Supporting Information

# Toward Heterostructured Transition Metal Hybrids with Promoted Electrochemical Hydrogen Evolution

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**Experimental**

**Chemicals and materials**

$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (99.95%, J&K Scientific), $MoS_2$ powder, $WS_2$ powder, n-methyl--pyrrolidone (NMP), thiourea, Nafion® perfluorinated resin solution (5 wt. % in lower aliphatic alcohols and water), Pt/C (10 wt. % Pt, matrix activated carbon support) are purchased from Sigma-Aldrich. And $H_2SO_4$ (98%), KCl ($\geqslant$85%), HCl (72%), $HNO_3$ (68%), ethanol (99.7%), IPA ($\geqslant$99.5%) are supplied from Shanghai lingfeng Chemical Reagent Co. LTD. The ultrapure water with a resistivity of 18.2 MΩ·cm is applied in the experiment. All the chemicals are used as received without further purification.

**Characterization**

Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) images and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and STEM-EDS mapping images are performed with a FEI Tecnai G2 F20 S-Twin microscope at an acceleration voltage of 200 kV.

Cross-sectional method preparing TEM sample: Cross-sections of exfoliated $MoS_2$ and $WS_2$ sheets transfered onto Si substrates respectively are prepared by using the standard strategy of mechanical grinding and dimpling (dimple grinder II Model 657, Gatan) the specimen followed by Ar-ion beam milling with the Precision ion polishing system (PIPS, model 691, Gatan) down to electron transparency. TEM imagings are performed with a JEOL 2100F field emission microscope operated at 200 kV. The microscope is equipped with a Gatan Ultra Scan 4000 CCD camera for image recording.

X-ray diffraction (XRD) analysis is conducted with a Bruker D8 Advance with Cu Kα radiation (λ = 1.54178 Å). X-ray Photoelectron Spectrometer (XPS) is carried out with a Thermo Fisher ESCALAB 250Xi. The sonication equipment is adopted with a sonicator Fisherbrand FB15061, 750 W. The higher power sonicator is supplied with a Coleparmer 1200 W.

**Electrocatalytic performance**

Electrochemical measurements are conducted with a three electrode system on a CHI 660D electrochemical workstation (Shanghai Chenhua Instruments). The working electrode is a glassy-carbon electrode (GCE, CHI104, diameter: 3 mm, area: 0.071 $cm^2$), Pt wires and an Ag/AgCl are used as counter and reference electrodes respectively.

**The preparation of working electrodes**: 4 mg catalyst with 30 $\mu L$ Nafion solution are dispersed into 1 mL DI water/ethanol (1:3 in volume) mixture, ultrasonicating for 30 minutes to obtain a homogeneous dispersion. Then 5 $\mu L$ the above dispersion (containing 20 $\mu g$ catalyst) is transferred onto the glassy-carbon electrode, dry naturally for investigating afterwards.

**RHE calibration**: In all electrochemical measurements, we use an Ag/AgCl as the reference electrode. It is calibrated with respect to RHE. The calibration is performed in the high-purity argon saturated electrolyte with a Pt foil as the working electrode. Cyclic voltammetry (CV) is run at a scan rate of 5 mV/s, and the average of the two potentials at which the current crossed 0 is taken to be the thermodynamic potential for the hydrogen electrode reaction. In 0.5 M $H_2SO_4$ solution,

$E_{RHE} = E_{Ag/AgCl} + 0.213V$.

**Electrochemical performance:** Before the electrochemical measurement, the electrolyte (0.5 M $H_2SO_4$) is degassed by pure argon for 30 minutes to remove the dissolved oxygen. The polarization curves are acquired by a scan rate of 5 mV/s sweeping the potential from -0.6 to 0.2 V (vs Ag/AgCl) at room temperature.

The electrochemical active surface area (ECSA) measurements are determined by integrating the hydrogen adsorption charge on the cyclic voltammetry (CV) at room temperature in argon saturated 0.5 M $H_2SO_4$ solution. The potential scan rate was 50 mV/s for the CV measurement. The Tafel plots are investigated via replotting the polarization curves as overpotential ($\eta$) vs log current ($\log j$) to assess the HER kinetics of obtained catalysts.

