Supporting Information

Design multifunctional Co and Fe co-doped MoS$_2$ nanocubes electrodes for dye-sensitized, perovskite solar cells, and supercapacitor

Chang Xu, Wenlu Yang, Jiaxin Zhao, Jingyuan Ma*, Mingxing Wu*

Hebei Key Laboratory of Inorganic Nanomaterials, College of Chemistry and Material Science, Hebei Normal University, No. 20 Rd. East of 2nd Ring South, Yuhua District, Shijiazhuang City, Hebei Province 050024, China. mingxing.wu@hebtu.edu.cn
E-mail: minxing.wu@hebtu.edu.cn; majingyuan@hebtu.edu.cn

Synthesis of Co-Fe PBA nanocubes

First, a certain amount of K$_3$[Fe(CN)$_6$] (2 mmol) was dissolved in deionized water (100 mL), achieving a uniform yellow solution A. Meanwhile, Co(NO$_3$)$_2$·6H$_2$O (3 mmol) and sodium citrate dihydrate (4.5 mmol) were dissolved in deionized water (100 mL), obtaining a red solution B. Next, the solution B was poured into solution A with vigorously stirring for 8 min. The resulted solution was aged for 24 h at room temperature, and the Co-Fe PBA nanocubes were collected by centrifugation and washed with deionized water and ethanol for several times.

Synthesis of (NH$_4$)$_2$Mo$_7$N$_6$O$_{24}$·4H$_2$O

H$_2$Mo$_7$N$_6$O$_{24}$·4H$_2$O (15 g) was dispersed into ammonia (10 mL) with stirring to form a suspension. Then, a certain amount of (NH$_4$)$_2$S aqueous solution (120 g, 20 wt%) was
added to the above suspension, which was heated at 60 °C for 2 h. The \((\text{NH}_4)_2\text{MoS}_4\) crystals can be collected under ice-bath.

**Synthesis of Co-Fe-MoS\(_x\) nanocubes**

Solid, core-shell, and hollow structured Co-Fe-MoS\(_x\) nanocubes were synthesized by solvothermal method using \((\text{NH}_4)_2\text{MoS}_4\) and Co-Fe PBA nanocubes as precursors with different mass ratios of 1:2, 1:1 and 2:1, and the generated products denoted as s-Co-Fe-MoS\(_x\), c-Co-Fe-MoS\(_x\), and h-Co-Fe-MoS\(_x\), respectively. The synthesis route is listed as following: A certain mount (50, 100, and 200 mg) of \((\text{NH}_4)_2\text{MoS}_4\) and Co-Fe PBA (100 mg) were dissolved in DMF (50 mL) with ultrasonic treatment for 15 minutes. Next, the solution was transferred into an autoclave and react at 200 °C for 20 h. After being centrifugated and washed with deionized water and ethanol for several minutes, the Co-Fe-MoS\(_x\) nanocubes were collected.

**Fabrications of dye-sensitized solar cells (DSCs)**

The Co-Fe-MoS\(_x\) electrodes are prepared as following: Add Co-Fe-MoS\(_x\) (100 mg) to isopropanol (5 mL), with ultrasonic dispersion for 30 min, resulting in Co-Fe-MoS\(_x\) suspension. Then, the prepared suspension was sprayed onto a FTO glass substrate, which sintered under N\(_2\) at 300 °C for 10 min and the Co-Fe-MoS\(_x\) electrodes were achieved. The photoanode was prepared as following: A precleaned FTO glass was immersed into an aqueous TiCl\(_4\) solution (40 mM) for 20 min, followed by washed with deionized water and sintered at 480 °C for 30 min, generating a blocking layer. A 5.0 µm thick TiO\(_2\) layer was coated on the TiO\(_2\) blocking layer, and sintered at 480 °C for
30 min to form a mesoporous TiO$_2$ film. The prepared TiO$_2$ film was preheated to 80 °C and immersed in a 2 x 10^{-4} M solution of YD2-o-C8 dye for 20 h, and the photoanode was achieved. The Co$^{3+/2+}$ electrolyte was comprised of 0.25 M Co (II) tris (bipyridyl) tetracyanoborate, 0.05 M Co (III) tris (bipyridyl) tetracyanoborate, 0.5 M TBP, and 0.1 M LiTFSI in acetonitrile. The DSCs was fabricated with a photoanode and a counter electrode sandwiching the cobalt electrolyte and the active surface of the DSCs were 0.16 cm$^2$. The dummy cell was assembled with two identical Co-Fe-MoS$_x$ electrodes sandwiching the electrolyte for specific EIS and Tafel polarization tests.

