Supporting information

Morphological and Electronic Modulation of NiSe Nanosheets Assemblies by Mo, S-codoping for Efficient Hydrogen Evolution Reaction

Shan Zhang,^{ab} Xiaoyan Zhang,^{ab} Jing Li*^a and Erkang Wang*^a

a. State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin, 130022, P. R. China. *E-mail: lijingce@ciac.ac.cn, ekwang@ciac.ac.cn; Tel: +86-431-85262003

b. University of Science and Technology of China, Hefei, Anhui, 230029,P. R. China.

Experimental section

Reagents: Sulfur (S) powder and ammonium molybdate tetrahydrate $((NH_4)_6Mo_7O_{24}\cdot 4H_2O)$ were purchased from Xilong Scientific Co., Ltd. (Guangdong, China). Selenium (Se) powder was taken from Sigma-Aldrich (USA). Hydrazine hydrate (80%) was taken from Yongsheng Fine Chemicals Co., Ltd. (Tianjin, China). Ethanol was obtained from the Beijing Chemical Works (China) and water underwent purification process by Millipore system (Bedford, MA, USA).

Preparation of Mo, S-codoped NiSe/NF-T materials: In a typical experiment, 0.01 g Se powder and 0.0041 g S powder (molar ratio of S : Se labeled as X was 1 : 1) were dissolved in 5 mL hydrazine hydrate under stirring, then aged for at least 10 h to prepare the solution A. 0.0112 g (NH₄)₆Mo₇O₂₄·4H₂O was carefully dissolved in 30 mL mixed solvent of water and ethanol (volume ratio 1:1) to obtain the homogeneous

solution B. Afterwards, the pre-treated nickel foam (NF, 2×2 cm²) was immersed in

the solution B and kept stirring for 10 min. Subsequently, solution A was added dropwisely to solution B containing NF. After reaction 30 min, the mixture was transferred to a 50 mL Teflon-lined autoclave and kept at various temperatures (140-

200 $^\circ$ C) for 12 h. Then, the product was cooled down naturally, sonicated in water and

ethanol for several minutes, and dried under vacuum at 60 °C. For comparison,

similar procedure was carried out when S/Se powder or $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was missed to prepare ternary products, that was Ni-Mo-S/NF-160 NSs, Ni-Mo-Se/NF-160 NSs and Ni-S-Se/NF-160 NRs, respectively. Finally, if the reaction was conducted in the absence of NF, only Mo-S-Se-160 NPs could be obtained. Note that the molar ratio of Mo : S remained 1 : 2 during all the fabrication process. Additionally, to examine the influence of weight percentages of Mo and S on the performance of HER, products with various molar ratios of S : Se (more or less than 1)

was prepared at the reaction temperature of 160 °C. Moreover, the actual weight

percentage of S/Mo was obtained by XPS and summarized in Table S1. For clarity, we still took X as representative in our report.

Characterizations: Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) measurements were carried out on JEM-2100F high-resolution transmission electron microscope (200 kV, Netherlands). Scanning electron microscope (SEM) images and X-ray (EDX) spectra were obtained by an XL30 ESEM FEG SEM operated at 20 kV (Philips, Netherlands). The XRD pattern was measured on D8 ADVANCE (Bruker, Germany) with Cu K α X-ray radiation (λ = 0.15406 nm). The XPS patterns were recorded on an ESCALAB-MKII 250 photoelectron spectrometer (VG Co. UK) with Al K α radiation.

Electrochemical measurements: Electrochemical measurements were conducted in a three-electrode system on an electrochemical workstation (CHI660E, Shanghai, China), with a graphite rod and Ag/AgCl electrode used as the counter electrode and the reference electrode, respectively. Before use, Ag/AgCl electrode was calibrated to a reversible hydrogen electrode (RHE) in 1 M KOH saturated with high purity hydrogen using Pt wire as both working electrode and counter electrode. Cyclic voltammetry (CV) was conducted between -1.2 and -0.8 V with a scan rate of 2 mV/s, and the data was recorded as Figure S1. The average potential at which the current crossed zero was considered as the thermodynamic potential needed for the hydrogen electrode reactions. In 1 M KOH, E (RHE) = E (Ag/AgCl) + 0.954 V. Linear sweep voltammetry (LSV) was carried out in nitrogen saturated electrolyte (1 M KOH) with a scan rate of 5 mV/s, and a flow of nitrogen was maintained during the testing process. AC impedance was measured over a frequency range from 100 kHz to 0.01 Hz at overpotential of 0 mV. The chronoamperometric response was recorded as a function of time under the overpotential of 108 mV vs. RHE. Catalysts loaded NF

