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Toward heterostructured transition metal hybrids with highly promoted electrochemical hydrogen evolution[†]

 Guanhui Gao, ^{‡*ab} Xiaobin Xie, ^{‡c} Shendong Kang, ^d Yanhua Lei, ^e Achim Trampert^b and Lintao Cai ^{‡*d}

It is essential to precisely develop low-cost and sustainable electrocatalysts for the hydrogen evolution reaction. Herein, we explore a robust and controllable hydrothermal approach to synthesize defect-rich MoS₂ nanoflakes on exfoliated MoS₂ and WS₂. Such well-designed hetero-structural hybrids of MoS₂/exfoliated MoS₂ and MoS₂/exfoliated WS₂ exhibit dramatically promoted electrochemical activity and high stability. The as-grown MoS₂ nanoflakes hybridized on exfoliated MoS₂ and WS₂ generate abundant active edge sites (rich in basal defects) and unsaturated sulfur atoms, resulting in highly enhanced electrocatalytic performance. This is expected to pave the way towards a significant improvement in transition metal dichalcogenide heterostructures as electrocatalysts.

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1 Introduction

Two-dimensional graphene-based atomic crystals and transition metal dichalcogenides (TMDs) have been attracting intense interest owing to their extraordinary chemical and physical properties,^{1–6} and they are expected to have a prosperous future in catalysis, water splitting, optic-electronic performance and energy storage devices.^{7–12} Very recently, TMD heterostructures with highly enhanced electrochemical performance have been suggested as efficient catalysts to substitute the scarce and expensive noble metals such as platinum-based catalysts, which could supply a promising strategy to generate sustainable hydrogen by electrochemical water splitting. In particular, layered molybdenum disulfide (MoS₂) and tungsten disulfide (WS₂) have been put forward as robust and efficient catalysts for the hydrogen evolution reaction (HER), attributed to their abundant catalytically active sites in the atomic superlattice structure.^{13–15} To date, anchoring massive sulfide nano-flakes

onto multi-layered TMD surfaces has been explored for building heterogeneous structural hybrids, which demonstrate promoted electrochemical performance and long-term stability.^{16,17} Hinnemann *et al.* simulated the Gibbs free energy (ΔG_H) at the edge sites of MoS₂ *via* density functional theory, which can be applied as a reasonable descriptor of HER activity for general catalysts. An optimal HER performance is considered to be achieved at a value of $\Delta G_H \approx 0$. A lower ΔG_H will lead to very high surface coverage of H_{ads}, while a higher ΔG_H will make the proton bonding on the catalyst surface tremendously fragile, resulting in slow HER kinetics.¹⁸ Prof. Song Jin's research group has instead engaged in efforts toward enriching defects on the basal planes and edges of TMD heterostructures to expose abundant active sites, triggering catalytic enhancement.^{19–24} Tuning 1T (octahedral) structural TMDs could result in the restoration of the 2H (trigonal prismatic) phase with a band gap ~ 2.0 eV, ideal for photocatalysis.^{13,25} Tailoring the electronic arrangement of TMD crystals by doping could significantly promote their catalytic activity.^{26–32}

Herein, defect-rich MoS₂ nanoflakes are synthesized *via* a chemical hydrothermal approach of loading onto the surface of exfoliated MoS₂/WS₂ layers to prepare extraordinary heterostructures. The exfoliated MoS₂/WS₂ layers act as scaffolds. The Mo source is generated from (NH₄)₆Mo₇O₂₄·4H₂O, and the S source is supplied by excessive thiourea triggering to obtain defect-rich MoS₂, as shown as Scheme 1 (details of the experiments are given in ESI[†]), which is expected to enhance their catalytic performance and stability for HER due to the abundant edges and defect active sites.³³ The aim is to supply a platform for designing TMD-based heterostructures as alternatives for noble metal catalysts with increased catalytic properties.

