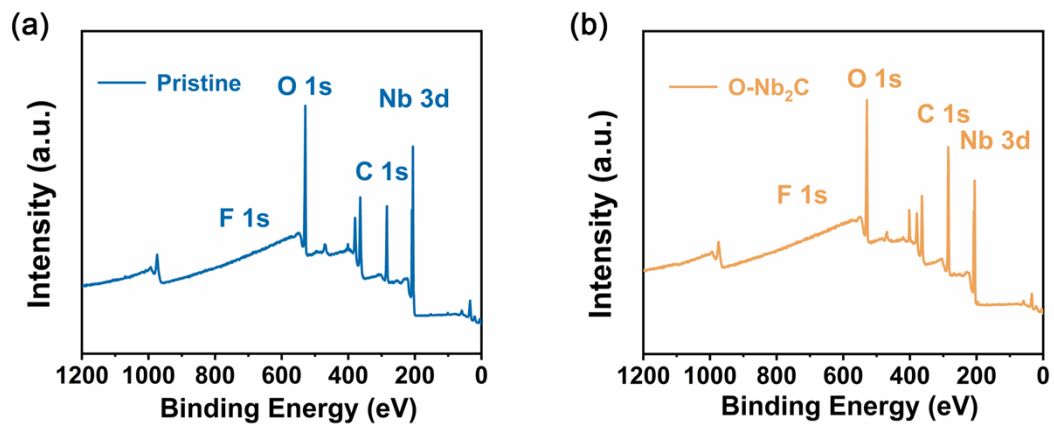


Figure S1. The full scan XPS spectra of (a) pristine Nb_2CT_x and (b) $\text{O-Nb}_2\text{C}$.

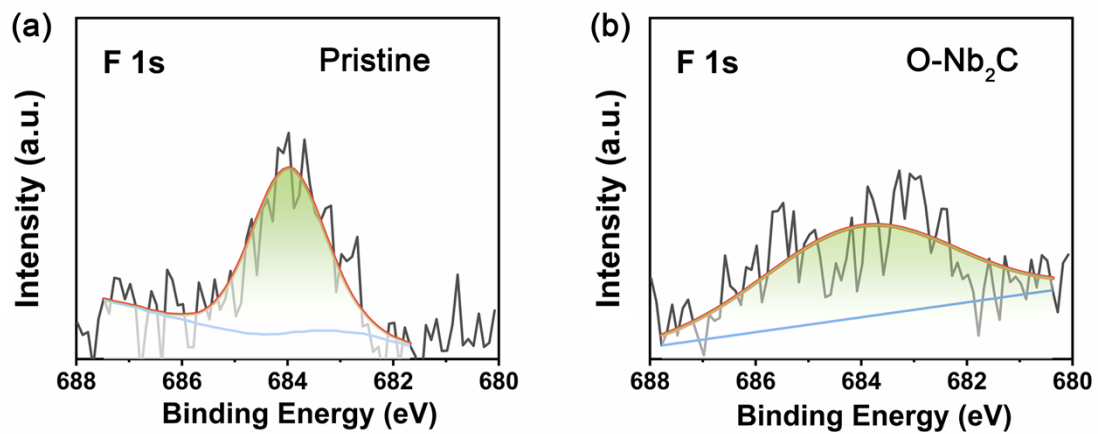


Figure S2. The fitted F 1s core-levels spectra of (a) pristine Nb₂CT_x and (b) O-Nb₂C.

