

## Electronic Supplementary Information

### CNT/VS<sub>2</sub>-MoS<sub>2</sub> with multi-interface structure for improved hydrogen evolution reaction

Xianpei Ren,<sup>\*a,b,d</sup> Qingbo Wei,<sup>\*c</sup> Fei Wu,<sup>a</sup> Yonghua Wang,<sup>a</sup> Liangjun Zhao<sup>a</sup>

<sup>a</sup>School of Physics and Electronic Engineering, School of computer science and Engineering, Sichuan University of Science and Engineering, Zigong 643000, China

<sup>b</sup>Key Lab of Process Analysis and Control of Sichuan Universities, Yibin University, Yibin 644000, China

<sup>c</sup>Key Laboratory of Chemical Reaction Engineering of Shaanxi Province; College of Chemistry & Chemical Engineering, Yan'an University, Yan'an 716000, China

<sup>d</sup>Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, China.

\*Corresponding author: E-mail: renxianpei@163.com, E-mail: qbwei2011@126.com.

#### Experimental Section

##### *Reagents and materials*

Sodium orthovanadate and thioacetamide were purchased from Aladdin Industrial Inc. Thiourea and molybdenum chloride were purchased from Sinopharm Chemical Reagent Co., Ltd. Carbon nanotube (CNT) was purchased from Nanjing XFNANO Materials Tech Co., Ltd. Nafion (5 wt%) was purchased from Sigma-Aldrich. Pt and glassy carbon electrodes were purchased from Tianjin Aidahengsheng Technology. Co. Ltd. All chemicals were used as received without further purification. All chemicals were used as received without further purification.

##### *Synthesis of CNT/VS<sub>2</sub>*

The CNT/VS<sub>2</sub> was synthesized by a hydrothermal process. At first, 370 mg

sodium orthovanadate and 600 mg thioacetamide were dissolved in 30 mL deionized water and ultrasonication for 0.5 h to form homogenous solution. Then 24 mg CNT was added in the above solution to fabricate CNT/VS<sub>2</sub>, after being magnetically stirring for 1 h, the whole mixed solution transferred into a 50 mL Teflon-lined stainless steel autoclave and maintained at 160 °C for 20 h. After natural cooling, the precipitate was collected by centrifugation, washed with DI water and ethanol, and dried in a vacuum oven at 60 °C for overnight. The VS<sub>2</sub> powder could be prepared with the same procedure without CNT adding into the starting materials solution.

### ***Synthesis of CNT/VS<sub>2</sub>-MoS<sub>2</sub> and VS<sub>2</sub>-MoS<sub>2</sub>***

The CNT/VS<sub>2</sub>-MoS<sub>2</sub> and VS<sub>2</sub>-MoS<sub>2</sub> were synthesized by a sol-gel process. Firstly, 110 mg molybdenum chloride and 182 mg thiourea were mixed in a 50 mL beaker. Excessive ethanol was slowly added into the beaker and ultrasonication for 0.5 h to form homogenous solution, then 100 mg the as-prepared CNT/VS<sub>2</sub> (or 90.5 mg VS<sub>2</sub>) was added to the solution and ultrasonication for 30 min. The gel-like precursor powders were formed after drying and transferred into a corundum boat and heated in a homemade quartz tube furnace for 2 h under argon gas (150 sccm) flow at 600 °C. After that, the products were cooled to room temperature under the protection of argon gas and collected from the quartz tube. With the same method described above, without CNT/VS<sub>2</sub> or VS<sub>2</sub> adding into the starting materials solution, the MoS<sub>2</sub> powder could be obtained after annealing at 600 °C for 2 hours in Ar atmosphere.

