

Electronic Supplementary Information

Hydrothermal synthesis of ternary $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheets for electrocatalytic hydrogen evolution

Congli Zhen,^a Bin Zhang,^{*a} Yuhong Zhou,^a Yunchen Du^a and Ping Xu^{*a}

^a. MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, China. Email: p xu@hit.edu.cn (P.X.); zhangbin_hit@aliyun.com (B.Z.)

Supplementary Figures and Tables

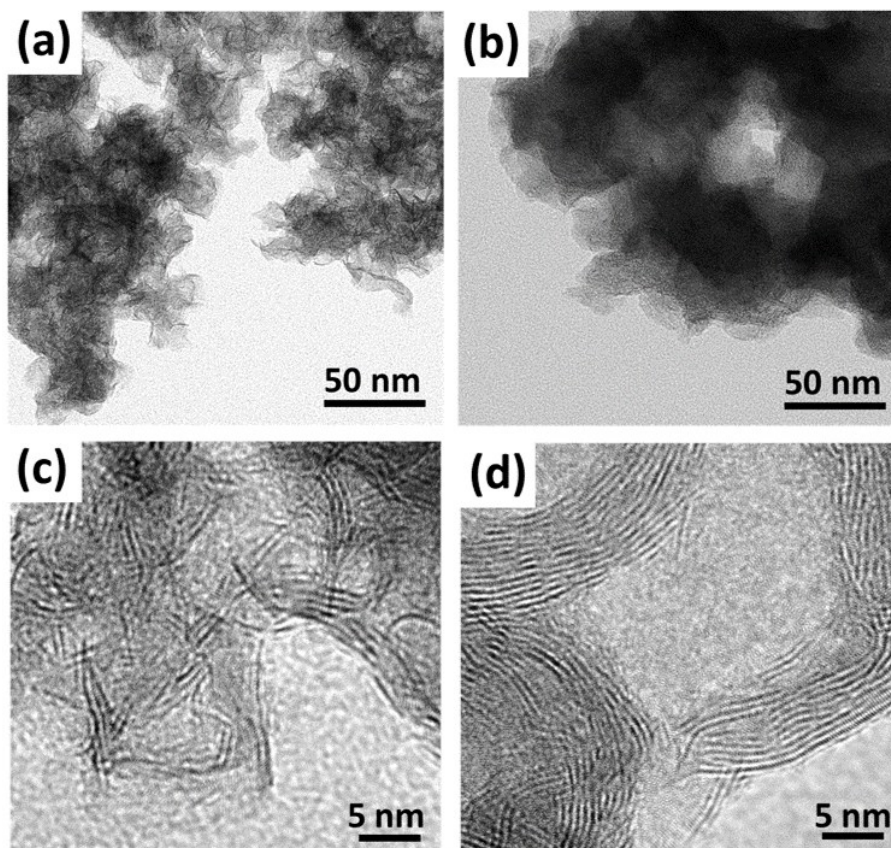


Fig. S1 (a) TEM and (b) HRTEM images of MoSe₂, (c) TEM and (d) HRTEM images of MoS₂.

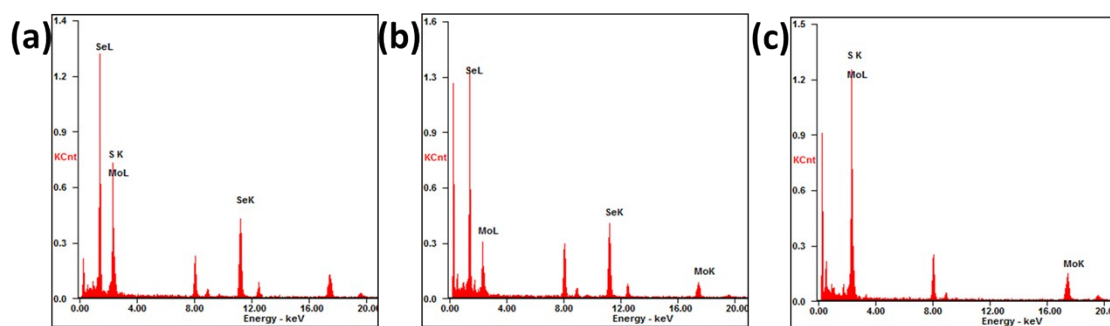


Fig. S2 EDX spectra of the (a) MoS_{2x}Se_{2(1-x)} (b) MoSe₂ and (c) MoS₂.

