

Supporting Information for (c8ta11072g)

An Fe-doped nickel selenide nanorod/nanosheet hierarchical array for efficient overall water splitting

Zexian Zou,[‡] Xiangyu Wang,[‡] Jiansong Huang, Zhengcui Wu* and Feng Gao*

Anhui Laboratory of Molecule-Based Materials (State Key Laboratory Cultivation Base), The Key Laboratory of Functional Molecular Solids, Ministry of Education, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241002, P. R. China.

[‡] These authors contributed equally to this work.

*Corresponding author. E-mail: zhengcui@mail.ahnu.edu.cn; fgao@mail.ahnu.edu.cn.

Tel.: +86 553 3869302; Fax: +86 553 3869302.

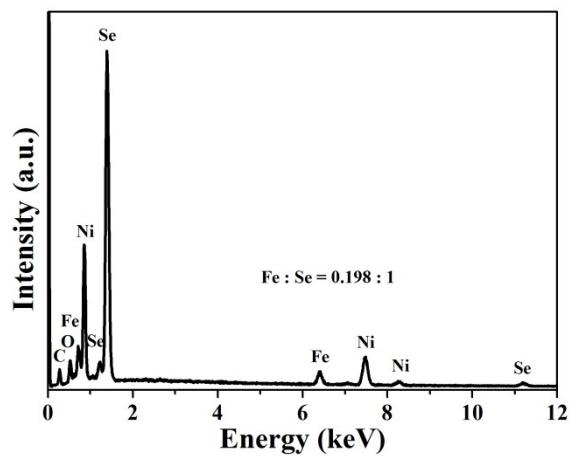


Fig. S1 The EDX result of $\text{Fe}_{7.4\%}\text{-NiSe}$.

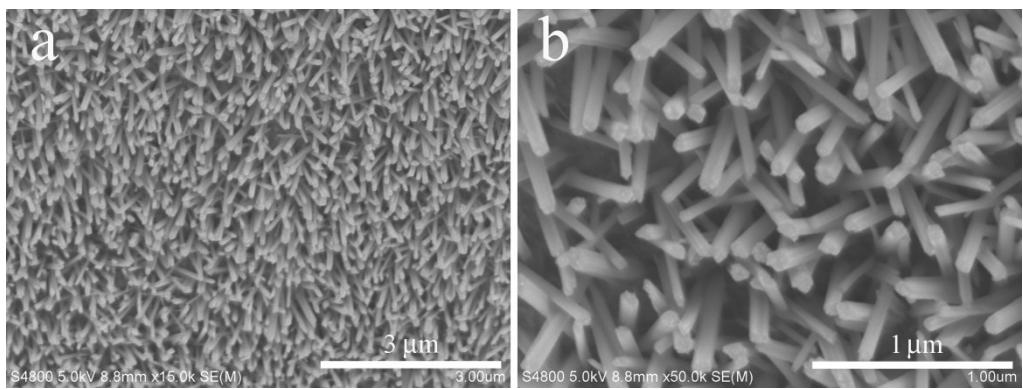


Fig. S2 The SEM images of NiSe nanorods array.

