Electronic Supplementary Information

3D graphene-supported MoS_2 nanosphere and nanosheet heterostructure as highly efficient free-standing hydrogen evolution electrode

Xuewan Wang*

School of Chemical and Biomedical Engineering, Nanyang Technological University, 70 Nanyang Drive, 637457, Singapore.

1. Synthesis of 3D graphene

3D graphene was prepared by a previously-reported CVD method.[1, 2] In a typical synthesis route, nickel foam (Alantum Advanced Technology Materials, China) with a thickness of 0.5 mm was heated to 950 °C in tube furnace under argon (Ar, 55 sccm) and hydrogen (H_2, 27 sccm) atmosphere, and maintained for 10 min. Ethanol was employed as carbon source and bubbled into the tube furnace at that temperature for 15 min. After the bubbling process, the furnace was quickly cooled to room temperature. Ni foam was removed by 3 M hydrochloric acid (HCl) and the remained 3D graphene was completely washed before drying at 100 °C.

2. Preparation of 3D graphene-MoS_2 free-standing electrode

For the synthesis of 3D graphene/MoS_2 composites, certain amount of ammonium tetrathiomolybdate (ATTM, Sigma-aldrich) was added into 20 mL DMF which contained 0.1 mL hydrazine monohydrate (Sigma-Aldrich, 64-65%). After ultrasonication for 30 min, the resultant clear solution was transferred into 80 mL Teflon-lined autoclave. Two pieces of 3D graphene (~2.5 cm × 3 cm) fixed on glass slides using silicone rubber were immersed into the precursor solution and heated at 200 °C for 12 h. The products were washed with deionized water and ethanol completely and dried at 50 °C. Pure MoS_2 was prepared by the same procedure in the absence of 3D graphene. Free-standing electrode was prepared by connecting hybrid foam with copper wire using silver paint. To avoid the possible HER interference, silver paint and copper wire was further insulated to the electrolyte with silicone rubber.

3. Characterization

The morphologies of 3D graphene and 3D graphene-MoS_2 were observed by field-emission scanning electron microscope (FESEM, Model JSM-6700F, JEOL) and transmission electron microscope (TEM) (JSM-6700F, JEOL). X-ray diffraction (XRD) patterns were carried out on D2 phaser X-ray diffractionmeter (Bruker) using Cu Kα radiation. The Raman spectra were obtained by using Raman-Renishaw system with a laser wavelength of 514 nm.

4. Electrochemical measurements

All electrochemical measurements were performed using a CHI 660D electrochemical workstation (Chenhua, Shanghai) in a standard three electrode setup. Pt foil and saturated Ag/AgCl electrode were used as counter and reference electrode, respectively. Free-standing 3D graphene/MoS_2 electrode was directly used as work electrode. For comparison, pure 3D graphene electrode and Pt foil were also prepared as working electrodes. The precise area of working electrode equalled to the size of 3D graphene/MoS_2 pieces which was carefully measured on each of as-fabricated electrodes. The weight of 3D graphene-supported MoS_2 nanosphere and nanosheet heterostructure (sample C) was *ca.* 1.86 mg cm^{-2} with MoS2 of *ca.* 1 mg cm^{-2}. The electrocatalytic performance of all electrodes was examined by polarization curves and Tafel plots *via* linear sweep voltammetery (LSV) at scan rate of 2 mV/s in 0.5 M H_2SO_4. Electrochemical impedance measurements were carried out at open circuit potential in the frequency range of 0.1 to 10^5 Hz with AC voltage amplitude of 10 mV. Ag/AgCl electrode was calibrated in H_2-satured 0.5 M H_2SO_4 using Pt foil as the working electrode (see Fig. S5). Thus, all the potentials were recorded with respect to reversible hydrogen electrode (RHE) and with IR compensation.