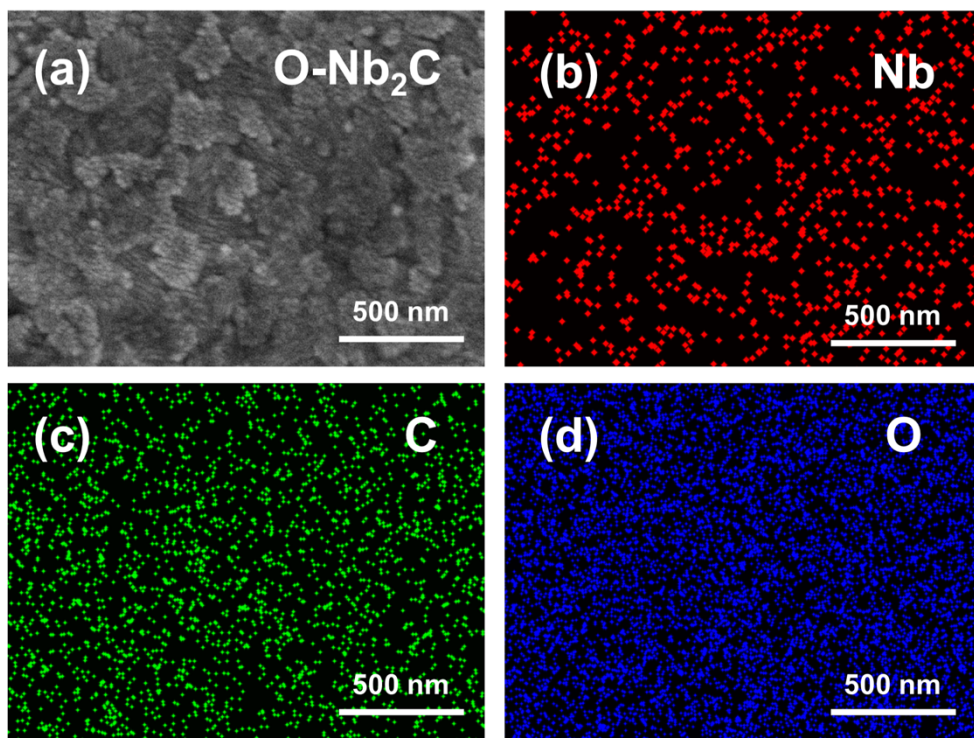


Figure S3. EDX elemental mapping images of (b) Nb (c) C (d) O for (a) O-Nb₂C film fabricated by spin-coating.

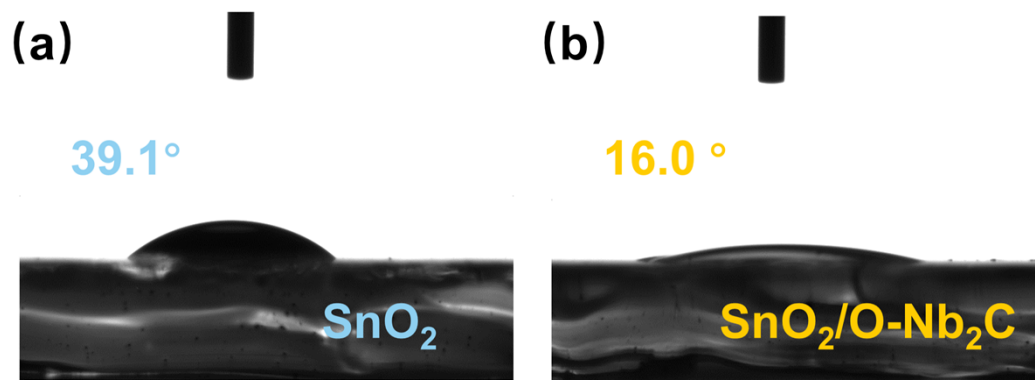


Figure S4. The contact angle measurements of water on (a) SnO_2 and (b) $\text{SnO}_2/\text{O-Nb}_2\text{C}$ substrates.

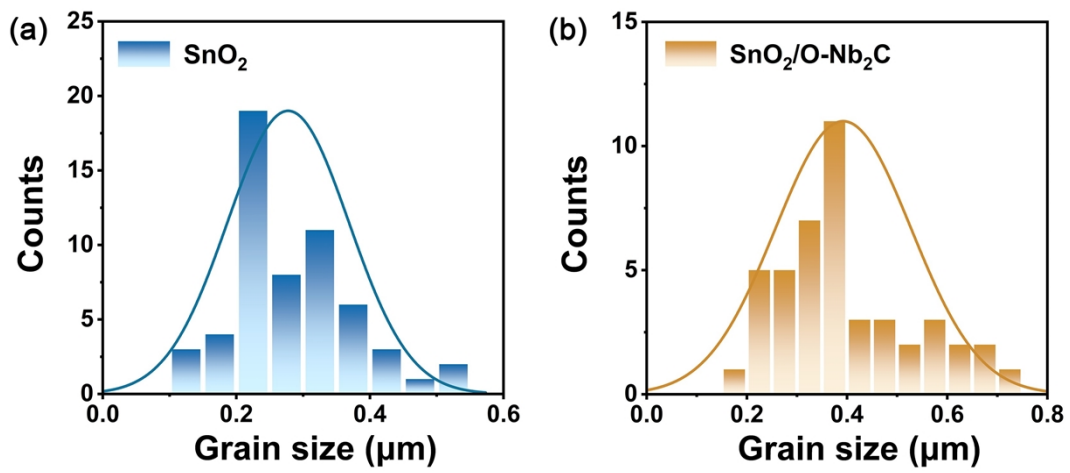


Figure S5. Grain size distributions calculated from the corresponding SEM images of the perovskite films based on (a) SnO₂ and (b) SnO₂/O-Nb₂C.

