Supplementary Information

Economical and effective sulfide catalysts for dye-sensitized solar cells as counter electrodes

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Synthesis of MoS_2 Na_2MoO_4 (2.42 g, 10 mmol), thiourea (3.12 g, 40 mmol) and 0.5 g PEG-600 were dissolved in distilled water (60 mL). Stir for 30 min and then transfer the solution into a teflon-lined stainless autoclave. After heated at 200 ˚C for 48 h, the autoclave was cooled to room temperature. The precipitates were collected by filter. And the precipitates were washed with ethanol and water and the dried at 300 ˚C. The purified MoS_2 was obtained.

Synthesis of WS_2 Na_2WO_4 (0.99 g, 3 mmol), thioacetamide (0.68 g, 9 mmol), and cetyltrimethylammonium bromide (CTAB, 3.28 g, 9 mmol) were dissolved in distilled water (60 mL). The solution was stirred for 2 h and then transformed into an autoclave. The autoclave was heat at 200 ˚C for one week and the intermediate was prepared. Then the intermediate was sintered at 850 ˚C for 12 h in N_2 atmosphere and WS_2 was obtained.

Electrodes and Cells fabrication Five layers of TiO_2 (solaronix D, Swiss) nanocrystalline film sensitized with N719 (Solaronix, Swiss) were used as photoanodes. A thin layer of TiO_2 was coated on F-doped tin oxide (FTO) conductive

glass using the screen printing technique. The TiO_2 film was sintered at 200 ˚C for 15 min. The process was repeated four times and five layers of TiO_2 film were obtained. After sintering at 500 °C for 10 min and the subsequent cooling to room temperature, the TiO_2 film was treated with 40 mM $TiCl_4$ aqueous solution and washed with distilled water. After sintering at 500 °C for 30 min, the mesoporous nanocrystalline TiO_2 film was completely fabricated with a thickness of approximately 12 μm. The photoanode was obtained after the TiO_2 film was pre-heated to 80 °C and immersed in a 5 x 10^{-4} M solution of N719 dye (Solaronix SA, Switzerland) in acetonitrile/*tert*-butyl alcohol (1:1 volume ratio) for 20 h and the photoanode was obtained. Two kinds of redox couples were used in this research. The first is triodide/iodide. The triodide/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 guanidiniumthiocyanate in acetonitrile. The second is 5-mercapto-1-methyltetrazole di-5-(1-methyltetrazole) disulfide/ *N*-tetramethylammonium salt ($^{+}NMe_4T^{-}$) (T_2/T^{-}, Fig. S2). The T_2/T^{-} electrolyte contains 0.4 M $^{+}NMe_4T^{-}$, 0.4 M di-5-(1-methyltetrazole) disulfide (T_2,), 0.05M $LiClO_4$ and 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile/ethylene carbonate (6:4, volume ratio). MoS_2 and WS_2 counter electrodes was fabricated with spray-coating technique as follow. 200 mg of the as-prepared MoS_2 or WS_2 was dispersed in 4 mL isopropanol. The solution was then ultrasonically dispersed for 30 min and the pastes for the spraying were obtained. The prepared pastes were sprayed onto an FTO glass with an air brush. Subsequently, the FTO glass coated with sulfide pastes was sintered in N_2 atmosphere at 500 °C for 30

min and the CEs were prepared. The thickness of sulfide CEs is around 20μm. Pt deposited on FTO glass was used as Pt CE. [1] A DSC was assembled with a photoanode and counter electrode clipping the electrolyte. And the DSC was sealed with a double-faced insulated adhesive tape. A symmetrical cell was assembled with two identical counter electrodes clipping the electrolyte used for EIS and Tafel-polarization measurements.

Measurements XRD tests were carried out with an automatic X-ray powder diffractometer (D/Max 2400, RIGAKU). Surface morphologies of the sulfides powder were checked by scanning electron microscopy (SEM, FEI QUANTA 450). Cyclic voltammetry (CV) was carried out in a three-electrode system in an argon-purged acetonitrile solution which contained 0.1 M $LiClO_4$, 10 mM LiI, and 1 mM I_2 at a scan rate of 10, 20, 50, or 100 mV s^{-1} using a electrochemical analyzer (CHI630, Chenhua, Shanghai). Pt served as a counter electrode, and Ag/Ag^+ as a reference electrode. 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 carried out 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. Tafel-polarization measurements were measured with an electrochemical workstation system (CHI 630, Chenhua, Shanghai) in a symmetrical dummy cell. The scan rate was 10 mV s^{-1}.