The durability tests are evaluated at room temperature in 0.5 M $H_2SO_4$ solution by applying cyclic potential between -0.6 and 0.2 V versus Ag/AgCl electrode at a sweeping rate of 50 mV/s for 3000 cycles.

**Methods**

**Exfoliation of layered $MoS_2$ and $WS_2$**

The preparation for exfoliation layered $MoS_2$ and $WS_2$ is referred with previous reported [1,2]. Pristine $MoS_2$ ($WS_2$) powder is dissolved into NMP solvent (initial concentration of 1.0 mg/mL) sonicating in a low power sonication bath for 1 h and keep the bath temperature 50 °C. Then the above mixture is transferred to a higher power sonicator and continually to be sonicated for 6 h. Finally, the mixture is centrifuged at 8000 rpm for 15 minutes, the supernatant is collected by pipette and filtered with filtration system (PTFE membrane, diameter with 47 mm, pore diameter with $0.22 \mu m$, Millipore filter). The above exfoliated $MoS_2$ nanosheets are then dispersed into IPA uniformly, dried at 60 °C in vacuum. Finally, the exfoliated $MoS_2$ layers containing single, double and multi-layered are stored in vacuum to be investigated further characteristics.

**Preparation for hybrids of $MoS_2$ growth on exfoliation of $MoS_2$, $WS_2$ via chemical hydrothermal approach**

**Exfoliated $MoS_2$ ($WS_2$) dispersion:** 20.00 mg as-exfoliated $MoS_2$ ($WS_2$) dissolves into 20.00 mL IPA, respectively, sonicating for 30 min to obtain homogeneous $MoS_2$ ($WS_2$)/IPA mixture (1 mg/mL).

3

**Precursor:** To prepare 0.03 mM/mL $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ solution and 0.1 mM/mL Thiourea solution.

The synthesis of $MoS_2$ hybridized $MoS_2$ ($WS_2$) heterostructures is referred by the literature [3]: add 20 mL ultrapure water into 5 mL above $MoS_2$ ($WS_2$)/IPA mixture (1 mg/mL), 0.03 mM/mL $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ solution 0.5 mL is mixed with 0.1 mM/mL Thiourea solution 0.5 mL, sonicating for 10 minutes, transferring to 45 mL PTFE reactor and reacting for 12 h at 210℃, then the reactant is centrifugated (12000 rpm) at room temperature for 10 min, remove supernatant solution, and continuously wash the precipitate three times using ultrapure water to remove precursor residues and surface adsorption contaminations. Finally, the obtained products are freeze-dried for investigation.

**Table S1** the corresponding relationship between Tafel slope and hydrogen evolution reaction controlling steps[4]

| Reactions | $b_a$ Low overvoltage | $b_a$ High overvoltage | Kinetics |
|---|---|---|---|
| $M + H_3O^+ + e^- \rightleftharpoons M{\cdots}H_{ads} + H_2O$ | 120 | 120 | Volmer |
| $M{\cdots}H_{ads} + H_3O^+ + e^- \rightleftharpoons M + H_{2(g)} + H_2O$ | 40 | 120 | Heyrovsky |
| $2M{\cdots}H_{ads} \rightleftharpoons 2M + H_{2(g)}$ | 30 | $\infty$ | Tafel |

