Electronic Supplementary Material (ESI) for Nanoscale.

Metal (Co, Ni) Selenium Nanosheets on Metal Fibers as Counter Electrodes toward Low-cost, High-Performance Fiber-shaped Dye-sensitized Solar Cells

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Supporting Information

1 Experimental Section

(1) Fabrication of $Ni_{0.85}Se$ and $Co_{0.85}Se$ nanosheets

0.2 g of metal (Ni, Co) fiber (127 μm diameter) was ultrasonically cleaned with 10 wt% nitric acid aqueous solution several minutes and then in ethanol for 30 min. 0.2 g Se powder and 15 mL of hydrazine hydrate were added into a stainless Teflon-lined autoclave of 50 mL inner volume and stirred for 30 min. The cleaned metal (Ni, Co) fiber was soaked in the solution. The sealed autoclave would be placed into an electric oven at 150ºC for 5 h. After synthesis, the sealed autoclaves cool down to room temperature, naturally. The as-prepared fiber was taken out, washed with de-ionized water and ethanol several times.

(2) Solar cells fabrication

TiO_2 nanotube grew on Ti fiber (diameter of 250 μm) which was treated by electrochemical anodization in ethylene glycol mixed with NH_4F (0.2 wt%) and H_2O (1 wt%). This anodization was performed under constant voltage 60 V and temperature 25 ºC for 7~8 h in a two-electrode system. The anode and cathode electrodes are Ti fiber and carbon rod, respectively. TiO_2 nanotube was obtained though annealing the anodized Ti fiber at 450 ºC in air for 2 h (Figure S1). The resulting Ti fiber was heated at 70 ºC in 0.2M $TiCl_4$ solution for 30 min. Following, it was sintered at 450 ºC in air for 30 min. After that, the obtained Ti fiber cooled were soaked in 0.5 mM N719 dye solution (solvent mixture of acetonitrile and tert-butyl alcohol in volume ratio of 1:1) and kept for 24~48h at room temperature. Herein, the redox electrolyte is consist of 1.0 M 1–Butyl–3–methylimidazolium iodide (BMIMI), 50 mM LiI, 30 mM I_2 and 0.5 M tert–butylpyridine in a mixed solvent of acetonitrile and 85 valeronitrile (v/v, 85:15). Finally, the dye-sensitized Ti fiber coated with TiO_2 naotube and counter electrode (Ni-$Ni_{0.85}Se$, Co-$Co_{0.85}Se$ or Pt fiber) were inserted into a transparent

capillary filled with electrolyte in order to assemble into a fiber-shaped dye-sensitized solar cell (FDSSC). The effective active area of the cell is calculated by multiplying the diameter (0.03 cm) of photoanode and effective length (3 cm) of the cell. The active area of FDSSCs is about 0.09 cm^2.

2 Characterization

Field-emission scanning electron microscopy (FE-SEM) images were obtained on an S－4800 scanning electron microscopy operating at 5 kV. The transmission electron microscopy (TEM), High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) images were observed on a JEM 200CX TEM instrument. The crystallographic phase of the as-prepared products was determined by powder X-ray diffraction (XRD) (Rigaku Ultima III, Japan) using Cu-Ka radiation (λ=0.154178 nm) with scan rate of 100 min^{-1} at 40 kV and 40 mA. Photocurrent-Voltage (I–V) measurements were carried out, with the length FDSSC of 3 cm, on a Keithley 236 source measurement unit under AM 1.5 illumination cast by an Oriel 92251A-1000 sunlight simulator calibrated by the standard reference of a Newport 91150 silicon solar cell. Electrochemical impedance spectroscopic (EIS) curves of the symmetric cells fabricated with two identical electrodes (CE/electrolyte/CE) were observed by PAR2273 workstation (Princeton Applied Research, USA) with a 10 mV amplitude perturbation and the frequency range was from 100 mHz to 100 kHz. The cyclic voltammetry measurements (CV) are conducted in a three-electrode system at a scan rate of 50 $mV•S^{-1}$ by using PAR2273 workstation (Princeton Applied Research, USA). The counter and reference electrode are Pt and Ag/AgCl composite electrode, respectively. In CV testing, the I_3^-/I^- electrolyte contained 0.1 M $LiClO_4$, 10 mM LiI, and 1 mM I_2 in acetonitrile.

3 Figure

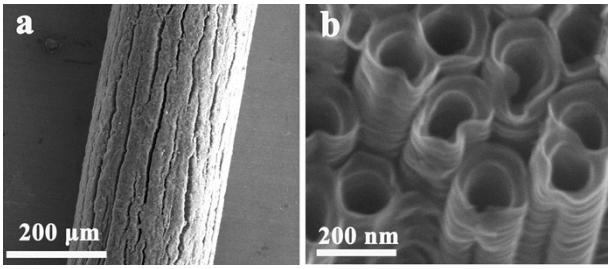

Figure S1. a) FE-SEM images of Ti fiber coating with TiO_2 nanotube, b) high magnification FE-SEM images of TiO_2 nanotube.

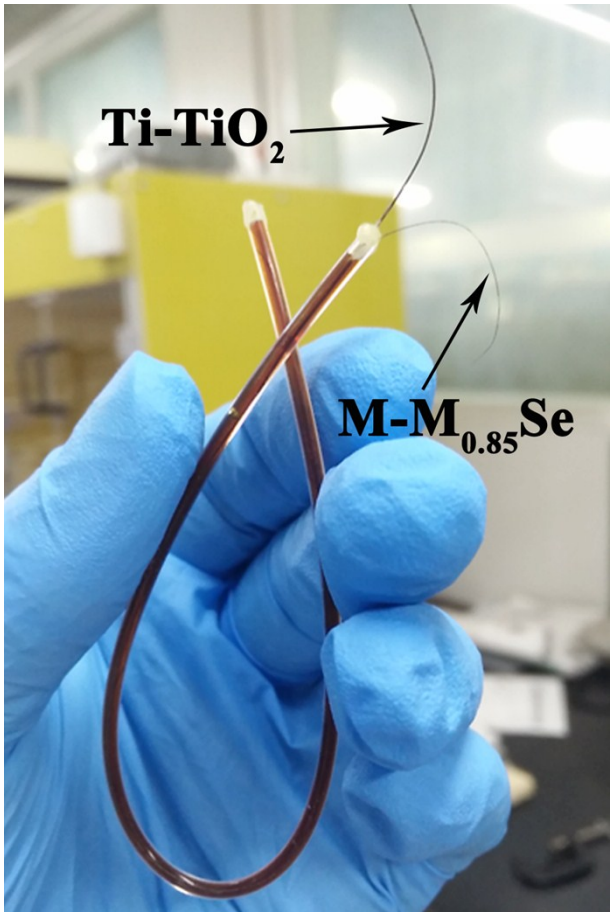

Figure S2. Photograph of FDSSC based on the $Ni_{0.85}Se$ CE.