Electronic Supplementary Information

A nonstoichiometric $SnO_{2-\delta}$ nanocrystal based counter electrode for remarkably improving performance of dye-sensitized solar cell

Experimental Details

Synthesis of $SnO_{2-\delta}$ nanocrystals. In a typical experiment, 0.2 g of tin dichloride dihydrate ($SnCl_2$ $2H_2O$) was added to 40 ml mixed solvent consisting of ethanol and de-ionized water in a 1 : 1 volume ratio to reach a tin (II) concentration of 25 mM. White suspension obtained was magnetically stirred for 1 h before being transferred to a Teflon-lined stainless steel autoclave and then heated in an electric oven at 120 ºC for 6 h. A yellow product was obtained after centrifugation and dried at 80 ºC for 24 h.

Characterization. X-ray diffraction patterns of the samples were recorded on a Rigaku diffractometer using Cu kα irradiation. Their morphology was determined using transmission electron microscopy (TEM, JEOL 2010) and scanning electron microscopy (SEM, Nova NanoSEM 430). The Brunauer-Emmett-Teller (BET) surface area was determined by nitrogen adsorption- desorption isotherm measurements at 77 K (ASAP 2010). Chemical compositions and valence band spectra of TiO_2 were analyzed using X-ray photoelectron spectroscopy (XPS) (Thermo Escalab 250, a monochromatic Al K_α X-ray source). All binding energies were referenced to the C 1s peak (284.6 eV) arising from adventitious carbon. Room-temperature ESR spectra of tin oxide powder were obtained using a JEOL JES-FA200 ESR spectrometer (300 K, 9.063 GHz, X-band).

Counter electrode fabrication. As-prepared $SnO_{2-\delta}$ nanocrystals were deposited on a fluorine-doped tin oxide (FTO) transparent conductive glass substrate by electrophoretic deposition. In detail, 40 mg of the $SnO_{2-\delta}$ nanoparticles was suspended in 50 mL of acetone solution containing 10 mg of iodine under ultrasonic treatment. The deposition

was conducted with a two electrode process at the applied bias of 20 V for 20 min, where both electrodes were FTO substrates (the surface area coated in the solution is 4 × 4 mm or 8 × 8 mm). The deposited electrode was then heated at 500 ºC for 30 min in argon or air.

Photoanode fabrication. A 3 layers of TiO_2 (Dyesol) nanocrystalline film sensitized with N719 dye (Dyesol) was used as photoanode. In detail, a thin layer TiO_2 was coated on FTO conductive glass with screen printing technique. Then the TiO_2 film was sinter at 110 ˚C for 15 min. Repeat this process another two times and a 3 layers of TiO_2 film was obtained. Then, the film was calcined at 475 ˚C for 30 min. Then the TiO_2 film was pre-heated to 80 ˚C and immersed in a 0.3mM solution of N719 dye in acetonitrile/tert-butyl alcohol (1:1 volume ration) for 20 h and the photoanode was obtained.

Cells fabrication. DSSCs was assembled with a photoanode and a counter electrode clipping the electrolyte and sealed by 60 μm hot-melt surlyn film. A symmetrical cell was assembled with two counter electrodes. The active area of the DSSCs is 16 mm^2. The active area of the symmetrical cells is 64 mm^2. The DSSCs were used for the photocurrent density-voltage test, and the symmetrical cells were used for the electrochemical impedance spectroscopy and Tafel-polarization measurement test.

Photovoltaic and electrochemical measurement. The photocurrent density-voltage (*J-V*) curve measurements were conducted with an AM 1.5 solar simulator (Newport 100mW cm^{-2}). The light intensity of the solar simulator was adjusted by using an optical power meter (Newport, 1918-c) with a detector (818P-040-25). *J-V* curves were obtained by applying an external bias to the cell and measurements were recorded by a Keithley model 2420 digital source meter. The voltage step and delay time of photocurrent were 10 mV and 10 ms, respectively. Electrochemical impedance spectroscopy (EIS) measurements were characterized with symmetrical cells using a PARSTAT 2273 electrochemical workstation (Princeton Applied Research). The applied bias voltage and ac amplitude were set around the open-circuit 0.7 V and 10 mV, and the frequency range was from 0.1 to 10^5 Hz.

