Supporting Information for

Thermodynamically Driven Surface De-Doping of Nb-Doped TiO₂ for Stable Perovskite Solar Cells

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Figure S1. Transmission electron microscopy image (a) and X-ray diffraction pattern (b) show that the average size of common TiO_2 with phase-pure anatase is ~33 nm.



Figure S2. Linear sweeping voltammetry behaviors of TiO_2 and de-Nb- TiO_2 electrodes. The voltammetry behaviors suggest that the treatment of TiO_2 with niobium doping and surface dedoping do not aggravate the charge leakage. The electrochemical measurements were conducted in a tri-electrode system, in which TiO_2 and de-Nb- TiO_2 that deposited on FTO substrate were used as working electrodes, Pt sheet was used as the counter electrode, and platinum wire, the reference electrode.



Figure S3. The *J-V* curves of the perovskite solar cells made from de-Nb-TiO₂ with different niobium concentration of starting Nb-doped TiO₂ materials. For a comparison, the *J-V* behaviors of the cells made from common TiO₂ and Dyesol-18-NRT paste are also shown. The de-Nb-TiO₂-based cells with 1 % of niobium doping in the starting material exhibits best photovoltaic performance (PCE: 21.12 %). Cell made from common TiO₂ delivers a PCE of 20.03 %, which is higher than that of 17.28 % for the cell with Dyesol-18-NRT.



Figure S4. Effect of sintering temperature and time on the photovoltaic behaviors of the resultant cells. For the cells made from common TiO₂, it shows that the sintering temperature has only slight influence to the photovoltaic behaviors (a, Table S2). For the cells made of Nb-TiO₂ as the starting material, the sintering temperature and time play crucial role. The cells made from the Nb-TiO₂ film with higher sintering temperature (500 °C) exhibits much higher PCE value than that with 450 °C. The *J-V* behaviors shows that the optimized time for heat treatment is 30 min when sintering temperature is 500 °C (b, Table S2).



Figure S5. Photovoltaic behaviors of the perovskite solar cell made of de-Nb-TiO₂ at powermaximum-output point. The plateau photocurrent density is 21.12 mA/cm^2 under the bias of 998 mV, delivers a power conversion of 21.08 %. The PCE of 21.08 % is slightly lower than that of 21.12 % obtained from the *J-V* measurement.



Figure S6. XRD patterns and SEM images of the perovskite layer deposited on de-Nb-TiO₂ (upper panel of a, b) and common TiO_2 skeletons (bottom panel of a, c). The phase (a) and morphologies (b, c) for the perovskite film deposited on de-Nb-TiO₂ and common TiO_2 are similar.



Figure S7. Hysteresis behaviors of the cells made of de-Nb-TiO₂ and common TiO₂. Due to efficient interfacial electron extraction, the efficiency difference for the cell made from de-Nb-TiO₂ (3.22 %) is lower than that with common TiO₂ (7.59 %).



Figure S8. The stability of unencapsulated cells based on de-Nb-TiO₂ and common TiO₂ in dark (relative humidity: 8-12%, temperature: 23-25 °C, oxygen content: 21%). For the cells with common TiO₂, the PCE decreases from 17.15% to 15.44% after 1000 h. For the situation of de-Nb-TiO₂, the PCE remain >95 % of its initial value after 1000 h (decrease from 18.21% to 17.38%).



Figure S9. Schematic diagram illustrating the variation of lattice mismatching upon change in temperature. According to the lattice constants, the lattice mismatching of the perovskite {110} and anatase {101} is a positive value at room temperature (a).¹ As the temperature increase, the interface lattice mismatching becomes severe (b), because the thermal expansion coefficient for perovskite is higher than that of anatase TiO₂.²⁻⁴ For the situation of de-Nb-TiO₂, the strain resulted from the doped interior can act on the surface and would expand the lattice even after surface de-doping (c). Thus, the lattice mismatching would be alleviated upon temperature increase (d), as compared with the case of common TiO₂ (b).



