Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Coupling MoS_2 nanosheets with CeO_2 for efficiently electrocatalytic hydrogen evolution at large current densities

Rui-Qing Li,[a]* Changming Wang,[a] Shuixiang Xie,[a] Tianyu Hang,[a] Xiaoyu Wan,[a] Jinjue Zeng,[b]* and Wei Zhang[a]*

[a] School of Textile and Clothing, Nantong University, Nantong 226019, China

E-mail: liruiqing@ntu.edu.cn; zhangwei@ntu.edu.cn

[b] National Laboratory of Solid State Microstructures (NLSSM), Collaborative Innovation Center of Advanced Microstructures, Jiangsu Key Laboratory of Artificial Functional Materials, College of Engineering and Applied Sciences, Nanjing University, Nanjing, 210093, China

E-mail: zengjinjue@smail.nju.edu.cn

1. Experient

1.1 Chemicals and materials

$NaMoO_4$ was purchased from Sinopharm Chemical Reagent Co. Ltd. $CS(NH_2)_2$ and $Ce(NO_3)_2{\cdot}6H_2O$ were provided by Aladdin Chemical Reagent Co. Ltd. Potassium hydroxide (KOH) and ethanol were supplied from Adamas-beta®. Commercial Pt/C (platinum, 20% on carbon) was provided by Alfa Aesar.

1.2 Synthesis of MoS_2/CeO_2 electrode

In a typical preparation process, 0.4839 g $Na_2MoO_4{\cdot}2H_2O$, 0.6090 g $CS(NH_2)_2$ and 0.0434 g $Ce(NO_3)_2{\cdot}6H_2O$ were added into 35 mL deionized water under stirring to obtain clear aqueous, which was transferred into a stainless-steel autoclave. Then, a piece of Ti mesh (3 × 2 cm) was immersed into above aqueous, sealed and kept at 200 °C for 24 h. After cooling down to room temperature, the $MoS_2/CeO_2/Ti$ was obtained by washing for several times, and dried at 70 °C for 6 h. The MoS_2/Ti was synthesized under similar conditions without adding $Ce(NO_3)_2{\cdot}6H_2O$.

1.3 Material characterization

X-ray diffraction patterns were characterized chemical components and crystal structure on X-ray diffraction (XRD, Bruker D8). The field-emission scanning electron microscopy equipped with energy-dispersive X-ray analysis (SEM, Thermo Fisher Scientific FIB-SEM GX4) and Transmission electron microscopy (TEM, FEI Tecnai G20) were tested to analyze morphological and structural characteristics. The composition and valences are studied out on a X-ray photo-electron spectrometer (XPS, Thermo ESCALAB 250).

1.3. Electrochemical measurements

The electrochemical measurements were performed on an electrochemical workstation (CHI 760E) by employing a typical three-electrode system in 1 M KOH. The synthesized electrode, saturated calomel electrode and graphite rod were used as the working, reference and counter electrodes. All potentials were converted to the reversible hydrogen electrode (E_{RHE}) according to the Nernst equation: $E_{RHE} = E_{SCE} + 0.242 + 0.059 \times pH$. To evaluate HER performance, linear sweep voltammetry was recorded with a fixed scan rate of 2 mV s^{-1}. The electrochemical impedance

spectroscopy was tested over a frequency range of 0.1-100 kHz. The electrochemical double-layer capacitance of catalysts was evaluated using cyclic voltammetry curves in a non-Faradic region at different rates from 10 to 120 mV s^{-1}. The Faradaic efficiency (FE) was evaluated by comparing the actually collected and theoretically generated H_2 amount during the HER process. To obtain the FE for HER, the actually generated H_2 was collected by a water drainage method at a constant current density of 50 mA cm^{-2}. The volumes of collected gas are 3.2, 5.1, 6.8 and 8.5 ml at 10, 15, 20, and 25 min, respectively, which was calculated as a corresponding molar amount using the ideal gas law. The theoretically generated gas amount was calculated using the Faraday law by assuming that only HER process happens at the electrode, in which states that the passage of 96485.4 C charge causes 1 equivalent reaction.