5. Supplementary figures and table

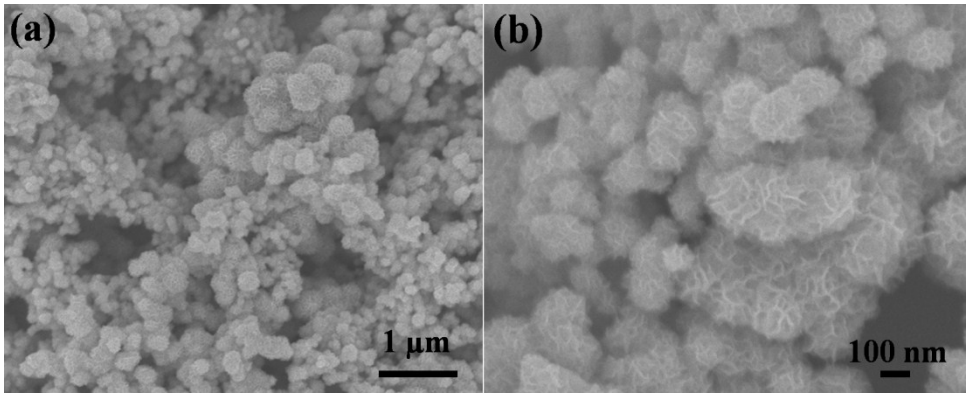

Fig. S1 SEM images of bare MoS_2 synthesized in the absence of 3D graphene.

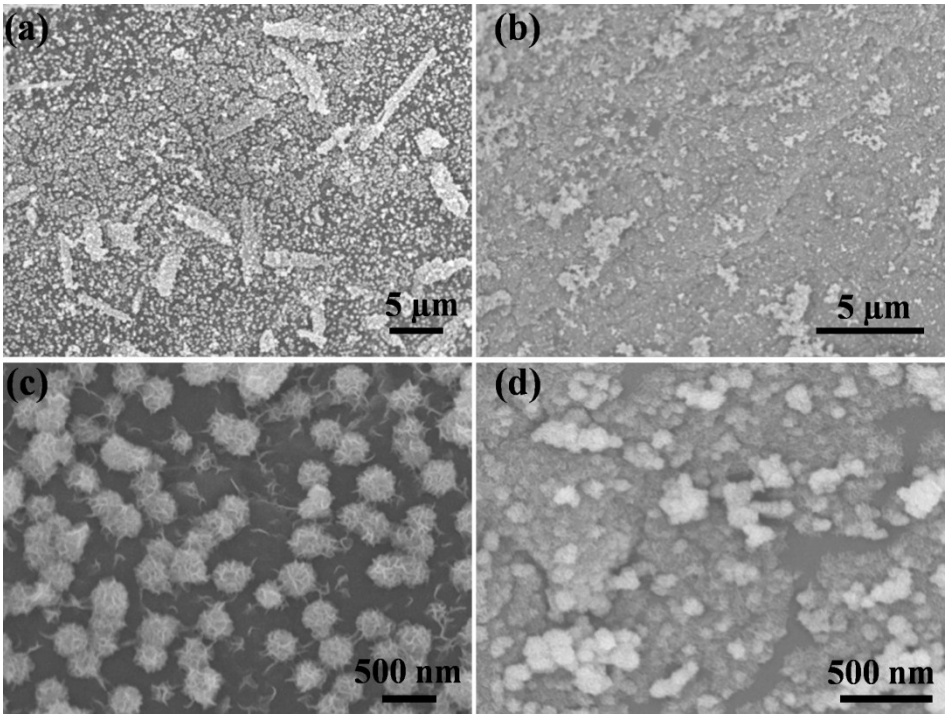

Fig S2 SEM images of 3D graphene/MoS_2 sample B and D prepared at AMT concentration of (a and c) 1.1 mg/mL and (b and d) 4.4 mg/mL, respectively.

