

Supporting Information

Cs-doped TiO₂ Nanorod Array Enhances Electron Injection and Transport in Carbon-Based CsPbI₃ Perovskite Solar Cells

*Jiaming Liu[†], Liqun Zhu[†], Sisi Xiang[†], Hailiang Wang[†], Huicong Liu[†], Weiping Li[†],
and Haining Chen^{†*}*

[†] School of Materials Science and Engineering, Beihang University, No. 37 Xueyuan Road, Haidian District, Beijing 100191, People's Republic of China.

** Corresponding E-mail: chenhaining@buaa.edu.cn (Haining Chen)*

Number of pages: 14

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Materials

The CsNO_3 (99.99%), IPA (99.5%), and DMF (anhydrous, 99.8%) were purchased from Alfa Aesar. The CsI (99.9%), HI (57 wt.% in H_2O) and titanium diisopropoxide bis-(acetylacetonate) (75 wt.% in isopropanol) were purchased from Sigma-Aldrich. The PbI_2 (99.9%), hydrochloric acid (37%), 1-butanol (99.5%), titanium (IV) isopropoxide (99.9%), ethanol (99.5%), and ultrasonic cleaning solution were purchased from Aladdin. The FTO glass (TEC15, NSG) and the commercial carbon paste (MTW-CE-C-003) were purchased from Shanghai MaterWin New Materials Co., Ltd. All the chemicals are used as received.

Characterization

Surface and cross-section morphologies were performed on a Zeiss Supra 55 field emission scanning electron microscopy (FESEM). X-ray diffraction (XRD) patterns were collected with a Rigaku D/MAX-2500 X-ray diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.1541 \text{ nm}$) with the speed of $6^\circ/\text{min}$. Chemical states and valence band spectrum of film surface were evaluated by an X-ray photoemission spectroscopy (XPS, ESCALab250Xi). Absorption spectra were measured on a UV-3600 ultraviolet and visible (UV-vis) spectrophotometer. Static contact angle of CsPbI_3 precursor solution on the surface of TiO_2 nanorods substrate were measured by sessile drop method with an optical contact angle meter system DSA20 (KRÜSS, Germany) at room temperature. The photoluminescence (PL) spectra were obtained on a lifetime and steady state spectrometer (FLS980, Edinburgh Instruments Ltd.)

with the excitation wavelength of 475 nm at the room temperature. The Mott–Schottky (M-S) plots were acquired using a CHI 660E electrochemical analyzer in a three-electrode system. The TiO₂ nanorods substrate, an Ag/AgCl electrode and a Pt wire served as the working, reference and counter electrodes, respectively. The electrolyte used for this measurement contained 0.1 M Na₂SO₄ and the frequency was set at 5 kHz.

The J-V measurements were recorded on a Zahner photo-electrochemical workstation by the scans (a voltage step of 50 mV and a delay time of 100 ms) under the illumination of a solar simulator (Newport SOL3A 94023A, 100 mW cm⁻², AM 1.5), intensity was calibrated with a certified Si-reference cell (Newport). The intensity-modulated photocurrent/photovoltage spectroscopy (IMPS/IMVS) was also performed on the Zahner photo-electrochemical workstation and the wavelength of the illumination light was 417 nm. The active area of solar cell was masked to about 6.25 mm². IPCE spectra were recorded on an IPCE kit (E0201, Institute of Physics, Chinese Academy of Sciences). For the stability test at room temperature (20-30 °C), the devices were stored in ambient air (relative humidity~20-30%) without encapsulation.

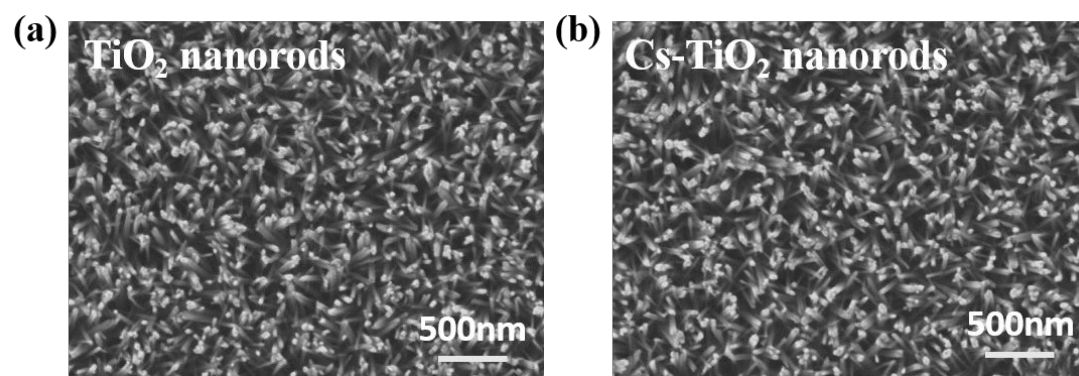


Figure S1 Top-view SEM images of TiO₂ and Cs-TiO₂ nanorods arrays.