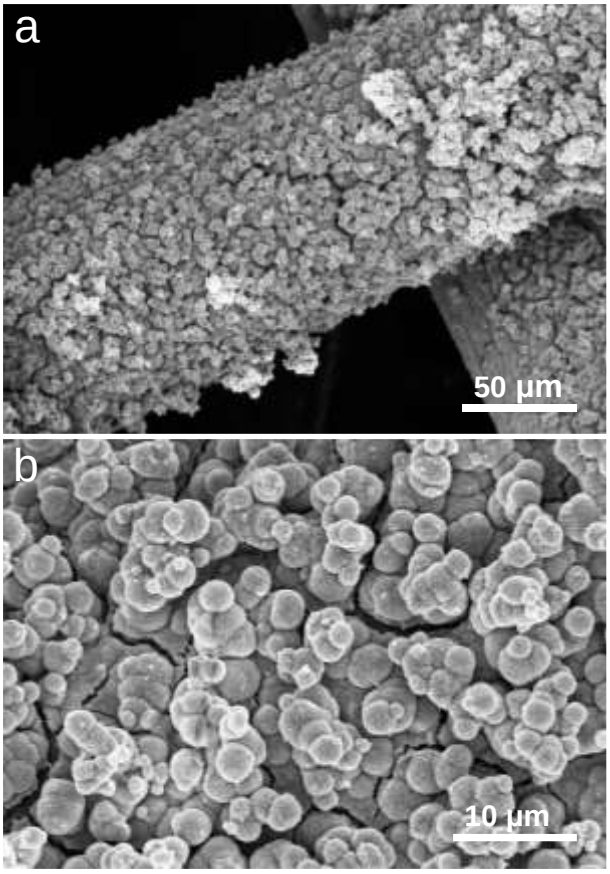

Fig. S1. (a,b) SEM images of MoS_2/CeO_2.

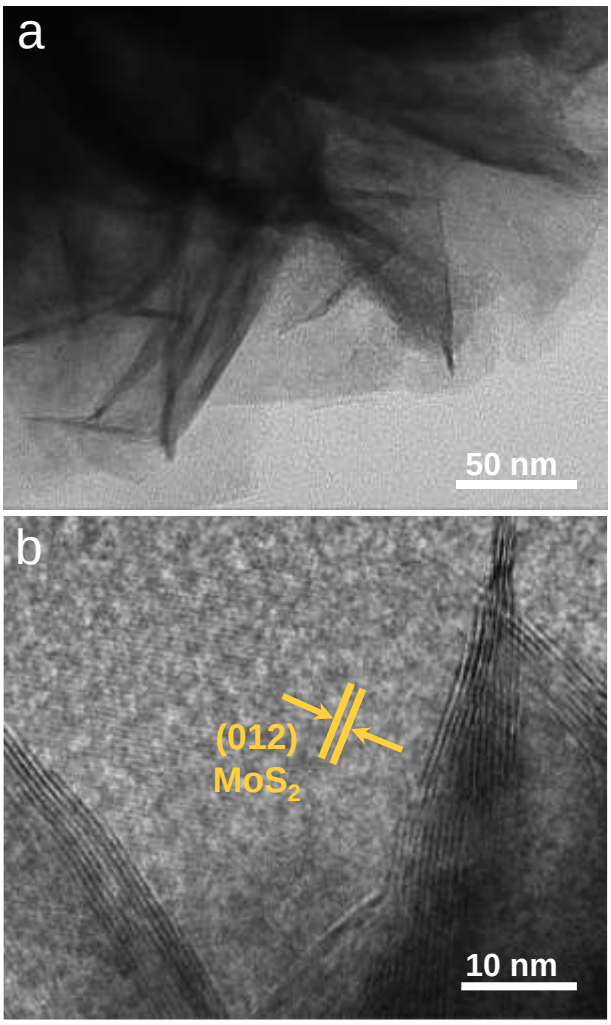

Fig. S2. (a) TEM and (b) HRTEM images of MoS_2.