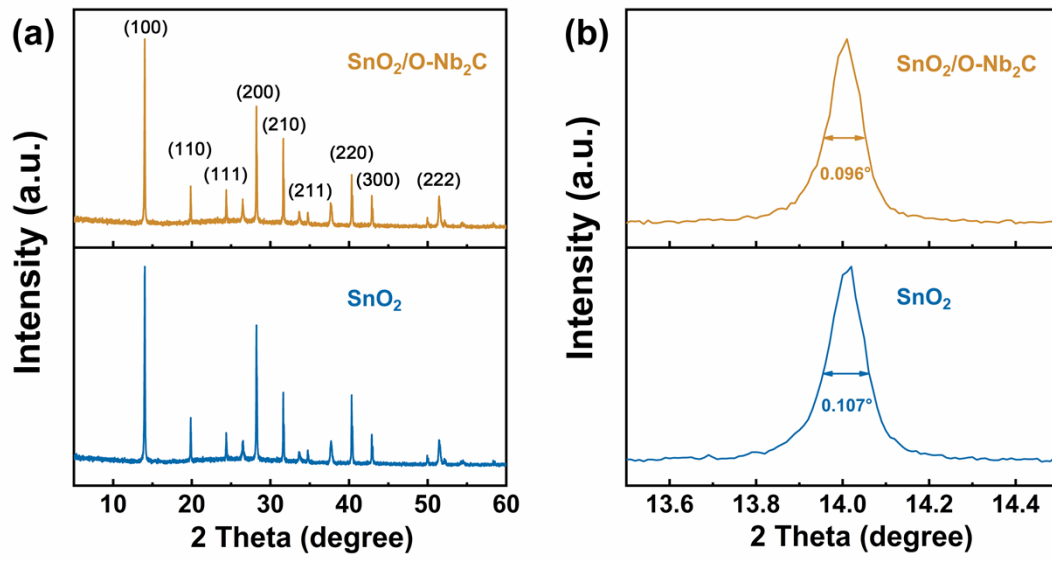


Figure S6. (a) XRD patterns and (b) their FWHM of the diffraction peak at about 14° of perovskite films based on SnO_2 and $\text{SnO}_2/\text{O-Nb}_2\text{C}$.



Figure S7. Cross-sectional SEM image of the PSC device based on SnO₂ ETL.

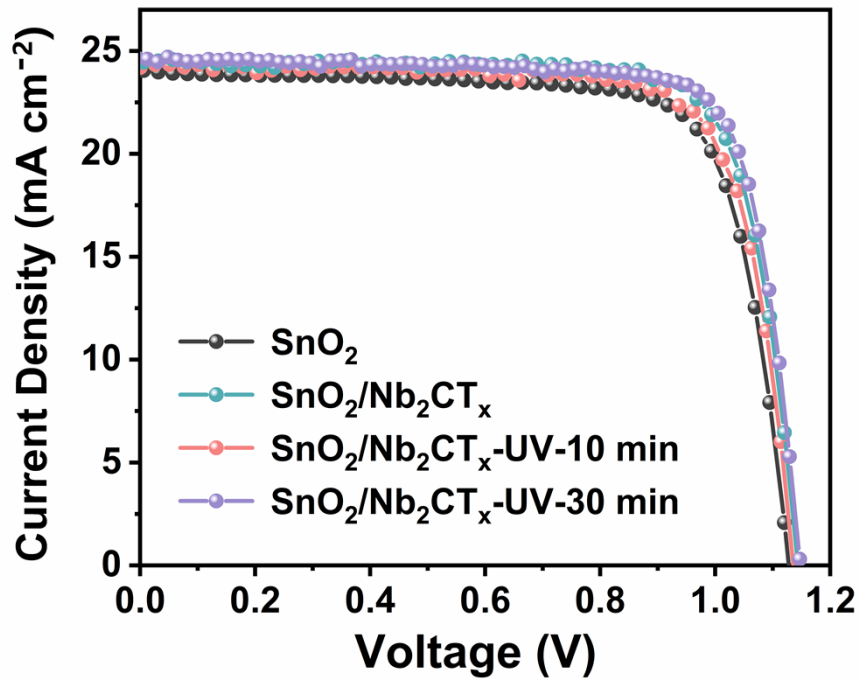


Figure S8. J - V curves of devices based on Nb₂CT_x regulation without oxidation under AM 1.5 G simulated illumination