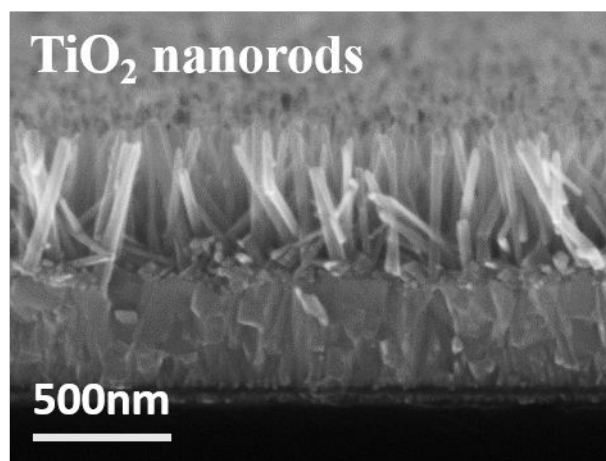


Figure S2 Cross-sectional SEM images of pure TiO₂ nanorods arrays.

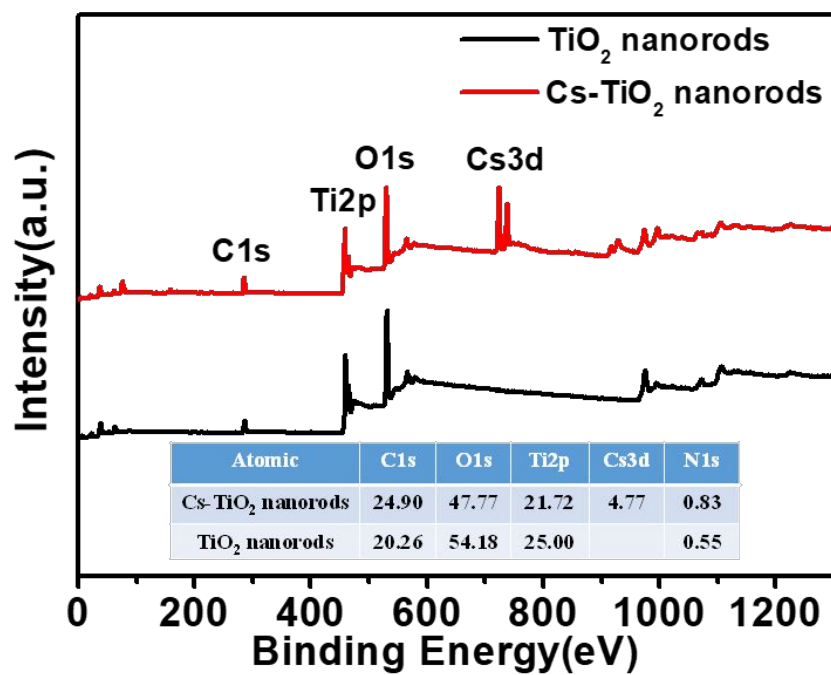


Figure S3 Full range XPS spectra of TiO₂ and Cs-TiO₂ nanorods, inserted table shows the atomic percent obtained from the XPS survey.