Fabrications of perovskite solar cells (PSCs)

The PSCs is fabricated as following: A compact TiO$_2$ layer is first coated on FTO glass by spin-coating the TiO$_2$ sol at 3000 rpm for 30 s, with sintered at 450 °C for 25 min. Then a mesoporous TiO$_2$ layer is coated by spin-costing a diluted TiO$_2$ paste at 5000 rpm for 25 s, with sintered at 500 °C for 30 min. The CH$_3$NH$_3$PbI$_3$ layer is prepared with a two-step sequential deposition method. Finally, the sulfide counter electrodes were deposited by doctor-blading sulfide paste on the perovskite layer with sintered at 80 °C for 30 min. The photovoltaic performance of PSCs was tested using a mask with active surface of 0.09 cm$^2$

Fabrications of supercapacitor electrode

The Co-Fe-MoS$_x$ electrode for supercapacitor was prepared by coating the Co-Fe-MoS$_x$ (80.0 wt%), acetylene black (10.0 wt%) and PTFE (10.0 wt%) onto a nickel foam. After drying in a vacuum oven at 80 °C for 10 h, the nickel foam coated with Co-Fe-MoS$_x$
nanocubes was pressed under a pressure of 10.0 MPa for 30 s and the electrode was obtained.

**Materials Characterizations**

The crystalline structures of the Co-Fe-MoS$_x$ samples were characterized by X-ray diffraction (XRD, D8 advance, Bruker) with scan rate of 5° min$^{-1}$ in the range of 10–80°. The surface chemical states of the samples were evaluated with an XPS spectrometer (ESCALAB250, Thermo VG). The morphologies were characterized by scanning Electron microscopy (SEM, S-4800, Hitachi) and transmission electron microscopy (TEM, H-7650, Hitachi). N$_2$ adsorption–desorption measurements were carried out isothermally at 77 K with an automated surface area analyzer (Antosorb-1, Quantachrome).

**Electrochemical Characterizations**

In this DSCs system, the CV measurements were carried out in a three-electrode system at a scan rate of 20 mV s$^{-1}$ using an electrochemical workstation system (CHI 660E, Chenhua). Pt wire acted as counter electrode and Ag/Ag$^+$ as the reference electrode. The Co$^{3+/2+}$ electrolyte is acetonitrile solution composed of 0.01 M Co$^{2+}$, 0.001 M Co$^{3+}$, and 0.1 M LiClO$_4$. The EIS measurements were conducted with dummy cell with an electrochemical workstation system (CHI 660E, Chenhua). The frequency is controlled ranged from 100 mHz to 1 MHz and the amplitude of the alternating current was 5 mV. Tafel polarization curve experiments were performed in a dummy cell with scan rate of 10 mV s$^{-1}$. The current density–voltage (J-V) curves of the DSCs and PSCs were tested.
under simulated AM 1.5 illumination ($I = 100\text{mWcm}^{-2}$, PEC-L01, Peccell, Yokohama, Japan). To evaluate the capacitive ability of the Co-Fe-MoS$_x$ electrodes, the CV and EIS measurements were carried out in neutral electrolyte of saturated Na$_2$SO$_4$ with a three-electrode system in which Pt foil worked as counter electrode oversized with respect to the working electrode, Hg/HgCl$_2$ as the reference electrodes. The EIS tested frequency was set at 100 kHz to 10 mHz and the amplitude of the alternating current was set at 5 mV. The galvanostatic charge-discharge and long-term cycle stability tests were carried out with a charge-discharge tester (CT2001A, LANHE, Wuhan, China).

Figure S1. SEM image of the prepared Co-Fe PBA.
Figure S2. EDS spectra of the prepared Co-Fe-MoS\textsubscript{x} nanocubes.

Figure S3. XPS spectra of the prepared Co-Fe-MoS\textsubscript{x} nanocubes.
Figure S4. XPS spectra of Fe 2p for the prepared Co-Fe-MoS\textsubscript{x} nanocubes.

Figure S5. XPS spectra of Co 2p for the prepared Co-Fe-MoS\textsubscript{x} nanocubes.
Figure S6. Nitrogen adsorption desorption curve and pore size distribution of the prepared s-Co-Fe-MoS$_x$.

Figure S7. Nitrogen adsorption desorption curve and pore size distribution of the prepared c-Co-Fe-MoS$_x$. 
Figure S8. Nitrogen adsorption desorption curve and pore size distribution of the prepared h-Co-Fe-MoS$_x$.

Figure S9. Cyclic voltammograms of the s-Co-Fe-MoS$_x$ in neutral electrolyte (saturated Na$_2$SO$_4$).
Figure S10. Cyclic voltammograms of the C-Co-Fe-MoS\textsubscript{x} in neutral electrolyte (saturated Na\textsubscript{2}SO\textsubscript{4}).

Figure S11. Cyclic voltammograms of the H-Co-Fe-MoS\textsubscript{x} in neutral electrolyte (saturated Na\textsubscript{2}SO\textsubscript{4}).
Figure S12. GCD curves of the s-Co-Fe-MoS$_x$ in neutral electrolyte (saturated Na$_2$SO$_4$).

Figure S13. GCD curves of the c-Co-Fe-MoS$_x$ in neutral electrolyte (saturated Na$_2$SO$_4$).
Figure S14. GCD curves of the h-Co-Fe-MoS$_x$ in neutral electrolyte (saturated Na$_2$SO$_4$).