were cut into 0.5×2 cm² before serving as working electrodes. For measurements on

bare NF and glass carbon (GC) electrode, the working electrodes with the same loading (0.002 g cm⁻²) were prepared by dropping the ethanol/water/Nafion dispersion of Mo-S-Se-160 NPs on either electrode and dried naturally. To estimate electrical double-layer capacitance (C_{dl}), CV tests were performed in the 0.1-0.2 V vs. RHE region with various scan rates (20, 40, 60 mV/s, etc.). The C_{dl} was evaluated by fitting curves of the ΔJ (Ja-Jc) at 0.15 V (vs. RHE) against the scan rate, and the slope was twice C_{dl}. All the potentials reported here were against RHE, and all currents were iR-corrected.



Figure S1. Cyclic voltammogram of Pt wire in 1 M KOH.



Figure S2. EDX spectrum of the Mo, S-codoped NiSe/NF-160 NSs and the corresponding element ratio of Ni and Se.



Figure S3. SEM image and the corresponding element mapping of the Mo, S-codoped NiSe/NF-160 NSs in larger size.



Figure S4. Low-magnification (A), (B), (C) and high-magnification (D) SEM images of product when the reaction was conducted at the temperature of 140 $^{\circ}$ C.



Figure S5. Low-magnification (A), (B) and high-magnification (C), (D) SEM images of product when the reaction was conducted at the temperature of 180 $^{\circ}$ C.



Figure S6. Low-magnification (A), (B), (C) and high-magnification (D) SEM images of product when the reaction was conducted at the temperature of 200 $^{\circ}$ C.



Figure S7. SEM images of (A), (B) Ni-Mo-S/NF-160 NSs; (C), (D) Ni-Mo-Se/NF-160 NSs and (E), (F) Ni-S-Se/NF-160 NRs.



Figure S8. (A) The typical SEM image of as-prepared Ni-Mo-S/NF-160 NSs. Insert: the corresponding element mapping. Scale bar: 1 μ m. (B) EDX spectrum of the obtained Ni-Mo-S/NF-160 NSs.



Figure S9. (A) The representative SEM image of as-prepared Ni-Mo-Se/NF-160 NSs. Insert: the corresponding element mapping. Scale bar: 1 μ m. (B) EDX spectrum of the obtained Ni-Mo-Se/NF-160 NSs.



Figure S10. (A) The typical SEM image of as-prepared Ni-S-Se/NF-160 NRs. Insert: the corresponding element mapping. Scale bar: 2.5 μ m. (B) EDX spectrum of the obtained Ni-S-Se/NF-160 NRs.



Figure S11. TEM and SEM images of Mo-S-Se-160 NPs.



Figure S12. (A) The typical SEM image of as-prepared Mo-S-Se-160 NPs. Insert: the corresponding element mapping. Scale bar: 500 nm. (B) EDX spectrum of the obtained Mo-S-Se-160 NPs.



Figure S13. (A) Polarization curves of the as-prepared Ni-S-Se/NF-160 NRs; Mo, S-codoped NiSe/NF-160 NSs; Ni-Mo-S/NF-160 NSs and Ni-Mo-Se/NF-160 NSs and (B) the corresponding Tafel plots.



Figure S14. Polarization curves of products with various molar ratio of S : Se (X) in the reactants with the reaction temperature of 160 $^{\circ}$ C, note that the target material (Mo, S-codoped NiSe/NF-160 NSs) was produced when X = 1.



Figure S15. Polarization curves of Mo-S-Se-160 NPs loaded on the GC electrode and bare NF with the same loading weight (0.002 g cm⁻²) as the prepared Mo, S-codoped NiSe/NF-160 NSs.



Figure S16. Cyclic voltammetry curves of the Mo, S-codoped NiSe/NF-T catalysts in the 0.1-0.2 V vs. RHE region.



Figure S17. The differences in current density variation ($\Delta J=Ja-Jc$) at an overpotential of 0.15 V vs. RHE plotted against scan rate fitted to a linear regression allowed for the estimation of C_{dl}. Ja and Jc meant the current density of anode and cathode at an overpotential of 0.15 V vs. RHE, respectively.



Figure S18. Cyclic voltammetry curves of the (A) Ni-Mo-S/NF-160 NSs; (B) Ni-Mo-Se/NF-160 NSs and (C) Ni-S-Se/NF-160 NRs in the 0.1-0.2 V vs. RHE region. (D) The differences in current density variation (ΔJ =Ja-Jc) at an overpotential of 0.15 V vs. RHE plotted against scan rate fitted to a linear regression allowed for the estimation of C_{dl}. Ja and Jc meant the current density of anode and cathode at an overpotential of 0.15 V vs. RHE, respectively.



