Electronic Supplementary Information

Notable Catalytic Activity of Oxygen-vacancy-rich WO_{2.72} Nanorod Bundles as the Counter

Electrode for Dye-sensitized Solar Cells

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1. Experimental Section:

Synthesis: In a typical procedure, WCl_6 (0.982 g) was dissolved in propyl alcohol (150 ml), and the clear yellow solution was transferred to a teflon-lined stainless-steel autoclave and heated at 200 °C for 24 h. Subsequently, WO₃ powder was obtained by oxidation of WO_{2.72} at 500 °C for 30 min in air.

Preparation of WO_{2.72}, WO₃, and Pt CEs: WO_{2.72} or WO₃ powder (300 mg) and zirconium dioxide pearl (4 g) were dispersed in isopropanol (5 mL) and milled for 2 hours. Then the obtained suspension was sprayed on FTO glass. The film coated with WO_{2.72} or WO₃ was then sintered in a tube furnace in N₂ atmosphere at 500 °C for 30 min. Noble metal Pt CE were prepared by pyrolysis H₂PtCl₆ as previously reported.

Photoanode preparation and cell fabrication: A layer of 20 nm-sized TiO₂ (P25, Degussa, Germany) layer (12 μ m) was loaded on FTO glass by printing technique method and used in this study.² The obtained film was sintered at 500 °C. After cooling to 90 °C, the TiO₂ films were

immersed in a solution of N719 dye (5 x 10^{-4} M) in acetonitrile/tert-butyl alcohol (1:1 volume ration) for 20 h. The triiodide/iodide electrolyte for cell testing is composed of LiI (0.03 M), 1-butyl-3-methylimidazolium iodide (0.6 M), I₂ (0.03 M), 4-tert-butyl pyridine (0.5 M), guanidinium thiocyanate in acetonitrile (0.1 M). The T₂/T⁻ electrolyte for cell testing is composed of T₂ (0.4 M), T (0.4 M), LiClO₄ (0.05 M) and 4-tert-butyl pyridine (0.5 M) and in acetonitrile–ethylene carbonate (6:4 volume ratios). DSSCs were assembled by a TiO₂photoanode with corresponding counter electrode sandwiching redox couple in the electrolyte. The symmetrical cells with effective area (0.64 cm²) were carried out in the Tefal-polarization test and the EIS experiments.

Characterization: To analyze the composition of as-synthesized samples, we obtained X-ray diffraction (XRD) patterns using PANalyticalX Pert diffractometer (Cu K α radiation at $\lambda = 1.54$ Å) sampling at 8°/ min, 40 kV and 100 mA. The as-prepared micro or nanostructures were characterized and analyzed by scanning electron microscopy (SEM, Nova Nano SEM 450), transmission electron microscopy (TEM, FEI Tecnai G2 F30) with an accelerating voltage (300 Kv). The absorption spectroscopy of WO₃ and WO_{2.72} were obtained using an UV-vis spectrophotometer (Jasco, UV-550) equipped with an integrating sphere. The films thicknesses were measured using film-thickness measuring device (Surfcom 130A, Japan). The photocurrent-voltage performance of the flexible DSSCs was measured by a Keithley digital source meter (Keithley 2601, USA) and equipped with a solar simulator (PEC-L15, Peccell, Yokohama, Japan). EIS experiments were measured in the dummy cells in the dark at corresponding open-circuit voltage of DSSCs using a computer-controlled potentiostat (ZenniumZahner, Germany). Cyclic voltammetry (CV) was measured in a three-electrode system. The triiodide/iodide electrolyte for CV testing is composed of LiI (2 mM), LiClO₄ (20 mM) and I_2 (0.2 mM). The T_2/T^- electrolyte for CV testing is composed of T_2 (0.01 M), T^- (0.1 M) and LiClO₄ (0.2 M) in acetonitrile-ethylene carbonate (6:4 volume ratios).

