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## Supporting Information

# Modification of TiO<sub>2</sub> nanowire arrays with Sn doping as photoanode for highly efficient dye-sensitized solar cells

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## EXPERIMENTAL SECTION

### Preparation of Sn-doped TiO<sub>2</sub> nanowire arrays (NWAs)

First, preparation a TiO<sub>2</sub> seed layer on the clean FTO glass by an aqueous solution with 0.2 M of TiCl<sub>4</sub>. After maintaining at 70 °C for 30 min, the FTO glass was annealing at 550 °C for 60 min in air. The reaction solution with 3 mL of TiCl<sub>4</sub>, 30 mL of concentrated HCl (36~38 wt%) and 30 mL of ethanol was prepared. Then 1.35, 2.7, 4.05 and 5.4 mmol SnCl<sub>4</sub>·6H<sub>2</sub>O were mixed into reaction solution, respectively. Subsequently, the FTO glass with seed layer was put in a mixed solution in a 100 ml Teflon-lined stainless steel autoclave. Then keep the autoclave heated at 150 °C for 12 h in a constant temperature electric oven. After the autoclave naturally cooling down to ambient temperature, swilling out the obtained samples with DI water and absolute ethyl alcohol for three times is indispensable. Then named the as-prepared samples TS1, TS2, TS3, and TS4, respectively. The pure TiO<sub>2</sub> NWAs named as TS0.

### Assembling of DSSCs

The as-prepared pure TiO<sub>2</sub> NWAs and Sn-doped TiO<sub>2</sub> NWAs on FTO glass were prepared photoanodes for DSCs similar to previous report. The photoanodes were stained by immersing them into a dye solution containing N719 (Desol) (0.5m M) in the mixture of acetonitrile and tert-butanol (volume ratio: 1/1) for 24 h. The dye-coated TiO<sub>2</sub> electrode was subsequently washed with acetonitrile, and then assembled with a thermally platinized FTO positive electrode. The two active electrodes were separated with a 25 μm-thick Surlyn (DuPont) hot-melt gasket and sealed up by heating. The internal space was filled with electrolytes using a vacuum back filling system. The electrolyte-injecting hole on the counter electrode made with a sand-blasting drill was sealed with a Surlyn sheet and a thin glass cover by heating. The electrolyte is composed of 1.0 M 1,3-dimethylimidazolium (DMII), 50 mM LiI, 30 Mm I<sub>2</sub>, 1.0 M 4-tert-butylpyridine (TBP), and 0.1 M guanidinium thiocyanate (GNCS) in the 85/15 (volume ratio) mixture of acetonitrile and valeronitrile.

### Characterization.

X-ray power diffraction (XRD) analysis was conducted on a Rigaku D/max-2500 x-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The Raman spectra were collected on an EZRaman-N benchtop Raman spectrometer (Enwave Optronics, Inc.). X-Ray photoelectron spectroscopy (XPS) measurements of the material binding energy distributions are carried out by the ESCALAB 250Xi spectrometer from the American Thermo Fisher Scientific. Field emission scanning electron microscopic (FESEM) images were obtained on a JEOL JEM-6700F microscope operating at 5 KV. Transmission electron microscope (TEM) and high-resolution TEM (HRTEM) observations were carried out with a JEOL JEM-2100 microscope operating at 200 kV. A model LS1000-4S-AM1.5G-1000W solar simulator (Solar Light Company, USA) in combination with a metal mesh was employed to give an irradiance of 100 mW cm<sup>-2</sup>. The light intensity was tested with a PMA2144 pyranometer and a calibrated PMA 2100 dose control system. The photocurrent density-hotovoltage (J-) characteristics were recorded by a Keithley 2400 source meter. The external quantum efficiency (EQE) spectra were measured on the basis of a Zolix Omni-300 monochromator and a Keithley 2400 source meter, where a 500 W xenon lamp (Zolix) was used a light source for generating monochromatic beam. An antireflection

