Supplementary Information

A novel catalyst of WO_2 nanorod for the counter electrode of dye-sensitized solar cells

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X-ray diffractograms peaks assignment of the synthesized WO_2 and WO_3

In Fig. 1a, the diffraction peaks of 18.4 º, 25.8 º, 31.6 º, 37.0 º, 41.4 º, 49.7 º, 53.0 º, 59.8 º, 63.3 º, 66.3 º, 72.7 º, 73.6 º, 78.5 º, 78.8 º 80.9 º and 84.0 º are attributed to the planes of (101), (011), (101), (211), (210), (301), (220), (310), (321), (231), (411), (413), (004), (233), (041) and (033) for WO_2 (32-1393, PDF 2 database). And in Fig. 1b the diffraction peaks of 13.9 º, 23.2 º, 24.3 º, 26.8 º, 28.1 º, 33.9 º, 36.7 º, 39.3 º, 42.0 º, 44.6 º, 47.4 º, 48.9 º, 49.7 º, 53.5 º, 55.6 º, 58.1 º, 62.0 º, 67.2 º, 71.3 º, 76.1 º and 83.2 º are attribute to the planes of (100), (002), (110), (111), (200), (112), (202), (211), (300), (212), (004), (302), (220), (311), (222), (400), (214), (410), (224), (106) and (324) for WO_3 (85-2460, PDF 2 database).

Preparation of WO_2, WO_3, and Pt electrodes

200 mg of WO_2 or WO_3 powder and 4 g of zirconium dioxide pearl were dispersed in 3 mL isopropanol and milled for 4 hours. Then the obtained solution was sprayed on FTO glass (Asahi Glass, type-U, 14 Ω/□, Japan). The FTO glass was coated with WO_2 or WO_3 film and then sintered in a tube furnace in N_2 atmosphere at 500 °C for 30 min. Pt electrodes were prepared according to our previous work.[1]

Photoanode preparation and cell fabrication

A 12 μm thick layer of 20 nm-sized TiO_2 layer (P25, Degussa, Germany) was loaded on FTO glass by doctor-blading technique. After sintering at 200 °C, the obtained layer was further coated with a 4 μm thick scattering layer of 160 nm-sized TiO_2 (ST-41, Ishihara, Japan) followed by sintering at 500 °C. After cooling to 80 °C, the TiO_2 films were immersed in a 5 x 10^{-4} M solution of N719 dye (Solaronix SA, Switzerland) in acetonitrile/*tert*-butyl alcohol (1:1 volume ration) for 14 h. The triiodide/iodide electrolyte contains 0.06 M of LiI, 0.6 M 1-butyl-3-methylimidazolium iodide, 0.03 M I_2, 0.5 M 4-*tert*-butyl pyridine, and 0.1 M guanidinium thiocyanate in acetonitrile. A DSC was assembled by a photoanode, with a counter electrode sandwiching the electrolyte. A symmetrical cell was assembled with two identical WO_2, WO_3, and Pt electrodes sandwiching the

electrolyte. The two electrodes were sealed by double-faced insulated adhesive tapes. The DSCs were used for the photocurrent-voltage test with an effective area of 0.2 cm^2. The symmetrical cells with effective area of 0.25 cm^2 were used in the Tefal-polarization test and the EIS experiments.

Characterization

The X-ray diffraction experiment was carried out with an automatic X-Ray powder diffractometer (D/Max 2400, RIGAKU). The surface morphologies of WO_2 and WO_3 powder were characterized using SEM (FEI HITACHI S-4800). Cyclic voltammetry (CV) was carried out in a three-electrode system in an Ar-purged acetonitrile solution containing 0.1 M $LiClO_4$, 10 mM LiI, and 1 mM I_2 at a scan rate of 100 mV s^{-1} using a BAS 100B/W electrochemical analyzer. Pt worked as a counter electrode and Ag/Ag^+ worked as a reference electrode. Photocurrent-voltage performance of the DSCs was conducted in simulated AM 1.5 illumination (I=100mM cm^{-2}, Solar Light Co., INC., USA) with a Keithley digital source meter (Keithley 2601, USA). The EIS experiment was conducted in the dark with dummy cells using a computer-controlled potentiostat (Zenium Zahner, Germany). The measured frequency ranged from 100 m Hz to 1 M Hz, and the AC amplitude was set at 10 mV. The spectra were fitted by Zview software. The equivalent circuit diagrams were shown in Fig. S1. Tafel-polarization measurements were carried out with an electrochemical workstation system (LK-9805, Tianjin Lanli Inc.) in a symmetrical dummy cell. The scan rate was 50 mV s^{-1}.

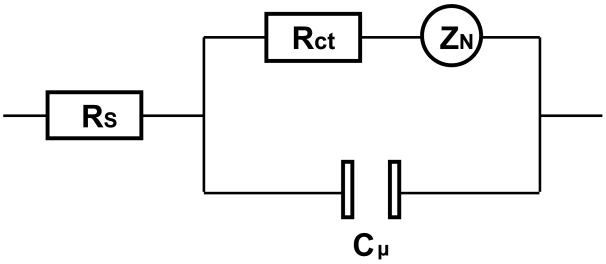

Fig. S1 Equivalent circuit for fitting EIS plots. R_s: series resistance, R_{ct}: charge transfer resistance in the electrode/electrolyte interface, $C\mu$: corresponding capacitance in the electrode/electrolyte interface, Z_N: Nernst diffusion resistance.

References

1 X. M. Fang, T. L. Ma, G. Guan, M. Akiyama, E. Abe, *J. Photochem. Photobiol.* A 2004, **164**, 179.