^aMaterials Science and NanoEngineering Department, Rice University, Houston, 77005, USA. E-mail: gg13@rice.edu

^bPaul-Drude Institut Für Festkörperelektronik, Leibniz-Institut Im Forschungsverbund Berlin, Berlin, 10117, Germany

^cSoft Condensed Matter, Debye Institute for Nanomaterials Science, Utrecht University, Utrecht, 3584CC, Netherlands

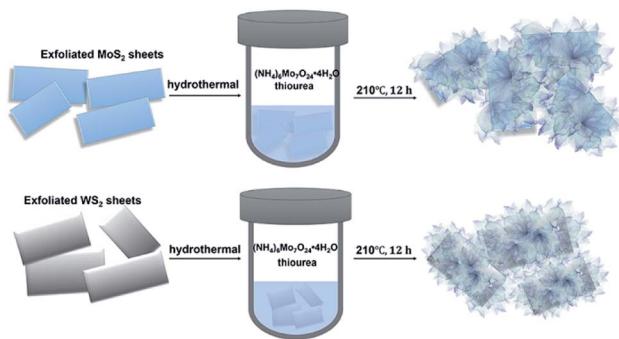
^dGuangdong Key Laboratory of Nanomedicine, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen, 518055, China. E-mail: lt.cai@siat.ac.cn

^eCollege of Ocean Environment and Engineering, Shanghai Maritime University, 1550 Haigang Ave, Shanghai, 201306, China

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[‡] Dr Guanhui Gao and Xiaobin Xie contributed equally to this work.





Scheme 1 Schematic illustration of the fabrication of defect-rich MoS₂ nanoflakes grown on exfoliated MoS₂ and WS₂ hybrids, respectively.

2 Experiment

2.1 Exfoliation of layered MoS₂ and WS₂

Pristine MoS₂ (WS₂) powder is dissolved into NMP solvent (initial concentration of 1.0 mg mL⁻¹) sonicated in a low-power sonication bath for 1 h with the bath temperature kept at 50 °C. Then the above mixture is transferred to a higher power sonicator and continually sonicated for 6 h. Finally, the mixture is centrifuged at 8000 rpm for 15 minutes. The supernatant is collected with a pipette and filtered with a filtration system (PTFE membrane, diameter 47 mm, pore diameter 0.22 µm, Millipore filter). The above exfoliated MoS₂ nanosheets are then uniformly dispersed into IPA, and dried at 60 °C in a vacuum. Finally, the exfoliated MoS₂ layers containing single, double and multi-layers are stored under vacuum for their characteristics to be investigated further.

2.2 Preparation of hybrids of MoS₂ grown on exfoliated MoS₂ or WS₂ via a hydrothermal approach

Exfoliated MoS₂ (WS₂) dispersion: 20.00 mg of as-exfoliated MoS₂ (WS₂) is dissolved into 20.00 mL of IPA, sonicated for 30 min to obtain a homogeneous MoS₂ (WS₂)/IPA mixture (1 mg mL⁻¹). Precursor: prepare 0.03 mM mL⁻¹ (NH₄)₆Mo₁₂O₄₂·4H₂O solution and 0.1 mM mL⁻¹ thiourea solution. The synthesis of MoS₂ hybridized MoS₂ (WS₂) heterostructures: add 20 mL of ultrapure water into 5 mL of the above MoS₂ (WS₂)/IPA mixture (1 mg mL⁻¹), 0.5 mL of 0.03 mM mL⁻¹ (NH₄)₆Mo₁₂O₄₂·4H₂O solution is mixed with 0.5 mL of 0.1 mM mL⁻¹ thiourea solution, sonicated for 10 minutes, transferred to a 45 mL PTFE reactor and reacted for 12 h at 210 °C. Then the reactant is centrifuged (12 000 rpm) at room temperature for 10 min, the supernatant solution removed, and the precipitate continuously washed three times using ultrapure water to remove precursor residues and surface adsorption contamination. Finally, the obtained products are freeze-dried for investigation.

2.3 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 cm²); Pt wires and an Ag/AgCl are used as counter and reference electrodes, respectively. The preparation of working electrodes: 4 mg catalyst with 30 µL Nafion solution are dispersed into 1 mL of DI water/ethanol (1 : 3 in volume) mixture, and ultrasonicated for 30 minutes to obtain a homogeneous dispersion. Then 5 µL of the above dispersion (containing 20 µg of catalyst) is transferred onto the glassy-carbon electrode, and dried naturally for later investigation.