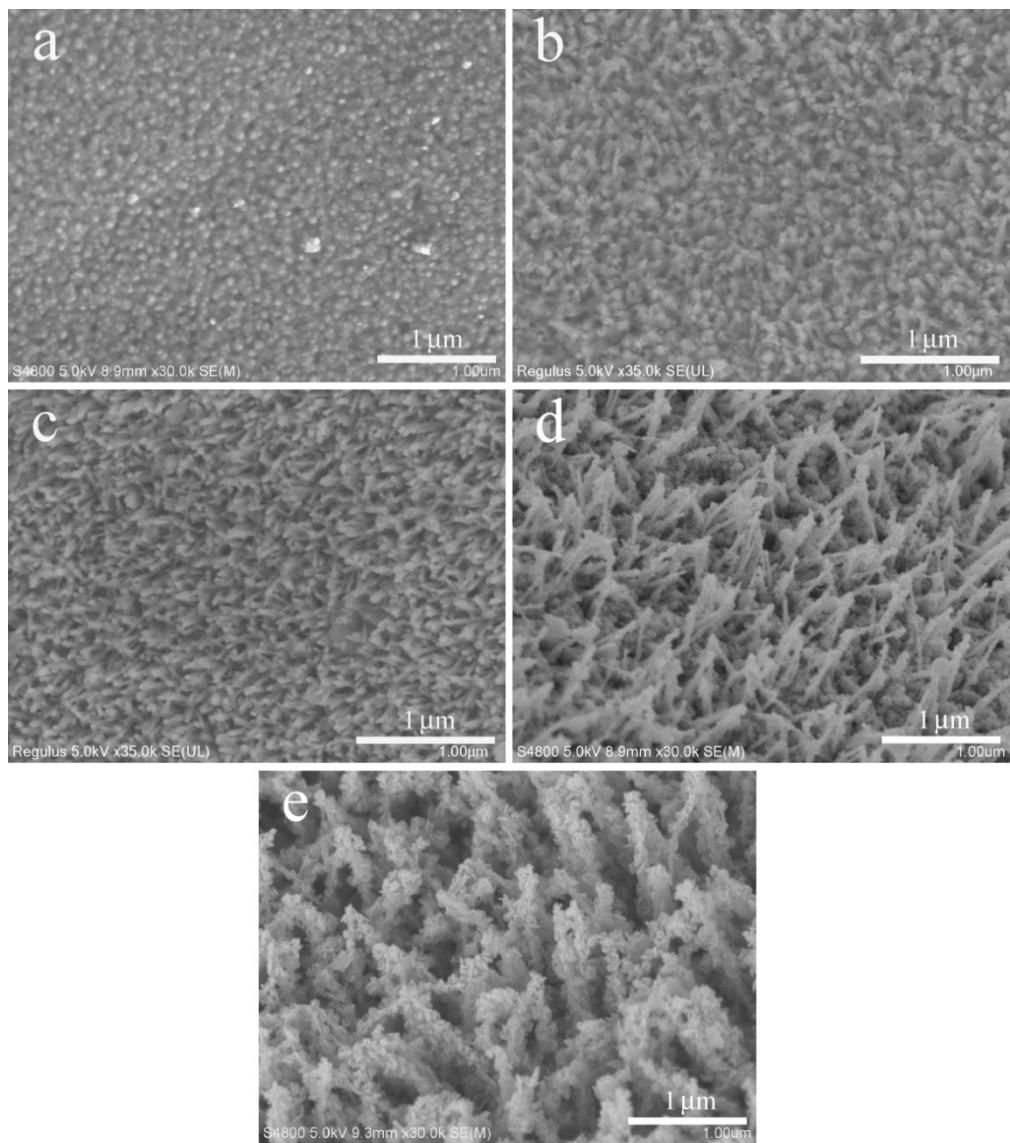


Fig. S3 Time resolved experiments of $\text{Fe}_{7.4\%}\text{-NiSe}$ nanorod/nanosheet hierarchical array. (a) 0.5 h. (b) 1 h. (c) 2 h. (d) 3 h. (e) 8h.

Table S1 The comparison of OER activity of Fe_{7.4%}-NiSe with some representative Ni-based selenide catalysts.

Catalyst	Electrolyte	Loading (mg cm ⁻²)	η (mV) @j (mA cm ⁻²)	Tafel Slope (mV dec ⁻¹)	Electrode	Reference
Fe-doped NiSe/Ni ₃ Se ₂ nanorods	1 M KOH	3.0	290@60	61	Ni foam	¹
Porous (Ni _{0.75} Fe _{0.25})Se ₂ nanosheets	1 M KOH	~1.5	255@35	47.2	Carbon fiber cloth	²
Rose-like Ni _{0.76} Fe _{0.24} Se	1 M KOH	6.6	197@10, 294@200	56	Ni foam	³
NiSe@NiOOH	1 M KOH	-	332@50	162	Ni foam	⁴
Urchin-like Ni _{1.12} Fe _{0.49} Se ₂	1 M KOH	0.45	227@10	37.9	Glassy Carbon	⁵
Ni ₃ Se ₂	0.1 M KOH	0.2	470@1.32	46	Glassy Carbon	⁶
NiSe nanowire	1 M KOH	-	400@35	54	Ni foam	⁷
Ni ₃ Se ₂ film	0.3 M KOH	-	~270@10	142.8	Ni foam	⁸
Ni ₃ Se ₂ nanoforest	1 M KOH	8.87	242@20, 353@100	144	Ni foam	⁹
NiSe nanowire film	1 M KOH	2.8	270@20	64	Ni foam	¹⁰
NiSe–NiO _x	1 M KOH	4.25	243@10	128	Ni foam	¹¹
Co-doped nickel selenide/C	1 M KOH	-	275@30, 300@50	63	Ni foam	¹²
Fe _{7.4%} -NiSe	1 M KOH	3.1	231@50, 254@200	43.0	Ni foam	This work