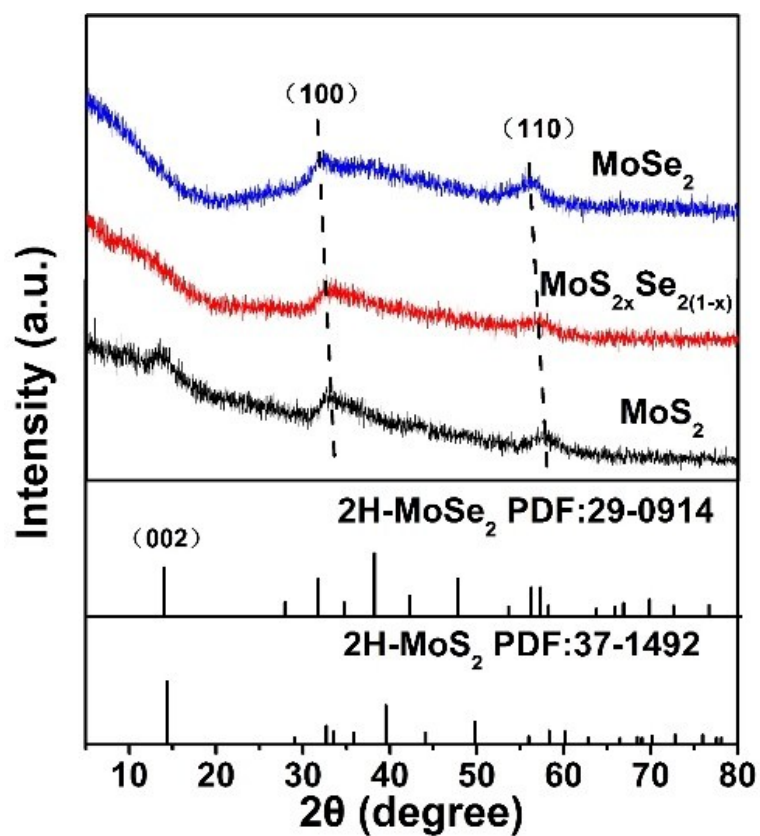


Fig. S3 XRD patterns of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$, MoSe_2 and MoS_2 .

