

## Electronic Supplementary Information

### **Superior Electrocatalytic Hydrogen Evolution at Engineered Non-Stoichiometric Two-Dimensional Transition Metal Dichalcogenide Edges**

Guoxiang Hu\*, Victor Fung, Xiahan Sang, Raymond R. Unocic, and P. Ganesh\*

[hug1@ornl.gov](mailto:hug1@ornl.gov), [ganeshp@ornl.gov](mailto:ganeshp@ornl.gov)

Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge,  
Tennessee 37831, US

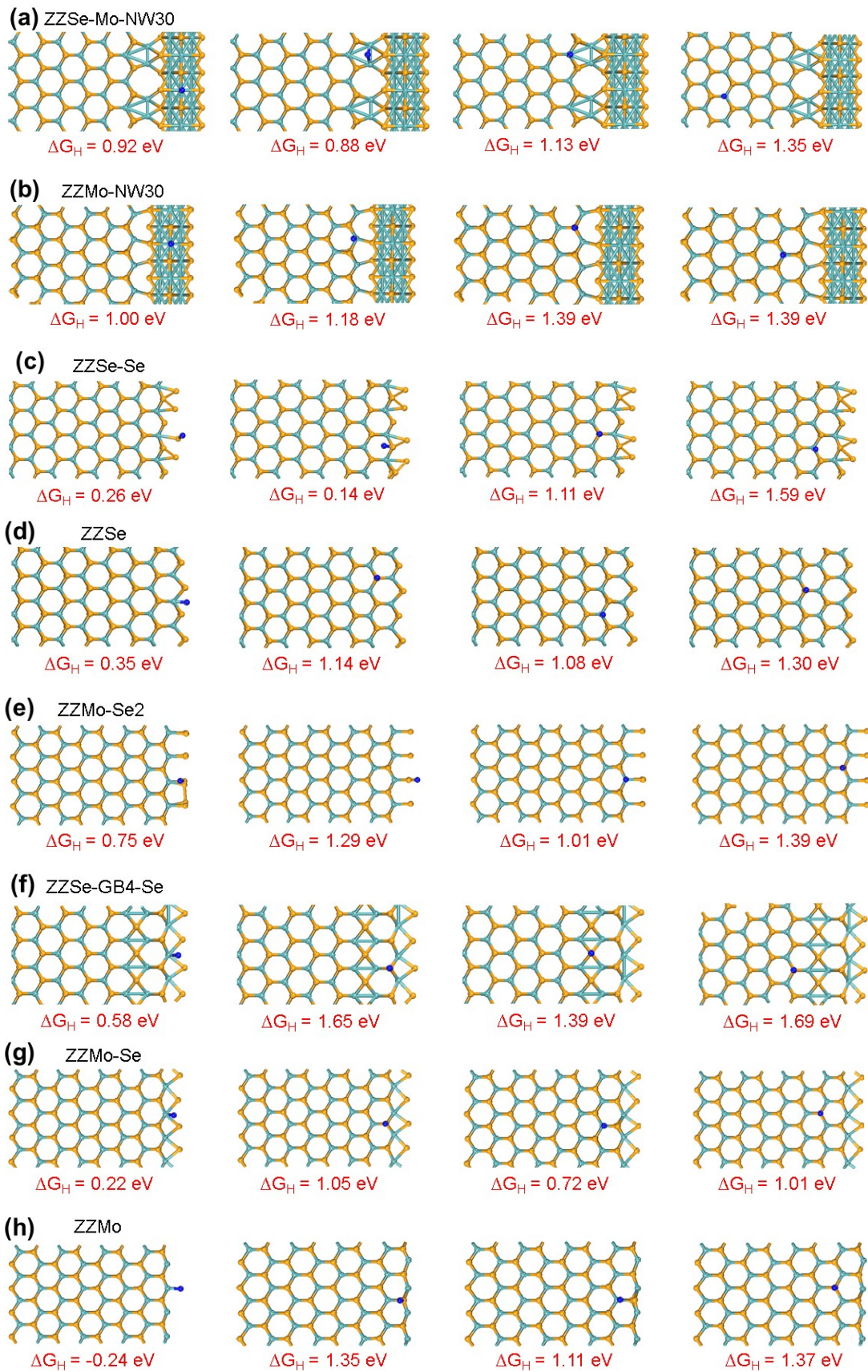


Fig. S1 The other H adsorption structures and their  $\Delta G_H$  on the six non-stoichiometric and two stoichiometric edges.