## References

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3. J. Xie, H. Zhang, S. Li, R. Wang, X. Sun, M. Zhou, J. Zhou, X. W. Lou, Y. Xie. *Adv. Mater.* **2013**, *25*, 5807-5813.
4. M. R. Gao, J. X. Liang, Y. R. Zheng, Y. F. Xu, J. Jiang, Q. Gao, J. Li, S. H. Yu. *Nat. Comm.* **2014**, *6*, 1-7
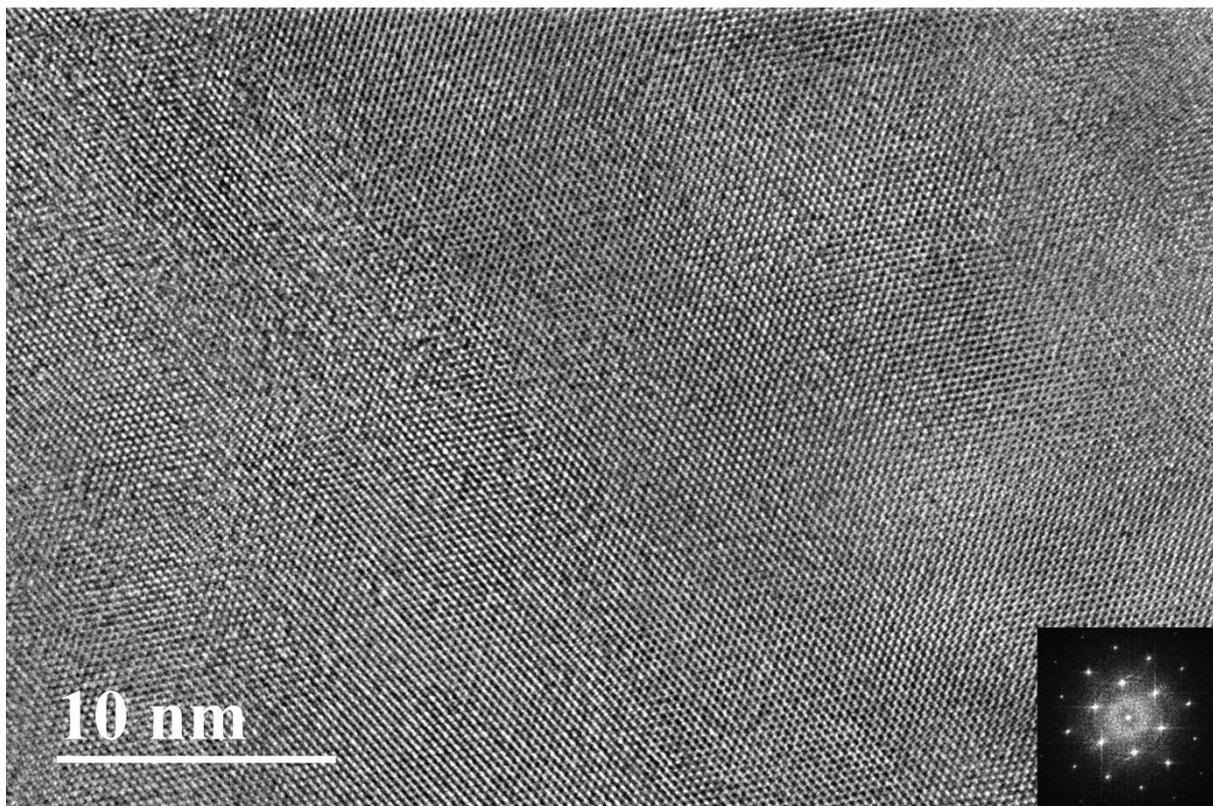
## Supplementary Figure
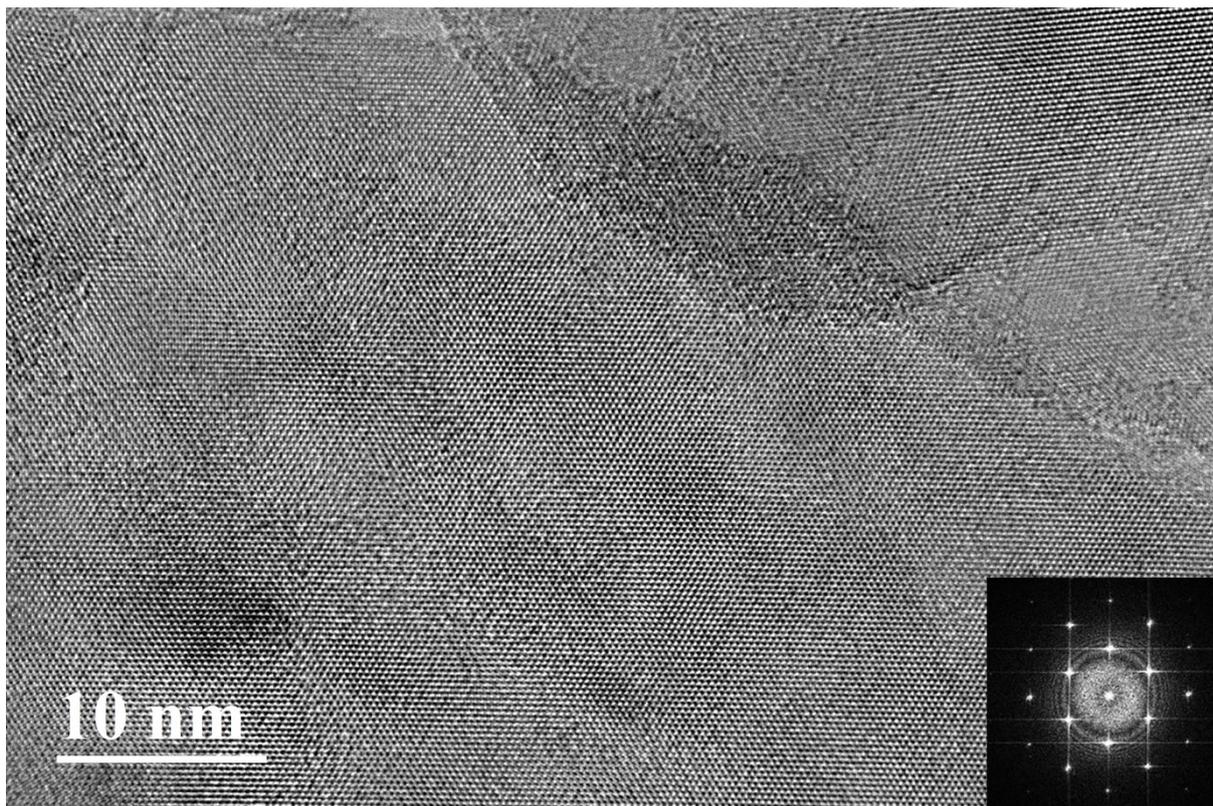
**Figure S1** high-resolution TEM image of the exfoliated $MoS_2$ nano-sheets by chemical liquid approach, insert with fast Fourier transform (FFT) pattern.
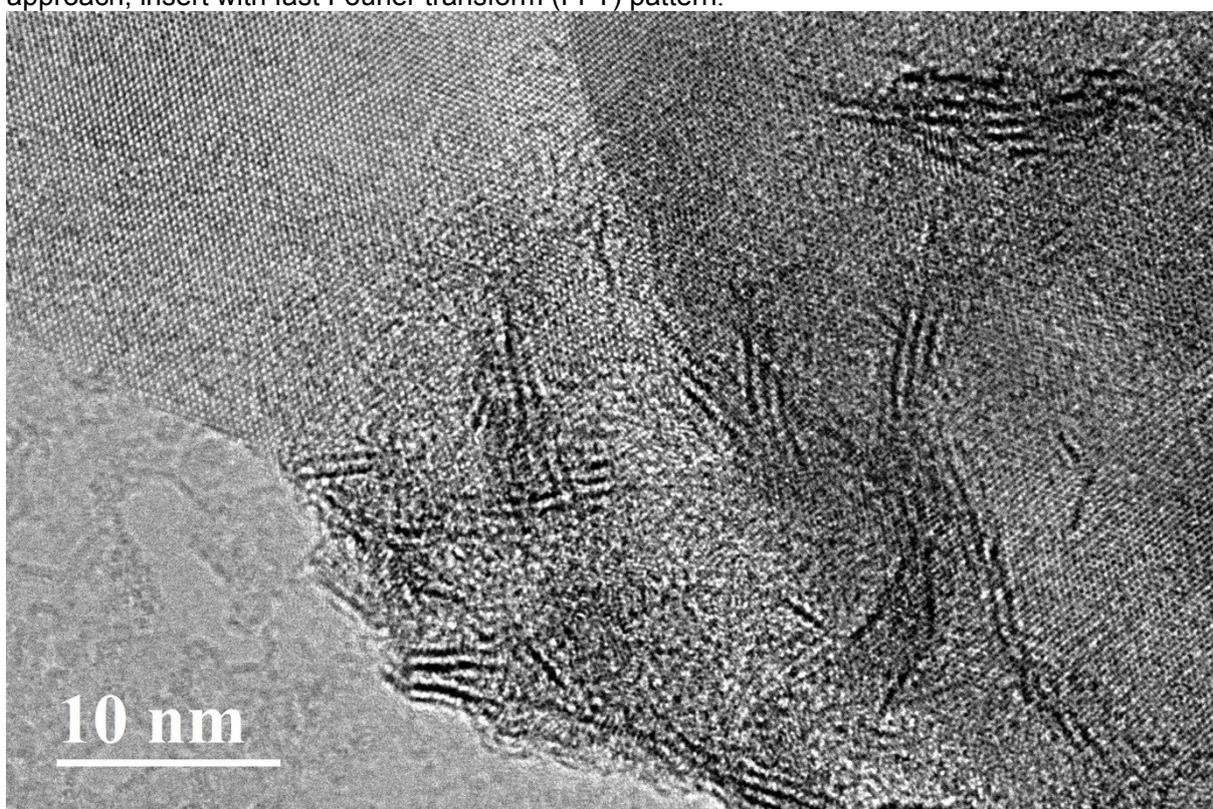