Figure S10. The scheme for measurement of heat stability for the perovskite solar cells. Initially, we measured the photocurrent-voltage (*J-V*) behaviors prior to stressing the perovskite solar cells at high temperature (initial photovoltaic parameters). For each cycle, the cells were firstly stressed at high temperature (80 °C) for 2 h; subsequently, the hot perovskite solar cells were placed at room temperature (RT) for 30 min following with *J-V* measurement.



Figure S11. XRD patterns show that both TiO_2 and Nb- TiO_2 are of phase-pure anatase (a). The significant broadening and slight shifting toward low-angles of (101) (b), (004) (c), and (200) (d) diffraction peaks for the Nb- TiO_2 sample suggest distortion and expanding of the TiO_2 lattice, resulting most likely from Nb doping.⁵ The XRD patterns were calibrated by the blended CaF₂ powders (with diffraction angle of 2 theta = 47.1° for the (333) and (511) planes).



Figure S12. The photocatalytic degradation of methylene blue (MB). It shows that the photocatalytic activity of de-Nb-TiO₂ is lower than that of TiO_2 .



Figure S13. Effect of heat treatment temperature on the surface de-segregation of niobium in the Nb-TiO₂. When the temperature is not sufficiently high (e.g.: 450 °C), surface de-segregation cannot occur evidently.



Figure S14. Effect of sintering temperature on the stability of cells with Nb-TiO₂ upon UV soaking. For the Nb-TiO₂ sintered at 450 °C for 30 min, the photovoltaic performance of the resultant cell decays rapidly (e.g.: PCE decreases from 16.21% to 2.26% after 200 min of UV soaking). For the situation of de-Nb-TiO₂ formed by heat treatment of the film at 500 °C for 30 min, the PCE decreases from 17.51 % to 11.82 % after 250 min of UV soaking.



Figure S15. Effect of sintering temperature on the stability of cells with common TiO_2 upon UV soaking. For the TiO_2 sintered at 450 °C (30 min), the PCE decreases fast (0-150 min) and remain to be a constant (160-200 min). The PCE value after 160 min is 2.72 %, which is similar to that for the cell with TiO_2 sintered at 500 °C (30 min).

Mesoporous layer	V _{OC} (V)	J_{SC} (mA/cm ²)	FF	PCE (%)
Dyesol-18NRT	1.103	22.45	0.698	17.28
common TiO ₂	1.141	23.85	0.736	20.03
0.5% de-Nb- TiO ₂	1.118	23.87	0.722	19.26
1.0% de-Nb- TiO ₂	1.181	23.67	0.756	21.12
1.5% de-Nb- TiO ₂	1.141	23.86	0.723	19.68
2.0% de-Nb- TiO ₂	1.122	23.79	0.721	19.25

Table S1. Effect of initial concentration of niobium in the starting Nb-TiO₂ materials on the photovoltaic behaviors of resultant perovskite solar cells.

Table S2. Effect of sintering temperature and time on the photovoltaic parameters of perovskite solar cells made from the (de-)Nb-TiO₂ and common TiO_2 .

Mesoporous layer	Sintering		V_{OC}	J_{SC}	FE	PCE
	Temp. (°C)	Time (min)	(V)	(mA/cm^2)	1'1'	(%)
Nb-TiO ₂	450	30	1.138	23.81	0.722	19.56
TiO ₂	500	30	1.141	23.85	0.736	20.03
	450		1.132	23.80	0.714	19.24
de-Nb-TiO ₂	500	10	1.079	22.23	0.676	16.21
	500	20	1.107	22.89	0.706	17.89
	500	30	1.181	23.67	0.756	21.12
	500	40	1.162	23.85	0.751	20.81

Mesoporous layer	Scanning direction	<i>V_{OC}</i> (V)	J_{SC} (mA/cm ²)	FF	PCE (%)
de-Nb-TiO ₂	forward	1.181	23.67	0.756	21.12
de-Nb-TiO ₂	reversed	1.158	23.82	0.741	20.44
TiO ₂	forward	1.141	23.85	0.736	20.03
TiO ₂	reversed	1.104	23.89	0.702	18.51

Table S3. Hysteresis parameters of cells based on de-Nb-TiO₂ and common TiO_2 .

