Surname *et al. Microstruct* Year;Volume:Number
DOI: 10.20517/microstruct.xxx.xx

Microstructures

Open Access

Supplementary Material
Atomic modulation and phase engineering of MoS_2 for boosting N_2 reduction

Yansong Jia[1,2,#], Guining Shao[1,2,#], Yang Li[1,2], Ruizhe Yang[3], Ming Huang[3], Hua Huang[4], Min Liu[5], Gai Huang[4], Qunjie Lu[4], Chaohua Gu[1,2]

[1]Institute of Process Equipment, College of Energy Engineering, Zhejiang University, Hangzhou 310000, Zhejiang, China.

[2]Hydrogen Energy Institute, Zhejiang University, Hangzhou 310000, Zhejiang, China.

[3]Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 611731, Sichuan, China.

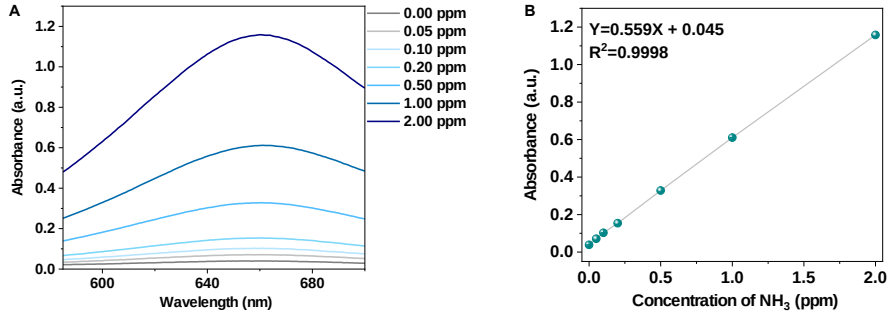
[4]National energy key laboratory for new hydrogen-ammonia energy technologies, Foshan Xianhu Laboratory, Foshan 528200, Guangdong, China.

[5]State Grid Zhejiang Electric Power CO., LTD. Research Institute, Hangzhou 310000, Zhejiang, China.

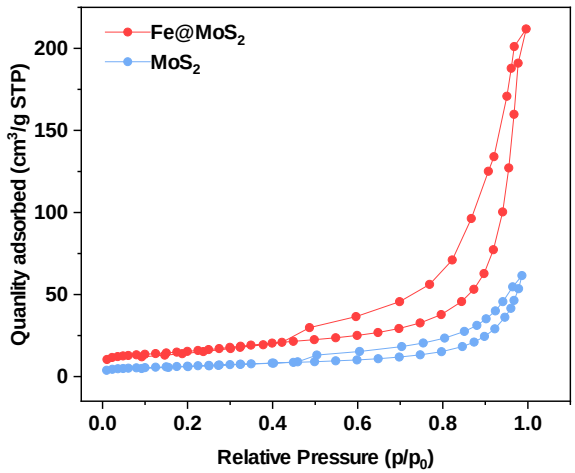
[#]Authors contributed equally.

Characterization methods

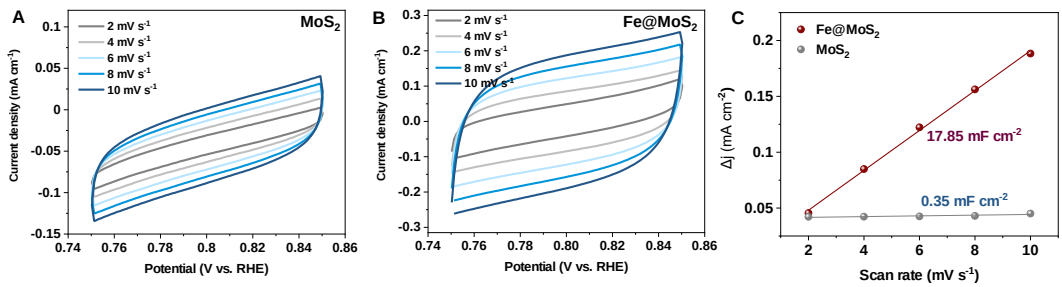
The phase data were analyzed by X-ray powder diffraction (XRD) on an MMA diffractometer equipped with Cu *K*α radiation (GBC, MMA), which operated from 10° to 80° in continuous scan mode with a scan rate of 1° min^{-1}. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a VG Scientific ESCALAB 2201XL instrument using aluminum *K*α X-ray radiation. X-ray absorption studies (XAS) were performed at the BL11B beamline at the Shanghai Synchrotron Radiation Facility (SSRF), Shanghai, PR China. Raman spectra were collected on a JOBIN YVON HR800 Confocal Raman System with 632.8 nm diode laser excitation on a 300 lines mm^{-1} grating under ambient conditions. The specific surface areas were determined using the Brunauer-Emmett-Teller (BET, Micro for TriStar II Plus 2.02) method, with a degassing pretreatment of N_2 at 200 °C for 24 h. The structure and morphology of the sample were investigated on a field emission scanning electron microscope (FESEM; JEOL JSM-7500) and a transmission electron microscope (TEM; JEOL-2010). Atomic resolution analytical microscope investigations were conducted using scanning TEM (STEM; JEOL ARM 200F), which was operated at 80 kV and equipped with a cold field emission high-resolution pole piece and a Centurio energy dispersive spectroscopy (EDS) detector. The electrochemical operando ATR-SEIRAS was measured by INVENIO R FTIR spectrometer (Bruker) equipped with a mercury-cadmium-telluride (MCT) detector.



