Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

for

Defective MoS_2 Monolayer as an Efficient Electrocatalyst for Nitrogen Reduction Reaction: A Combined Theoretical and Experimental Study

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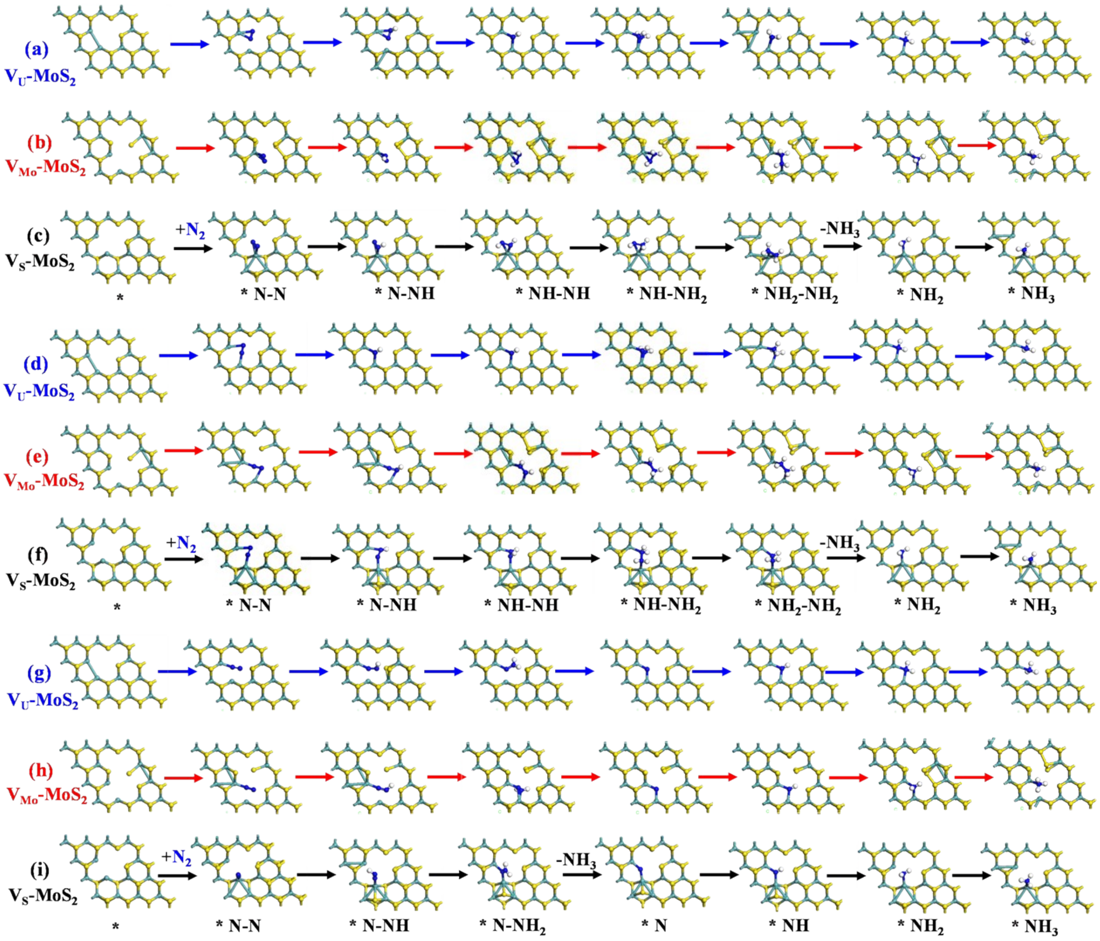

Fig S1. The optimized structures of all intermediates during the electrochemical NRR catalyzed by V_U-MoS_2, V_{Mo}-MoS_2, and V_S-MoS_2 through enzymatic (a ~ c), alternating (d ~ f), and (g ~ i) distal pathways.