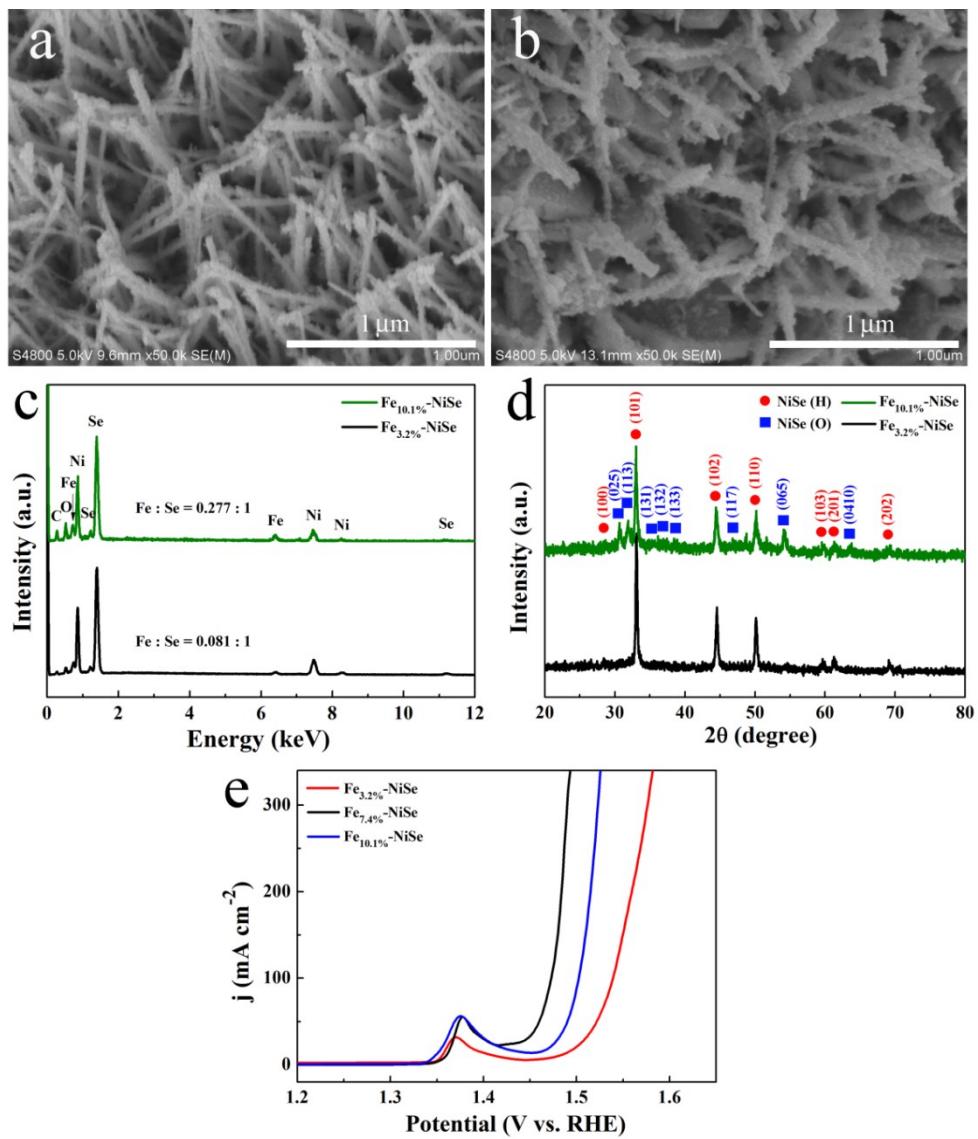


Fig. S4 (a, b) The SEM images of the Fe-doped NiSe products with Fe content of 3.2% and 10.1%, respectively.

(c, d) The EDX spectra and the XRD patterns of the Fe-doped NiSe products with Fe content of 3.2% and 10.1%, respectively. (e) The OER polarization curves of the Fe-doped NiSe products with different Fe content.