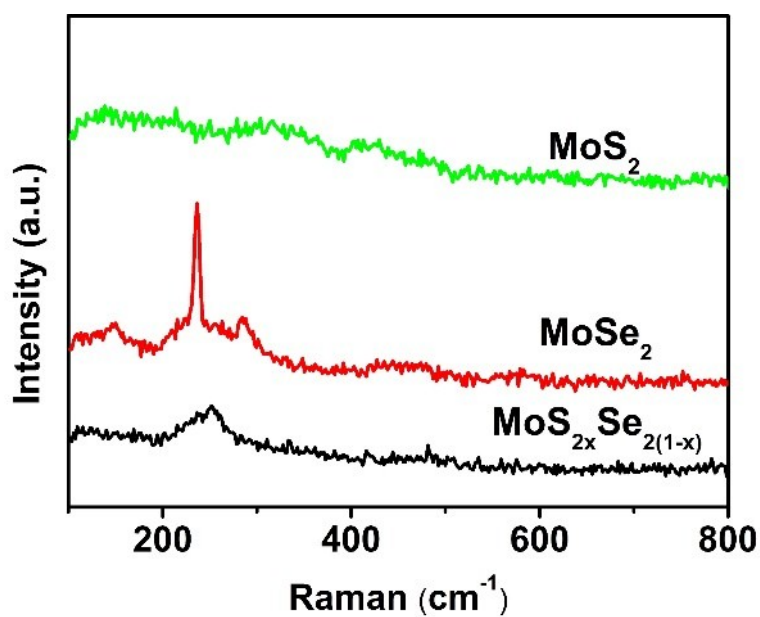


Fig. S4 Raman spectra of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$, MoSe_2 and MoS_2 .

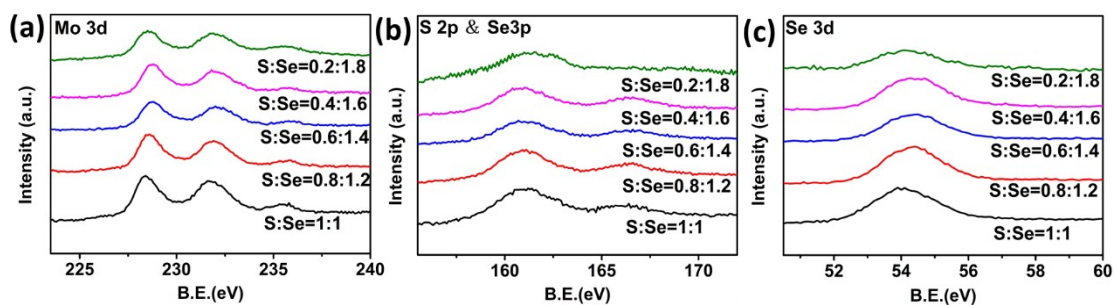


Fig. S5 High resolution XPS spectra of (a) Mo 3d, (b) S 2p and Se 3p, and (c) Se 3d regions of the five $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ samples.

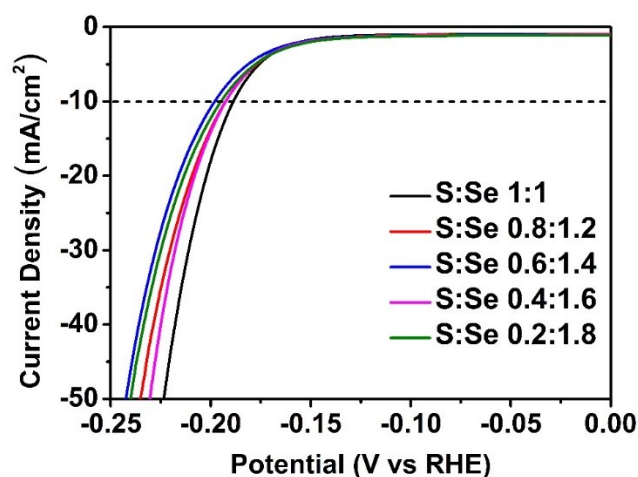


Fig. S6 Linear sweep voltammetry curves (after iR correction) of five $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ products prepared from different molar ratios of S and Se (the total amount of S and Se powder was 2 mmol).