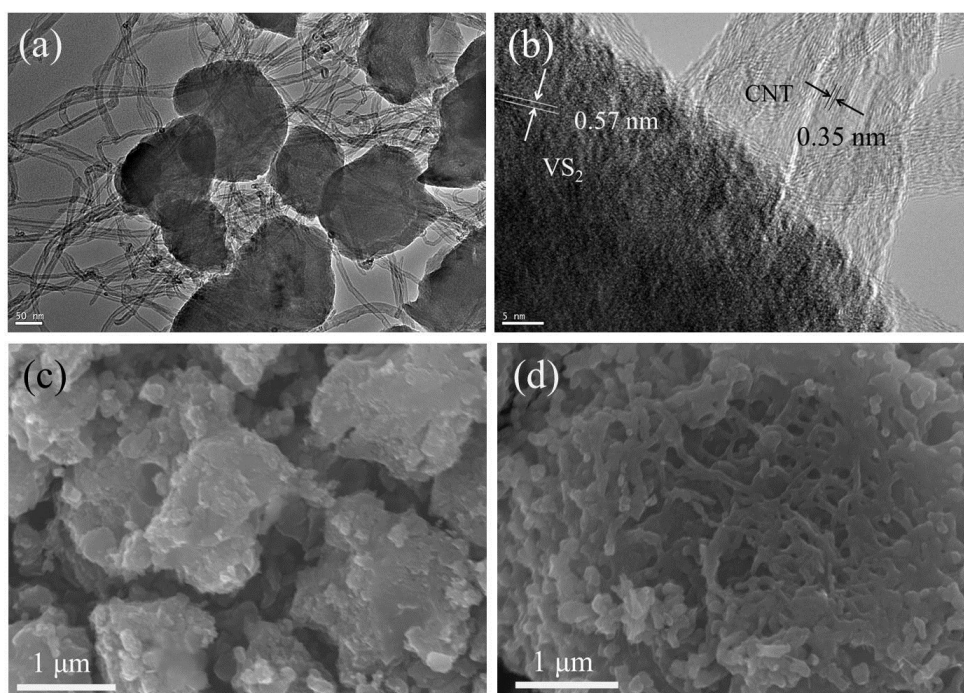
### ***Characterization***

The surface morphology and particle size of the samples was recorded on a JSM-7610F scanning electron microscopy (SEM), with an operating voltage of 20 kV. The morphology and fine structure were observed by transmission electron microscopy (TEM; FEI, Tecnai G2). Powder X-ray diffraction (XRD) tests were carried out by Bruker D8 ADVANCE with Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). The surface composition and chemical environment of the samples were analyzed via X-ray photoelectron spectroscopy (XPS, Thermo-VG Scientific, ESCALAB 250) using an

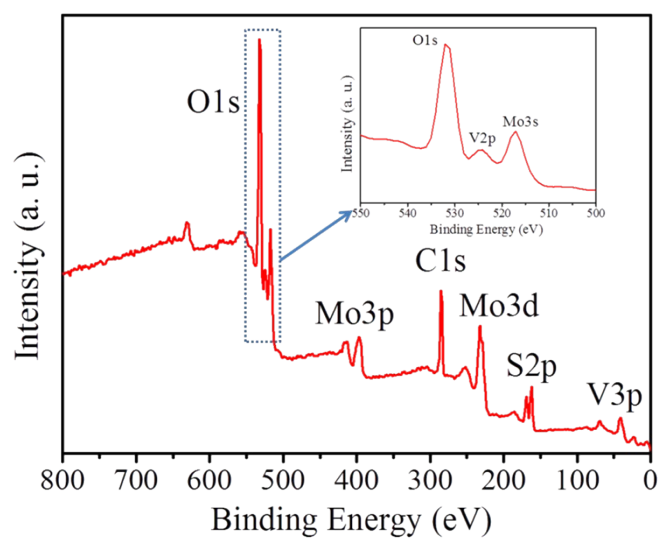
Al K $\alpha$  X-ray source.