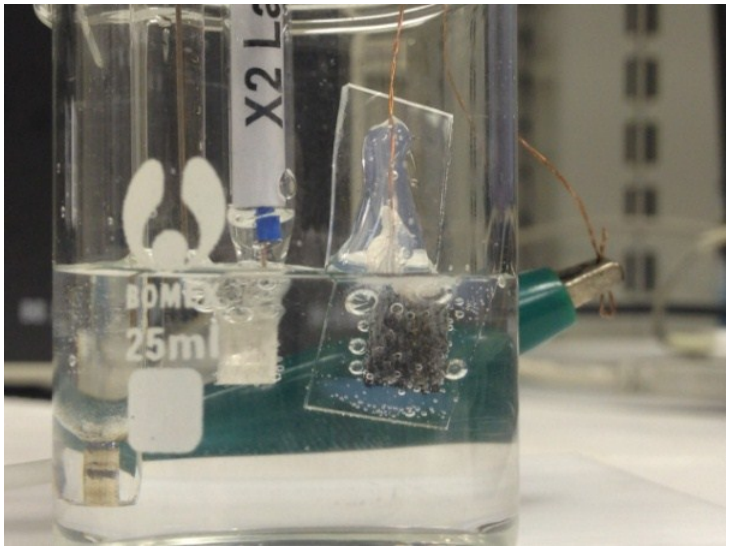

Fig. S3 Optical photograph of 3D graphene/MoS_2 C electrode at -0.6 V vs. Ag/AgCl.

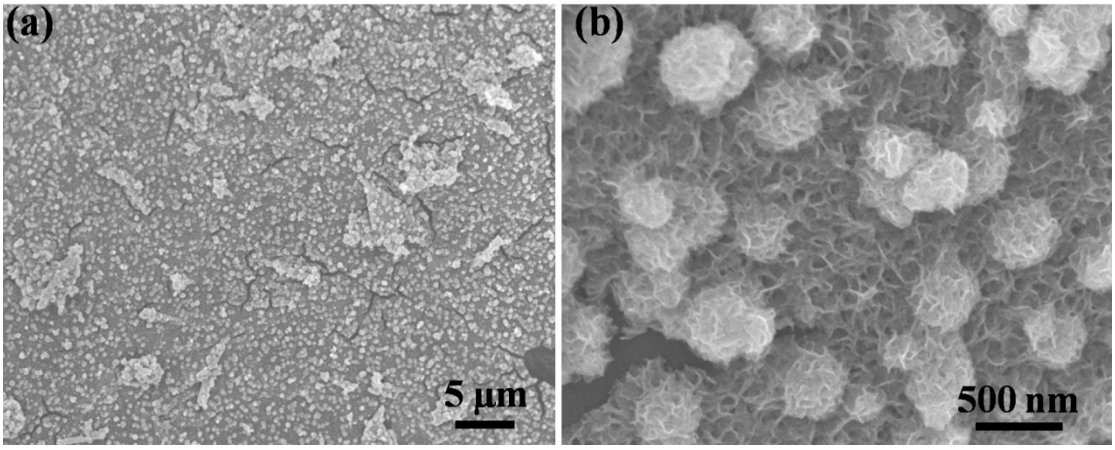

Fig. S4 SEM images of 3D graphene/MoS_2 C electrode after stability measurement.

