Electronic Supplementary Information (ESI)

One-dimensional hierarchical structured MoS_2 with nanosheets ordered stacking: a facile template-free hydrothermal synthesis strategy and application as an efficient hydrogen evolution electrocatalyst

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Experimental section

Reagents and materials

Sodium molybdate ($Na_2MoO_4·2H_2O$), thioglycollic acid (TGA) and molybdenum trioxide (MoO_3) were obtained from Shanghai Aladdin Reagents Co. Ammonia water ($NH_3·H_2O$, 25–28% w/w), thiacetamide, thiourea, urea, and ethanol were purchased from Shanghai Chemical Reagents Co. All reagents used in this work were analytical reagents (A. R.) without any further purification.

Synthesis of nanosheets ordered stacking one-dimensional hierarchical MoS_2

A typical procedure was as follows: 0.1 mmol of $Na_2MoO_4·2H_2O$ was dissolved in 30 mL of distilled water. Subsequently, 200 μL of TGA and 0.5 mL of $NH_3·H_2O$ were added slowly to the solution with stirring until a clear mixture was formed. The above mixture was transferred to a Teflon-lined autoclave (50 mL capacity), which was sealed and heated in an oven at 220 °C for 12 h, then allowed to cool naturally to room temperature. The products were subsequently isolated by centrifugation and cleaned by several cycles of centrifugation/washing/redispersion in distilled water and in ethanol. Finally, the products were dried in a vacuum at 60 °C for 6 h.

Synthesis of flower-like MoS_2 with nanosheets unordered stacking

Flower-like MoS_2 with nanosheets unordered stacking was prepared by a modified hydrothermal method reported in the literature.[1, 2] Typically, 30 mg of MoO_3, 35 mg of thiacetamide and 0.3 g of urea were added to the mixture of 15 mL of distilled water and 25 mL of absolute ethanol under vigorous stirring. After stirring for 1 h, the mixture was then transferred into a Teflon-lined autoclave (50 mL capacity), which was sealed and heated in an oven at 200 °C for 24 h. The autoclave was cooled to room temperature naturally, and then the precipitates were separated by centrifugation, washed with distilled water and absolute ethanol, and dried in a vacuum oven at 60 °C for 6 h.

Characterization

X-ray powder diffraction (XRD) pattern of the products were recorded using a Bruker D8 ADVANCE X-ray diffractometer with graphite monochromatized $Cu_{K\alpha}$

radiation (λ = 1.5418 Å). Field emission scanning electron microscopy (FESEM) was performed on a Hitachi S-4800 scanning electron microscope. Transmission electron microscopy (TEM) images were obtained using a HITACHI HT-7700 transmission electron microscope at an accelerating voltage of 120 kV. High-resolution transmission electron microscopy (HRTEM) images were obtained using a FEI Tecnai G20 transmission electron microscope at an accelerating voltage of 200 kV. The energy dispersive X-ray (EDX) spectrum was recorded with a Hitachi S-4800 scanning electron microscope equipped with an INCAx-Sight OXFORD energy-dispersion X-ray fluorescence analyzer. Raman spectrum was recorded using a Renishaw inVia confocal Raman microscope spectrometer equipped with a 532 nm laser as the exciting radiation. X-ray photoelectron spectroscopy (XPS) was recorded on a UlVAC-PHI PHI 5000 VersaProbe X-ray photoelectron spectrometer equipped with a nonmonochromatic $Al_{K\alpha}$ excitation source (hv = 1486.6 eV). Fourier transform infrared (FTIR) spectrum was recorded on a Shimadzu IR Prestige21 FTIR spectrometer in the wave numbers of 500-4000 cm^{-1} at room temperature, with the sample in a KBr disk.

Electrochemical measurements

All electrochemical measurements were performed with a CHI 660E electrochemical analyzer (Chenhua Instruments, Inc., Shanghai) in a standard three-electrode system at room temperature. A Pt foil and a saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively. The working electrode was prepared as follows. 4mg of the products and 40 μl of Nafion solution (5wt%, Sigma-Aldrich) were dispersed in 1 ml of 3:1 v/v water/ethanol mixture by about 30 min of ultrasonication to generate a homogeneous ink. Next, 10 μl of the ink was loaded onto a glassy carbon electrode (GCE) of 3 mm in diameter. Linear sweep voltammetry (LSV) at a scan rate of 5 mV/s was subsequently conducted in an electrolyte solution of 0.5 M H_2SO_4. All potentials reported in our manuscript were referenced to reversible hydrogen electrode (RHE). In 0.5 M H_2SO_4, E (RHE) = E (SCE) + 0.28 V. AC impedance measurements were performed in the

same configuration at η = 200 mv from 10^5 to 0.01 Hz with an AC voltage of 5 mV.