2. Results and discussion

X-ray diffraction peaks assignment of the synthesized WO_{2.72} and WO₃

In Fig. 1a, the diffraction peaks of 23.37° , 26.184° , 35.435° , and 47.968° are attributed to the planes of (010), (503), (513) and (020) for WO_{2.72} (65-1291, PDF 2 database). And in Fig. 1b the diffraction peaks of 23.118° , 23.579° , 24.319° , 26.542° , 28.779° , 33.279° , 34.101° , 35.560° ,

41.676°, 44.857°, 47.265°, 48.247°, 49.918°, 50.702°, 53.695°, 54.150°, 54.725° and 55.782° are attribute to the planes of (002), (020), (200), (120), (200), (112), (022), (202), (122), (222), (132), (004), (040), (140), (114), (024), (042), (240) and (142) for WO₃ (43-1035, PDF 2 database).



Fig.S1. UV/Vis absorption spectra of WO_{2.72} NRBs and WO₃ prisms.

Discussion of the reason for the notable catalytic activity of oxygen-vacancy-rich $WO_{2.72}$

NRBs compared to WO₃

In our previous study¹, it was noted that the catalytic activities of the SnO₂ and Nb₂O₅ CEs prepared in N₂ atmosphere were much higher than those prepared in air. The DSSCs using Air-SnO₂ and Air-Nb₂O₅ show PCEs of 1.84% and 0.97%. This means that the SnO₂ and Nb₂O₅ CEs prepared in air cannot be used as eligible catalysts for DSSCs. In contrast, the SnO₂ and Nb₂O₅ CEs prepared in N₂ produce high catalytic activity, and the DSSCs yield PCEs of 6.09% (N₂-SnO₂) and 4.65% (N₂-Nb₂O₅), giving improvements of 231% and 379%, respectively. Based on the analysis of the XPS results, the N₂-SnO₂ and Air-SnO₂ and Nb₂O₅ CEs prepared in air catalytic activity variation. The SnO₂ and Nb₂O₅ CEs prepared in N₂ can maintain more surface oxygen-vacancy compared to those prepared in air. Thus, the above result is one of the supporting data for the role of surface oxygen-vacancy in the catalytic activity. As emphasized in the text, among the tungsten oxides WO_{2.625}-WO₃, WO_{2.72} possesses the largest oxygen deficiency has been reported as the only oxide that can be isolated in a pure form.² W⁶⁺, W⁵⁺ and W⁴⁺ are the typical oxidation states found in WO_{2.72} nanomaterials surface.³

Therefore, a large number of oxygen deficiencies exist on the WO_{2.72} surface. WO₃ was obtained by annealing our as-synthesized WO_{2.72} in air at 500 °C for 30 min. The change of oxygen-vacancy before and after annealing in air was confirmed by the visible and near-infrared regions in ultraviolet/visible absorption spectra.⁴ In Figure S1, the sample after annealing in air has a weak adsorption in the visible and near-infrared regions when compared with WO_{2.72}, which demonstrates that the oxygen-vacancy was filled after annealing in air. When applied them as CEs prepared in same condition, the catalytic activity of the sample annealed in air declined obviously, which were proved by CV, EIS and Tafel-polarization measurements (Fig.S2, S3, S4, S5, S6). The performance of nanomaterial in various heterogeneous catalytic processes has been found to be highly dependent on the exposed facets, which determines the surface atomic arrangement and coordination.⁵ Based on this result, the surface oxygen-vacancy in WO_{2.72} is produced by the nanostructure [010] specific facets exposed. Thus, nanostructure [010] specific facets determining the large surface oxygen-vacancy in WO_{2.72} was thought to be one of the factors to the notable catalytic activity of WO_{2.72}.

Electro-catalytic activities of $WO_{2.72}$, WO_3 and Pt based CEs for I_3 ⁻/I⁻ and organic redox couples.