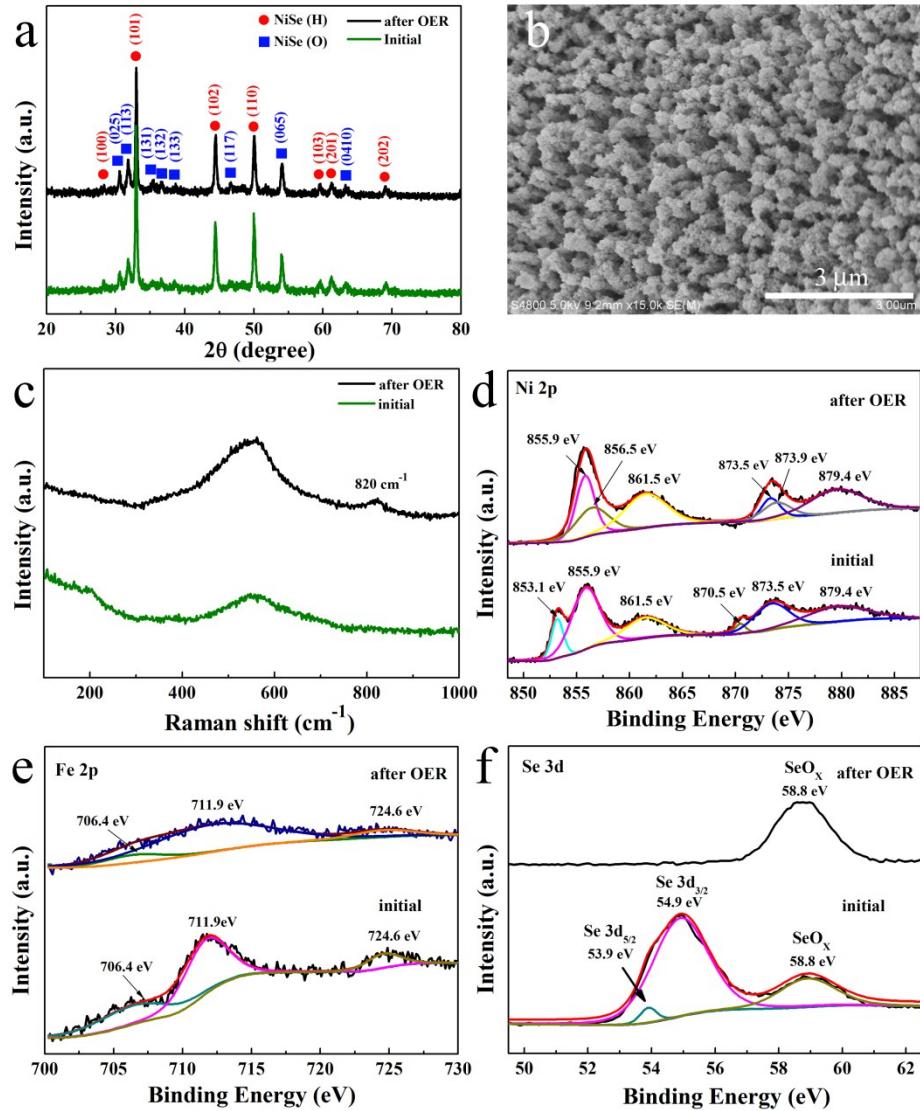


Fig. S5 The XRD pattern (a), the SEM image (b), the Raman spectrum (c), the XPS spectra of Ni 2p (d), Fe 2p (e), and Se 3d (f) of Fe_{7.4%}-NiSe after 22 h OER chronopotentiometry test at an overpotential of 217 mV.

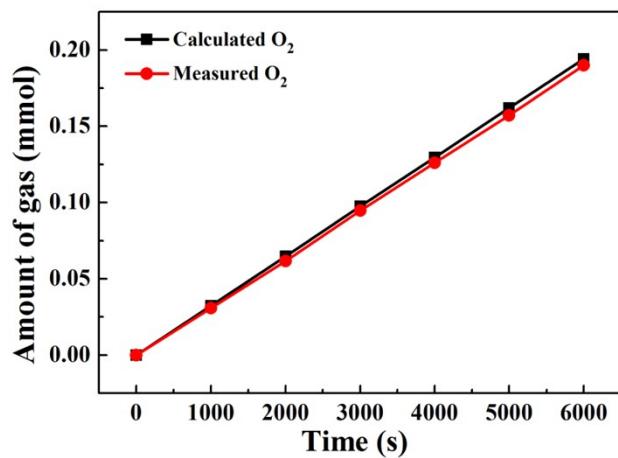


Fig. S6 The electrocatalytic efficiency of Fe_{7.4%}-NiSe for OER at 50 mA cm⁻².

Table S2 The comparison of HER activity of Fe_{7.4%}-NiSe with some representative Ni-based selenide catalysts.

Catalyst	Electrolyte	Loading (mg cm ⁻²)	η (mV) @j(mA cm ⁻²)	Tafel Slope (mV dec ⁻¹)	Electrode	Reference
Fe-doped NiSe/Ni ₃ Se ₂ nanorods	1 M KOH	3.0	140@10	-	Ni foam	¹
Ni ₃ Se ₂ nanoforest	1 M KOH	8.87	203@10, 279@100	79	Ni foam	⁹
NiSe Nanowire film	1 M KOH	2.8	96@10	120	Ni foam	¹⁰
CoNi ₂ Se ₄ nanoflake film	1 M KOH	4.7	220@10	-	Carbon fiber Paper	¹³
Porous NiSe ₂ nanosheets	1 M KOH	~ 0.46	184@10	76.6	Ni foam	¹⁴
NiSe ₂ nanocrystals	1 M KOH	1	540@10	139	Rotating disk electrode	¹⁵
Cactuslike Ni ₃ Se ₄	1 M KOH	2.45	206@50	156	Ni foam	¹⁶
MoSe ₂ –NiSe	0.5 M H ₂ SO ₄	~ 0.285	210@10	56	glassy carbon electrode	¹⁷
Fe _{7.4%} -NiSe	1 M KOH	3.1	163@10, 265@100	71.4	Ni foam	This work

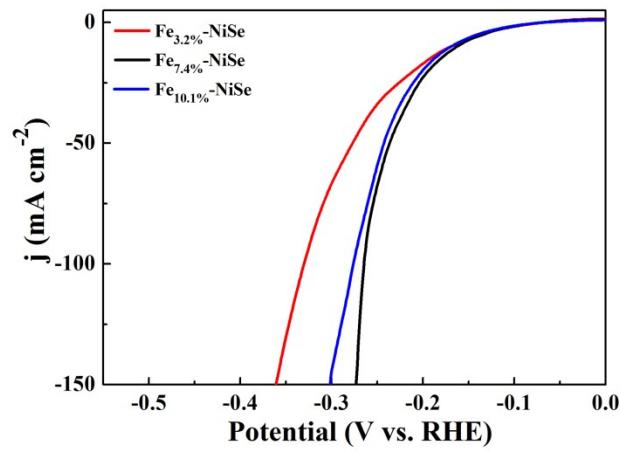


Fig. S7 The HER polarization curves of the Fe-doped NiSe products with different Fe content.