References

1. H. L. Yu, C. L. Zhu, K. Zhang, Y. J. Chen, C. Y. Li, P. Gao, P. P. Yang and Q. Y. Ouyang, *J. Mater. Chem. A*, 2014, **2**, 4551-4557.
2. H. L. Yu, C. Ma, B. H. Ge, Y. J. Chen, Z. Xu, C. L. Zhu, C. Y. Li, Q. Y. Ouyang, P. Gao, J. Q. Li, C. W. Sun, L. H. Qi, Y. M. Wang and F. H. Li, *Chem. -Eur. J.*, 2013, **19**, 5818-5823.

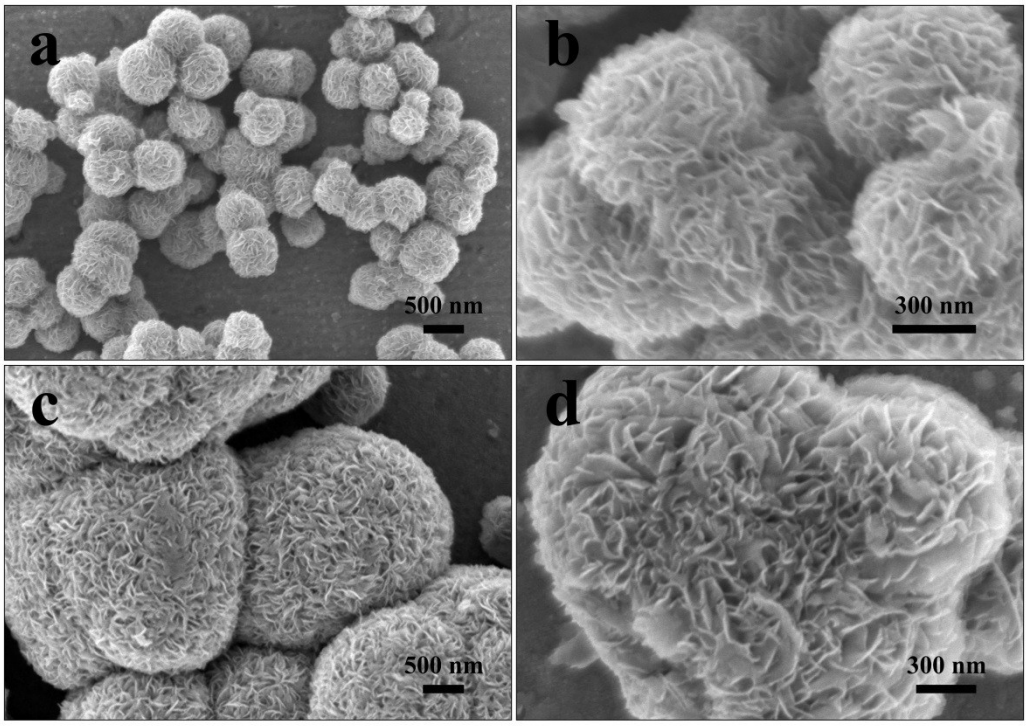

Fig. S1 FESEM images of the products prepared with (a, b) thiacetamide and (c, d) thiourea as sulfur source