Figure S19. EIS Nyquist plots of the as-prepared Ni-Mo-S/NF-160 NSs; Ni-Mo-Se/NF-160 NSs and Ni-S-Se/NF-160 NRs.



Figure S20. Randle equivalent circuit applied to model the process of HER on the studied system.



Figure S21. Polarization curves of Mo, S-codoped NiSe/NF-160 NSs before and after 1000 and 2000 CV cycles.



Figure S22. (A) SEM and (B) TEM images of Mo, S-codoped NiSe/NF-160 NSs after 12 h chronoamperometric measurement.



Figure S23. XPS patterns of Mo, S-codoped NiSe/NF-160 NSs before and after 12 h chronoamperometric measurement: (A) Ni 2p; (B) Se 3d; (C) Mo 3d and (D) S 2p.

Table S1. Weight percentages of Mo and S (At. %) obtained by XPS spectra.

	Мо	S
X = 0.5	0.07	0.29
X = 1	1.26	0.37
X = 2	1.78	0.31
X = 3	3.05	0.63
X = 4	7.32	0.99

	Ni	Мо	S	Se
Ni-Mo-S/NF-160 NSs	71.35	3.10	25.56	-
Ni-Mo-Se/NF-160 NSs	61.81	2.64	-	35.55
Ni-S-Se/NF-160 NRs	63.61	-	27.94	8.44
Mo-S-Se-160 NPs	-	30.54	30.04	39.42

Table S2. Element atomic ratio of Ni-Mo-S/NF-160 NSs; Ni-Mo-Se/NF-160 NSs; Ni-S-Se/NF-160 NRs and Mo-S-Se-160 NPs obtained by EDX spectra.

Table S3. Comparison of the HER performance of various catalysts in 1 M KOH.¹⁻¹⁰

Catalysts	η1 (mV)	η ₁₀ (mV)	Tafel Slope (mV dec ⁻¹)	reference
Mo, S-codoped NiSe/NF-160 NSs	60	88	82	This work
Ni ₃ Se ₄	N.A.	203	156	1
Co-Ni-Se/C/NF	N.A.	90	81	2
NiSe ₂ NSs	N.A.	184	77	3
NiSe ₂ NCs	N.A.	540	139	4
NF-Ni ₃ Se ₂ /Ni	97	203	79	5
NiSe/NF	N.A.	96	120	6
Chevrel-phase NiMo ₃ S ₄	59	257	98	7
Ni ₃ Se ₂ /CF	N.A.	100	98	8
nickel oxysulfide nanospheres	50	140	81.63	9
MoC _x	92	151	59	10

Table S4. ICP-OES results of electrolyte after stability measurement.

Elements	Ni	Se	Mo	S
Concentration /ppm	0	6.264	1.496	43.48

References

- 1. S. Anantharaj, J. Kennedy and S. Kundu, ACS Appl. Mater. Interfaces, 2017, 9, 8714-8728.
- 2. F. Ming, H. Liang, H. Shi, X. Xu, G. Mei and Z. Wang, J. Mater. Chem. A, 2016, 4, 15148-15155.
- H. Liang, L. Li, F. Meng, L. Dang, J. Zhuo, A. Forticaux, Z. Wang and S. Jin, *Chem. Mater.*, 2015, 27, 5702-5711.
- 4. I. H. Kwak, H. S. Im, D. M. Jang, Y. W. Kim, K. Park, Y. R. Lim, E. H. Cha and J. Park, *ACS Appl. Mater. Interfaces*, 2016, **8**, 5327-5334.
- 5. R. Xu, R. Wu, Y. Shi, J. Zhang and B. Zhang, *Nano Energy*, 2016, **24**, 103-110.
- 6. C. Tang, N. Cheng, Z. Pu, W. Xing and X. Sun, *Angew. Chem., Int. Ed.*, 2015, **54**, 9351-9355.
- 7. J. Jiang, M. Gao, W. Sheng and Y. Yan, *Angew. Chem., Int. Ed.*, 2016, **55**, 15240-15245.
- 8. J. Shi, J. Hu, Y. Luo, X. Sun and A. M. Asiri, *Catal. Sci. Technol.*, 2015, **5**, 4954-4958.
- 9. J. Liu, Y. Yang, B. Ni, H. Li and X. Wang, *Small*, 2017, **13**, DOI: 10.1002/smll.201602637.
- H. B. Wu, B. Y. Xia, L. Yu, X. Y. Yu and X. W. Lou, *Nat. Commun.*, 2015, 6, DOI: 10.1038/ncomms7512.