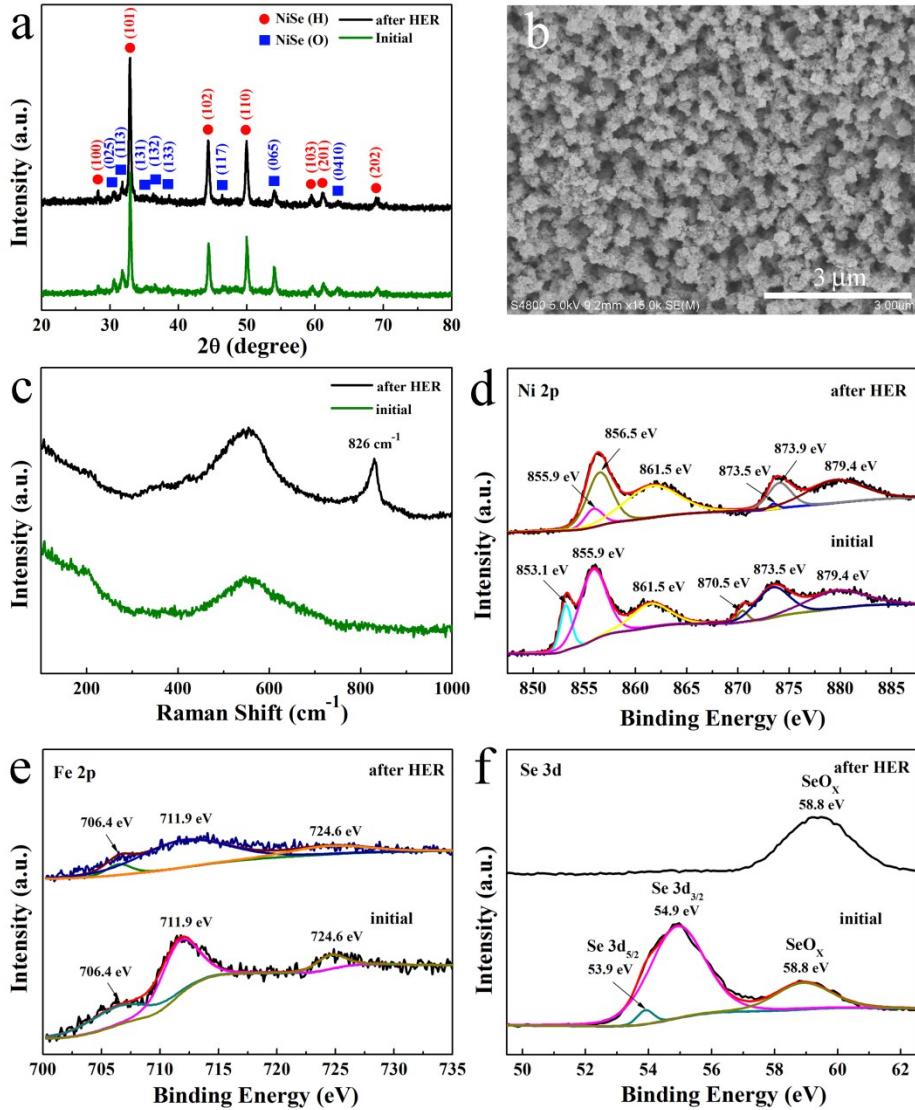


Fig. S8 The XRD pattern (a), the SEM image (b), the Raman spectrum (c), the XPS spectra of Ni 2p (d), Fe 2p (e) and Se 3d (f) of Fe_{7.4%}-NiSe after 22 h HER chronopotentiometry test at an overpotential of 195 mV.

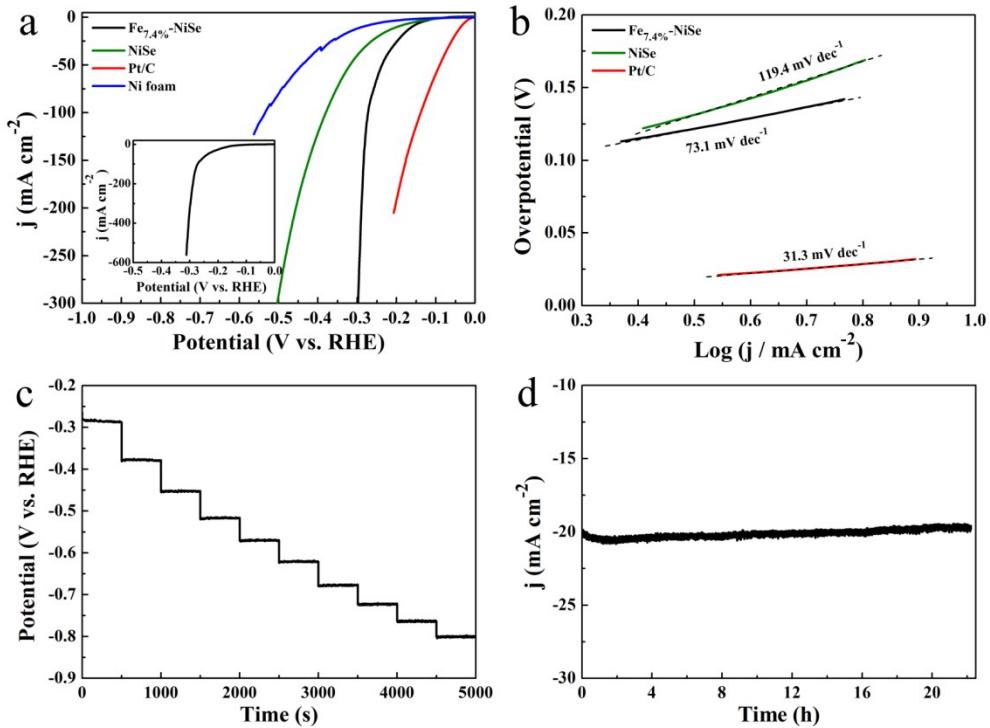


Fig. S9 The HER performances of the catalysts with a carbon rod as the counter electrode. (a) The HER polarization curves of Fe_{7.4%}-NiSe, NiSe, Pt/C, and Ni foam. (b) The corresponding Tafel plots of Fe_{7.4%}-NiSe, NiSe, and Pt/C. (c) The multi-step chronopotentiometric curve of Fe_{7.4%}-NiSe without iR-compensation. (d) The chronoamperometric curve of Fe_{7.4%}-NiSe for 22 h.