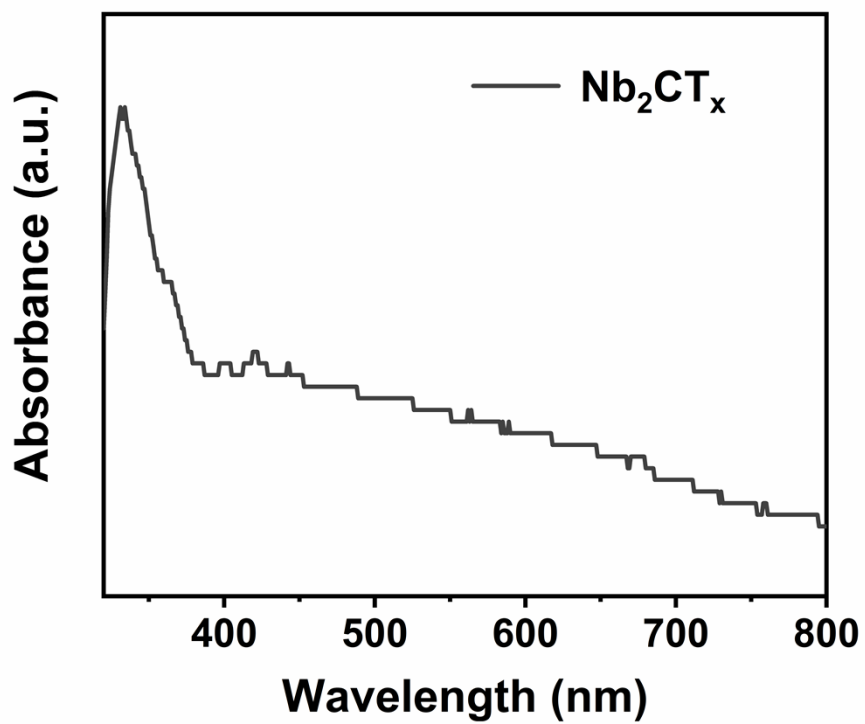


Figure S9. UV-vis absorption measurement of pristine Nb₂CT_x film.

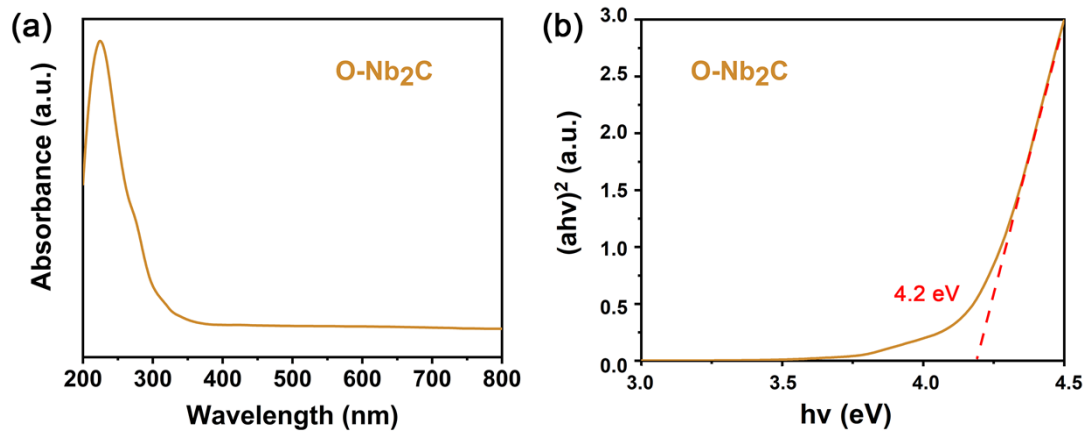


Figure S10. (a) UV-vis absorption measurement of O-Nb₂C and (b) the curves of $(ah\nu)^2$ versus $h\nu$ derived from the optical absorption spectra.

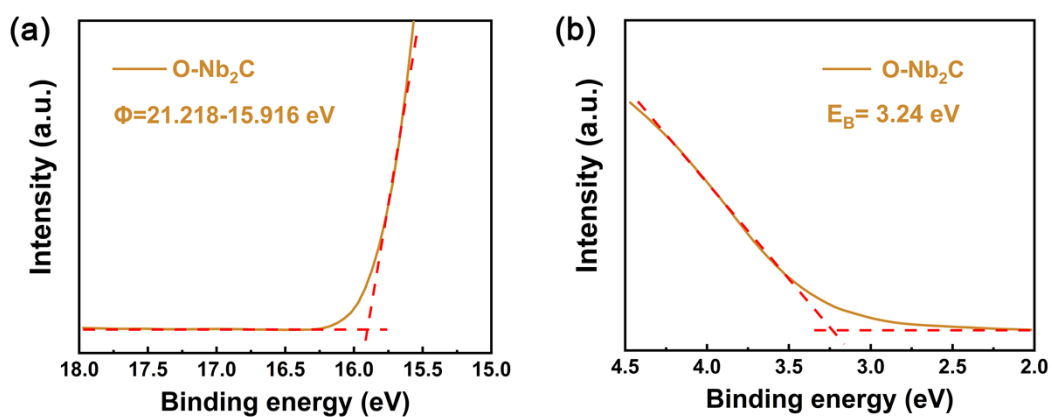


Figure S11. UPS results of O-Nb₂C film. The HOMO energy levels were determined by the intersection of baseline with the tangent line of the spectra, that is, HOMO = –

