Electronic Supplementary Information

A bismuth-based ternary nanowires as an efficient electrocatalyst for dye sensitized solar cells

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Experimental Section

Chemicals. Oleylamine (OLA, 70%), oleic acid (OA, 90%), and Bis(trimethylsilyl) sulfide (TMS) were purchased from Sigma-Aldrich. Aluminum(III) acetylacetonate (Al(acac)_3, 99%), were obtained from J&K. Bismuth(III) Bromide (BiBr_3, 99%), Bismuth(III) Iodide (BiI_3, 99.999%), 1-Octadecene (ODE, 90%) were obtained from Alfa Aesar. Ethanol (99.7%), isopropanol (99.7%) and n-hexane (97%) were supplied by Sinopharm chemical Reagent Co., Ltd. OLA, OA and ODE were dried under vacuum at 120 °C for 10 h before use.

Synthesis of Bi_{19}S_{27}Br_3 (Bi-S-Br) NWs. In a typical synthesis, 97 mg (0.3 mmol) of Al(acac)_3 and 180 mg (0.4 mmol) of BiBr_3, 400 μL of OLA, 400 μL of OA, and 4.5 mL of ODE were first loaded into a flask of 50 mL capacity. The flask was degassed by a vacuum pump for 30 min to remove water and other low-boiling point impurities at 100 °C and then backfilled with argon. Afterwards, the temperature was subsequently increased to 180 °C, 158 μL TMS and 1 mL dried ODE solution were injected and maintained at this temperature for 30 min to finish the reaction. Subsequently, the solution was cooled down to 60 °C and then precipitated with 10 mL of isopropanol and centrifuged at 8000 rpm for 5 min. The upper solution was discarded and n-hexane was added to disperse the nanocrystals. Then the product was further purified by adding a certain amount of isopropanol and centrifuging. This process was repeated for three times to yield the nanocrystal product that could be dispersed in common organic solvents such as toluene. The obtained nanocrystals product was dispersed into 10 mL of n-hexane as stock solution for later use.

Synthesis of Bi_{19}S_{27}I_3 (Bi-S-I) NWs was carried out under otherwise identical conditions to Bi_{19}S_{27}Br_3 NWs, while using BiI_3 as Bi precursor.

Fabrication of photovoltaic devices

Sputtered Pt layer (~50 nm) on a FTO glass was used as the Pt CE in this study. Bi-S-Br CEs were prepared as follows: 3.5 mL of the above stock solution and carbon black (5 wt.%) were ultrasonically dispersed for 30 min, resulting in slurry, which was subsequently sprayed at 120 °C onto 8 piece (1.2 × 2 cm^2) of FTO substrates to form Bi-S-Br CE for DSSCs followed by sintering at 350 °C for 30 min under N_2 atmosphere.

The commercial TiO_2 photoanodes (Ying kou Opvtech New Energy Co., Ltd) were first annealed at 500 °C for 30 min. After being cooled to 70 °C, the TiO_2 photoanodes were immersed in a 0.5 mM ethanol solution of N719 dye (Solaronix SA, Switzerland) for 24 h. The TiO_2 photoanodes were assembled with various CEs to fabricated DSSCs. The dye-sensitized TiO_2 photoanode and the CE were separated by a hot-melt Surlyn film (60 μm thick) and sealed through hot-pressing. The redox electrolyte (0.1 M LiI, 0.05 M I_2, 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide, and 0.5 M 4-tert-butylpyridine in anhydrous acetonitrile) was injected into the interspace between the photoanode and CE. Finally, the holes on the back of the CE were sealed with a Surlyn film covered with a thin glass slide under heat. The as-assembled DSSCs with an active area of 0.16 cm^2 were used for photovoltaic performance tests. A dummy cell was assembled with two identical counter electrodes in a sandwich fashion containing the same electrolyte as used in the assembled DSSCs. The as-assembled symmetrical cell was used for the electrochemical impedance spectroscopy and Tafel polarization measurements.