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film (~380 nm, ARKTOP, ASAHI Glass) is adhered to the photoanode during *J-V* and IPCE measurements. The amount of adsorbed dye was estimated by immersing the film into an ethanol-water mixed solution (1:1, v/v) with 0.1 M NaOH and testing the absorption spectrum of desorbed dye by a UV-vis spectrophotometer (Shimadzu 3600). PL characterizations were recorded in CCD spectroscopy at fixed excitation intensity by a He–Cd laser line of 325 nm at room temperature. Transient photoelectrical experiments were performed on an utolab-PGSTAT302N electrochemical workstation with the DC10M high-speed module, which can satisfy 100 ns time-resolved current and voltage tests. The static and perturbing lights were supplied with home-made white and red light-emitting diode arrays. We employed a red light to generate a photovoltage perturbation near the open circuit photovoltage of a testing cell under the irradiation of a certain white light and measured the voltage decay thereafter. The modulated photovoltage by the red pulse of a testing cell was below 5 mV and the transient signals follow a mono-exponential decay. Fitting an exponential function to the photovoltage decay can produce the electron lifetime. The electron density was estimated by the charge extraction method. A testing cell was first kept at open circuit under white light and subsequently the white light was turned off upon switching the cell from open circuit to short circuit to record the resulting current transient, and the electron density was obtained by current integration.