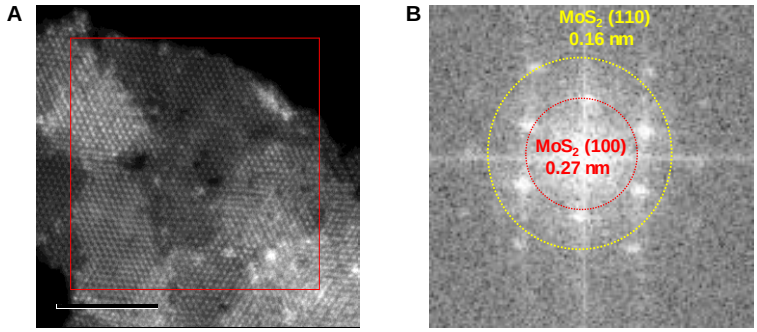
Supplementary Figure 1. Standard curves. (A) UV-Vis absorption spectra of NH_3 standard solutions; (B) Calibration curve for colorimetric NH_3 assay using salicylic acid.



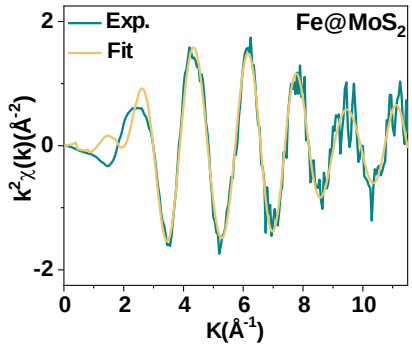
Supplementary Figure 2. N_2 adsorption and desorption isotherms of MoS_2 and Fe@MoS_2.



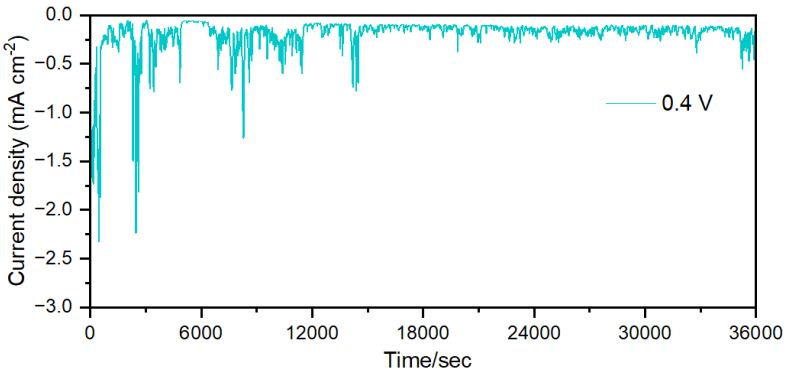
Supplementary Figure 3. CV curves of (A) MoS_2, (B) Fe@MoS_2 at potential from 0.75 V to 0.85 V at a scan rate of 2, 4, 6, 8, 10 mV s^{-1}. (C) The measured capacitive currents are plotted as a function of the scan rate.



Supplementary Figure 4. STEM image of A) Fe@MoS_2, and B) the corresponding Fourier transform.



Supplementary Figure 5. The corresponding EXAFS fitting curves of Fe@MoS_2.



Supplementary Figure 6. Long-term stability test of Fe@MoS_2.

Supplementary Table 1. BET surface area and pore volume of ENRR catalysts.

ENRR catalysts	MoS_2	Fe@MoS_2
Specific area (m^2 g^{-1})	22.63	54.034
Pore volume (cm^3 g^{-1})	0.09	0.32

Supplementary Table 2. Fe *K*-edge EXAFS curve Fitting Parameter.

Sample	Path	C.N.	R (Å)	$\sigma^2\times10^3$ ($Å^2$)	*R* factor

Fe Foil	Fe-Fe1	8.0	1.96±0.03	2.3±0.5	0.004
	Fe-Fe2	6.0	2.67±0.01	2.3±0.5	
Fe@MoS_2	Fe-S	5.5±0.4	2.29±0.05	3.3±0.7	0.004
	Fe-Mo	0.7±0.1	2.83±0.025	1.9±0.5	

Supplementary Table 3. Comparison of ENRR performance.

