Supplementary Information

Novel counter electrode catalysts of niobium oxides supersede Pt for dye-sensitized solar cells

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X-ray diffractograms peak assignments of the synthesized Nb_2O_5, NbO_2

In Fig. 1, for H-Nb_2O_5, the diffraction peaks at 22.58°, 28.60°, 36.74°, 46.16°, 50.74°, 55.25°, and 56.16±are assigned to the crystal planes (001), (100), (101), (002), (110), (102), and (111), respectively (28-0317, PDF 2 database). For O-Nb_2O_5, the diffraction peaks at 22.58°, 28.30°, 28.82°, 36.54°, 36.99°, 46.14°, 49.88°, 50.94°, 55.06°, 56.32°, and 58.66±are assigned to the crystal planes (001), (180), (200), (181), (201), (002), (0160), (380), (182), (381), and (2160), respectively (27–1003, PDF 2 database). The diffraction peaks at 17.98°, 23.68°, 25.14°, 31.96°, 38.80°, 43.98°, 47.38°, 51.06°, 54.38°, and 58.62±for M-Nb_2O_5 are assigned to the crystal planes (401), (004), ($\bar{8}$03), ($\bar{7}$12), ($\bar{5}$16), (514), (020), (023), ($\bar{8}$23), and ($\bar{1}$511), respectively (74-0298, PDF 2 database). Last, the peaks T-NbO_2 at 24.46°, 26.00°, 27.77°, 35.18°, 36.00°, 37.10°, 39.94°, 41.68°, 45.82°, 47.86°, 48.92°, 50.84°, 52.06°, 53.48°, 56.28°, 57.03°, and 58.74° are assigned to the crystal planes (301), (400), (321), (222), (341), (440), (402), (620), (103), (213), (701), (721), (262), (800), (741), (503), and (253), respectively (43-1043, PDF 2 database).

Morphological Characterization of the synthesized Nb_2O_5 and NbO_2

The morphologies of the three synthesized Nb_2O_5 and the NbO_2 samples are shown in Figure S1. H-Nb_2O_5 is composed of several sphere-like particles, whereas O-Nb_2O_5 shows oblique prisms. M-Nb_2O_5 has an exposed molten state and consists of various irregular grains. T-NbO_2 has formed a typical honeycomb structure with various incorporated channels. Moreover, the average sizes of the particles or pores are approximately 100, 200, 500, and 300 nm, respectively.

Preparation of Nb_2O_5, NbO_2, and Pt CEs as well as TiO_2 Photoanode

The preparation of Nb_2O_5 and NbO_2 CEs can be described as follows: 200 mg of Nb_2O_5 or NbO_2 powder and 5 g of zirconium dioxide pearl were dispersed in 5 mL isopropanol and milled for 8 h. The obtained solution was then sprayed on an FTO glass (Asahi Glass, type-U, 14 Ω/ϒ, Japan)

using an airbrush (TD-128, Tiandi Co., Ltd.). The FTO glass coated with Nb_2O_5 or NbO_2 film was

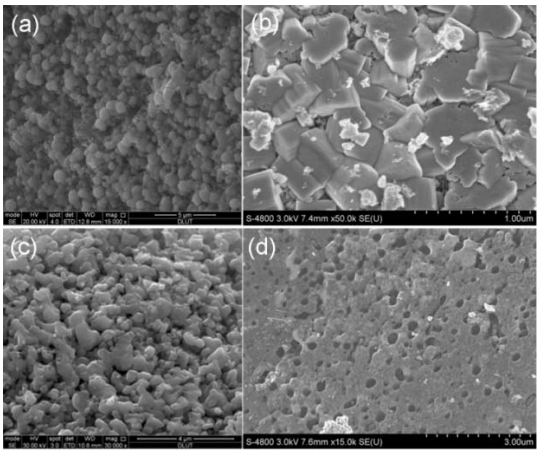

Fig. S1 SEM images of the as-prepared Nb_2O_5 and NbO_2 samples. (a) H-Nb_2O_5, (b) O-Nb_2O_5, (c) M-Nb_2O_5, and (d) T-NbO_2.

Table S1 Crystal structures, space groups, lattice parameters, sizes, and morphologies of the three Nb_2O_5, and one NbO_2.