RHE calibration. In all electrochemical measurements, we use Ag/AgCl as the reference electrode. It is calibrated with respect to RHE. The calibration is performed in a high-purity argon saturated electrolyte with Pt foil as the working electrode. Cyclic voltammetry (CV) is run at a scan rate of 5 mV s⁻¹, 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 H₂SO₄ solution,

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

Electrochemical performance. Before the electrochemical measurement, the electrolyte (0.5 M H₂SO₄) is degassed with pure argon for 30 minutes to remove the dissolved oxygen. The polarization curves are acquired at a scan rate of 5 mV s⁻¹, sweeping the potential from -0.6 to 0.2 V (vs. Ag/AgCl) at room temperature.

The electrochemically 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 H₂SO₄ solution. The potential scan rate is 50 mV s⁻¹ for the CV measurement. The Tafel plots are investigated by replotting the polarization curves as overpotential (η) vs. log current (log j) to assess the HER kinetics of the obtained catalysts. The durability tests are evaluated at room temperature in 0.5 M H₂SO₄ solution by applying a cyclic potential between -0.6 and 0.2 V versus Ag/AgCl electrode at a sweeping rate of 50 mV s⁻¹ for 3000 cycles.

2.4 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 MoS₂ and WS₂ sheets transferred onto Si substrates 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 imaging measurements 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 K α radiation ($\lambda = 1.54178 \text{ \AA}$). X-ray



Photoelectron Spectrometry (XPS) is carried out with a Thermo Fisher ESCALAB 250Xi. The sonication equipment is adapted with a sonicator, Fisherbrand FB15061, 750 W. The higher power sonicator is supplied with a Cole-Parmer 1200 W.

3 Results and discussion

Exfoliated MoS₂ layers are observed by TEM measurement, as shown in Fig. 1A. The size distribution has a rather large range, mostly with multi-layers. The lattice structure of MoS₂ nano-sheets is obtained (Fig. 1B) and hardly any defects are found. The inset indicates the MoS₂ simulated lattice structure with the yellow standing for S atoms and the blue being Mo atoms. And the typical layered structure with an interlayer spacing distance of 0.635 nm is shown in Fig. 1C, which is evaluated *via* a cross-sectional method with the sample prepared by using the standard strategy of mechanical grinding and dimpling the specimen followed by Ar-ion beam milling down to electron transparency. The high-resolution TEM (HRTEM) image with fast Fourier transform (FFT) pattern given in ESI (Fig. S1†) illustrates the complete hexagonal atomic arrangement with 2H phase.³¹ From the TEM and high-angle annular dark-field (HAADF) STEM images, a large quantity of defect-rich MoS₂ nanoflakes grown on the exfoliated MoS₂ layers can clearly be observed (Fig. 1D and E). The hexagonal lattice of this well-designed 3D hybrid is characterized by selected area electron diffraction (SAED), as shown as Fig. 1F, indicating its polycrystalline structure. The HRTEM images provide more obvious proof of the lattice structures of both synthesized MoS₂

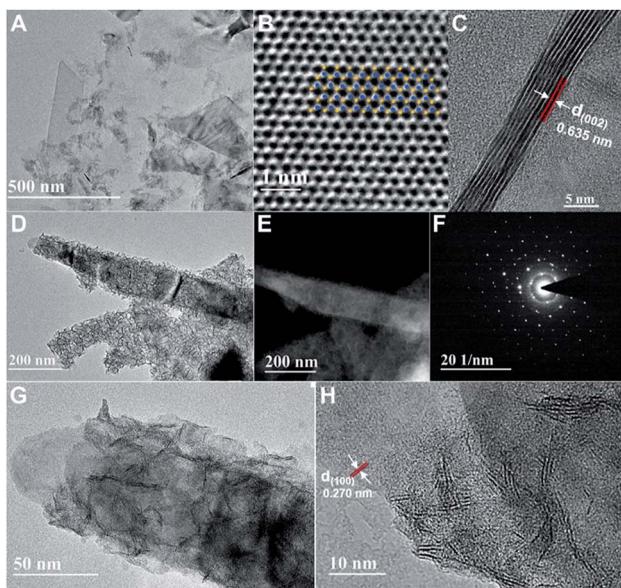


Fig. 1 (A) TEM image of the exfoliated MoS₂ nano-sheets produced by a chemical liquid method. (B) Lattice structure of the exfoliated MoS₂ sheets. (C) Cross-sectional HRTEM image of exfoliated MoS₂ sheets. (D) The TEM image of defect-rich MoS₂ hybridized exfoliated MoS₂ layers. (E) High-angle annular dark-field (HAADF)-STEM image of (D). (F) SAED pattern of (D). (G and H) HRTEM images of local defect-rich MoS₂ hybridized exfoliated MoS₂ layers.