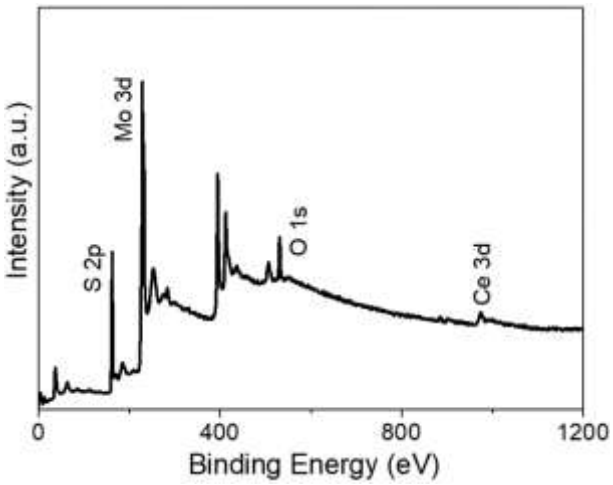

Fig. S3. XPS survey spectrum of MoS_2/CeO_2.

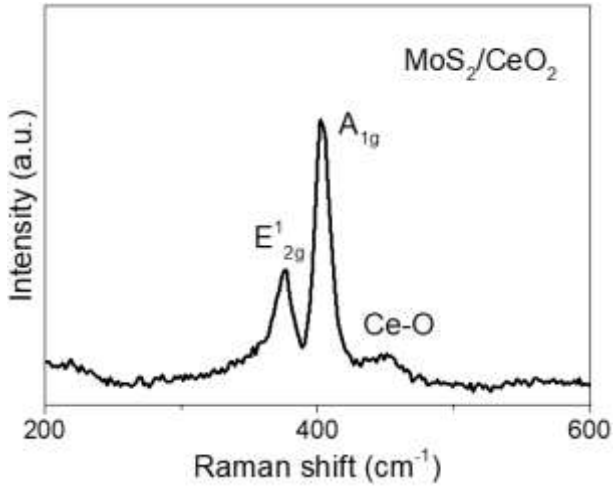

Fig. S4. Raman spectra of MoS_2/CeO_2.

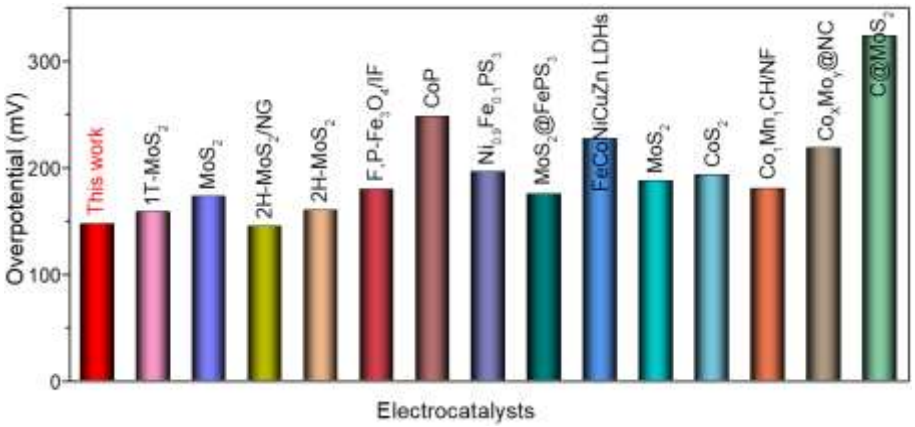

Fig. S5. Comparison of HER activities of MoS_2/CeO_2 with developed catalysts.[1-14] -