Experimental section

Preparation of TiO₂ **Paste.** Niobium-doped TiO₂ nanoparticles were prepared by solvothermal treatment of NbCl₅ and tetrabutyl titanate that dissolved into acetic acid. Briefly, 10.35 mL of tetrabutyl titanate containing desired amount of NbCl₅·5H₂O (with Nb/Ti ratios of 0, 0.5, 1, 1.5, and 2 at. %) were dissolved into 3.36 ml of CH₃COOH under stirring. The resulted solution was then transferred into a Teflon reactor. After that, the sealed reactors were heated at 220 °C for 12 h. After reaction, the products were washed with anhydrous ethanol for several times and collected by centrifugation. After dried in vacuum, the white powders (1.0 g) were mixed with ethyl cellulose (4.0 g) that dissolved in terpinol (2.0 g) and ethanol (3 mL) for 6 h. Then, 1.0 g of the obtained mixture was dispersed into 8.5 mL of ethanol to obtain the TiO₂ paste.

Solar Cell Preparation. The TiO₂ compact layer was deposited on the pre-cleaned FTO by spray pyrolysis using air as the carrying gas at 450 °C from a precursor solution of 1.3 ml titanium diisopropoxide and 0.07 mL bis(acetylacetonate) in 9 ml C₂H₅OH. Mesoporous TiO₂ layers were prepared by spin-coating the TiO₂ paste onto the substrate with a speed of 5000 rpm for 30 s with a ramp rate of 2000 rpm/s. Then the substrates were sintered at 500 °C for 30 min. The optimized thickness of TiO₂ films is ~400 nm.

The perovskite film was deposited by spin-coating the perovskite precursor solution onto the TiO₂ substrate with a speed of 5000 rpm for 30 s with a ramp-up of 1000 rpm/s in a glovebox. The perovskite precursor solution was prepared by dissolving PbI₂ (528.99 mg), PbBr₂ (74.3 mg), FAI (formamidine hydrochloride, 187.96 mg), and MABr (22.65 mg) into 100 mL of mixture of DMF: DMSO (4: 1 in volume) in a glovebox. After spin-coating of the perovskite precursor, ethyl acetate (100 mL) was dropped onto the spinning substrate during the spincoating step 5s before the end of the procedure. The substrate was then heated at 100 °C for 60 min on a hot plate, after then cooling down to the room temperature in the glovebox. Spiro-OMeTAD was subsequently deposited on top of the perovskite layer by spin-coating at 3000 rpm for 30 s. Finally, gold was deposited by thermal evaporation using a shadow mask to pattern the electrodes.

Characterization. The photovoltaic properties of perovskite solar cells were characterized by recording the photocurrent-voltage (*J-V*) curves under A.M. 1.5 G illumination (100 mW/cm²). The scanning rate for the *J-V* measurement is 50 mV/s. The illumination was provided by a San-EiXES-301S solar simulator. Scanning electron microscopy (SEM) investigation was carried out by performing a JEOL field-emission scanning electron microscope (JSM-7001F). Xray diffraction (XRD) characterizations were carried out on a Bruker X-ray diffractometer (D8 Advance) using Cu K_a radiation. X-ray photoelectron spectroscopy (XPS) investigation was performed using a Kratos instrument (Axis Ultra DLD, Al K α source, UK), which was calibrated by the C1s reference binding-energy (284.8 eV). Time integrated photoluminescence (TIPL) and time-resolution photoluminescence (TRPL) spectra were obtained under excitation and laser wavelengths of 390 and 385 nm, respectively (Horiba, Fluorolog-3).

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