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Supplementary information

Great improvement of electrochemical catalytic activity of the oxide counter electrodes fabricating in nitrogen atmosphere for dye-sensitized solar cells

Mingxing Wu,* Xiao Lin, Wei Guo, Yudi Wang, Lingling Chu, Tingli Ma* and Kezhong Wu*

Counter electrode fabrication: The method for preparing the SnO_2 and Nb_2O_5 electrodes is the same. As an example of SnO_2 electrode, a mixture of 2 g SnO_2 powder and 15 g zirconium dioxide pearl was dispersed in 10 mL absolute alcohol inside an agate pot. The mixture was milled for 4 h. Then it was ultrasonically dispersed for 30 min. The SnO_2 paste was prepared. The SnO_2 paste was sprayed on FTO glass (Asahi Glass, Japan) at room temperature with an airbrush (TD-128, Tiandi Co., Ltd.) connected to an air compressor (TC-118, Aihui Co., Ltd.). The prepared SnO_2 film was sintered at 500 °C in air or N_2 for 30 min. The film can be directly used as a counter electrode.

Photoanode fabrication: A 5 layers of TiO_2 (solaronix D, Switzerland) nanocrystalline film sensitized with N719 dye (Solaronix, Switzerland) 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 200 ˚C for 15 min. Repeat the process above mentioned four times and a 5 layers of TiO_2 film was obtained. After sintered at 500 ˚C for 10 min, cool to room temperature, the TiO_2 film was treated with 40 mM $TiCl_4$ aqueous solution, and then washed with distilled water. Sintered at 500 ˚C for 30 min, the mesoporous nanocrystalline TiO_2 film was completely fabricated. The thickness of the nanocrystalline TiO_2 film was 12 μm. Then the TiO_2 film was pre-heated to 80 ˚C and immersed in a 5 x 10^{-4} M solution of N719 dye in acetonitrile/tert-butyl alcohol (1:1 volume

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ration) for 20 h and the photoanode was obtained. The electrolyte contains 0.06 M of LiI, 0.6 M 1-propyl-3-methylimidazolium iodide, 0.03 M I_2, 0.5 M 4-*t*ert-butyl pyridine, and 0.1 M guanidinium thiocyanate in acetonitrile.

Cells fabrication: DSCs was assembled with a photoanode and a counter electrode clipping the electrolyte and sealed by hot-melt surlyn film. A symmetrical cell was assembled with two identical electrodes. The active area of the DSCs is 16 mm^2. The active area of the symmetrical cells is 56 mm^2. The DSCs were used for the photocurrent density-voltage test, and the symmetrical cells were used for the electrochemical impedance spectroscopy (EIS) test.

Measurements: XRD measurements were conducted using an automatic X–ray powder diffractometer (D/Max 2400, RIGAKU). The XPS measurements were carried with a surface analysis system (ESCALAB250, Thermo VG, USA). The surface morphologies of the oxide films were achieved by scanning electron microscopy (FEI QUANTA 450). The photocurrent density -voltage performance of the DSCs was tested in simulated AM 1.5 illumination (I =100 mW cm^{-2}, PEC-L15, Peccell, Japan) with a digital source meter (Keithley 2601, USA). EIS experiments were characterized with symmetrical cells using a computer-controlled potentiostat (Zennium Zahner, Germany) in the dark. The measured frequency ranged from 100 m Hz to 1 M Hz. The amplitude of the alternating current was set at 10 mV, and the bias was -0.75 V. The spectra were fitted by Zview software. The IR measure was carried out with FT-IR spectrometer (FT-IR 430, JASCO, Japan).

Table S1 Photovoltaic parameters of the DSCs with SnO_2 and Nb_2O_5 counter electrodes fabricated in air or N_2 atmosphere.