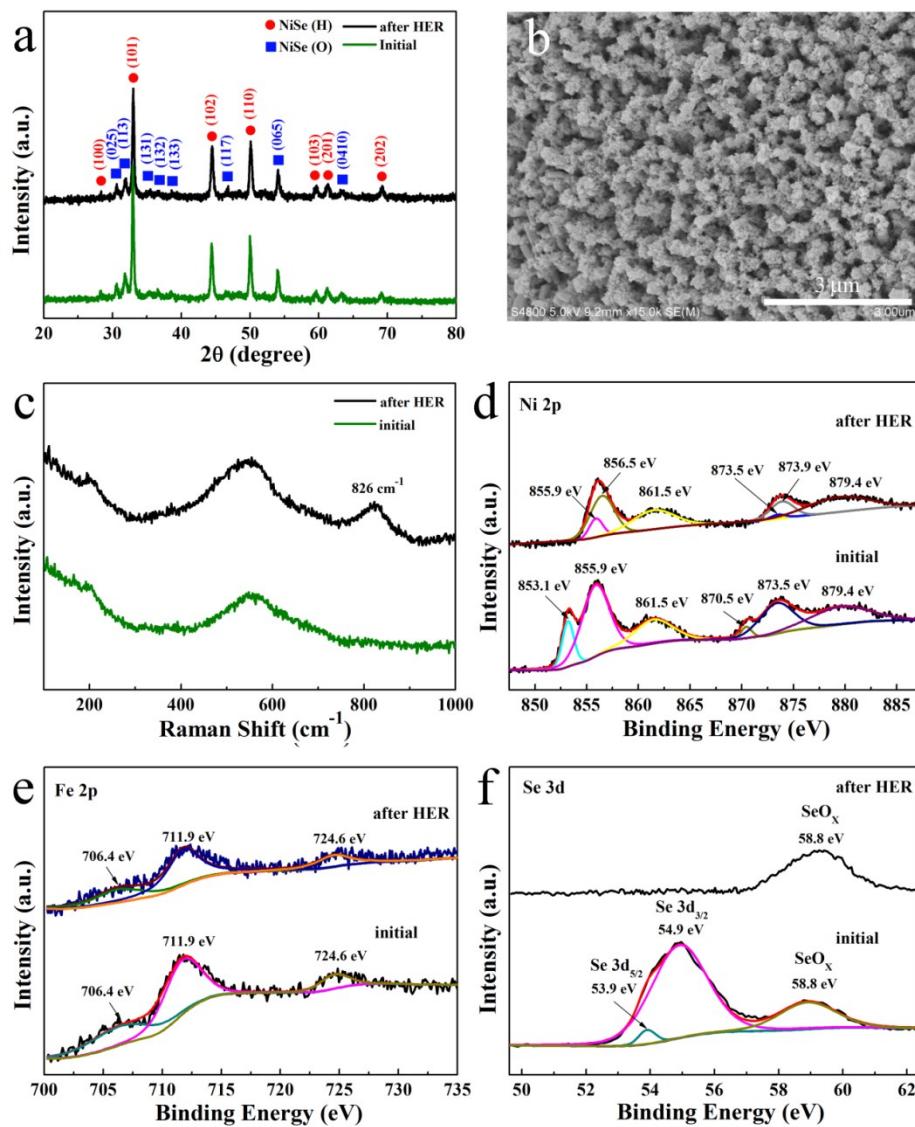


Fig. S10 The XRD pattern (a), the SEM image (b), the Raman spectrum (c), the XPS spectra of Ni 2p (d), Fe 2p (e) and Se 3d (f) of $\text{Fe}_{7.4\%}\text{-NiSe}$ after 22 h HER chronopotentiometry test with a carbon rod as the counter electrode.

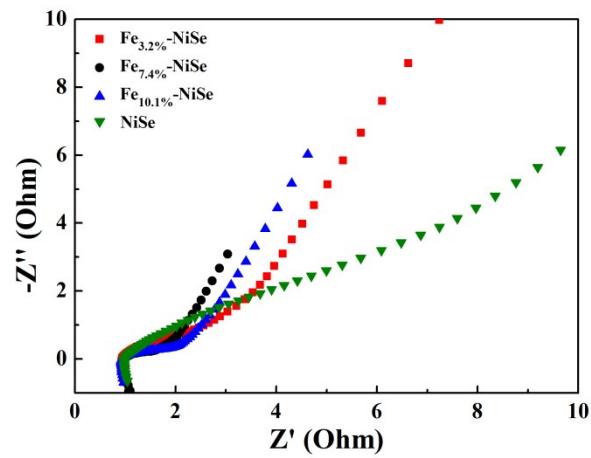


Fig. S11 The Nyquist diagrams of the Fe-doped NiSe with different Fe content and undoped NiSe.