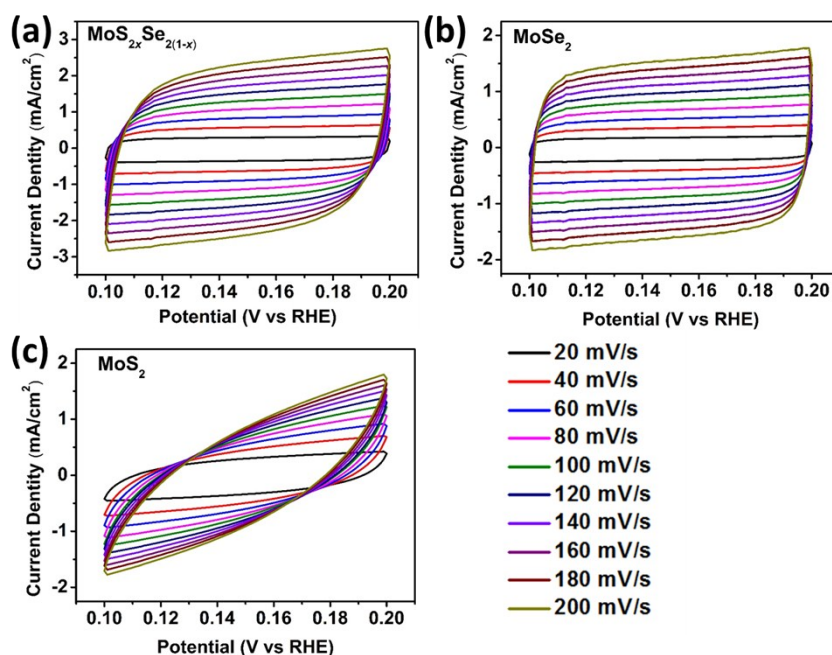


Fig. S7 Cyclic voltammetry curves of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$, MoSe_2 and MoS_2 under different scan rate, in the region of 0.1-0.2 V vs. RHE. These data were used to present the plots showing the extraction

of the C_{dl} as shown in Fig. 4(c) in the main text.

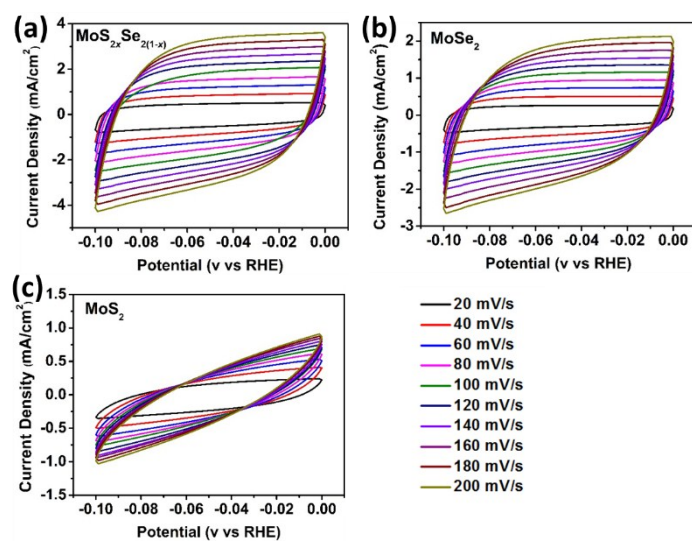


Fig. S8 Cyclic voltammetry curves of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$, MoSe_2 and MoS_2 under different scan rates in the range of 0 ~ -0.1 V vs. RHE.