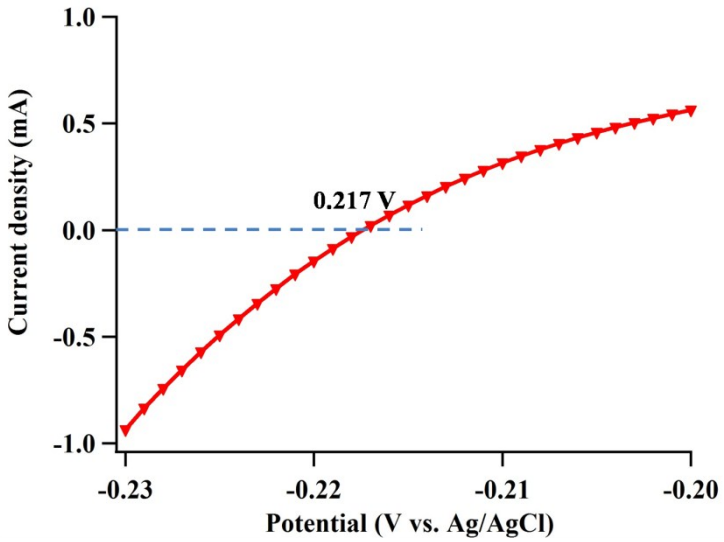

Fig. S5 Ag/AgCl reference electrode calibration in H_2-satured 0.5 M H_2SO_4

Table S1 Summary of HER parameters for various molybdenum sulfide catalysts

Catalysts	Onset potential (mV)	Exchange current density ($\mu A\ cm^{-2}$)	Tafel slope ($mV\ dec^{-1}$)	Tafel region (mV)	Current density at -200 mV ($mA\ cm^{-2}$)	Ref.
MoS_2 on Au electrode	90	9.3	69	90~190	4~6	3
Defect rich MoS_2	120	8.91	50	120~180	13	4
MWCNT/MoS_2	90	—	44.6	135~180	17	5
Carbon cloth/crumpled RGO/MoS_x	100~120	10~100	51.9	135~180	75	6
RGO/MoS_2	100	—	41	100~140	—	7
Ni foam/ graphene/MoS_x	90~100	—	42.8	109-141	40~50	8
Core-shell MoS_2/MoO_3 nanowire	150~200	—	50~60	—	< 2	9
MoSx/glassy carbon electrode	100~120	0.04~0.15	40	120~200	14	10
MoS_2 quantum dots/MoS_2 sheets	—	32	74	—	—	11
Mesoporous RGO/MoS_2	100	3	42	90~120	100	12
3D graphene/MoS_2	110	3.5	47	122-181	50	Our work

6. Reference

1. X. C. Dong, H. Xu, X. W. Wang, Y. X. Huang, M. B. Chan-Park, H. Zhang, L. H. Wang, W. Huang and P. Chen, *Acs Nano*, 2012, **6**, 3206-3213.
2. X. C. Dong, X. W. Wang, L. H. Wang, H. Song, H. Zhang, W. Huang and P. Chen, *Acs Appl. Mater. Interfaces*, 2012, **4**, 3129-3133.
3. T. Y. Wang, L. Liu, Z. W. Zhu, P. Papakonstantinou, J. B. Hu, H. Y. Liu and M. X. Li, *Energy Environ. Sci.*, 2013, **6**, 625-633.
4. J. F. Xie, H. Zhang, S. Li, R. X. Wang, X. Sun, M. Zhou, J. F. Zhou, X. W. Lou and Y. Xie, *Adv. Mater.*, 2013, **25**, 5807-5813.

5. Y. Yan, X. M. Ge, Z. L. Liu, J. Y. Wang, J. M. Lee and X. Wang, *Nanoscale*, 2013, **5**, 7768-7771.

6. A. J. Smith, Y. H. Chang, K. Raidongia, T. Y. Chen, L. J. Li and J. X. Huang, *Adv. Energy Mater.*, 2014, **4**, 1400398.

7. Y. G. Li, H. L. Wang, L. M. Xie, Y. Y. Liang, G. S. Hong and H. J. Dai, *J. Am. Chem. Soc.*, 2011, **133**, 7296-7299.

8. Y. H. Chang, C. T. Lin, T. Y. Chen, C. L. Hsu, Y. H. Lee, W. J. Zhang, K. H. Wei and L. J. Li, *Adv. Mater.*, 2013, **25**, 756-760.

9. Z. B. Chen, D. Cummins, B. N. Reinecke, E. Clark, M. K. Sunkara and T. F. Jaramillo, *Nano Lett.*, 2011, **11**, 4168-4175.

10. D. Merki, S. Fierro, H. Vrubel and X. L. Hu, *Chem. Sci.*, 2011, **2**, 1262-1267.

11. D. Gopalakrishnan, D. Damien and M. M. Shaijumon, *Acs Nano*, 2014, **8**, 5297-5303.

12. L. Liao, J. Zhu, X. J. Bian, L. N. Zhu, M. D. Scanlon, H. H. Girault and B. H. Liu, *Adv. Funct. Mater.*, 2013, **23**, 5326-5333.