Low-Cost and High-Performance CoMoS₄ and NiMoS₄ Counter Electrodes for Dye-Sensitized Solar Cells

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Experimental details

Synthesis of CoMoS₄, NiMoS₄, CoMoS₄-C, NiMoS₄-C:

Ammonium thiomonomolybdate $(NH_4)_2MoS_4$ was obtained by the reaction of $(NH_4)_6Mo_7O_{24}$ • $4H_2O$ and $(NH_4)_2S$ aqueous solution at ambient temperature. The product was stored in an N₂ atmosphere glove box. An amount of 2.5 mmol (0.73 g) of Co(NO₃)₂ $6H_2O$ (Sigma–Aldrich, 99.9%) was dissolved in 20 mL of formamide. Ammonium tetrathiomolybdate (2.5 mmol, 0.61 g) was dissolved in 20 mL of formamide. The Co precursor solution was added into the tetrathiomolybdate solution and kept undisturbed for 7 days and rigid black chalcogel was obtained. ¹ The remaining formamide was decanted and the rigid gel was rinsed with ethanol/ H₂O (4:1) solution, ethanol and isopropanol three times for each to remove byproducts and impurities. CoMoS₄-C was synthesized in the similar way except 6mg graphite was added in the Co precursor before it mixed with the etrathiomolybdate solution. The NiMoS₄ and NiMoS₄-C were obtained in similar way.

Preparation of CEs:

The resultant CoMoS₄, NiMoS₄, CoMoS₄-C or NiMoS₄-C was suspended in isopropanol with zirconium dioxide pearl and milled with a star ball mill (QM-QX04, Nanjing NanDa Instrument Plant) for 4 h. Then the slurry was sprayed onto FTO glass (14 Ω sq⁻¹, Nippon Sheet Glass, Japan) with an air brush connected to a minicompressor. Before assembled in DSSCs, the obtained film was annealed under N₂ atmosphere at 300 °C for 30 min in a tube furnace to form the expected CoMoS₄, NiMoS₄, CoMoS₄-C and NiMoS₄-C CEs. Sputtered Pt layer (100 nm) on a FTO glass substrate was used as a Pt CE in this study.

Assembly of DSSCs:

The 12 µm thick TiO₂ film (P25, Degussa, Germany) on FTO glass substrate was prepared by the screen-printing technique. Then the resultant TiO₂ film was soaked in a 5×10^{-4} M of N719 dye (Solaronix SA, Switzerland) in acetonitrile/tert-butyl alcohol (1:1 volume ration) for 21 h after sintered at 500 $^{\circ}$ C for 30 min. The TiO₂ photoanodes were assembled with various CEs to fabricated DSSCs. The redox electrolyte (contains 0.06 LiI, 0.6 Μ Μ 1-butyl-3-methylimidazolium iodide, 0.03 M I₂, 0.5 M 4-tert-butyl pyridine, and 0.1 M guanidinium thiocyanate in acetonitrile solution) was injected into the cell. The as-assembled DSSCs with an active area of 0.16 cm² were used for photovoltaic performance tests. A dummy cell was assembled with two identical CoMoS₄, NiMoS₄, CoMoS₄-C, NiMoS₄-C or Pt 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 measurement.

Characterization and measurements:

Scanning electron microscopy (SEM) images were obtained from FEI Quanta 200F microscope operated at an accelerating voltage of 20 kV. Elemental analysis of the electrodes were conducted using an energy dispersive X-ray spectroscopy (EDS) analyzer (QUANTA 200FEG) attached to the FEI Quanta 200F SEM microscope. High resolution (HR) TEM were carried out with a FEI TECNAI F30 microscope operating at 300 kV. X-ray diffraction (XRD) analyses were performed at a scanning rate of 2 %min on a Rigaku RINT D/Max-2500 powder diffraction system using Cu K α radiation source ($\lambda = 1.54$ Å) operating at 40 kV and 200 mA.

Cyclic voltammetry (CV) for the Γ/I_3^- system was measured in an anhydrous acetonitrile solution consisting of 0.1 M LiClO₄, 10 mM LiI, and 1 mM I₂, and conducted over the potential range from -0.2 V to 0.8 V at a scan rate of 50 mV s⁻¹, using a 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.

Symmetric dummy cells were used for the electrochemical impedance spectroscopy (EIS) measurements and Tafel polarization tests. The electrochemical impedance spectroscopy measurements were conducted using a computer-controlled electrochemical workstation (Zennium Zahner, Germany) under dark conditions. The measured frequency ranged from 100 mHz to 1 MHz with a bias potential of -0.75 V, and the 10 mV of AC amplitude. The resultant impedance spectra were analyzed with an appropriate equivalent circuit by means of Z-view software. The Tafel polarization curves were measured using an electrochemical workstation (CHI630D, Chenhua, Shanghai) at a scan rate of 10 mVs⁻¹.

The photovoltaic performance of the DSSCs was evaluated with a Keithley digital source meter (Keithley 2601, USA) under simulated sunlight illumination conditions (Xe arc lamp, AM1.5G, 100 mW/cm², PEC-L15, Peccell, Japan).



Figure S1. X-ray diffraction patterns of the CoMoS₄, NiMoS₄, CoMoS₄-C and NiMoS₄-C.

The reflectance at 26.6° is attributed to graphite (JCPDS No. 26-1079).



Figure S2. The Raman spectrum of graphite, CoMoS₄-C and NiMoS₄-C.

Two prominent signals at around 1348 and 1580 cm⁻¹ correspond to the typical D and G modes of graphite, respectively[2]. The G mode revealed by Raman measurement indicates the existence of graphite in the composites. The disappearance of the D mode could be attributed to the low content of graphite in the composite.



Figure S3. SEM images for CoMoS₄, NiMoS₄, CoMoS₄-C and NiMoS₄-C.



Figure S4. The EIS data of the symmetrical cells based on graphite counter electrode.



Figure S5. The J–V characteristics of DSSCs with graphite counter electrode without the addition of CoMoS4 or NiMoS4.

Table S1. Energy dispersive X-ray spectroscopy (EDS) analysis of the element composition for

the CoMoS₄

Element	Со	Мо	S		
Wt%	21.16	34.72	44.12		
At%	17.13	17.25	65.62		

Table S2. Energy dispersive X-ray spectroscopy (EDS) analysis of the element composition for

the NiMoS₄

Element	Ni	Мо	S		
Wt%	20.69	33.65	45.66		
At%	16.57	16.49	66.94		

Sample	Ep _o (mV)	Ep _r (mV)	ip _o (mA cm ⁻²)	ip _r (mA cm ⁻²)	$\Delta \mathbf{E} \ (\mathbf{mV})$
Pt	235	120	2.219	-2.124	115
CoMoS ₄	240	100	1.509	-1.555	140
NiMoS4	220	110	1.575	-1.687	110
CoMoS ₄ -C	205	135	1.646	-1.785	70
NiMoS ₄ -C	206	130	1.654	-1.760	76

Table	S3 .	Electrochemical	performance	parameters	for	cyclic	voltammograms	of	I^{-}/I_{3}^{-}	redox
couple	with	n different CEs.								

References:

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