nanoflakes and exfoliated MoS₂ layers (Fig. 1G, H and S2†). The lattice structure of exfoliated MoS₂ layers uncovered at the edge is complete with a spacing distance of 0.270 nm, (100) facet. In comparison, the atomic arrangement of synthesized MoS₂ seems irregularly disordered, inducing surface defects, and is expected to supply more activate sites for improving catalytic function.

The energy dispersive X-ray spectrometry (EDS) mapping results indicate that the synthesized MoS₂ nanoflakes are uniformly deposited onto the exfoliated MoS₂ surface (Fig. 2A–D). Furthermore, X-ray diffraction (XRD) is conducted to explore the structural information between exfoliated MoS₂ layers and hybrids of defect-rich MoS₂ nanoflakes grown on exfoliated MoS₂ layers (MoS₂/exfoliated MoS₂), as shown as Fig. 3E. This reveals that the exfoliated MoS₂ layers are 2H phase, corresponding to JCPDS 65-0160.

Obviously, the crystallinity of the MoS₂/exfoliated MoS₂ hybrids is not as high as that of pure exfoliated MoS₂. Hybrids of MoS₂/exfoliated MoS₂ are produced to further evaluate the elements' binding mechanism using X-ray photoelectron spectroscopy (XPS). The main peaks of Mo 3d are at 227 eV and 232 eV, corresponding to Mo 3d_{5/2} and Mo 3d_{3/2}, respectively, which indicates the valence of Mo⁴⁺. The binding energies of 161 eV and 163 eV contribute to S 2p_{3/2} and S 2p_{1/2}, illustrating that the valence of S is –2 (Fig. 2F).

The exfoliated WS₂ nano-sheets, as shown in Fig. 3A and B, are obtained by a chemical liquid method which is the same as for the fabrication of layered MoS₂. The lattice structure of WS₂ nano-sheets is obtained (Fig. 3C). The inset shows the WS₂ simulated lattice structure where blue stands for a W atom, and yellow represents an S atom. Similarly, the cross-sectional lamellar structure of exfoliated WS₂ is investigated, and the number of WS₂ layers can clearly be seen. And the FFT mode exhibits the hexagonal structure of layered WS₂ with 2H phase (Fig. S3†). It is observed that the synthesized MoS₂ nanoflakes hybridize on layered WS₂ nano-sheets, as shown in Fig. 3D and

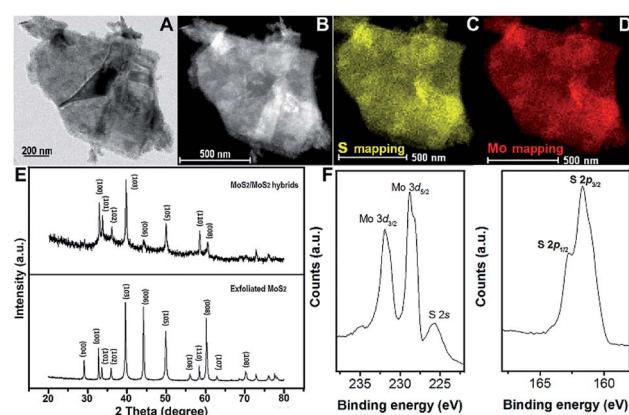


Fig. 2 (A) Bright-field TEM image of hybrids of defect-rich MoS₂ nanoflakes grown on exfoliated MoS₂. (B) HAADF-STEM image of (A). (C and D) S and Mo elemental mappings. (E) XRD spectra of exfoliated MoS₂ layers and MoS₂ nanoflakes grown on exfoliated MoS₂ hybrids. (F) High-resolution XPS spectra of MoS₂ nanoflakes grown on exfoliated MoS₂ hybrids, Mo 3d, S 2s and S 2p core level, respectively.