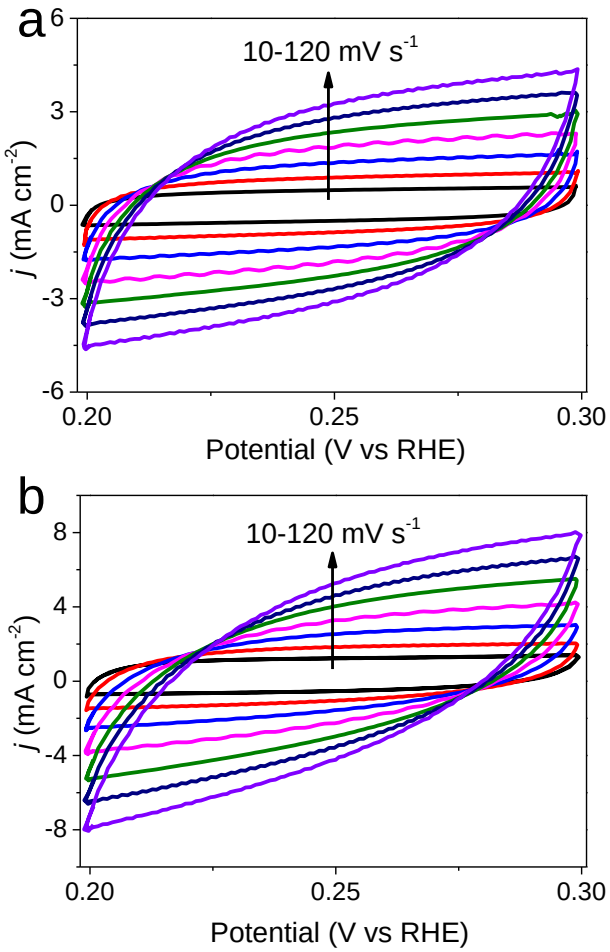

Fig. S6. Cyclic curves at different scan rates of (a) MoS_2 and (b) MoS_2/CeO_2.

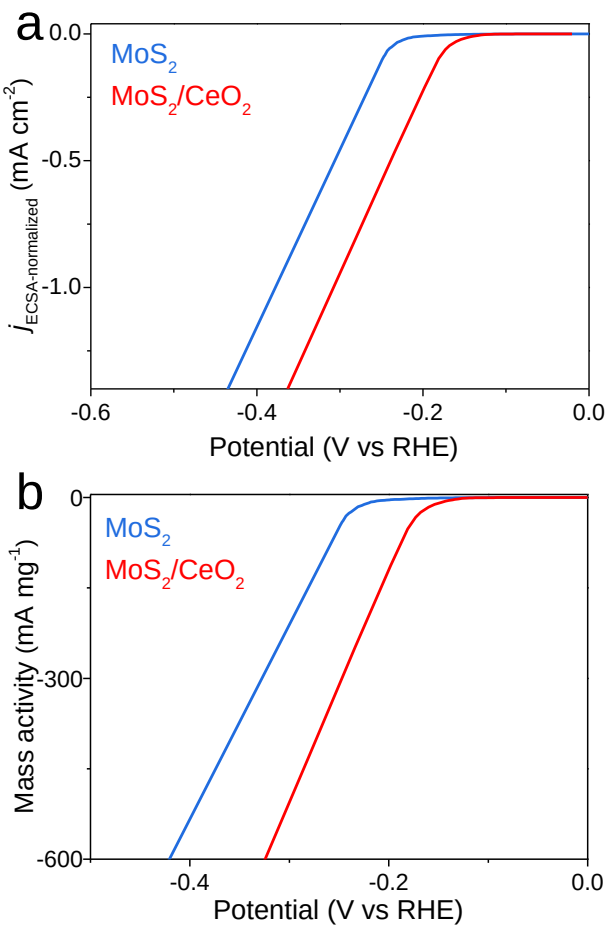

Fig. S7. (a) ECSA-normalized and (b) mass-normalized polarization curves of MoS_2 and MoS_2/CeO_2.