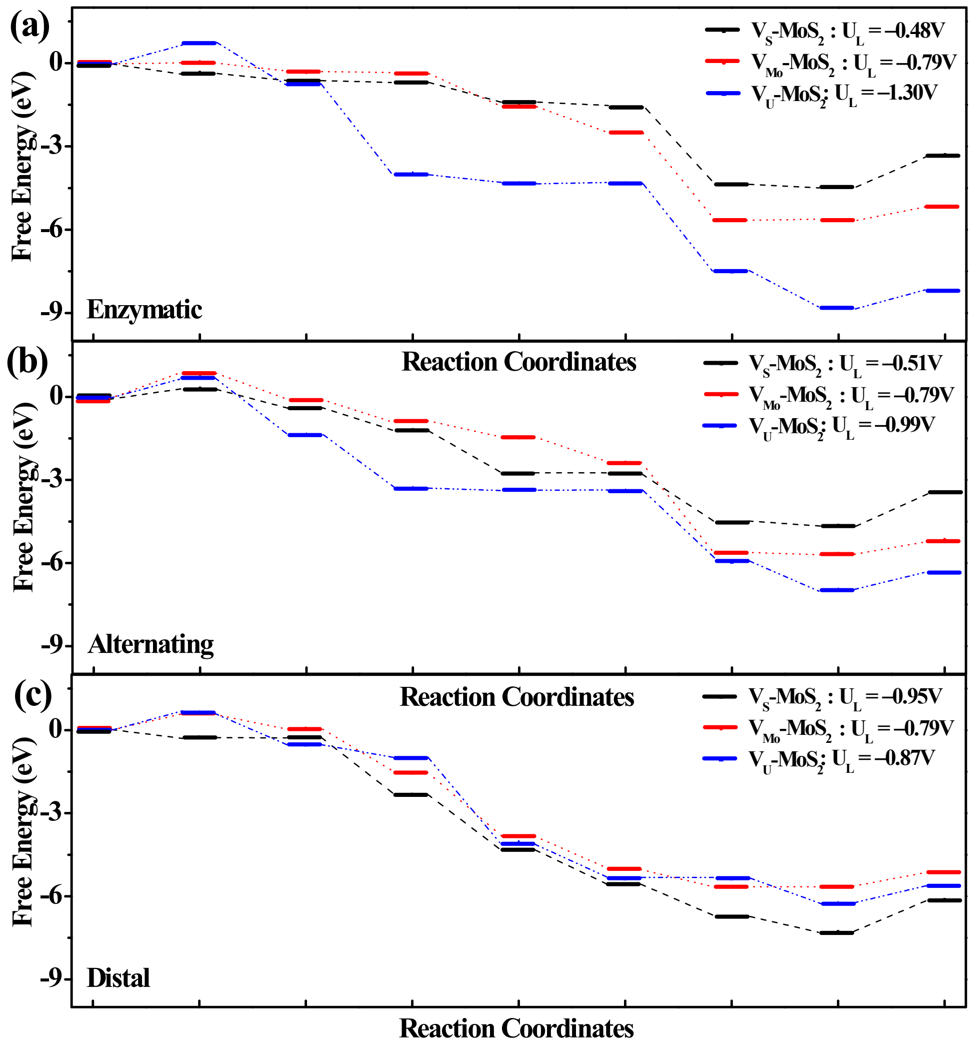

Fig S2. The calculated reaction free energy profiles of V_S-MoS_2, V_{Mo}-MoS_2, and V_U-MoS_2, with the limiting potential (U_L) through enzymatic, alternating, and distal pathways.

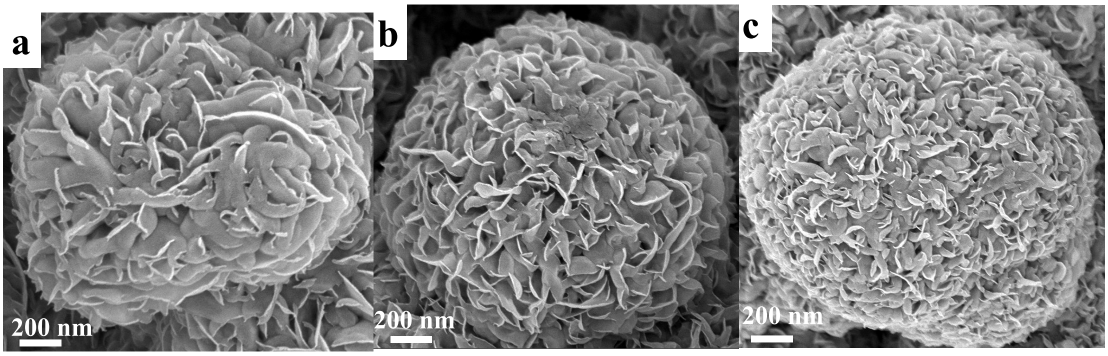

Fig S3. Scanning electron microscopy (SEM) image of (a) V_S-MoS_2, (b) V_{Mo}-MoS_2, and (c) V_U-MoS_2.

Table S1. Comparison of U_L for V_S-MoS_2 with recently reported NRR electrocatalysts under ambient conditions.