(a) ZZSe-Mo-NW30. (b) ZZMo-NW30. (c) ZZSe-Se. (d) ZZSe. (e) ZZMo-Se2. (f) ZZSe-GB4-Se. (g) ZZMo-Se. (h)

ZZMo. Mo, cyan; Se, orange; H, blue.

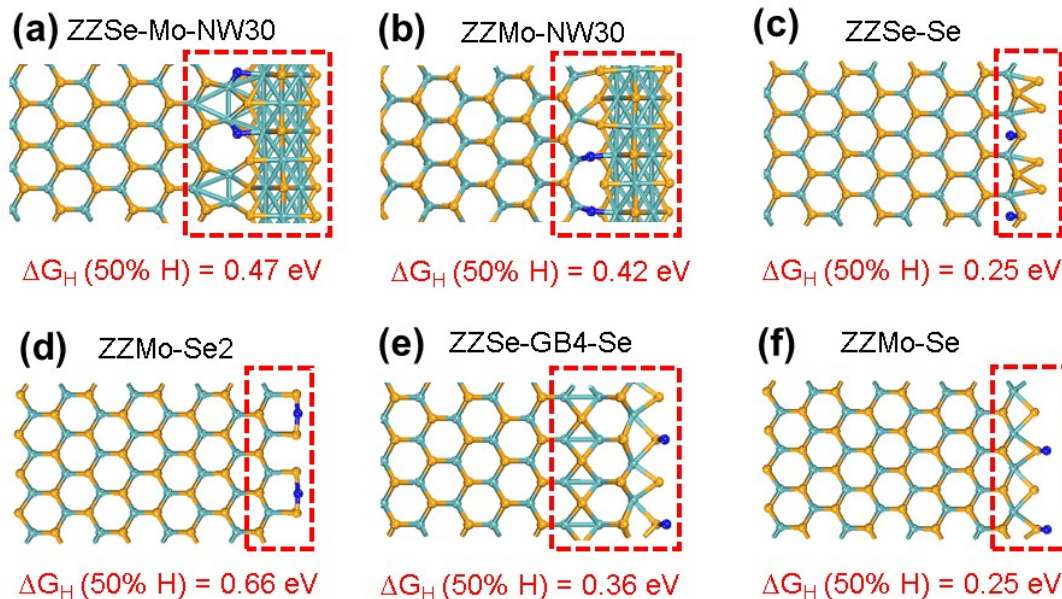


Fig. S2 The adsorption free energies and adsorption structures for the six non-stoichiometric edges at 50% H coverage.

(a) ZZSe-Mo-NW30. (b) ZZMo-NW30. (c) ZZSe-Se. (d) ZZMo-Se2. (e) ZZSe-GB4-Se. (f) ZZMo-Se. Mo, cyan; Se,

orange; H, blue.

Table S1. Comparison of HER performance for non-stoichiometric MoSe<sub>2</sub> edge with other 2D materials.

<b>Catalysts</b>	<b>Onset overpotential (V)</b>	<b>Tafel slope (mV/dec)</b>	<b>References</b>
<b>ZZSe-Se</b>	0.07	-	This work
<b>MoSe<sub>2</sub> films</b>	0.20	105-120	S1
<b>MoSe<sub>2</sub> NSs</b>	~0.15	101	S2
<b>MoS<sub>2</sub></b>	~0.17	94	S3
<b>1T-MoS<sub>2</sub> NSs</b>	0.187	43	S4
<b>Defect-rich MoS<sub>2</sub> sheets</b>	0.12	50	S5
<b>Amorphous MoS<sub>2</sub> film</b>	0.15	40	S6
<b>hydrogen-annealed MoS<sub>2</sub></b>	~0.30	147	S7
<b>1T-VS<sub>2</sub> NSs</b>	-	34	S8
<b>1T-WS<sub>2</sub> NSs</b>	0.10	60	S9
<b>1T'-MoTe<sub>2</sub> film</b>	-	44	S10
<b>MoSe<sub>2-x</sub> NSs</b>	0.17	98	S11
<b>MoS<sub>2</sub>/SnO<sub>2</sub></b>	0.15	59	S12
<b>MoS<sub>2</sub>/Au</b>	~0.10	61	S13
<b>S-doped MoSe<sub>2</sub></b>	0.09	58	S14
<b>Pt-doped MoS<sub>2</sub></b>	0.06	96	S15
<b>MoSe<sub>2</sub>/RGO</b>	~0.05	69	S2
<b>MoS<sub>2</sub>/RGO</b>	~0.10	41	S3
<b>WS<sub>2</sub>/rGO</b>	0.15-0.20	58	S16
<b>C<sub>3</sub>N<sub>4</sub>@NG</b>	-	51.5	S17
<b>LSTL NiPS<sub>3</sub></b>	~0.10	95	S18