Crystal structures	Space groups	Lattice parameters			d (nm) by SEM	Morphology
		a(Å)	b(Å)	c(Å)		
H-Nb_2O_5	P6/mmm	3.607	3.607	3.925	100	spherical
O-Nb_2O_5	Pbam(55)	6.168	29.312	3.936	200	oblique prism
M-Nb_2O_5	C2/m(12)	20.440	20.440	3.832	500	irregular particle
T-NbO_2	141/a(88)	13.696	13.696	5.981	300	honeycomb

then sintered under N_2 atmosphere at 500 °C for 30 min in a tube furnace. Pt electrodes were obtained by pyrolyzing platinum acid chloride isopropyl alcohol solution at 500 °C under air atmosphere.

A 12 μm thick layer of 20 nm TiO_2 (P25, Degussa, Germany) was attached to an FTO glass by screen printing technique. The obtained film was sintered at 500 °C for 30 min. After cooling to 80 °C, the TiO_2 films were immersed in 5 x 10^{-4} M solution of N719 dye (Solaronix SA, Switzerland) in ethanol solution for 20 h.

Fabrication of DSCs and symmetrical cells

A DSC with an active area of 0.16 cm^2 was assembled by a photoanode with a CE sandwiching the electrolyte. The electrolyte contains 0.06 M of LiI, 0.03 M I_2, 0.6 M 1-butyl-3-methylimidazolium iodide, 0.5 M 4-tert-butyl pyridine, and 0.1 M guanidinium thiocyanate, using acetonitrile as solvent. Last, the two electrodes were sealed with double-faced

insulated adhesive tapes. The symmetrical cells had an active area of 0.25 cm^2, assembled with two identical CEs filling the electrolyte, and then sealed with double-faced insulated adhesive tapes. The symmetrical cells were used in the EIS experiments and Tafel-polarization tests.

Characterization

The X-ray diffraction experiments were performed using an automatic X-Ray powder diffractometer (D/Max 2400, RIGAKU). The surface morphologies of H and M-Nb_2O_5 were observed using scanning electron microscopy (SEM, FEI HITACHI S-4800). The surface morphologies of O-Nb_2O_5 and T-NbO_2 were using also observed using SEM (QUANTA 450). Cyclic voltammetry was conducted using a CHI 660 (SHANGHAI, CHEN HUA) electrochemical analyzer in a three-electrode system, in which Pt was used as a CE and Ag/Ag^+ worked as a reference electrode. The scan rate is 10 mVs^{-1}. Photocurrent-voltage performance of the DSCs was measured with a Keithley digital source meter (Keithley 2601, USA) under illumination of an Xe lamp (AM 1.5, I=100 mW cm^{-2}, PEC-L15, Peccell, Japan). A computer-controlled potentiostat (Zennium Zahner, Germany) was used in the EIS experiments that were conducted in the dark. The measured frequency ranged from 100 mHz to 1 MHz, and the AC amplitude was set at 10 mV. The spectra were fitted by Zview software. The equivalent circuit diagram is shown in Fig. S2. Tafel-polarization was measured with an electrochemical workstation system (LK-9805, Tianjin Lanli Inc.).

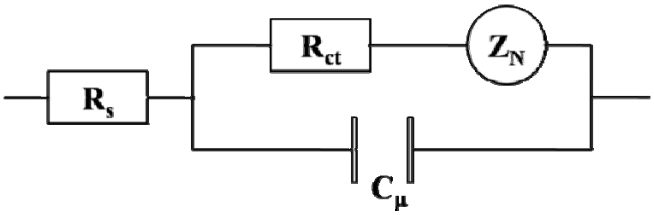

Fig. S2 Equivalent circuit of the symmetrical cells. R_s, series resistance; R_{ct}, charge transfer resistance in the electrode/electrolyte interface; C_μ, corresponding capacitance in the electrode/electrolyte interface; and Z_N, Nernst diffusion impedance.

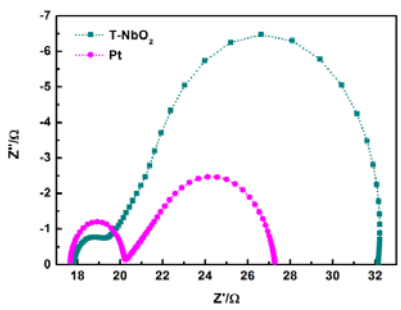

Fig. S3. The magnified Nyquist plots for symmetrical cells assembled with T-NbO_2 and Pt.