**Figure S2** high-resolution TEM image of defective $MoS_2$ nanoflakes growth onto exfoliated $MoS_2$ hybrids.

**Figure S3** high-resolution TEM image of the exfoliated $WS_2$ nano-sheets by chemical liquid approach, insert with FFT pattern.
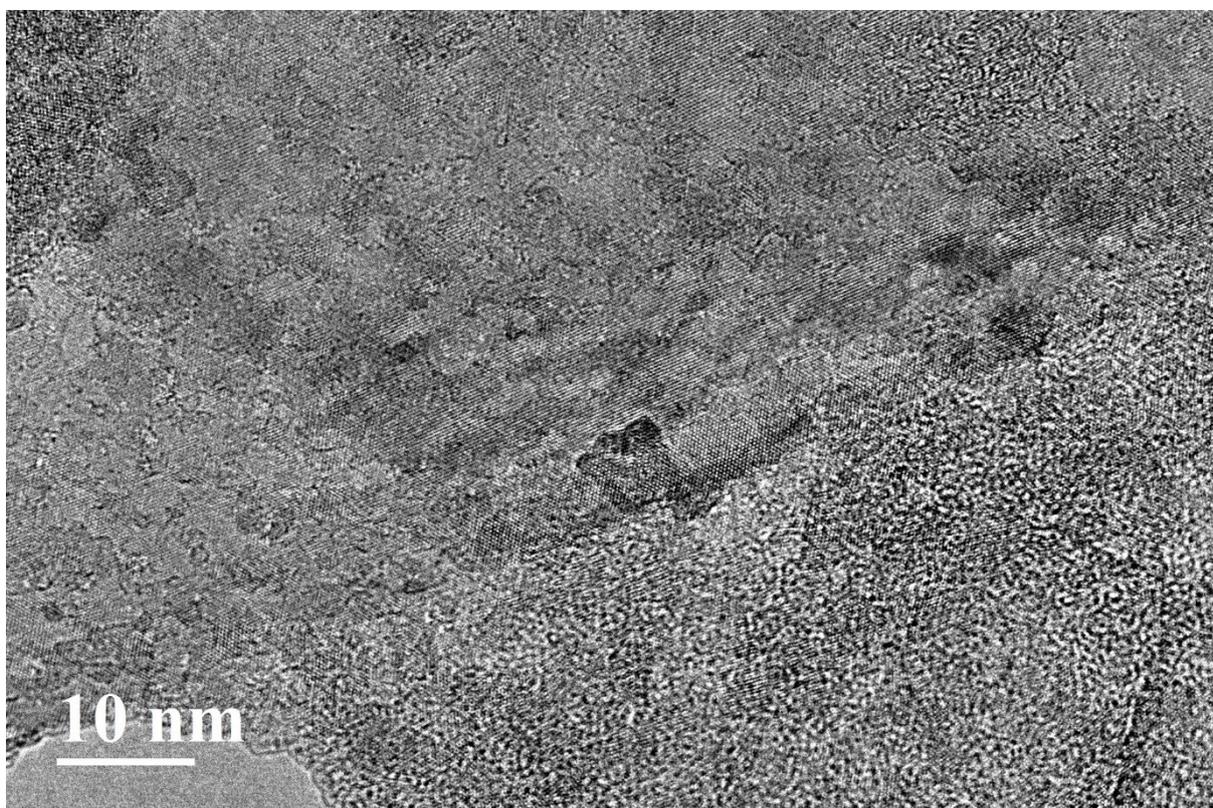


**Figure S4** high-resolution TEM image of defective $MoS_2$ nanoflakes growth onto exfoliated $WS_2$ hybrids.