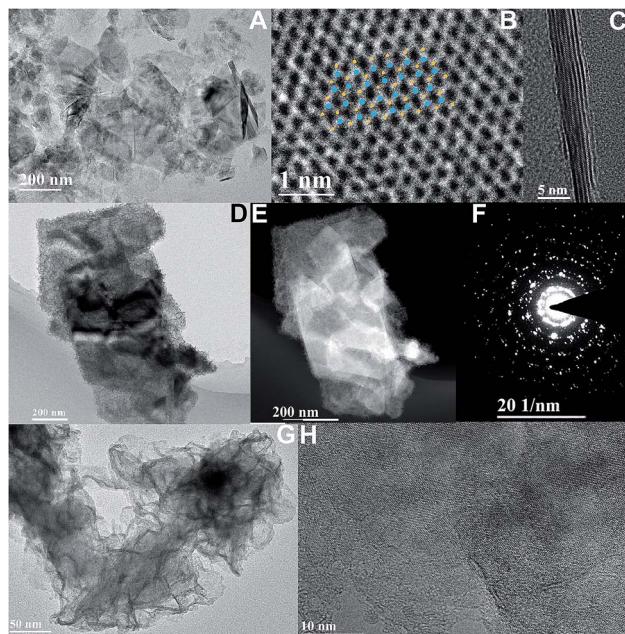


Fig. 3 (A) TEM image of the exfoliated WS_2 nano-sheets produced by a chemical liquid method. (B) Lattice structure of the exfoliated WS_2 layers. (C) Cross-sectional HRTEM image of exfoliated WS_2 nano-sheets. (D) The TEM image of the hybrids of defect-rich MoS_2 nanoflakes grown on exfoliated WS_2 via a hydrothermal strategy. (E) HAADF-STEM image of (D). (F) SAED pattern of (D). (G and H) HRTEM image of local defect-rich MoS_2 hybridized exfoliated WS_2 layers.

E. The hexagonal lattice with the polycrystalline structure of the hybrids is investigated by SAED, as shown as Fig. 3F. The high-resolution TEM images indicate defect-rich MoS_2 with a multi-layered morphology grown on exfoliated WS_2 (Fig. 3G). The clear boundary between as-grown MoS_2 and exfoliated WS_2 is demonstrated in Fig. 3H and S4[†] due to the obvious lattice mismatch.

A morphological image of MoS_2 grown on exfoliated WS_2 hybrids is shown in Fig. 4A, indicating that the branch-like grafted MoS_2 grows *in situ* on the surface of exfoliated WS_2 . This typical hetero-structure might be advantageous for enhancing electro-catalytical performance. STEM and EDS elemental mappings illustrate the spatial distribution of these S, Mo and W elements of the obtained hybrids (Fig. 4B–E). In comparison, the pixel density of W is more compact than that of Mo, revealing that the W content is locally higher than the Mo content. Moreover, the distribution area of Mo is larger than that of W, suggesting that Mo element is dominant in the external surface of the hybrids. XRD spectra are conducted to explore the structural information between exfoliated MoS_2 layers, exfoliated WS_2 layers and hybrids of MoS_2 grown on exfoliated WS_2 layers (MoS_2/WS_2), as shown as Fig. 4F. This indicates that the exfoliated WS_2 layer is 2H phase, corresponding to JCPDS 65-0160, but the crystallinity is not particularly high in comparison. In order to further investigate the variation in surface electron states of hetero-structural MoS_2/WS_2 hybrids, XPS measurement is conducted, as shown as Fig. 4G. The peaks located at 33 eV and 38 eV are assigned to W