### ***Electrochemical characterization***

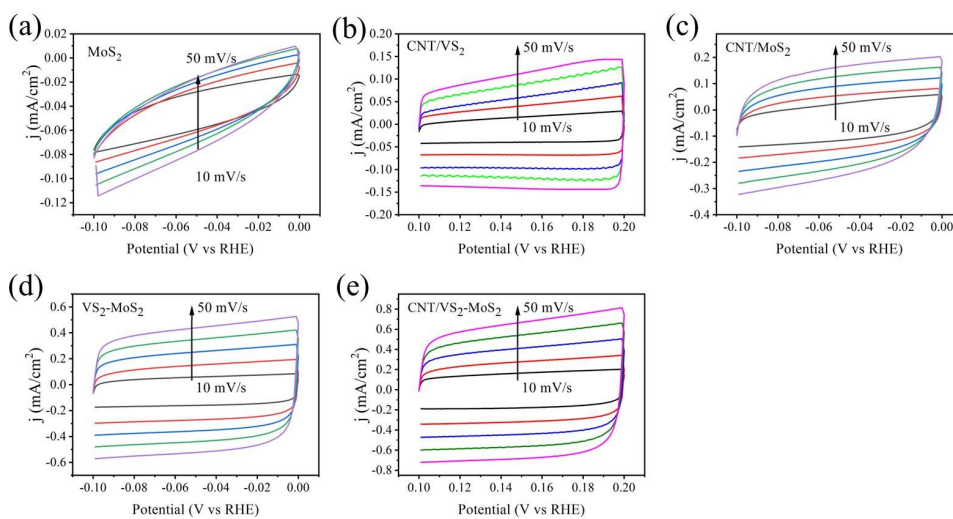
All electrochemical tests were carried out at room temperature by an electrochemical workstation (CHI604E, Shanghai Chenhua). The synthesized samples were used as working electrode, the graphite rod was used as the counter electrode and Ag/AgCl (saturated KCl filled) as the reference electrode. All measurements were performed in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. The dispersion was obtained by mixing the catalyst (4 mg) and 80  $\mu$ L of Nafion (5 wt %) with 1 mL solvent (4:1 v/v water/isopropanol) by sonication. The above dispersion (5  $\mu$ L) was transferred to the glassy carbon electrode with 3 mm diameter (loading ca. 0.285 mg cm<sup>-2</sup>), and then dried at room temperature. All linear-sweep voltammograms (LSV) were tested at a scan of 10 mV  $\cdot$  s<sup>-1</sup>, and the potential was converted by the use of equation  $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.205 + 0.0591 \times \text{pH}$ . All the potentials were calibrated with respect to a reversible hydrogen electrode. Nyquist plots were recorded under -0.3 V versus the RHE in the frequency range from 1 Hz to 100 kHz with an amplitude potential of 5 mV. The Cyclic voltammetry (CV) measurement for the electrochemical double-layer capacitance ( $C_{\text{dl}}$ ) estimation was performed in the range of potential between 0.10 V and 0.20 V at various scan rates from 10 to 50 mV/s.



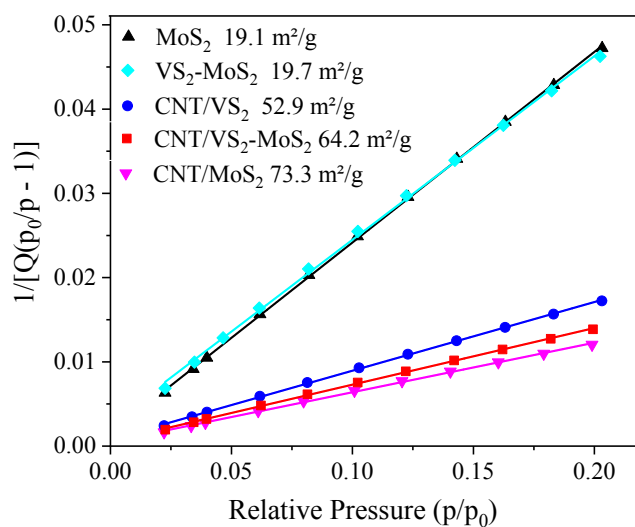
**Fig. S1** TEM (a) and HRTEM (b) image of CNT/VS<sub>2</sub>. SEM images of VS<sub>2</sub>-MoS<sub>2</sub> (c) and CNT/MoS<sub>2</sub> (d).



**Fig. S2** XPS survey spectrum of CNT/VS<sub>2</sub>-MoS<sub>2</sub>.



**Fig. S3** (a-e) Electrochemical cyclic voltammogram of as-grown catalysts at different potential scanning rates. The scan rates are 10, 20, 30, 40 and 50 mV/s. The selected potential range where no faradic current was observed is 0.10 to 0.2 V vs RHE.



**Fig. S4** The BET surface area of MoS<sub>2</sub>, CNT/MoS<sub>2</sub>, VS<sub>2</sub>-MoS<sub>2</sub>, CNT/VS<sub>2</sub> and CNT/VS<sub>2</sub>-MoS<sub>2</sub>.