Characterization

X-ray diffraction (XRD) analyses were performed on a Rigaku RINT D/Max- 2500 powder diffraction system using Cu Kα radiation source (λ = 1.541 Å) operating at 40 kV and 200 mA with a scanning rate of 5°/ min in the 20 range of 20-60° at a step size of 0.02 s. The TEM images showing the morphology of the NWs were obtained on a FEI TECNAI G^2 spirit microscope, operating at an accelerating voltage of 100 kV. HRTEM images were obtained with a FEI TECNAI F30 S-Twin (FEI company) with an accelerating voltage of 300 kV. Cyclic voltammetry (CV) for the I^-/I_3^- system was measured in an anhydrous acetonitrile solution consisting of 0.1 M LiClO_4, 10 mM LiI, and 1 mM I_2, and conducted over the potential range
from -0.25 V to 0.85 V at different scanning rates, using an electrochemical workstation (CHI760C, Chenhua, Shanghai) in a three-electrode electrochemical system. The resultant CEs acted as the working electrode, a Pt foil as the counter electrode, and a saturated calomel electrode as the reference electrode. The symmetrical dummy cells assembled with two identical CEs filled with the same electrolyte as used in the DSSCs were used for the electrochemical impedance spectroscopy (EIS) measurements and Tafel polarization tests. EIS experiments were carried out using an electro-chemical workstation (IM6 Zahner, Germany) at 0 V with a frequency range of 100 mHz ~1 MHz and a potential modulation of 20 mV under dark conditions. The resultant impedance spectra were analyzed with an appropriate equivalent circuit by means of Z-view software. The Tafel polarization curves were measured at a scanning rate of 10 mV s\(^{-1}\). Photovoltaic measurement was recorded with a Newport Oriel class AAA solar simulator (model 92250A-1000) equipped with a class A 300 W xenon light source powered by a Newport power supply (model 69907). The power output of the lamp was calibrated to 1 Sun (AM1.5G, 100 mW cm\(^{-2}\)) using a certified Si reference cell (SRC–1000–TC–QZ, VLSI standard, S/N 10510-0031). The current-voltage characteristics of each cell were recorded with a Keithley digital source meter (model 2400). Photovoltaic performance was measured using a metal mask displayed a square geography with the diameter of 3 mm.
**Table S1.** Electrochemical parameters of the dummy cells.

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<th>CEs</th>
<th>Rs (Ω cm$^2$)</th>
<th>Rct (Ω cm$^2$)</th>
<th>$Z_N$ (Ω cm$^2$)</th>
<th>Epp (mV)</th>
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**Table S2** Statistics of the photovoltaic parameters for DSSCs with different CEs.

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<th>Pt CE</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
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Fig. S1 EDAX spectra of bismuth based NWs: (a) Bi-S-Br, (b) Bi-S-I.
Fig. S2 XPS spectra of bismuth-based materials: (a) survey XPS spectrum of Bi-S-Br, (b) high-resolution spectra of Bi 4f and S 2p, (c) high-resolution spectrum of Br 3d, (d) survey XPS spectrum of Bi-S-I, (e) high-resolution spectra of Bi 4f and S 2p, and (f) high-resolution spectrum of I 3d.
Fig. S3 Calculated energetics for adsorption and desorption of I on Pt surface.

$E = -3.40 \text{ eV}$  \hspace{1cm}  $E = -0.10 \text{ eV}$
Fig. S4 The cyclic voltammograms of the Pt (a) and Bi-S-Br (b) electrode at different scanning rates.
Fig. S5 TEM image and XRD patterns of Bi-S-I NWs.

Fig. S6 The cyclic voltammograms of the Pt and Bi-S-I electrodes.
Fig. S7 Nyquist plots of EIS for the symmetrical cells with sputtered Pt and Bi-S-I electrodes.
Fig. S8 Tafel polarization curves of symmetrical cells with sputtered Pt and Bi-S-I electrodes.
Fig. S9 A total of 150 consecutive cyclic voltammograms for the I$_2$/$\text{I}^-_3$ system at a scanning rate of 50 mV s$^{-1}$ for (a) sputtered Pt, (b) Bi-S-Br CE, and (c) Bi-S-I CE.