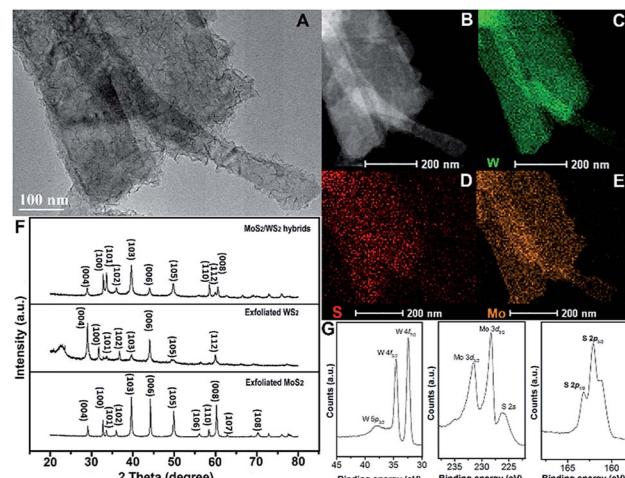


Fig. 4 (A) Morphology of the hybrids of MoS_2 grown on exfoliated WS_2 ($\text{MoS}_2/\text{exfoliated WS}_2$). (B–E) HAADF-STEM and STEM-EDS elemental mapping images of $\text{MoS}_2/\text{exfoliated WS}_2$ hybrids. (F) XRD pattern of exfoliated WS_2 , exfoliated MoS_2 layers and hybrids of defect-rich MoS_2 nanoflakes grown on exfoliated WS_2 . (G) XPS spectra of the hybrids of MoS_2 grown on exfoliated WS_2 , W 5p, W 4f, Mo 3d, S 2s and S 2p core level.

$4\text{f}_{5/2}$ and W $4\text{f}_{7/2}$, respectively, indicating the valence state of W with +4. The binding energies of S $2\text{p}_{3/2}$ and S $2\text{p}_{1/2}$ negatively shift to 161.9 eV and 163.1 eV (compared to pure MoS_2 layers with their binding energies of 162.7 eV and 163.9 eV for S $2\text{p}_{3/2}$ and S $2\text{p}_{1/2}$), illustrating the electron transfer from WS_2 to MoS_2 in MoS_2/WS_2 hybrids. And the typical peaks are located at 227 eV and 232 eV corresponding to Mo $3\text{d}_{5/2}$ and Mo $3\text{d}_{3/2}$, indicating the valence state of Mo is +4.

Electrocatalytic measurements were investigated at room temperature using a working electrode made of glassy-carbon electron (GCE, CHI104, $\varnothing = 3$ mm) in argon-saturated 0.5 M H_2SO_4 electrolyte (see ESI[†] for the experimental methods in detail). The polarization curves are acquired at a scan rate of 5 mV s^{-1} , sweeping the potential from -0.6 to 0.2 V (vs. Ag/AgCl) at room temperature. Subsequently, we evaluate the electro-catalytic performance for the hydrogen evolution reaction of the well-designed MoS_2/WS_2 hybrids, $\text{MoS}_2/\text{MoS}_2$ hybrids, exfoliated MoS_2 , and exfoliated WS_2 as investigated catalysts. Fig. 5A exhibits that the initial overpotentials of both MoS_2/WS_2 hybrids and $\text{MoS}_2/\text{MoS}_2$ hybrids are much lower than those of exfoliated MoS_2 , or exfoliated WS_2 , indicating that the electro-catalytic activities of MoS_2 hybridized layered MoS_2 and WS_2 heterostructures are promoted significantly. Comparably, the catalytic performance of the hetero-structural MoS_2/WS_2 hybrids is superior to that of the $\text{MoS}_2/\text{MoS}_2$ hybrids, a possible reason being that the structure of MoS_2 is not infected by MoS_2 hybridization, the lattice structure and constants of synthesized MoS_2 remain consistent with exfoliated MoS_2 layers, and thus the electronic effect would not be varied. But in terms of MoS_2/WS_2 hybrids, the banding energy and electronic property of exfoliated WS_2 are influenced dramatically after MoS_2 hybridization.³²