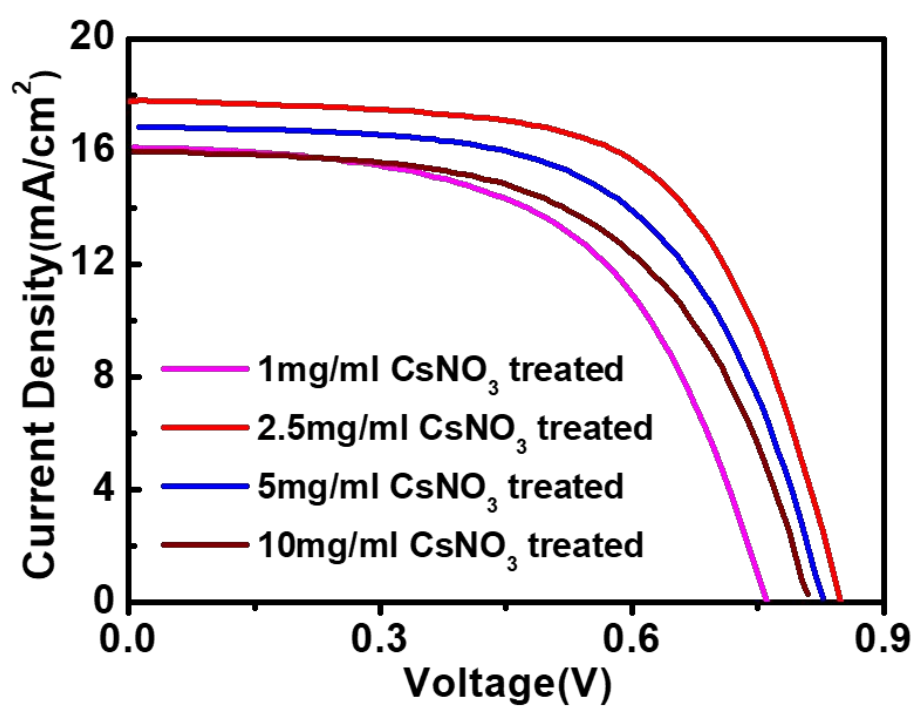


Figure S4 J-V curves of C-PSCs based on the Cs-TiO₂ nanorods with various CsNO₃ solution concentration.

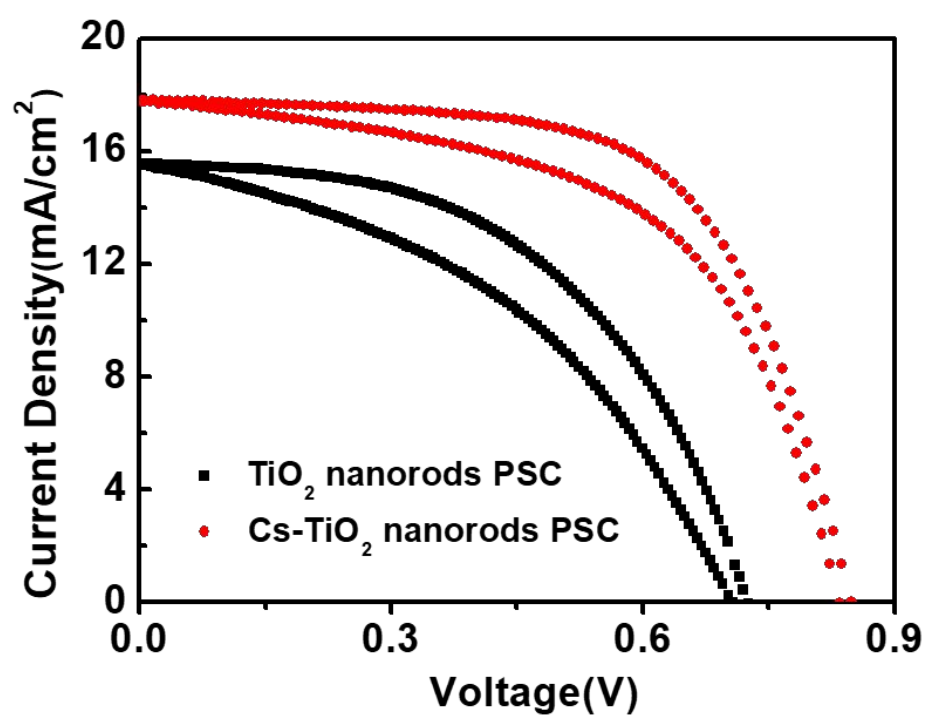


Figure S5 J-V curves of the champion C-PSCs based on TiO₂ and Cs-TiO₂ nanorods measured in forward and reverse scanning modes.