Counter electrodes	V_{OC}/V	J_{sc}/mA cm^{-2}	FF	*PCE*/%
Air-SnO_2	0.53	9.81	0.36	1.84
N_2-SnO_2	0.73	15.79	0.53	6.09
Air-Nb_2O_5	0.46	7.41	0.28	0.97
N_2-Nb_2O_5	0.70	14.49	0.46	4.65

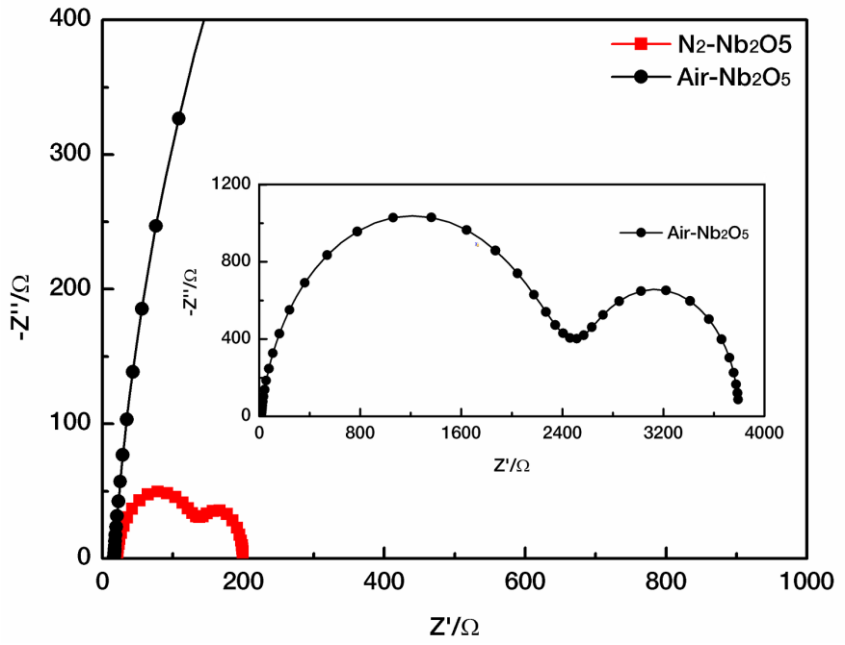

Fig. S1 Electrochemical impedance spectroscopy Nyquist plots of the symmetrical cells using Nb_2O_5 electrode fabricated in N_2 (■) or air (●) atmosphere, inset is the full scaled Nyquist plot of the Air-Nb_2O_5.

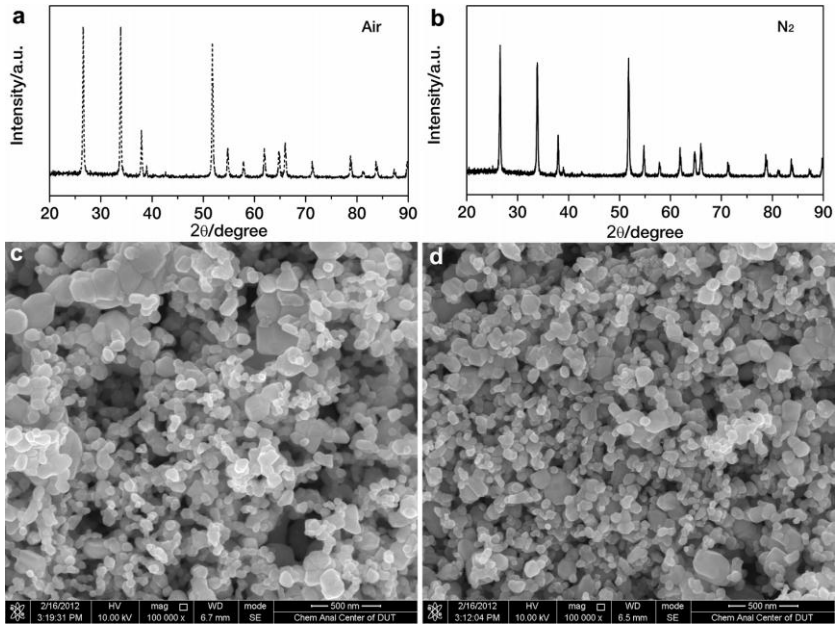

Fig. S2 XRD patterns of the SnO_2 sintered in (a) air and (b) N_2; SEM image of the SnO_2 sintered in (c) air and (d) N_2.