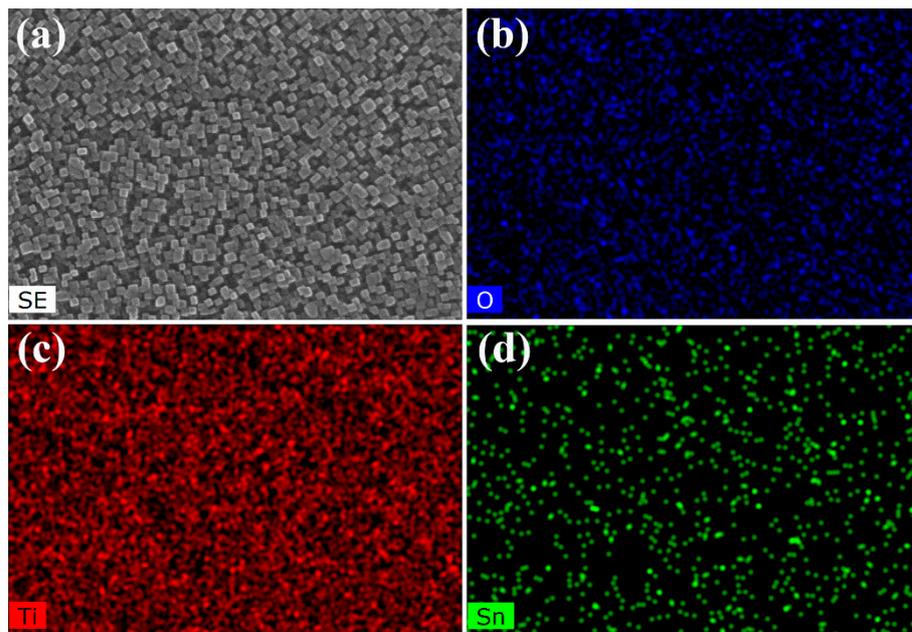
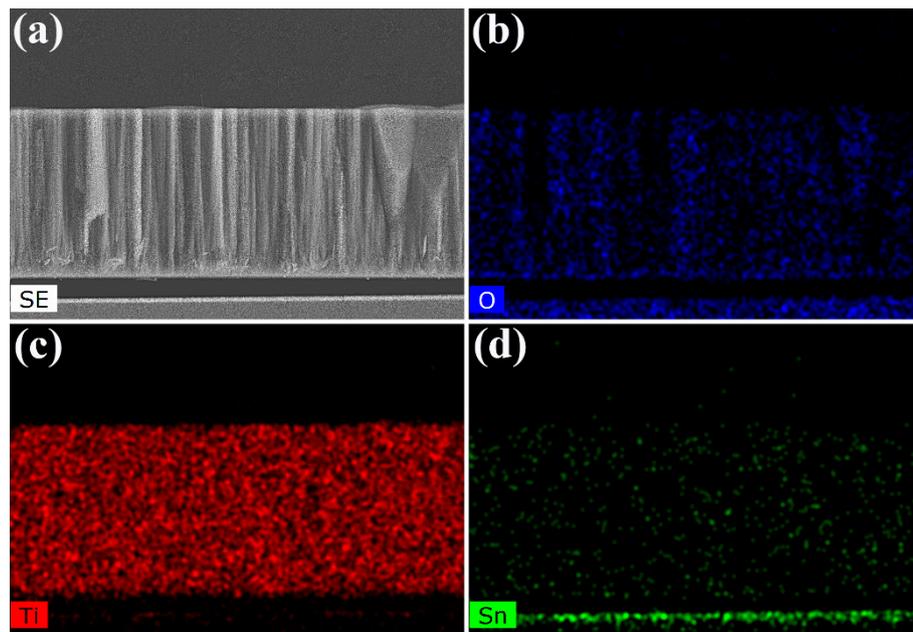
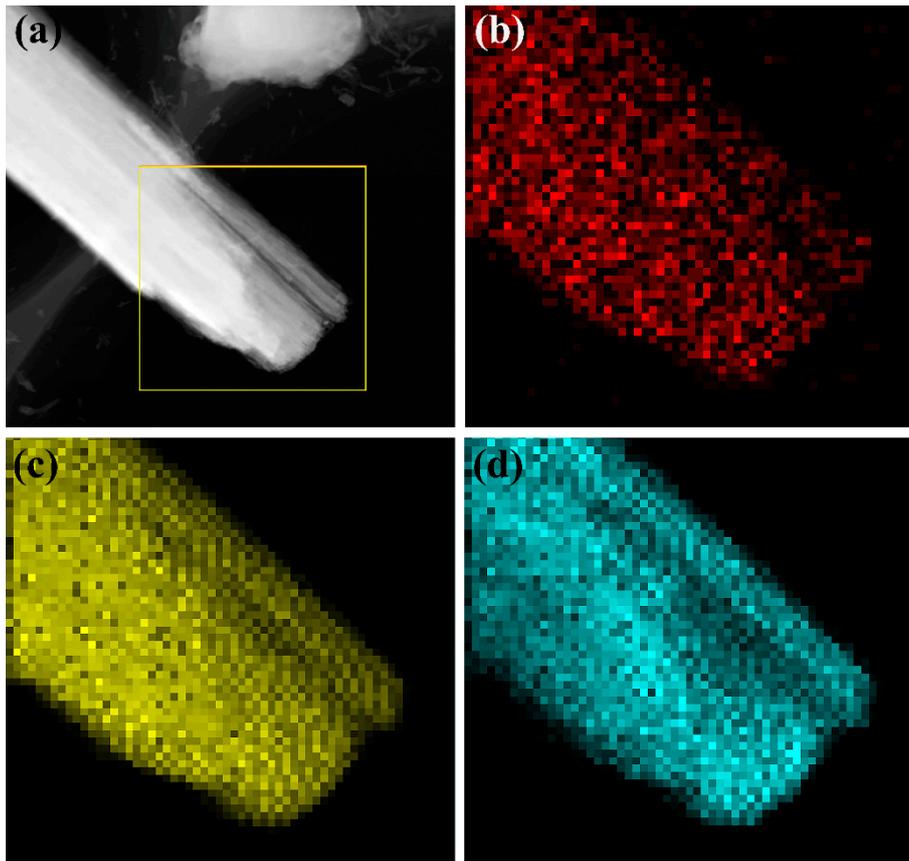


Figure S1 EDS elemental mapping images of cross section of Sn-doped TiO<sub>2</sub> NWAs (TS2)



**Figure S2** EDS elemental mapping images of top surface of Sn-doped TiO<sub>2</sub> NWAs (TS2)



**Figure S3** (a) the tip region of Sn-doped TiO<sub>2</sub> NWAs (TS2). Corresponding EELS elemental mapping images for b) Sn, c) Ti, and d) O, respectively