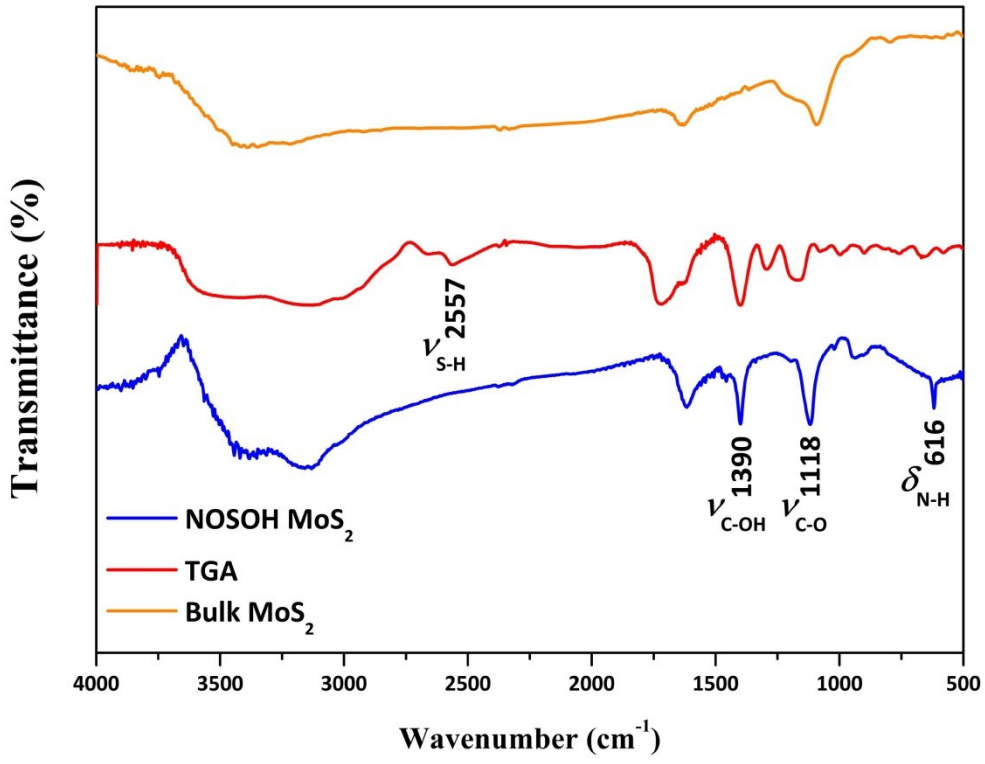

Fig. S2 FTIR spectra of the NOSOH MoS_2, TGA and bulk MoS_2

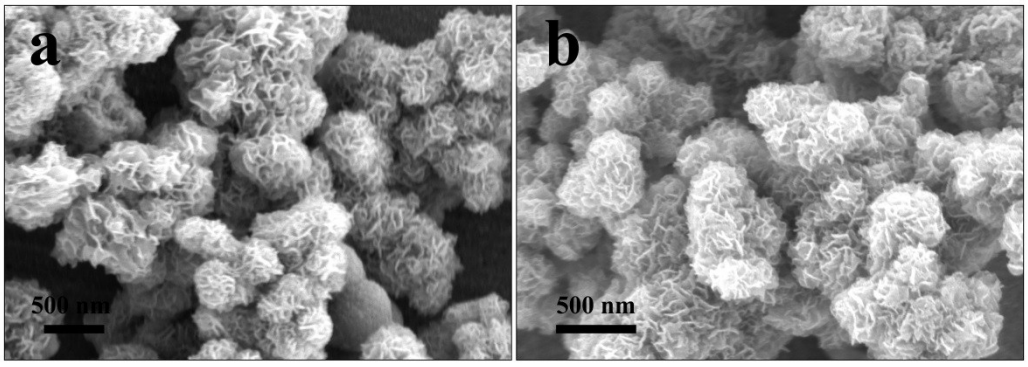

Fig. S3 FESEM images of the flower-like MoS_2 with nanosheets unordered stacking

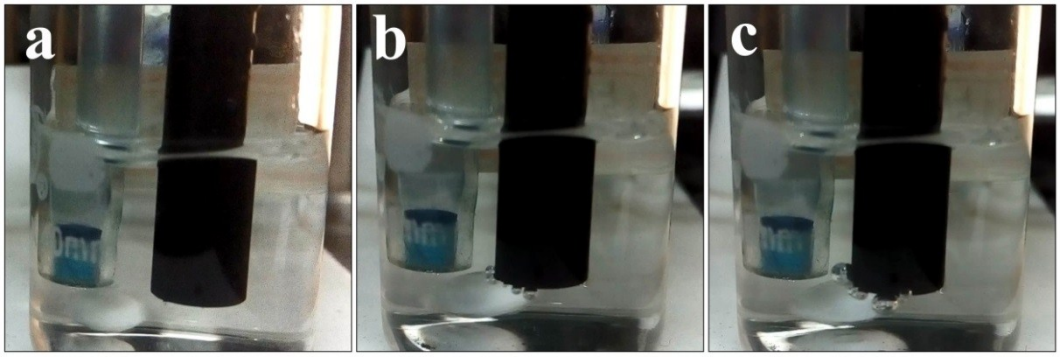

Fig. S4 Optical photograph showing the gradual generation of hydrogen bubbles on the NOSOH MoS_2 catalysts modified GCE: (a) 0, (b) 30 and (c) 60 s.