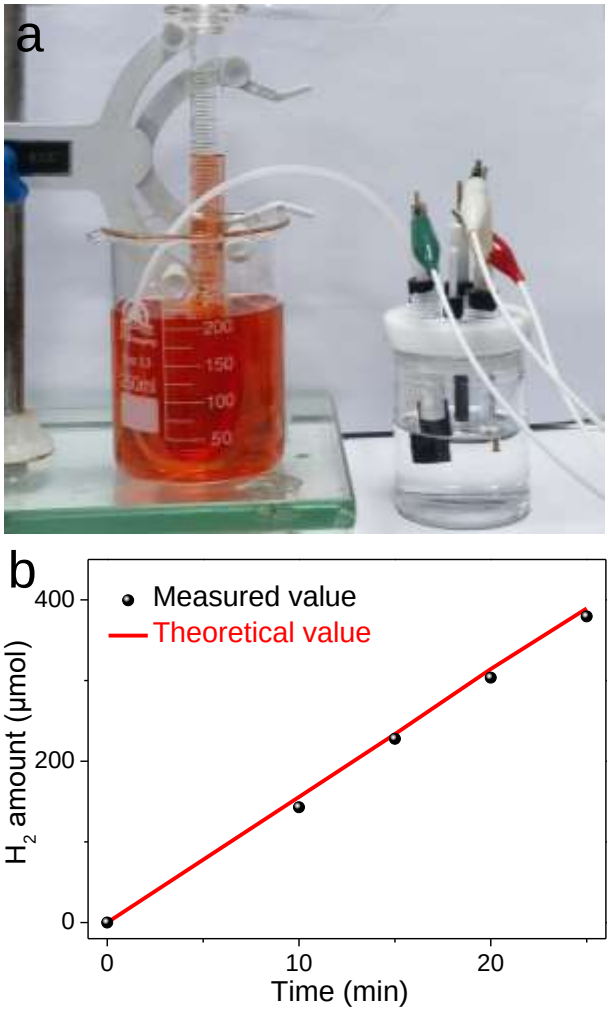

Fig. S8. Experimental and theoretical amount of H_2 production over the MoS_2/CeO_2.

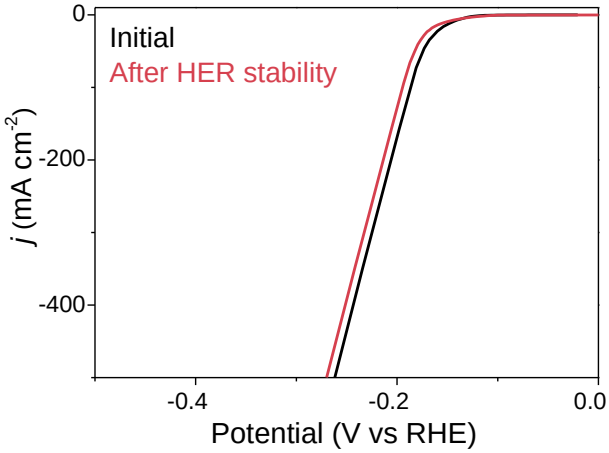

Fig. S9. Polarization curves recorded for MoS_2/CeO_2 before and after HER stability.

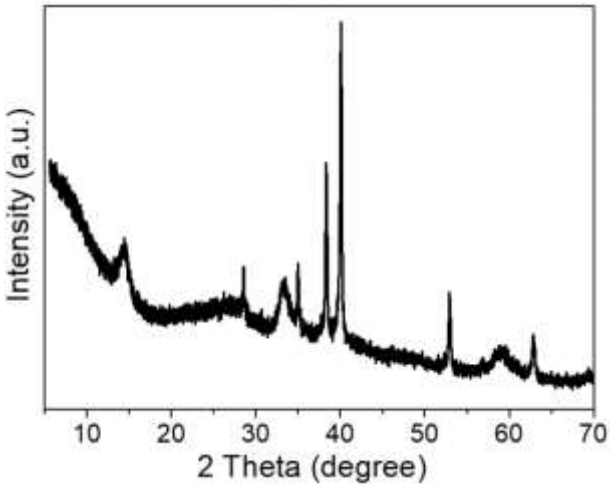

Fig. S10. XRD pattern of MoS_2/CeO_2 after HER test.