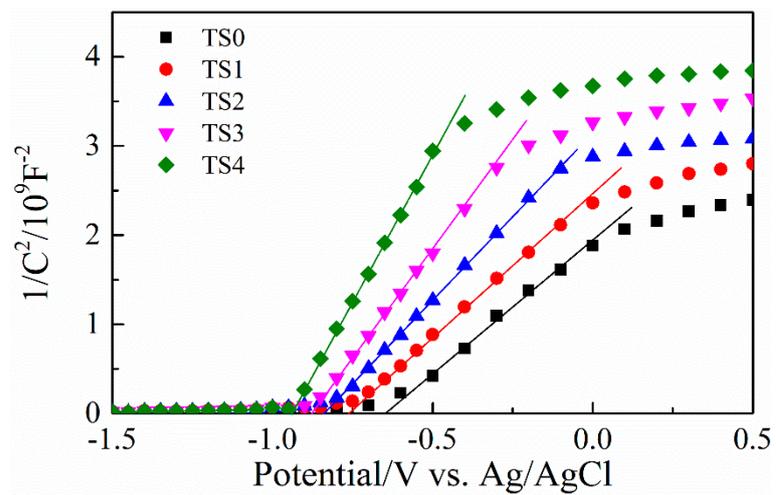
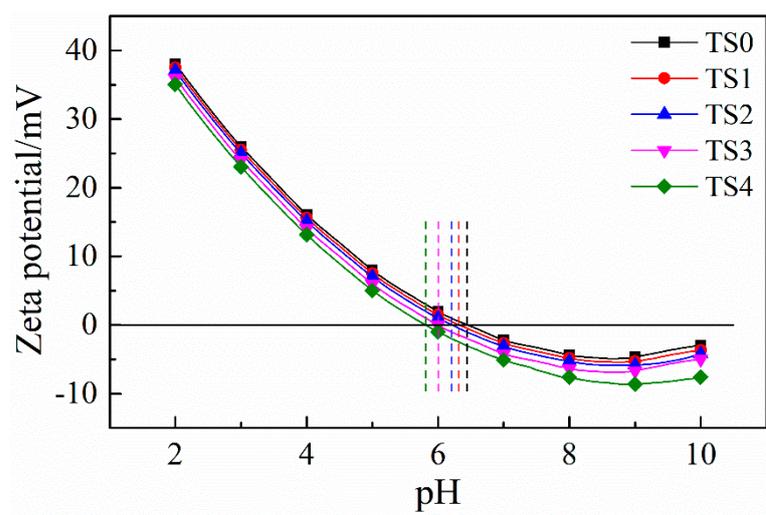
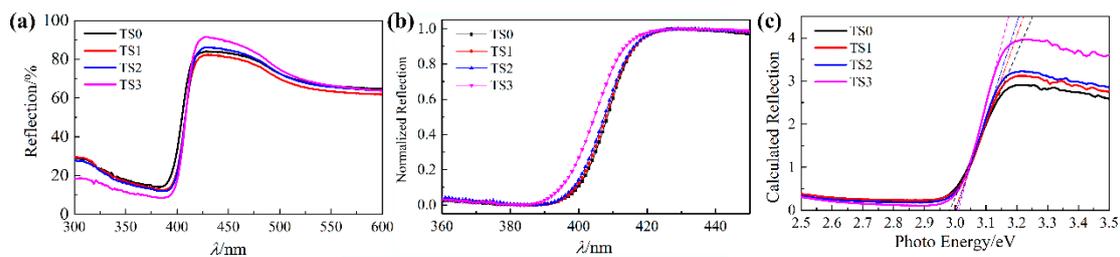


Figure S4 Mott-Schottky plots of the pure  $\text{TiO}_2$  NWAs (TS0) and Sn-doped  $\text{TiO}_2$  NWAs (TS1, TS2, TS3, TS4)



**Figure S5** The pH-dependent zeta-potential of the pure TiO<sub>2</sub> NWAs (TS0) and Sn-doped TiO<sub>2</sub> NWAs (TS1, TS2, TS3, TS4).



**Figure S6** (a) The UV-vis diffusive reflectance spectra of the pure TiO<sub>2</sub> NWAs (TS0) and Sn-doped TiO<sub>2</sub> NWAs (TS1, TS2, TS3), (b) normalized UV-vis diffusive reflectance spectra and (c) the plots of transforming the Kubelka–Munk function versus the energy of light.

According to previous work [1], the Kubelka–Munk function is applied to convert the diffuse reflectance into the equivalent band gap energy:

$$F(R_{\infty}) = (1-R)^2/(2R) \quad (4)$$

here R is the reflectance of the sample.