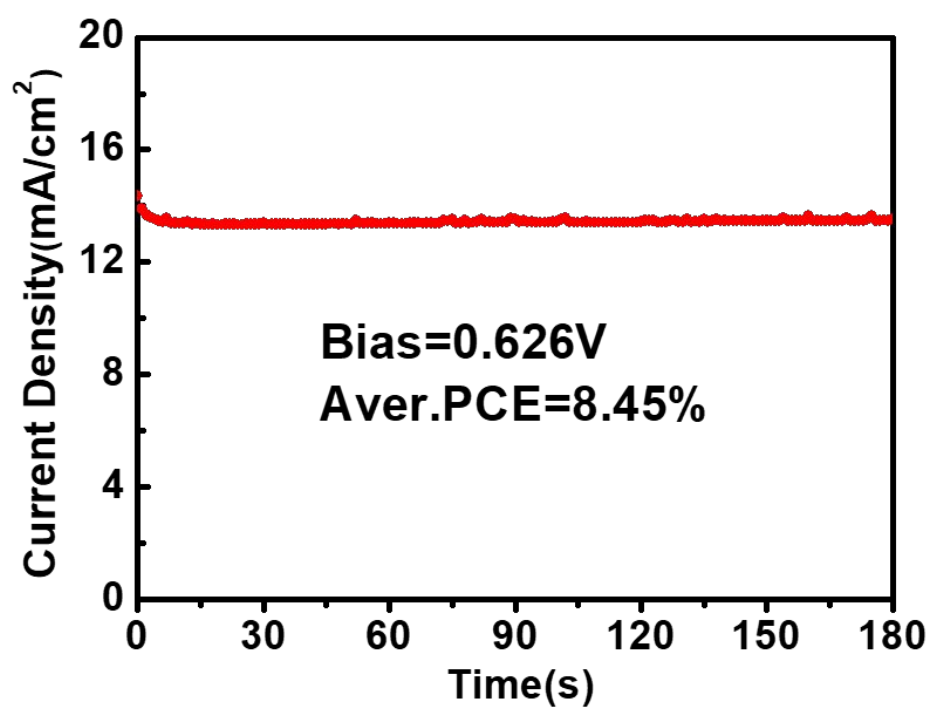


Figure S6 Steady current density at a voltage close to the maximum output point of the champion Cs-TiO₂ C-PSCs.

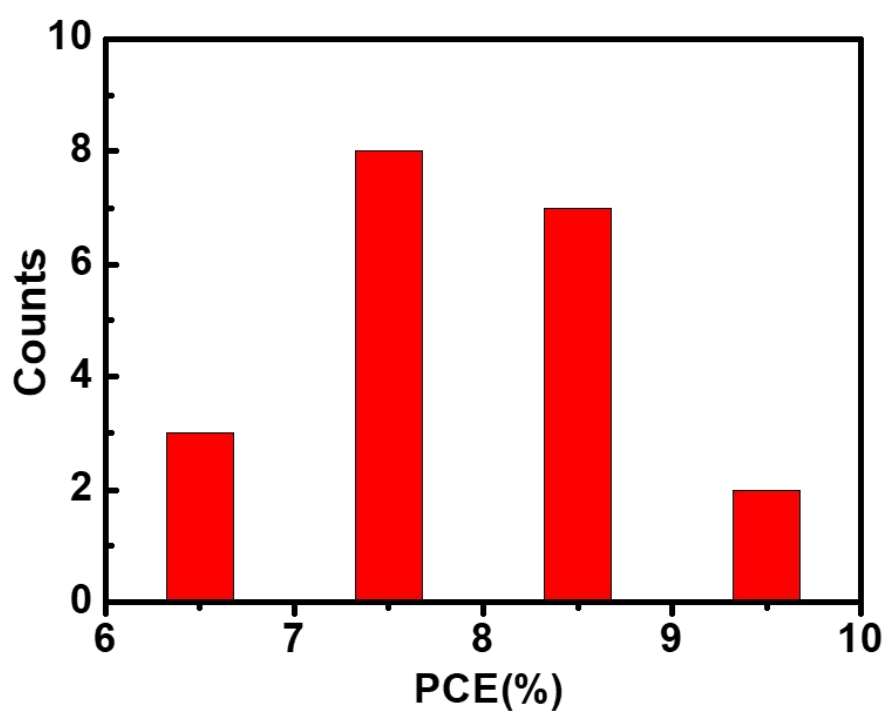


Figure S7 PCEs histogram of 20 individual devices with the same fabrication procedure to that of the champion Cs-TiO₂ device.