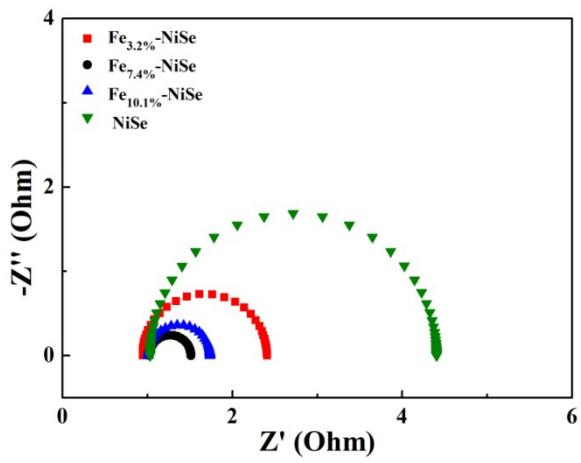


Fig. S12 The fitting results of the semicircles of EIS of the Fe-doped NiSe with different Fe content and undoped NiSe.

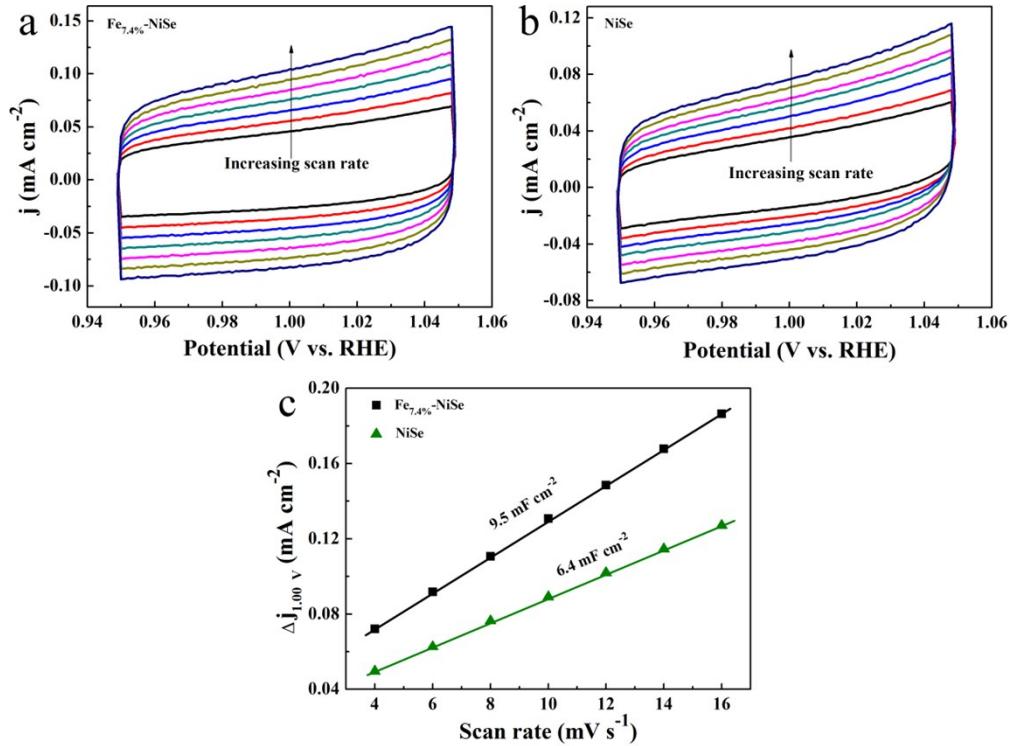


Fig. S13 The cyclic voltammograms of $\text{Fe}_{7.4\%}\text{-NiSe}$ (a) and NiSe (b) at different sweep rates of 4, 6, 8, 10, 12, 14, and 16 mV s^{-1} . (d) The capacitive currents at 1.00 V versus RHE with different sweep rates.