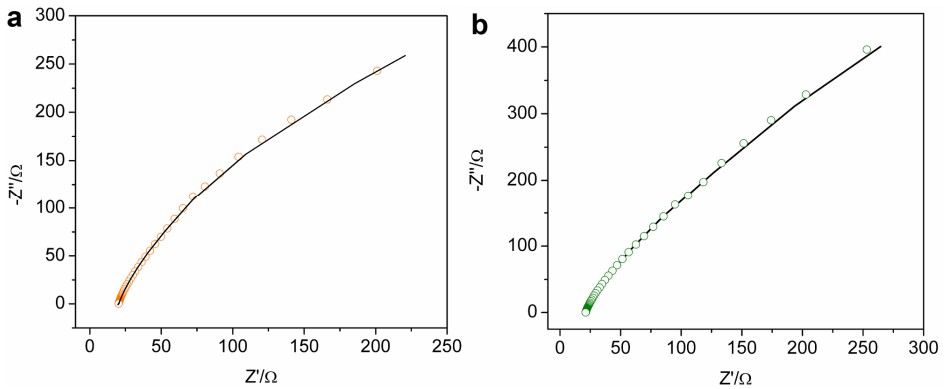
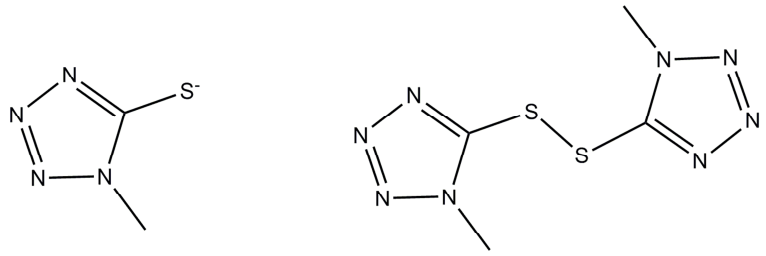


Fig. S1 Full–range of the Nyquist curve of the symmetrical cells based on WS_2 (a) and MoS_2 (b) electrodes. The solid line is the original plot and the circle is the fitted plot.



T^- T_2

Fig. S2 Chemical structure of the redox couple of disulfide/thiolate (T_2/T^-).

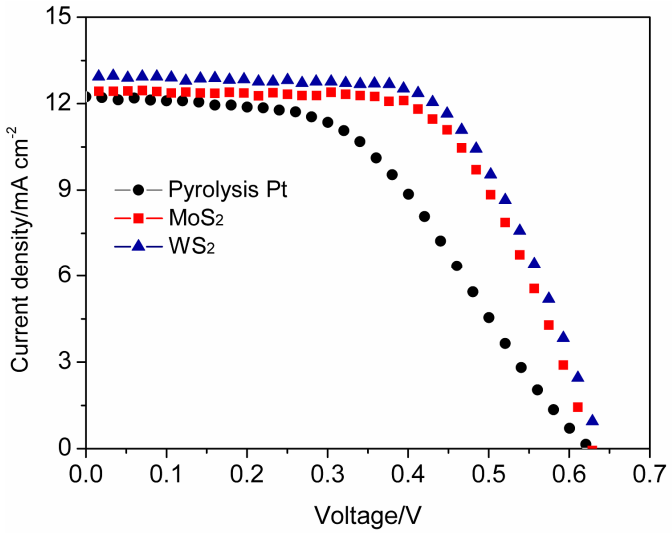


Fig. S3 Photocurrent density-voltage (*J-V*) curves of the T_2/T^- based DSCs using Pt, MoS_2 and WS_2 CEs.

Reference

1 T. L. Ma, X. M. Fang, M. Akiyama, K. Inoue, H. Noma and E. Abe, *J. Electroanal. Chem.*, 2004, **574**, 77.