Electronic Supplementary Information for

Ultra-small TiO₂ nanowire forests on transparent conducting oxide for solid-state semiconductor-sensitized 5 solar cells

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TiO₂ nanowire forest were synthesized on FTO glass (F: SnO₂, 13Ω/square, Aldrich) initially rinsed by water, acetone and ethanol successively, and finally treated by ultraviolet light for 30 min. In a typical process for synthesis of TiO₂ nanowires,
5 0.5 ml of titanium (IV) butoxide (97%, Aldrich) was first added into 6 M HCl solution, made by diluting HCl (36% by weight) using methanol, or ethanol, or isopropanol at 1:1 weight ratio, under vigorous stirring. The solution was then stirred for another 10 min before transferred to a 50 ml Teflon-lined stainless steel autoclave. Afterwards, the substrates were placed at an angle of 15 degree against the wall of the

- 10 Teflon liner with the conducting side facing down. Then the autoclave was sealed and placed in an oven at 150 °C for 4 h. After cooling the autoclave to room temperature, the TiO₂ structures were washed with deionized water and ethanol repeatedly and subsequently dried in nitrogen flow. Vertically aligned TiO₂ nanorod arrays were synthesized by replacing methanol with water, similar to the method developed by B.
- 15 Liu and E. S. Aydil. ¹ Other procedures were the same as the NWs.

Deposition of Sb_2S_3

Sb₂S₃ was used as a sensitizer, and was deposited on TiO₂ NWs by the following procedure. ² 650 mg SbCl₃ was first dissolved in 5 ml acetone, then 25 ml of 1 M Na₂S₃O₃ solution and enough deionized water was added to make the volume of the 20 mixture to 100 ml. Then the substrates with the TiO₂ NW were dipped into the solution against the beaker with the TiO₂ NW side facing down. After that, the system was kept at 7 °C for designated durations. The Sb_2S_3 crystals formed within 1 h, 2 h, and 3 h deposition time were annealed at 330 °C for 30 min in nitrogen and then cooled in air to form a Sb_2O_3 passivation layer for reduction of recombination.³

Material Characterization

5 The synthesized nanostructures were examined by field emission scanning electron microscopy (FESEM, Hitachi S-4800), X-ray diffractometry (XRD, X'Pert Pro MPD) using Cu Kα radiation (1.5405Å) operating at 40 kV and 40 mA, and transmission electron microscopy (TEM, JEM-2010HR) at an accelerating voltage of 200 kV.

Fabrication and Characterization of SSSCs

P3HT solution (15 mg/ml in 1,2-dichlorobenzene) was spin-coated onto Sb₂S₃-sensitized TiO₂ NRs at 2,500 rpm. In order to improve the contact between P3HT and the gold electrode, poly(3-4-ethylenedioxythiophene) doped with poly(4-stylenesulfonate) (PEDOT:PSS; Baytron AI 4083) diluted with two volumes of methanol was deposited onto the P3HT/Sb₂S₃/NR layer by spin-coating at 2,000 rpm.
The PEDOT:PSS/P3HT/Sb₂S₃/NR layer was then annealed at 90 °C for 30 min in a vacuum oven. Afterwards, a gold film was deposited by thermal evaporation and

Torr, and a metal mask was used to yield an active area of 16 mm² for each device.

acted as the counter electrode. The thermal evaporation was performed under 5×10^{-5}

SSSCs were characterized under illumination of AM 1.5 simulated sunlight at a 20 power density of 100 mW cm⁻², by using a solar simulator (Oriel 91192, Newport,

USA) calibrated with a standard crystalline silicon solar cell (PEC-SI01, Peccell Technologies, Inc., Japan). Electrochemical impedance spectra were recorded in the dark condition at a 600 mV bias voltage by using a CHI 650C electrochemical analyzer (CH Instrument Corp., USA).

5 **References**

1 B. Liu and E. S. Aydil, J. Am. Chem. Soc., 2009, 131, 3985-3990.

2 S. Messina, M. T. S. Nair and P. K. Nair, Thin Solid Films, 2007, 515 5777-5782.

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Figure S1. Zoomed-in SEM images of different areas through the cross sectional of the NWs-4hr. The zoomed-in images labled A, B, and C corresponded to the selected areas in the top left image.



Figure S2. Cross sectional SEM images of TiO_2 film obtained using different solvents. (a) ethanol (b) IPA. (c-f) ethanol mixed with H₂O at different ratios. (c) 2:1. (d) 1:1. (e) 1:2. (f) H₂O.

To investigate the influence of different alcohols on the growth of NWs, ethanol or IPA were used as the solvent instead of methanol while keeping other conditions unchanged. Figure S1a and S1b shows the SEM images obtained using ethanol and IPA as solvent, respectively. Obviously, they are totally fused, unlike that in the case of methanol. The fusion degree decreases when increasing the amount of water, replacing part of ethanol. And the NWs become gradually more independent as the ratio between ethanol and water turns from 100% to 2:1 to 1:1 to 1:2, finally 100% water (Figure S1(a, c-f)). The coverage density of the nanorods in Figure S1f is ~4.5 × 10⁹ /cm², almost two orders of magnititude smaller than that of the nanowire forest in

this paper.



Figure S3. (a) Cross sectional SEM images of TiO₂ NWs synthesized with 3 h (b)
5 Cross sectional SEM images of TiO₂ NWs synthesized with 8 h.



Figure S4. (a) Cross-sectional SEM image of TiO₂ NWs after 3 h deposition of Sb₂S₃
[Sb₂S₃-NW (3 h)]. (b) Top view SEM image of TiO₂ NWs after 3 h deposition of
Sb₂S₃ [Sb₂S₃-NW (3 h)].



Figure S5. Absorption spectra of Sb_2S_3 -NW-FTO with different Sb_2S_3 deposition times.



Figure S6. Reference device using TiO_2 NRs synthesized on bare FTO. The Sb_2S_3 deposition time is 2 h. (a) Top-view SEM image of the TiO_2 NRs on FTO (NR-FTO).

(b) Cross-sectional SEM image of Sb₂S₃-NR-FTO. (c) Cross-sectional SEM image of the SSSC using Sb₂S₃-NR-FTO. (d) J-V characteristics of such SSSC using Sb₂S₃-NR-FTO.