## References

- S1 D. Kong, H. Wang, J. J. Cha, M. Pasta, K. J. Koski, J. Yao and Y. Cui, *Nano Lett.*, 2013, 13, 1341-1347.
- S2 H. Tang, K. Dou, C.-C. Kaun, Q. Kuang and S. Yang, *J. Mater. Chem. A*, 2014, 2, 360-364.
- S3 Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong and H. Dai, *J. Am. Chem. Soc.*, 2011, 133, 7296-7299.
- S4 M. A. Lukowski, A. S. Daniel, F. Meng, A. Forticaux, L. Li and S. Jin, *J. Am. Chem. Soc.*, 2013, 135, 10274-10277.
- S5 J. Xie, H. Zhang, S. Li, R. Wang, X. Sun, M. Zhou, J. Zhou, X. W. Lou and Y. Xie, *Adv. Mater.*, 2013, 25, 5807-5813.
- S6 D. Merki, S. Fierro, H. Vrubel and X. Hu, *Chem. Sci.*, 2011, 2, 1262-1267.
- S7 G. Ye, Y. Gong, J. Lin, B. Li, Y. He, S. T. Pantelides, W. Zhou, R. Vajtai and P. M. Ajayan, *Nano Lett.*, 2016, 16, 1097-1103.
- S8 J. Yuan, J. Wu, W. J. Hardy, P. Loya, M. Lou, Y. Yang, S. Najmaei, M. Jiang, F. Qin and K. Keyshar, *Adv. Mater.*, 2015, 27, 5605-5609.
- S9 D. Voiry, H. Yamaguchi, J. Li, R. Silva, D. C. Alves, T. Fujita, M. Chen, T. Asefa, V. B. Shenoy and G. Eda, *Nat. Mater.*, 2013, 12, 850.
- S10 P. Zhuang, Y. Sun, P. Dong, W. Smith, Z. Sun, Y. Ge, Y. Pei, Z. Cao, P. M. Ajayan and J. Shen, *Adv. Funct. Mater.*, 2019, 1901290.
- S11 X. Zhou, J. Jiang, T. Ding, J. Zhang, B. Pan, J. Zuo and Q. Yang, *Nanoscale*, 2014, 6, 11046-11051.
- S12 Y. Huang, Y.-E. Miao, L. Zhang, W. W. Tjiu, J. Pan and T. Liu, *Nanoscale*, 2014, 6, 10673-10679.
- S13 J. Shi, D. Ma, G.-F. Han, Y. Zhang, Q. Ji, T. Gao, J. Sun, X. Song, C. Li and Y. Zhang, *ACS nano*, 2014, 8, 10196-10204.
- S14 C. Xu, S. Peng, C. Tan, H. Ang, H. Tan, H. Zhang and Q. Yan, *J. Mater. Chem. A*, 2014, 2, 5597-5601.
- S15 J. Deng, H. Li, J. Xiao, Y. Tu, D. Deng, H. Yang, H. Tian, J. Li, P. Ren and X. Bao, *Energy Environ. Sci.*, 2015, 8, 1594-1601.
- S16 J. Yang, D. Voiry, S. J. Ahn, D. Kang, A. Y. Kim, M. Chhowalla and H. S. Shin, *Angew. Chem. Int. Ed.*, 2013, 52, 13751-13754.

S17 Y. Zheng, Y. Jiao, Y. Zhu, L. H. Li, Y. Han, Y. Chen, A. Du, M. Jaroniec and S. Z. Qiao, *Nat. Commun.*, 2014, 5, 3783.

S18 X. Li, Y. Fang, J. Wang, B. Wei, K. Qi, H. Y. Hoh, Q. Hao, T. Sun, Z. Wang and Z. Yin, *Small*, 2019, 1902427.