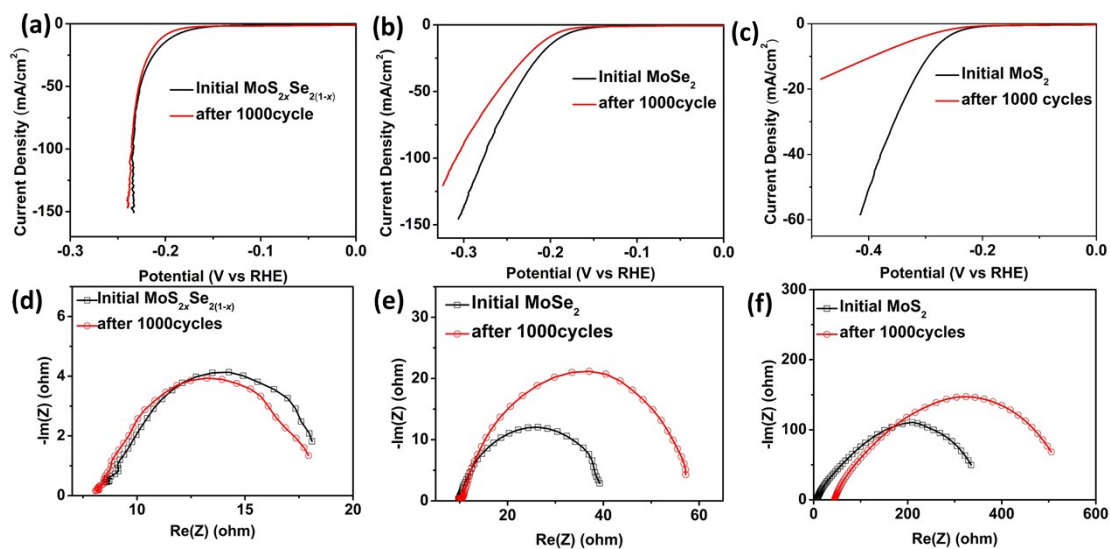


Fig. S9 Stability tests of the as-prepared materials. Polarization curves before and after 1000 cycles of (a) $\text{MoS}_{2x}\text{Se}_{2(1-x)}$, (b) MoSe_2 and (c) MoS_2 ; Electrochemical impedance spectroscopy (EIS) Nyquist plots for before and after 1000 cycles of (a) $\text{MoS}_{2x}\text{Se}_{2(1-x)}$, (b) MoSe_2 and (c) MoS_2 .

Table S1 A brief survey of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$, MoSe_2 and MoS_2 HER electrocatalysts reported in literature.

Catalyst	η/mV (at -10 mA cm^{-2})	Tafel slope (mV dec^{-1})	Ref
$\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheets	188	43	this work
MoSe_2 nanosheets	221	58	this work
MoS_2 nanosheets	268	68	this work
$\text{MoS}_{2x}\text{Se}_{2(1-x)}$ Nanotubes	219	55	1
Se-doped MoS_2 nanosheet	-	55	2
3D $\text{MoS}_{2(1-x)}\text{Se}_{2x}/\text{CF}$	183	55.5	3
Ultrathin $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ nanoflakes	164 ± 2	48 ± 2	4
few-layer alloys of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$	-	56	5
$\text{MoS}_{2(1-x)}\text{Se}_{2x}$	141	67	6
monolayered $\text{MoS}_{2(1-x)}\text{Se}_{2x}$	273	119	7
MoSSe/rGO	153	51	8
$\text{MoS}_{2(1-x)}\text{Se}_{2x}$ nanobelts	-	65	9
Se- MoS_2/CC	127	63	10
Active-site-rich MoS_2	220	53.5	11
Oxygen-incorporated MoS_2 nanosheets	-	55	12
2H c- MoS_2	191	64	13
a few layer MoS_2 nanodots	-	61	14
mesoporous MoS_2/Co foam	156	74	15
$\text{MoS}_2/\text{Graphene}$	110	67.4	16
Ultra-thin and porous MoSe_2 nanosheets	150	80	17
$\text{MoSe}_2/\text{carbon fiber paper}$	250	59.8	18
Mo-rich MoSe_2 nanosheets	-	98	19
$\text{MoSe}_2/\text{graphene}$	-	69	20
$\text{MoSe}_2/\text{graphene}$	195	67	21

Table S2 Summary of the x value from XPS analyses for the five $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ samples using different molar ratios of S and Se in the hydrothermal synthesis.

molar ratio of S and Se	x value of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$
1:1	0.68
0.8:1.2	0.65
0.6:1.4	0.66
0.4:1.6	0.65
0.2:1.8	0.62