$$(\Phi + E_B) \text{ (eV)}.$$

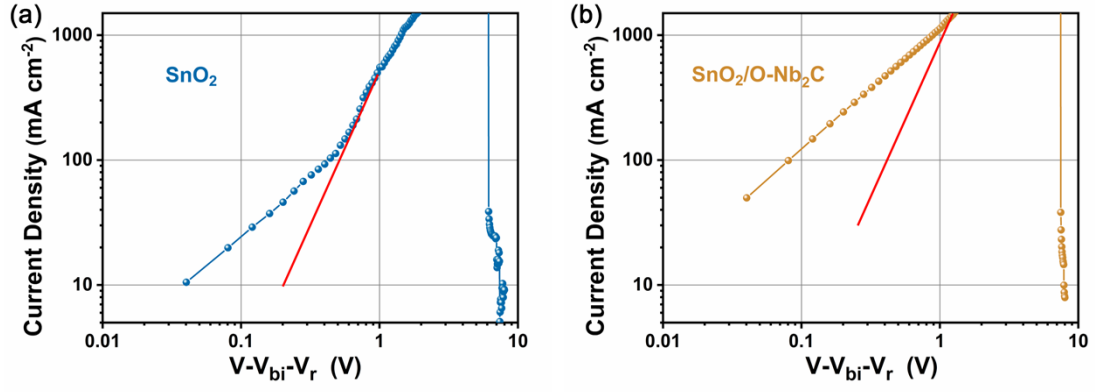


Figure S12. Typical J - V curves for the devices based on (a) SnO_2 and (b) $\text{SnO}_2/\text{O-Nb}_2\text{C}$.

The electron mobilities of ETLs were analyzed by the J - V curves with the electron-only structure under dark, and were calculated with the following equation:

$$J = 9\varepsilon_0\varepsilon_r\mu(V - V_{bi} - V_r)^2/8L^3$$

where μ is electron mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$), J represents the current density (mA cm^{-2}), ε_0 indicates the permittivity of free space ($\text{mA s V}^{-1} \text{cm}^{-1}$), ε_r represents the dielectric constant of ETLs, V is the applied voltage (V), V_r is the voltage drop (V) due to the series resistance and contact resistance across the electrodes, V_{bi} is the built-in voltage (V), $V - V_{bi} - V_r$ is obtained through a slope in the double log plot equals to 2, and L is the thickness of ETLs film.

Table S1. The photovoltaic performance parameters of the devices with and without Nb₂CT_x modification.

	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)
SnO ₂	1.128	24.02	0.76	20.51
SnO ₂ /Nb ₂ CT _x	1.136	24.23	0.77	21.19
SnO ₂ /Nb ₂ CT _x -UV-10 min	1.145	24.50	0.78	21.88
SnO ₂ /Nb ₂ CT _x -UV-30 min	1.148	24.66	0.78	22.08

Table S2. The fitted lifetime parameters originated from the TRPL measurements in Figure 5c.

Sample Structures	τ_1 (μ s)	A ₁	τ_2 (μ s)	A ₂	B	τ_{ave} (μ s)
Glass/perovskite	1.646	405.160	10.730	255.818	22.366	8.954
Glass/SnO ₂ /perovskite	1.582	462.754	8.217	256.817	10.016	6.508
Glass/SnO ₂ /O-Nb ₂ C/perovskite	0.718	274.226	6.393	255.308	10.599	5.782

The TRPL spectra are fitted using the bi-exponential decay function as equation below:

$$f(t) = A_1 \exp[-t/\tau_1] + A_2 \exp[-t/\tau_2] + B$$

where A_i is the decay amplitudes, τ_i is the decay lifetime, and B is constant. The average lifetimes (τ_{ave}) are calculated according to the equation:

$$\tau_{ave} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}$$

Table S3. EIS fitting results for the devices with and without the regulation of O-Nb₂C.

Sample	R_{tr} (k Ω)	R_{rec} (k Ω)
SnO ₂	140	1400
SnO ₂ /O-Nb ₂ C	33	1600