**Figure S6c** shows the plot of  $[F(R_{\infty})hv]^{1/2}$  vs.  $hv$ , in which linear segments are extended to intersect with the  $hv$ -axis to obtain the indirect band gap of the samples.

[1] H. A. Hamedani, N. K. Allam, H. Garmestani, M. A. El-Sayed, Electrochemical Fabrication of Strontium-Doped TiO<sub>2</sub> Nanotube Array Electrodes and Investigation of Their Photoelectrochemical Properties, *Journal of Physical Chemistry C* 115 (2011) 13480–13486.

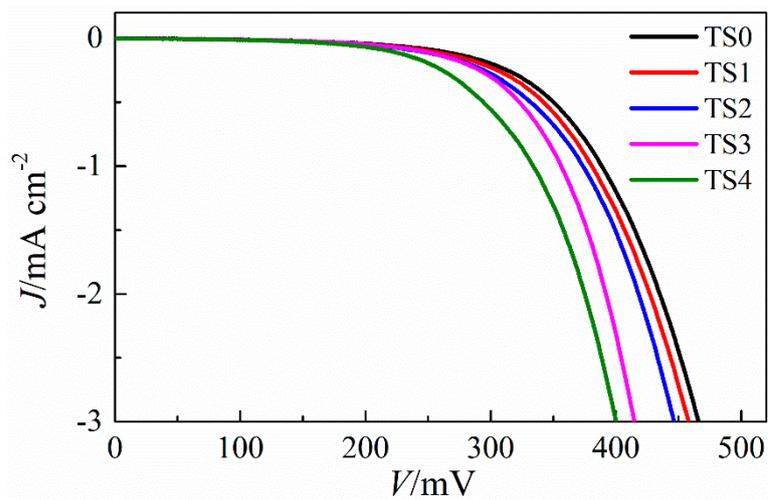


Figure S7 Dark current density–voltage of DSCs based on the pure TiO<sub>2</sub> NWAs (TS0) and Sn-doped TiO<sub>2</sub> NWAs (TS1, TS2, TS3, TS4).

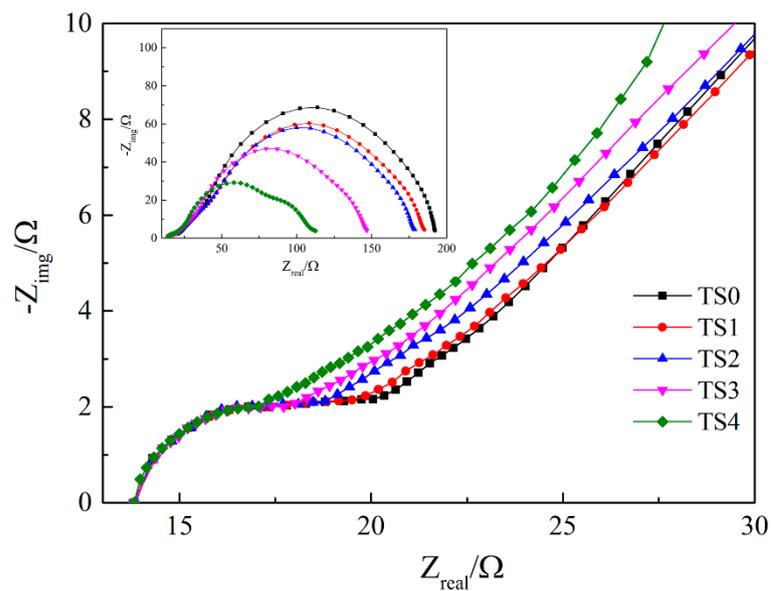


Figure S8 The enlarged low-frequency arc and full scale (inset graph) Nyquist plots of the DSSCs based on the pure  $\text{TiO}_2$  NWAs (TS0) and Sn-doped  $\text{TiO}_2$  NWAs (TS1, TS2, TS3, TS4) measured under 750 mV bias in the dark condition

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Table 1. Detailed simulative values of the charge transfer resistance from EIS spectra.

<b>Sample</b>	<b>the charge transfer resistance (<math>\Omega</math>)</b>
TS0	5.2
TS1	4.3
TS2	3.6
TS3	2.9
TS4	1.8

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