Reference

1. J. Zhang, M. H. Wu, Z. T. Shi, M. Jiang, W. J. Jian, Z. Xiao, J. Li, C. S. Lee and J. Xu, *Small*, 2016, **12**, 4379-4385.
2. X. Ren, Q. Ma, H. Fan, L. Pang, Y. Zhang, Y. Yao, X. Ren and S. F. Liu, *Chem Commun (Camb)*, 2015, **51**, 15997-16000.
3. X. Chen, Z. Wang, Y. Qiu, J. Zhang, G. Liu, W. Zheng, W. Feng, W. Cao, P. Hu and W. Hu, *J. Mater. Chem. A*, 2016, **4**, 18060-18066.
4. Q. Gong, L. Cheng, C. Liu, M. Zhang, Q. Feng, H. Ye, M. Zeng, L. Xie, Z. Liu and Y. Li, *ACS Catal.*, 2015, **5**, 2213-2219.
5. V. Kiran, D. Mukherjee, R. N. Jenjeti and S. Sampath, *Nanoscale*, 2014, **6**, 12856-12863.
6. S. Hussain, K. Akbar, D. Vikraman, K. Karuppasamy, H. S. Kim, S. H. Chun and J. W. Jung, *Inorg. Chem. Front.*, 2017, **4**, 2068-2074.
7. L. Yang, Q. Fu, W. Wang, J. Huang, J. Huang, J. Zhang and B. Xiang, *Nanoscale*, 2015, **7**, 10490-10497.
8. B. Konkena, J. Masa, W. Xia, M. Muhler and W. Schuhmann, *Nano Energy*, 2016, **29**, 46-53.
9. L. Yang, W. Wang, Q. Fu, J. Zhang and B. Xiang, *Electrochim. Acta*, 2015, **185**, 236-241.
10. Z. Pu, S. Wei, Z. Chen and S. Mu, *RSC Advances*, 2016, **6**, 11077-11080.
11. N. Liu, Y. Guo, X. Yang, H. Lin, L. Yang, Z. Shi, Z. Zhong, S. Wang, Y. Tang and Q. Gao, *ACS Appl. Mat. Interfaces*, 2015, **7**, 23741-23749.
12. J. Xie, J. Zhang, S. Li, F. Grote, X. Zhang, H. Zhang, R. Wang, Y. Lei, B. Pan and Y. Xie, *J. Am. Chem. Soc.*, 2013, **135**, 17881-17888.
13. Y. C. Chen, A. Y. Lu, P. Lu, X. Yang, C. M. Jiang, M. Mariano, B. Kaehr, O. Lin, A. Taylor, I. D. Sharp, L. J. Li, S. S. Chou and V. Tung, *Adv. Mater.*, 2017, **29**.
14. J. Benson, M. Li, S. Wang, P. Wang and P. Papakonstantinou, *ACS Appl. Mat. Interfaces*, 2015, **7**, 14113-14122.
15. J. Deng, H. Li, S. Wang, D. Ding, M. Chen, C. Liu, Z. Tian, K. S. Novoselov, C. Ma, D. Deng and X. Bao, *Nat. Commun.*, 2017, **8**, 14430.
16. L. Ma, Y. Hu, G. Zhu, R. Chen, T. Chen, H. Lu, Y. Wang, J. Liang, H. Liu, C. Yan, Z. Tie, Z. Jin and J. Liu, *Chem. Mater.*, 2016, **28**, 5733-5742.
17. Z. Lei, S. Xu and P. Wu, *Phys. Chem. Chem. Phys.*, 2016, **18**, 70-74.
18. H. Wang, D. Kong, P. Johanes, J. J. Cha, G. Zheng, K. Yan, N. Liu and Y. Cui, *Nano Lett.*, 2013, **13**, 3426-3433.
19. X. Zhou, J. Jiang, T. Ding, J. Zhang, B. Pan, J. Zuo and Q. Yang, *Nanoscale*, 2014, **6**, 11046-11051.
20. H. Tang, K. Dou, C.-C. Kaun, Q. Kuang and S. Yang, *J. Mater. Chem. A*, 2014, **2**, 360-364.
21. Z. Liu, N. Li, H. Zhao and Y. Du, *J. Mater. Chem. A*, 2015, **3**, 19706-19710.