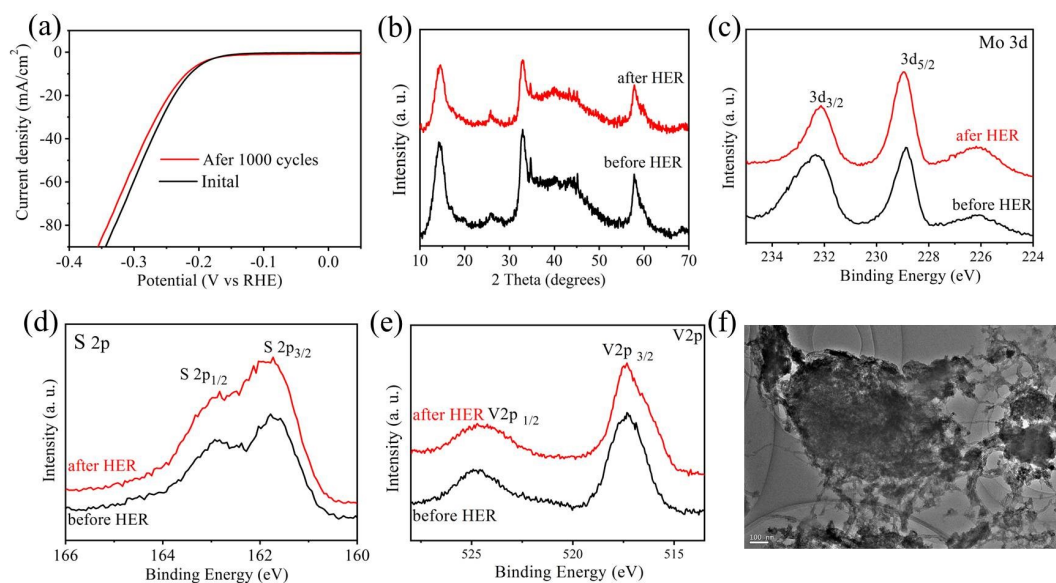


Fig. S5 (a) Stability of CNT/VS<sub>2</sub>-MoS<sub>2</sub> in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution after 1000 cycles. (b) XRD patterns of the CNT/VS<sub>2</sub>-MoS<sub>2</sub> electrocatalyst before and after HER measurement, (c-e) High-resolution Mo 3d, S 2p and V 2p XPS spectra of the CNT/VS<sub>2</sub>-MoS<sub>2</sub> electrocatalyst before and after HER measurement. (f) TEM image of CNT/VS<sub>2</sub>-MoS<sub>2</sub> after HER measurement.

**Table S1.** Comparison of HER performance in acidic media for CNT/VS<sub>2</sub>-MoS<sub>2</sub> with other state-of-the-art MoS<sub>2</sub>-based HER electrocatalysts.

catalyst	$\eta(\text{mV})$ for $j=10 \text{ mA cm}^{-2}$	Tafel (mV/dec)	slope	References
MoS <sub>2</sub> microflowers	-330.8	101.1		
VS <sub>2</sub> microflakes	-259.7	89.3		[1]
MoS <sub>2</sub> /VS <sub>2</sub> hybrid	-199.6	95.2		
pristine VS <sub>2</sub>	/	382.2		
MoS <sub>2</sub> NDs/VS <sub>2</sub>	-291	58.1		[2]
MoS <sub>2</sub> nanosheets	-979	133.7		
VS <sub>2</sub> nanoflowers	-611	105.6		[3]
VS <sub>2</sub> @MoS <sub>2</sub>	-177	54.5		
MoS <sub>2</sub> /MoO <sub>2</sub>	-380	113		[4]
MoS <sub>2</sub> -NiS <sub>2</sub>	-225	97		
MoS <sub>2</sub> -NiS <sub>2</sub> /NGF	-172	70		[5]
CNT/VS <sub>2</sub> -MoS <sub>2</sub>	-215	64		This work

MoS<sub>2</sub> NDs: MoS<sub>2</sub> nanodots; CNT: carbon nanotubes

NGF: nitrogen-doped graphene foam

## References

- [1] S. H. Yu, Z. Tang, Y. Shao, H. Dai, H. Y. Wang, J. Yan, H. Pan and D. H. C. Chua, *ACS Appl. Energy Mater.*, 2019, **2**, 5799-5808.
- [2] C. Du, D. Liang, M. Shang, J. Zhang, J. Mao, P. Liu and W. Song, *ACS Appl. Mater. Interfaces* 2017, **9**, 42139-42148.
- [3] X. Chen, K. Yu, Y. Shen, Y. Feng and Z. Zhu, *ACS Appl. Mater. Interfaces*, 2017, **9**, 42139-42148
- [4] J. Yan, A. Rath, H. Wang, S. H. Yu, S. J. Pennycook, D. H. C. Chua, *Mater. Res. Lett.*, 2019, **7**, 275-281.
- [5] P. Kuang, M. He, H. Zou, J. Yu and K. Fan, *Appl. Catal. B: Environ.*, 2019, **254**,

15-25.