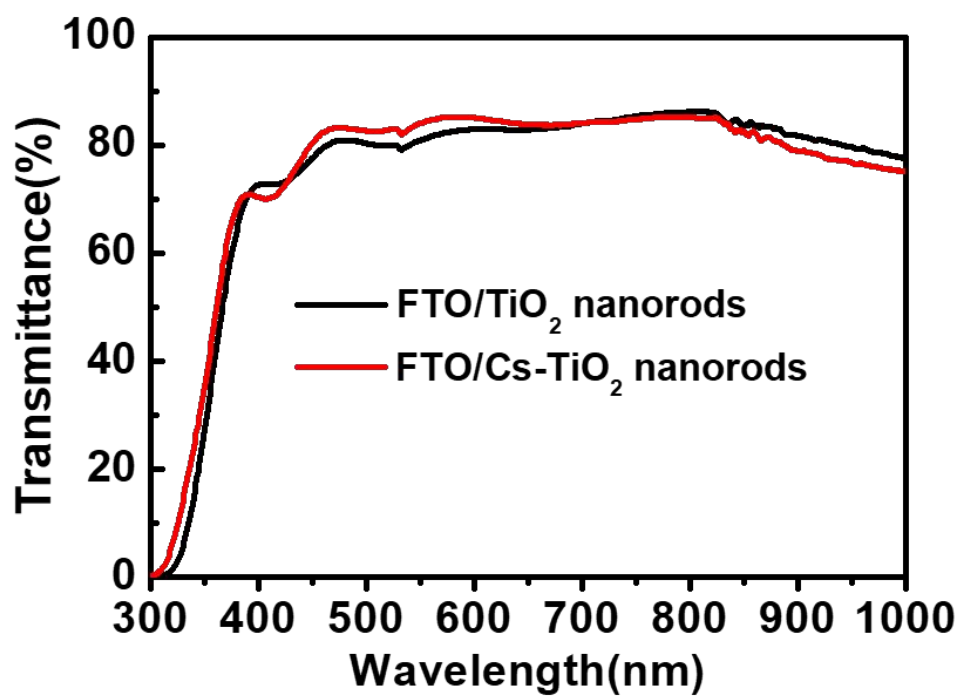


Figure S8 Optical transmission spectra of TiO₂ and Cs-TiO₂ nanorods arrays.

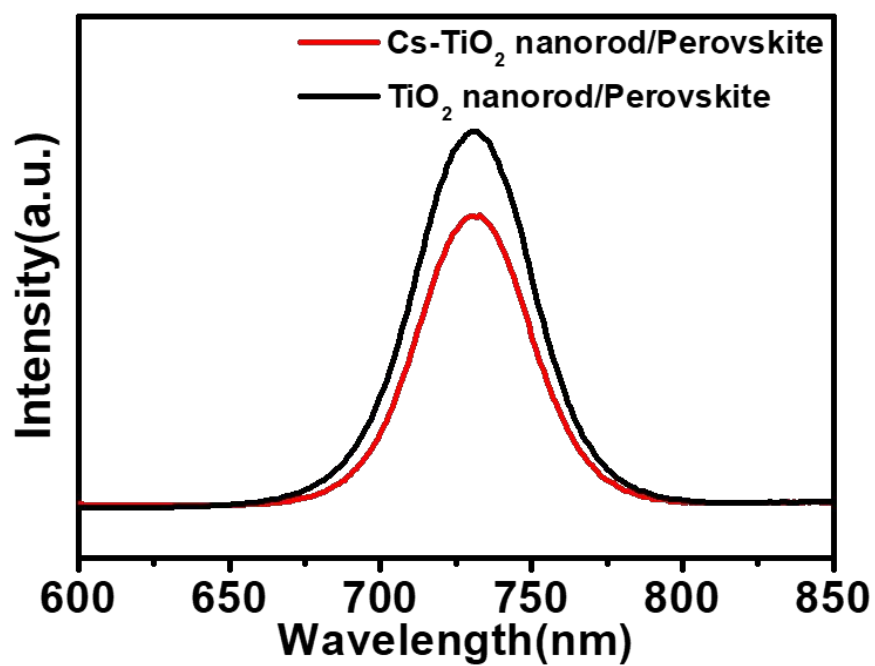


Figure S9 Steady-state PL spectra of the CsPbI₃ films over the TiO₂ and Cs-TiO₂ nanorods.

Table S1 Characteristics of C-PSCs based on the Cs-TiO₂ nanorods with various CsNO₃ solution concentrations.

	Jsc(mA/cm²)	Voc(V)	FF	PCE(%)
1mg/ml-PSC	16.2	0.76	0.56	6.9
2.5mg/ml-PSC	17.8	0.85	0.63	9.5
5mg/ml-PSC	16.9	0.83	0.60	8.4
10mg/ml-PSC	16.0	0.81	0.58	7.5

Table S2 Photovoltaic parameters obtained from the champion C-PSCs based on TiO₂ and Cs-TiO₂ nanorods measured in forward and reverse scanning modes.

Devices	Scanning direction	Jsc (mA/cm²)	Voc (V)	FF (%)	PCE (%)
TiO₂ C-PSC	Forward	15.5	0.70	43	4.7
	Reverse	15.5	0.72	52	5.8
Cs-TiO₂ C-PSC	Forward	17.8	0.84	56	8.3
	Reverse	17.8	0.85	63	9.5