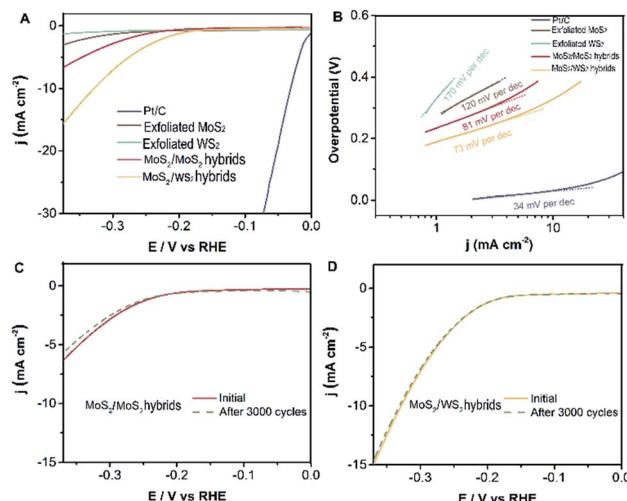
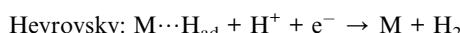
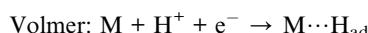


Fig. 5 Electrocatalytic hydrogen evolution of different catalysts. (A) Polarization curves for HER on pure exfoliated MoS₂, exfoliated WS₂, obtained MoS₂/WS₂ hybrids, MoS₂/MoS₂ hybrids and a high-quality commercial Pt/C catalyst for comparison. (B) Tafel plot for the different catalysts derived from (A). (C) Comparison of polarization curves for HER on MoS₂/MoS₂ hybrids and after 3000 cycles. (D) Comparison of polarization curves for HER on MoS₂/WS₂ hybrids and after 3000 cycles.

In principle, Tafel slopes demonstrate the hydrogen evolution reaction (HER) kinetics of the as-synthesized catalysts. In an acidic system, there are generally three stages to describe the procedure of H⁺ converting to H₂, famously the reactions of Volmer, Heyrovsky, Tafel, shown as follows:^{33,34}



The Tafel slope ($b = 2.3RT/\alpha F$) is a convenient and reasonable way to analyze electrode properties and the reaction mechanism. It is can be derived to be reversely proportional to the charge transfer coefficient (α), where T is temperature and F is the Faraday constant.

The charge transfer coefficient is a significant quantity in electrochemistry, reflecting the nature of electron transfer in an elementary reaction. While it is commonly assumed that the charge transfer coefficient of an elementary reaction is either 0.5 (single electron transfer) or 0 (nonelectron transfer). For instance, HER kinetic models suggest that a Tafel slope of about 120, 40 or 30 mV per decade will be obtained if the Volmer, Heyrovsky or Tafel reaction, respectively, is the rate-determining step. Likewise, the Tafel slope of Pt/C is 34 mV dec⁻¹, suggesting a Tafel-step-determined Volmer-Tafel mechanism at work in the Pt/C catalyst. Based on this analysis and the Butler-Volmer kinetics, we show that the Volmer-Heyrovsky mechanism is dominant for HER in these MoS₂ hybridized MoS₂ and MoS₂ hybridized WS₂ nanostructures due to their

Tafel slopes of 81 mV dec⁻¹ and 73 mV dec⁻¹ (Fig. 5B) respectively. (The Tafel slope is higher than 30 mV dec⁻¹, indicating there is no electron transfer, which is attributed to the reaction mechanism mainly being dominated by the Volmer-Heyrovsky mechanism.) However, this value of the Tafel slope is still higher than that of a Pt/C catalyst, the main possible reason for which is that the electrodes are extremely small in our electrochemical workstation system, resulting in an inefficient evaluation. Nevertheless, the building blocks of MoS₂ hybridized MoS₂ (WS₂) demonstrate superior catalytic performance compared with exfoliated MoS₂ (WS₂) layers. In order to further evaluate the durability of as-catalysts, the electrochemical activity of MoS₂ hybridized MoS₂ (WS₂) heterostructures are retained in the current after 3000 cycles, as shown in Fig. 5C and D. There is almost no variation in the polarization curves for HER before and after 3000 cycles. This confirms the outstanding stability and durability of MoS₂/exfoliated MoS₂ hybrids and MoS₂/exfoliated WS₂ hybrids.

4 Conclusions

In summary, we explored heterogeneous hybrids of MoS₂/exfoliated MoS₂ (WS₂) via a facile and high-yielding hydrothermal strategy. These well-designed heterostructures possess abundant edges and basal plane defects which could supply rather more active sites, triggering significant promotion of electrochemical performance and stability for HER as catalysts. This is expected to pave the way for the development of innovative efficient catalysts in transition metal dichalcogenides instead of rare noble catalysts.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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