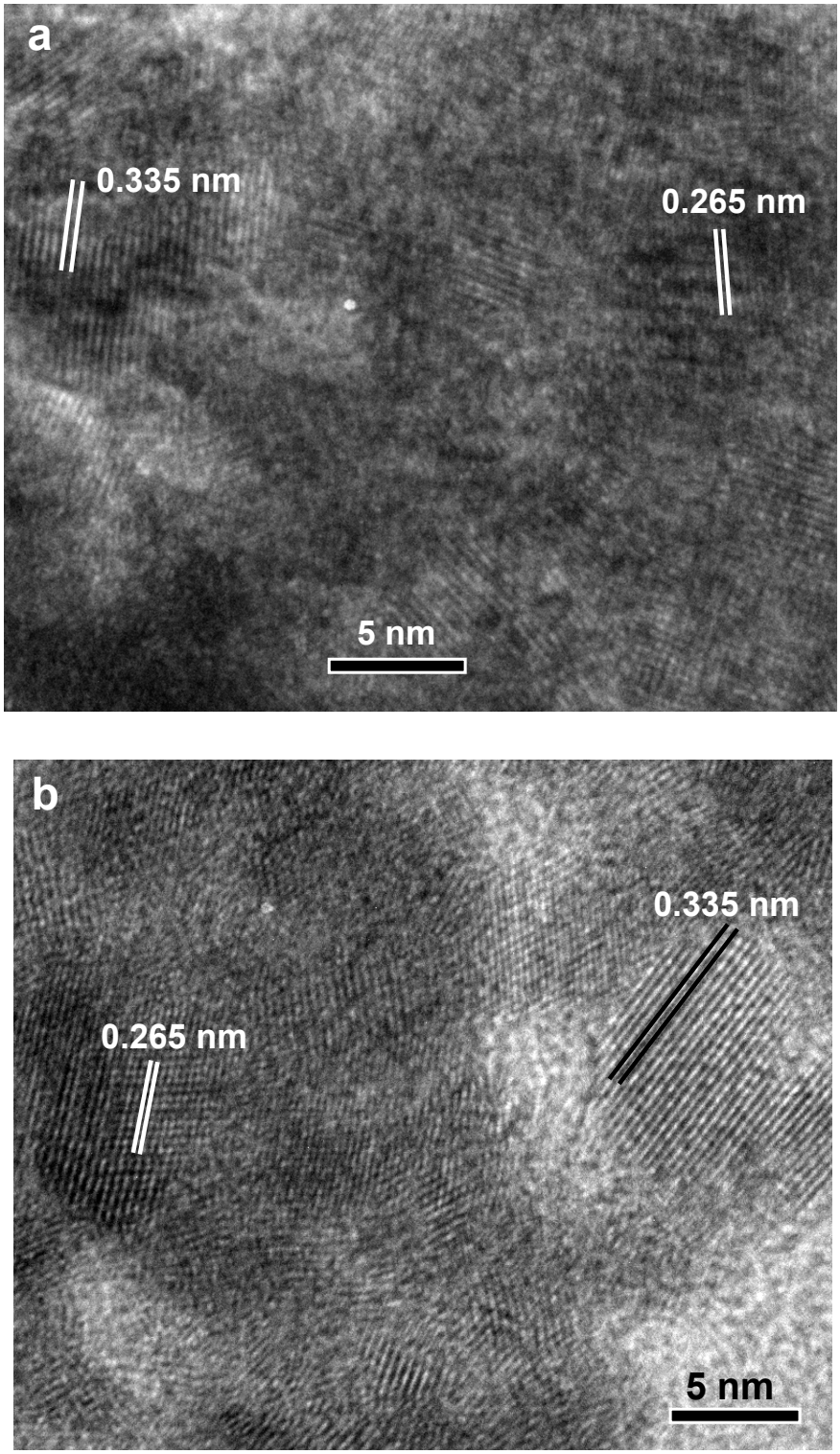

Fig. S1 High resolution TEM images of (a) SnO_2 and (b) $SnO_{2-\delta}$ nanocrystals.

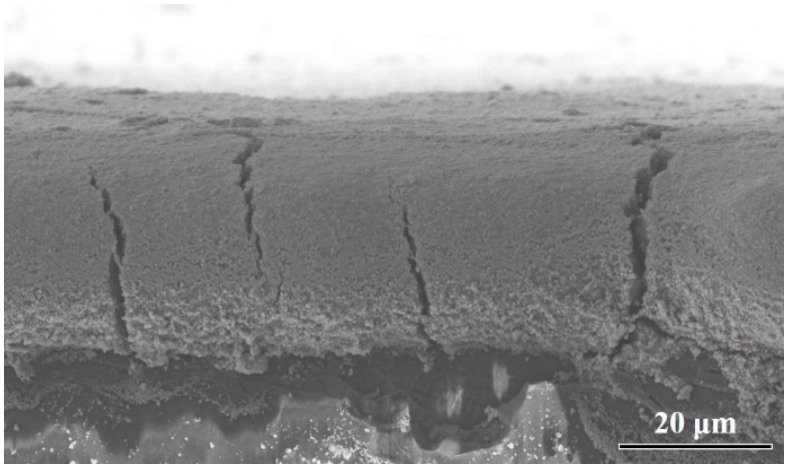

Fig. S2 SEM image of the cross section of the counter electrode.

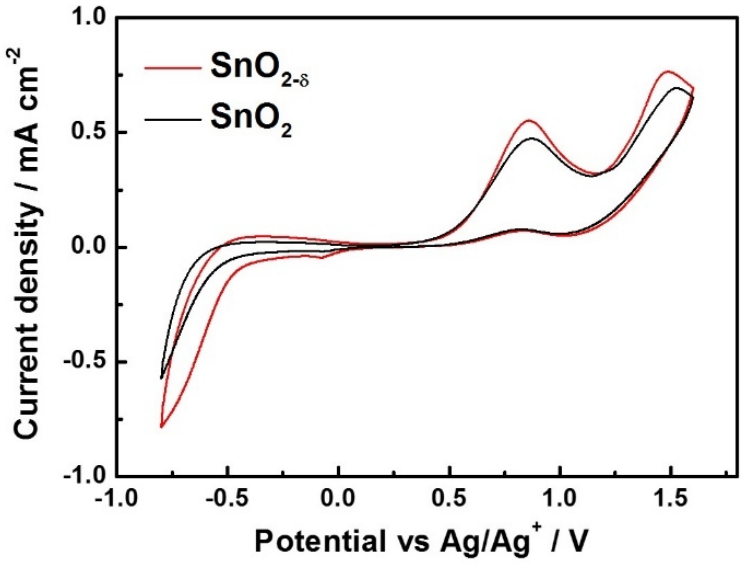

Fig. S3 Cyclic voltammetry curves of the symmetrical cells based on dual $SnO_{2-\delta}$ and SnO_2 electrodes.