Catalyst	**U_L (V)**	**Ref.**
V_S-MoS_2	-0.48	This work
Re (111)	-0.50	**[1]**
Ti-C_3N_4	-0.51	**[2]**
Mo-graphene	-0.54	**[3]**
Mo-MoP	-0.95	**[4]**
V-MoP	-0.65	**[4]**
FeB_6	-0.68	**[5]**
Tc-BN	-0.59	**[6]**

Table S2. Comparison of NH_3 yield and FE for V_S-MoS_2 with recently reported NRR electrocatalysts at ambient conditions

Catalyst	**NH_3 yield rate ($\mu g\ h^{-1}\ mg^{-1}_{cat.}$)**	**FE (%)**	**Ref.**
V_S-MoS_2	29.55	4.58	This work
VO_2	14.85	3.97	**[7]**
$Fe_2(MoO_4)_3$	7.5	1.0	**[8]**
Ru NPs	24.88	0.35	**[9]**
B-TiO_2	14.4	3.4	**[10]**
Cr-CeO_2	16.82	3.84	**[11]**
Mn_3O_4	11.6	3.0	**[12]**
PEBCD/C	2.01	2.91	**[13]**
Mn_3O_4/rGO	17.4	3.52	**[14]**
C-TiO_2	16.22	1.84	**[15]**
DR-fluorographene	9.3	4.2	**[16]**
V_O-CeO_2	16.4	3.7	**[17]**
Fe_2O_3 nanorods	15.9	0.94	**[18]**
TiO_2/rGO	15.13	3.3	**[19]**

References:

1 J. H. Montoya, C. Tsai, A. VojvodicJ. K. Nørskov *ChemSusChem,* 2015, ***8***, 2180-2186.

2 X. Chen, X. Zhao, Z. Kong, W.-J. OngN. Li *Journal of Materials Chemistry A,* 2018, ***6***, 21941-21948.

3 Z. W. Chen, X. Y. LangQ. Jiang *Journal of Materials Chemistry A,* 2018, ***6***, 9623-9628.

4 M. Han, G. Wang, H. ZhangH. Zhao *Physical Chemistry Chemical Physics,* 2019, ***21***, 5950-5955.

5 Q. Li, C. Liu, S. Qiu, F. Zhou, L. He, X. ZhangC. Sun *Journal of Materials Chemistry A,* 2019, ***7***, 21507-21513.

6 Z. Ma, Z. Cui, C. Xiao, W. Dai, Y. Lv, Q. LiR. Sa *Nanoscale,* 2020, ***12***, 1541-1550.

7 R. Zhang, H. Guo, L. Yang, Y. Wang, Z. Niu, H. Huang, H. Chen, L. Xia, T. Li, X. Shi, X. Sun, B. LiQ. Liu *ChemElectroChem,* 2019, ***6***, 1014-1018.

8 C. Chen, Y. LiuY. Yao *European Journal of Inorganic Chemistry,* 2020, ***2020***, 3236-3241.

9 L. Zhao, J. Zhao, J. Zhao, L. Zhang, D. Wu, H. Wang, J. Li, X. RenQ. Wei *Nanotechnology,* 2020, ***31***, 29LT01.

10 Y. Wang, K. Jia, Q. Pan, Y. Xu, Q. Liu, G. Cui, X. GuoX. Sun *ACS Sustainable Chemistry & Engineering,* 2018, ***7***, 117-122.

11 H. Xie, H. Wang, Q. Geng, Z. Xing, W. Wang, J. Chen, L. Ji, L. Chang, Z. WangJ. Mao *Inorganic Chemistry,* 2019, ***58***, 5423-5427.

12 X. Wu, L. Xia, Y. Wang, W. Lu, Q. Liu, X. ShiX. Sun *Small,* 2018, ***14***, 1803111.

13 G.-F. Chen, X. Cao, S. Wu, X. Zeng, L.-X. Ding, M. ZhuH. Wang *Journal of the American Chemical Society,* 2017, ***139***, 9771-9774.

14 H. Huang, F. Gong, Y. Wang, H. Wang, X. Wu, W. Lu, R. Zhao, H. Chen, X. Shi, A. M. Asiri, T. Li, Q. LiuX. Sun *Nano Research,* 2019, ***12***, 1093-1098.

15 K. Jia, Y. Wang, Q. Pan, B. Zhong, Y. Luo, G. Cui, X. GuoX. Sun *Nanoscale Advances,* 2019, ***1***, 961-964.

16 J. Zhao, J. Yang, L. Ji, H. Wang, H. Chen, Z. Niu, Q. Liu, T. Li, G. CuiX. Sun *Chemical Communications,* 2019, ***55***, 4266-4269.

17 B. Xu, L. Xia, F. Zhou, R. Zhao, H. Chen, T. Wang, Q. Zhou, Q. Liu, G. Cui, X. Xiong, F. GongX. Sun *ACS Sustainable Chemistry & Engineering,* 2019, ***7***, 2889-2893.

18 X. Xiang, Z. Wang, X. Shi, M. FanX. Sun *ChemCatChem,* 2018, ***10***, 4530-4535.

19 X. Zhang, Q. Liu, X. Shi, A. M. Asiri, Y. Luo, X. SunT. Li *Journal of Materials Chemistry A,* 2018, ***6***, 17303-17306.