Electronic Supplementary Information (ESI) for

Highly Efficient Telluride Electrocatalyst for Use as Pt-free Counter Electrode in Dye-Sensitized Solar Cells

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Experimental Section

Synthesis of tellurides.

CoTe and $NiTe_2$ crystals were synthesized by the composite-hydroxide-mediated (CHM) approach.[1] All chemicals are analytical grade. For the synthesis of $NiTe_2$, in a typical procedure, firstly, an amount of 18 g of mixed hydroxides (NaOH:KOH= 51.5:48.5, mole ratio) was added to a 80 mL Teflon-lined autoclave. Meanwhile, an amount of 1 mmol of $NiCl_2 \cdot 6H_2O$ was mixed with 1 mmol Te powder grinding with agate mortar. Then the reactant mixture was placed on the top of the hydroxides in the autoclave. 2 mmol $NaBH_4$ powder was then added in as reducing agent. Subsequently, the Teflon-lined autoclave was sealed and put into a furnace preheated to 200 ^{o}C. The autoclave maintained in the furnace at 200 ^{o}C for 48 h and then cooled naturally down to room temperature. Finally, the black solid product obtained was washed several times using deionized water and centrifugated, and then washed with diluted HCl (pH 3.0) to remove other hydroxides on the surface of the product. The clean $NiTe_2$ was thus obtained after being washed with deionized water repeatedly, dried under vacuum, and heated at 400 ^{o}C for 1h under N_2 atmosphere. For the synthesis of CoTe, all the synthesis procedures were the same as those stated above except that 1 mmol of $NiCl_2 \cdot 6H_2O$ was replaced by 1 mmol of $CoSO_4 \cdot 7H_2O$ as cobalt reagent.

Preparation of CEs and Assembly of DSCs

The preparation of CoTe and $NiTe_2$ CEs can be described as follows: 200mg of CoTe or $NiTe_2$ powder and 4g of zirconium dioxide pearl were dispersed in 4mL isopropanol and milled for 4h. The prepared telluride slurry was then sprayed onto the FTO glass (Asahi Glass, type-U, 14 U sq^{-1}, Japan) with an airbrush (TD-128, Tiandi Co., Ltd.) connected to a minicompressor. The FTO substrate coated with CoTe or $NiTe_2$ film was then annealed under N_2 atmosphere at 400 ^{o}C for 30 min in a tube furnace to obtain the expected CoTe or $NiTe_2$ CEs. The Pt CE was prepared according to our previous work.[2]

A semi-conductive TiO_2 (Degussa, Germany) film with 12 μm thickness on an ultrasonically cleaned FTO glass was fabricated using a screen-printing technique. The obtained TiO_2 film was sintered at 500 °C for 30 min, and subsequently cooled to 80 °C. Finally, the TiO_2 film was immersed in a 5×10^{-4} M of N719 dye (Solaronix SA, Switzerland) in acetonitrile/tert-butyl alcohol (1:1 volume ration) for 21 h to obtain the photoanode. DSCs were assembled together with the dye-sensitized TiO_2 electrode and the telluride CEs sandwiching the liquid electrolyte. The triiodide/iodide electrolyte was composed of 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 with acetonitrile as the solvent. The as-assembled DSCs were used for photovoltaic performance tests with an effective area of 0.16cm^2. A symmetrical dummy cell was assembled by stacking two identical CoTe, $NiTe_2$, and Pt electrodes facing each other and filling the electrolyte similar to that described above. The two electrodes were sealed by double-faced insulated adhesive tapes. The symmetrical cells were used in the electrochemical impedance spectroscopy (EIS) experiments and the Tefal-polarization test.

Characterization

The X-ray powder diffraction (XRD) patterns of the obtained telluride were recorded on an automatic X-ray powder diffractometer (D/Max 2400, RIGAKU, Japan) with Cu K α radiation (λ=0.154 nm) operating at 40 kV and 200 mA. The 2θ angular regions between 10° and 90° were investigated at a scan rate of 8° min^{-1} with a step of 0.02°. The surface morphology and microstructure of the telluride CEs were examined by field emission scanning electron microscopy (FESEM, S-4800, Hitachi). Cyclic voltammetry (CV) was conducted in a three-electrode system in an acetonitrile solution containing 0.1 M $LiClO_4$, 10 mM LiI, and 1 mM I_2 at a scan rate of 10 mV s^{-1} by using a CHI 630D (Chenhua, Shanghai) electrochemical analyzer. Platinum wire served as a counter electrode, Ag/Ag$^+$ was used as a reference electrode, and the as-prepared CE as the working electrode, respectively. The EIS measurements were carried out in the dark at room temperature using a computer-controlled potentiostat (Zennium Zahner, Germany) at a bias potential of -0.75V, an AC amplitude of 10 mV and frequencies from 100 mHz to 1 MHz. The obtained spectra were then fitted by Z-view software. The equivalent circuit diagram is shown in Fig. S1. The Tafel polarization curves were measured using an electrochemical workstation system (CHI630D, Chenhua, Shanghai) at a scan rate of 10 mV s^{-1}. The photocurrent–voltage (*J–V*) characteristics of the DSCs were measured in simulated AM 1.5 illumination (Xe arc lamp, 100 mW cm^{-2}; Peccell-L15, Peccell, Japan) using a Keithley digital source meter (Keithley 2601, USA).

X-ray diffractograms peak assignments of the synthesized CoTe, NiTe$_2$

In Fig.1, for CoTe, the diffraction peaks at 26.58°, 31.56°, 33.78°, 43.18°, 46.96°, 57.76°, 59.28°, 75.98°, and 77.70° are assigned to the crystal planes (100), (101), (002), (102), (110), (201), (112), (104), (203), and (300), respectively (34-0420, PDF 2 database). For NiTe$_2$, the diffraction peaks at 16.76°, 26.70°, 31.68°, 33.94°, 43.80°, 47.22°, 57.92°, 59.52°, 66.26°, 71.72°, 77.82°, and 79.32° are assigned to the crystal planes (001), (100), (101), (002), (102), (110), (201), (112), (202), (004), (104), and (203), respectively (08-0004, PDF 2 database).

Table S1 Crystal structures, space groups, lattice parameters, sizes, and morphologies of the CoTe, and NiTe$_2$.

Crystal structures	Space groups	Lattice parameters			d (nm) by SEM	Morphology
		a(Å)	b(Å)	c(Å)		
CoTe	P63/mmc(194)	3.893	3.893	5.375	500	octahedral
NiTe$_2$	P-3m1(164)	3.843	3.843	5.265	800	irregular plate

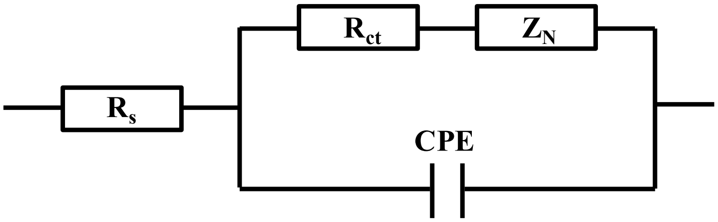

Fig.S1 Equivalent circuit model of the symmetrical cells. R_s, series resistance; R_{ct}, charge transfer resistance in the electrode/electrolyte interface; Z_N, Nernst diffusion impedance; CPE, corresponding capacitance in the electrode/electrolyte interface.

Reference

1 B.Wan, C. Hu, B. Feng, Y. Xi, X. He, *Materials Science and Engineering B*, 2009, **163**,57.

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