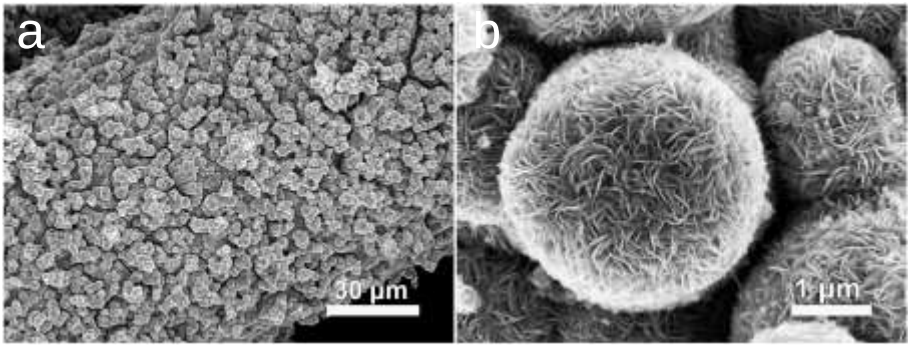

Fig. S11. (a,b) SEM images of MoS_2/CeO_2 after HER test.

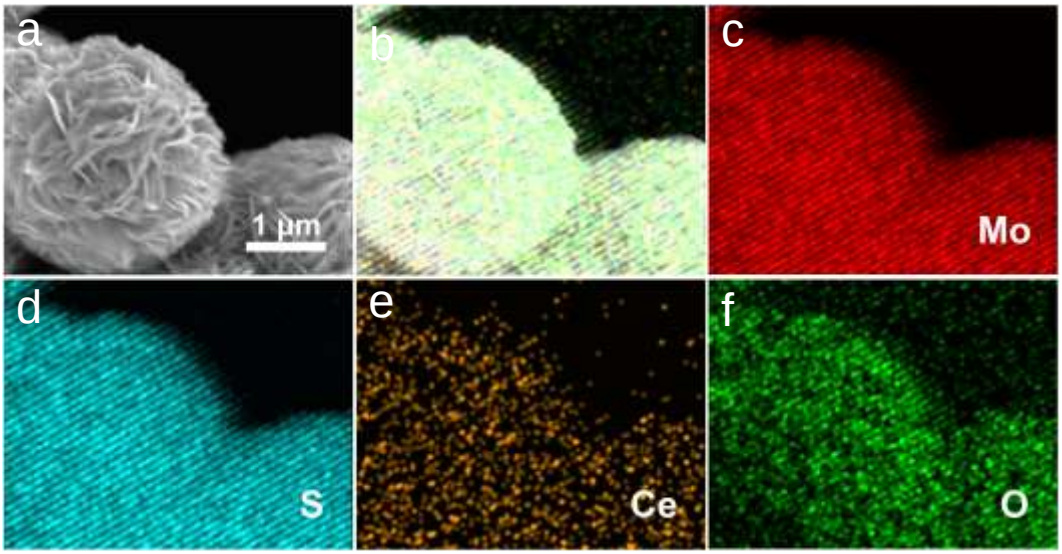

Fig. S12. (a) SEM and (b-f) corresponding element mapping images of MoS_2/CeO_2 after HER test.