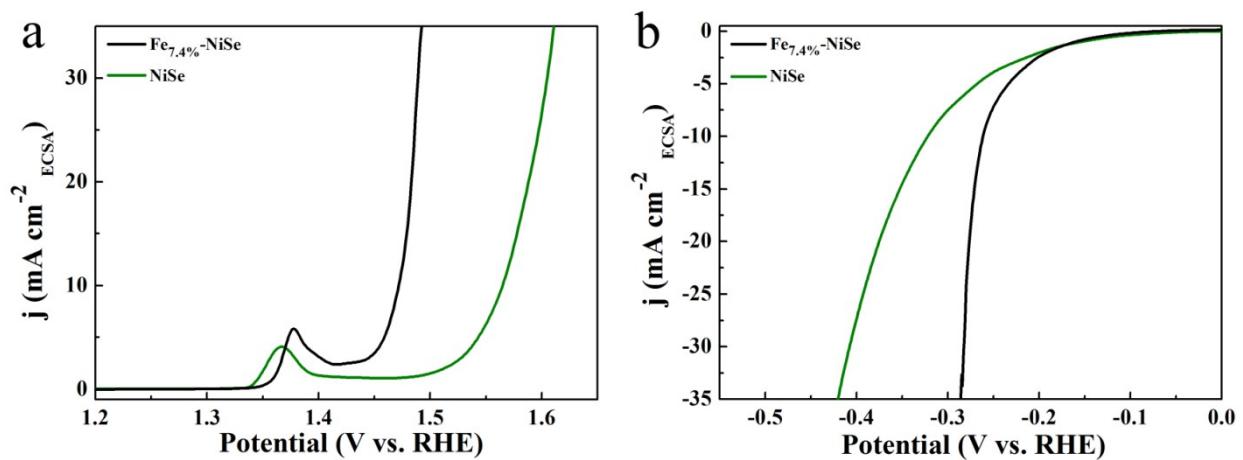


Fig. S14 The ECSA-normalized LSV curves of Fe_{7.4%}-NiSe and NiSe for OER (a) and HER (b) with Pt wire as the counter electrode.

Table S3 Comparison of overall water-splitting performance of Fe_{7.4%}-NiSe with some representative Ni-based selenide catalysts.

Catalyst	Electrolyte	Potential (V) @j(mA cm ⁻²)	Electrode	Reference
Fe-doped NiSe/Ni ₃ Se ₂ nanorods	1 M KOH	1.64@10	Ni foam	¹
Ni ₃ Se ₂ nanoforest	1 M KOH	1.612@10	Ni foam	⁹
NiSe nanowire film	1 M KOH	1.63@10	Ni foam	¹⁰
Co-doped nickel selenide/C	1 M KOH	1.6@10	Ni foam	¹²
CoNi ₂ Se ₄ nanoflake film	1 M KOH	1.61@10	Carbon fiber Paper	¹³
Co-doped NiSe ₂ nanoparticles	1 M KOH	1.62@10	Ti plate	¹⁸
Ni ₃ Se ₂ film	1 M KOH	1.65@10	Cu foam	¹⁹
Fe _{7.4%} -NiSe	1 M KOH	1.585@10	Ni foam	This work

References

- 1 J. Du, A. Yu, Z. Zou and C. Xu, *Inorg. Chem. Front.*, 2018, **5**, 814–818.
- 2 Z. Wang, J. Li, X. Tian, X. Wang, Y. Yu, K. A. Owusu, L. He and L. Mai, *ACS Appl. Mater. Interfaces*, 2016, **8**, 19386–19392.
- 3 J. Yu, G. Cheng and W. Luo, *Nano Res.*, 2018, **11**, 2149–2158.
- 4 X. Li, G. Q. Han, Y. R. Liu, B. Dong, W. H. Hu, X. Shang, Y. M. Chai and C. G. Liu, *ACS Appl. Mater. Interfaces*, 2016, **8**, 20057–20066.
- 5 Y. Du, G. Cheng and W. Luo, *Nanoscale*, 2017, **9**, 6821–6825.
- 6 K. Xu, H. Ding, H. Lv, S. Tao, P. Chen, X. Wu, W. Chu, C. Wu and Y. Xie, *ACS Catal.*, 2016, **7**, 310–315.
- 7 K. Xu, H. Ding, K. Jia, X. Lu, P. Chen, T. Zhou, H. Cheng, S. Liu, C. Wu and Y. Xie, *Angew. Chem. Int. Ed.*, 2016, **55**, 1710–1713.
- 8 A. T. Swesi, J. Masud and M. Nath, *Energy Environ. Sci.*, 2016, **9**, 1771–1782.

- 9 R. Xu, R. Wu, Y. Shi, J. Zhang and B. Zhang, *Nano Energy*, 2016, **24**, 103–110.
- 10 C. Tang, N. Cheng, Z. Pu, W. Xing and X. Sun, *Angew. Chem. Int. Ed.*, 2015, **54**, 9351–9355.
- 11 R. Gao, G.-D. Li, J. Hu, Y. Wu, X. Lian, D. Wang and X. Zou, *Catal. Sci. Technol.*, 2016, **6**, 8268–8275.
- 12 F. Ming, H. Liang, H. Shi, X. Xu, G. Mei and Z. Wang, *J. Mater. Chem. A*, 2016, **4**, 15148–15155.
- 13 B. G. Amin, A. T. Swesi, J. Masud and M. Nath, *Chem. Commun.*, 2017, **53**, 5412–5415.
- 14 H. Liang, L. Li, F. Meng, L. Dang, J. Zhuo, A. Forticaux, Z. Wang and S. Jin, *Chem. Mater.*, 2015, **27**, 5702–5711.
- 15 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.
- 16 S. Anantharaj, J. Kennedy and S. Kundu, *ACS Appl. Mater. Interfaces*, 2017, **9**, 8714–8728.
- 17 X. Zhou, Y. Liu, H. Ju, B. Pan, J. Zhu, T. Ding, C. Wang and Q. Yang, *Chem. Mater.*, 2016, **28**, 1838–1846.
- 18 T. Liu, A. M. Asiri and X. Sun, *Nanoscale*, 2016, **8**, 3911–3915.
- 19 J. Shi, J. Hu, Y. Luo, X. Sun and A. M. Asiri, *Catal. Sci. Technol.*, 2015, **5**, 4954–4958.