The electrochemical impendence spectroscopy (EIS) and Tafel-polarization measurements depicted the electric response of interfaces, were carried out to further elucidate the difference electro-catalytic activities of WO_{2.72} NRBs, WO₃ and Pt. Nyquist plots for I₃^{-/}/T redox couples shown in Fig. S3 were fitted to the equivalent circuit shown in Fig. 5S. The detail parameter of impendence is listed in Table S1. We could see that the values of R_s have almost identical for WO_{2.72} NRBs and WO₃. The value of R_{ct} of WO_{2.72} NRBs based CEs is much smaller than WO₃ based CEs, which indicated that the more catalytic sites on surface of WO_{2.72} NRWs based CEs than that of WO₃ based CEs. Note that the arch for the I₃⁻/T electrolyte diffusion is enlarged for WO₃ compared to WO_{2.72} NRWs based CEs. As shown in Fig S4, the Tafel plot in Tafel zone show the larger slope for the WO_{2.72} NRWs, indicating the higher Tafel exchange current density (J_0) on WO_{2.72} NRWs electrodes compared to WO₃. The slope of this region can be related to R_{ct} by the eq. (1)

$$R_{\rm ct} = \frac{RT}{nFJ_0} (1)$$

Where *R* is the gas constant, *T* is the temperature, *F* is Faraday's constant, and *n* is the number of electrons involved in the reaction at the electrode. According to eq. (1), WO_{2.72} NRBs has the smaller R_{ct} compared to WO₃, which is agree with the EIS result. Together with the CV, EIS and Tafel result, for the I₃⁻/T electrolyte, the WO_{2.72} NRBs based CEs have notable electro-catalytic activities compared to WO₃, nearly the same as the precious metal Pt-based CEs. For organic redox couples, the electrochemical impedance spectroscopy (EIS) results are listed in table S1. The R_{ct} (1.89) for WO_{2.72} NRBs is obviously smaller than that of WO₃ and Pt based CEs. As shown in Fig S6, the J–U plot in Tafel zone show the larger slope for the WO_{2.72} NRBs than that of WO₃ and Pt based CEs, which is good agree with the CV and EIS result. Therefore, our result is extraordinarily important considering that WO₃, WO_{2.72} and Pt can demonstrate selective catalytic activities for difference organic redox couples.



Fig.S2. Cyclic voltammograms of WO₃, WO_{2.72} NRBs and Pt electrodes for (a) I_3 ^{-/T} and (b) organic redox couples.



Fig.S3 Nyquist plots of the symmetrical cells fabricated with two identical a) WO_{3} ; b) $WO_{2.72}$ and Pt electrodes based on triiodide/iodide redox couple



Fig.S4 Tafel curves of the symmetrical cells fabricated with two identical WO_3 , $WO_{2.72}$ and Pt electrodes based on triiodide/iodide redox couple



Fig.S5 Nyquist plots of the symmetrical cells fabricated with two identical $WO_{2.72}$, WO_3 and Pt electrodes based on non-corrosive organic redox couple (T_2/T^-) ; the inset shows the corresponding equivalent circuit diagram



Fig.S6 Tafel curves of the symmetrical cells fabricated with two identical WO₃, WO_{2.72} and Pt electrodes based on non-corrosive organic redox couple (T_2/T^-)

Electrolyte	CE	$R_{ m s}/\Omega$	$R_{\rm ct}/\Omega$	$Z_{ m N}/\Omega$
I ₃ ⁻ /I ⁻	WO ₃	21.37	51.56	70.47
	WO _{2.72}	20.25	1.714	5.12
	Pt	9.85	2.21	2.50
T_2/T^-	WO ₃	11.85	12.15	12.41
	WO _{2.72}	13.88	1.89	4.12
	Pt	12.38	18.21	20.27

Table S1 Parameters of EIS and Tafel polarization of various CEs based on triiodide/iodide and non-corrosive organic redox couple (T_2/T^-) redox couple



Fig.S7 12 Consecutive CVs of $WO_{2.72}$ NRBs at a scan rate of 10 mVs⁻¹ in triiodide/iodide electrolyte. Inset: anodic and cathodic peak current densities versus cycle times.

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