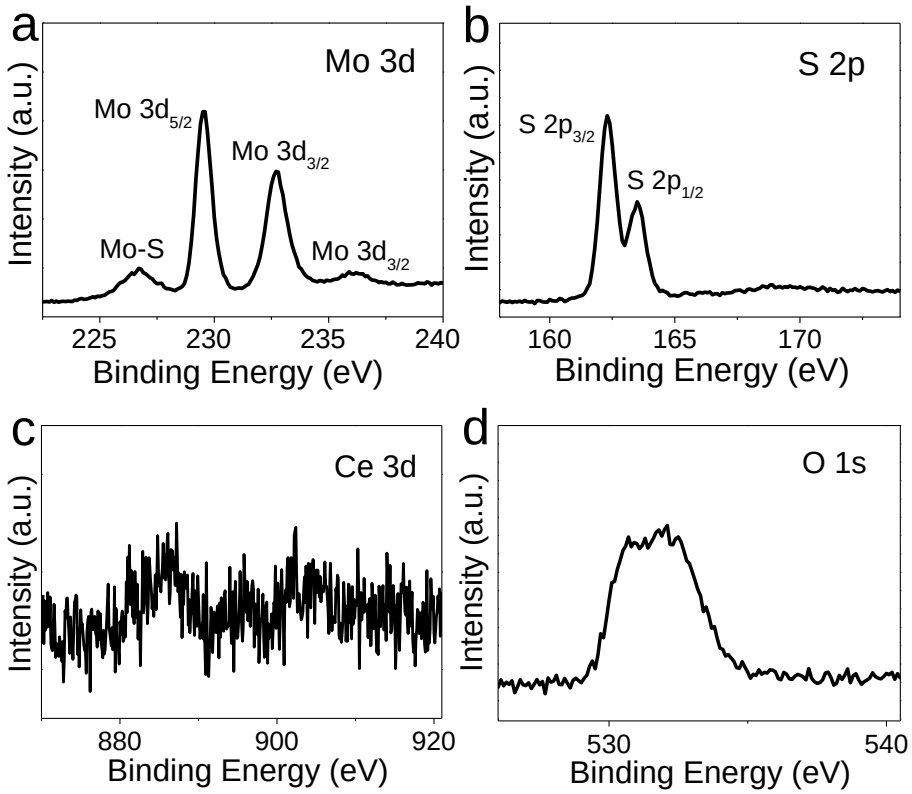

Fig. S13. XPS spectra of MoS_2/CeO_2 after HER test.

References

1 X. Guo, E. Song, W. Zhao, S. Xu, W. Zhao, Y. Lei, Y. Fang, J. Liu and F. Huang, *Nat. Commun.*, 2022, **13**, 5954.

2 B. Chen, P. Hu, F. Yang, X. Hua, F. Yang, F. Zhu, R. Sun, K. Hao and Z. Yin, *Small*, 2023, **19**, 2207177.

3 J. Qin, C. Xi, R. Zhang, T. Liu, P. Zou, D. Wu, Q. Guo, J. Mao, H. Xin and Jing Yang, *ACS Catal.*, 2021, **11**, 4486.

4 L. Li, Z. Qin, L. Ries, S. Hong, T. Michel, J. Yang, C. Salameh, M. Bechelany, P. Miele, D. Kaplan, M. Chhowalla and D. Voiry, *ACS Nano*, 2019, **13**, 6824.

5 X. Zhang, F. Li, R. Fan, J. Zhao, B. Dong, F. Wang, H. Liu, J. Yu, C. Liu and Y. Chai, *J. Mater. Chem. A*, 2021, **9**, 15836.

6 J. Xie, H. Liu, Y. Zhen, Y. Dong, R. Luan, N. Yu, D. Liu, Y. Chai and B. Dong, *J. Colloid Interf. Sci.*, 2022, **614**, 84.

7 C. Du, K. Dinh, Q. Liang, Y. Zheng, Y. Luo, J. Zhang and Q. Yan, *Adv. Energy Mater.*,

2018, **8**, 1801127.

8 H. Huang, J. Song, D. Yu, Y. Hao, Y. Wang and S. Peng, *Appl. Surf. Sci.*, 2020, **525**, 146623.

9 J. Yao, F. Wang, W. He, Y. Li, L. Liang, Q. Hao and H. Liu, *Chem. Commun.*, 2023, **59**, 3719.

10 J. Radhakrishnan, A. Kareem, S. Senthilkuma, K. Biswas, *J. Alloy. Compd.*, 2022, **917**, 165444.

11 X. Ma, W. Zhang, Y. Deng, C. Zhong, W. Hu and X. Han, *Nanoscale*, 2018, **10**, 4816.

12 T. Tang, W. Jiang, S. Niu, N. Liu, H. Luo, Y. Chen, S. Jin, F. Gao, L. Wan and J. Hu, *J. Am. Chem. Soc.*, 2017, **139**, 8320.

13 J. Jiang, Q. Liu, C. Zeng, L. Ai, *J. Mater. Chem. A*, 2017, **5**, 16929.

14 I. Amiinu, Z, Pu, X, Liu, K, Owusu, H, Monestel, F, Boakye, H, Zhang and Shichun Mu, *Adv. Funct. Mater.*, 2017, **27**, 1702300.