Catalysts	Electrolyte	Yield Rate	FE (%)	Ref
Fe@MoS_2	0.25 M $LiClO_4$	20.20 μg $h^{-1}mg^{-1}$	19.7%	This work
MoS_2/BCCF	0.1 M Li_2SO_4	43.4 μg $h^{-1}mg^{-1}$	9.81%	[1]
MoS_2/C_3N_4	0.1 M Na_2SO_4	19.86 μg $h^{-1}mg^{-1}$	6.87%	[2]
$Cu_{2-x}S/MoS_2$	0.1 M Na_2SO_4	22.1 μg $h^{-1}mg^{-1}$	6.06%	[3]
SnS_2/MoS_2	0.1 M Li_2SO_4	34.3 μg $h^{-1}mg^{-1}$	13.8%	[4]
V_S-MoS_2	0.1 M Na_2SO_4	29.55 μg $h^{-1}mg^{-1}$	4.58%	[5]
VS-Fe-MoS_2/C	0.1 M $LiClO_4$	17.8 μg $h^{-1}mg^{-1}$	9.2%	[6]
Fe–MoS_2/CC	0.1 M KOH	12.5 μg $h^{-1}mg^{-1}$	10.5%	[7]
MoS_2 NDs/RGO	0.1 M Na_2SO_4	16.41 μg $h^{-1}mg^{-1}$	27.93%	[8]
MoS_2–rGO	0.1 M $LiClO_4$	24.82 μg $h^{-1}mg^{-1}$	4.58%	[9]
MoS_2/CC	0.1 M Na_2SO_4	5.23 μg $h^{-1}mg^{-1}$	1.17%	[10]

REFERENCES

1. Liu Y, Han M, Xiong Q, Zhang S, Zhao C, et al. Dramatically Enhanced Ambient Ammonia Electrosynthesis Performance by In-Operando Created Li–S Interactions on MoS_2 Electrocatalyst. *Adv Energy Mater* 2019;9:1803935. https://doi.org/10.1002/aenm.201803935

2. Zhao Z, Luo S, Ma P, Luo Y, Wu W, et al. In Situ Synthesis of MoS_2 on C_3N_4 To Form MoS_2/C_3N_4 with Interfacial Mo–N Coordination for Electrocatalytic Reduction of N_2 to NH_3. *ACS Sustainable Chem Eng* 2020;8:8814-22. https://doi.org/10.1021/acssuschemeng.0c02763

3. Jiang T, Li L, Li L, Liu Y, Zhang D, et al. Ultra-thin shelled $Cu_{2-x}S/MoS_2$ quantum dots for enhanced electrocatalytic nitrogen reduction. *Chem Eng J* 2021;426:130650. https://doi.org/10.1016/j.cej.2021.130650

4. Xiang L, Liu S, Zhao L, Yuan S, Li X, et al. Modifying the electronic structure of MoS_2 via interface engineering to boost intrinsic activity for nitrogen fixation. *J Alloys Compd* 2023;945:169201. https://doi.org/10.1016/j.jallcom.2023.169201

5. Ma C, Yan X, He H, Liu B, Yan S. A defective MoS_2 monolayer as an efficient electrocatalyst for the nitrogen reduction reaction: a combined theoretical and experimental study. *Sustainable Energy Fuels* 2021;5:2415-8. https://doi.org/10.1039/D1SE00346A

6. He Z, Jiang Y, Cui X, Liu Z, Meng X, et al. Fe-Doped 1T/2H Mixed-Phase MoS_2/C Nanostructures for N_2 Electroreduction into Ammonia. *ACS Appl Nano Mater* 2022;5:5470-8. https://doi.org/10.1021/acsanm.2c00467

7. Zhao X, Zhang X, Xue Z, Chen W, Zhou Z, et al. Fe nanodot-decorated MoS_2 nanosheets on carbon cloth: an efficient and flexible electrode for ambient ammonia synthesis. *J Mater Chem A*

2019;7:27417-22. https://doi.org/10.1039/C9TA09264A

8. Liu Y, Wang W, Zhang S, Li W, Wang G, et al. MoS_2 Nanodots Anchored on Reduced Graphene Oxide for Efficient N_2 Fixation to NH_3. *ACS Sustainable Chem Eng* 2020;8:2320-6. https://doi.org/10.1021/acssuschemeng.9b07679

9. Li X, Ren X, Liu X, Zhao J, Sun X, et al. A MoS_2 nanosheet–reduced graphene oxide hybrid: an efficient electrocatalyst for electrocatalytic N2 reduction to NH_3 under ambient conditions. *J Mater Chem A* 2019;7:2524-8. https://doi.org/10.1039/C8TA10433F

10. Zhang L, Ji X, Ren X, Ma Y, Shi X, et al. Electrochemical Ammonia Synthesis via Nitrogen Reduction Reaction on a MoS_2 Catalyst: Theoretical and Experimental Studies. *Adv Mater* 2018;30:1800191. https://doi.org/10.1002/adma.201800191