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, and they are expected to have a prosperous future in catalysis, water splitting, opto-electronic performance and energy storage devices. 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 (MoS\(_2\)) and tungsten disulfide (WS\(_2\)) have been put forward as robust and layered molybdenum disulfide able to electrocatalyze the hydrogen evolution reaction (HER), attributed to their extraordinary chemical and physical properties.

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 MoS\(_2\)/exfoliated MoS\(_2\) and WS\(_2\). Such well-designed hetero-structural hybrids of MoS\(_2\)/exfoliated MoS\(_2\) and MoS\(_2\)/exfoliated WS\(_2\) exhibit dramatically promoted electrochemical activity and high stability. The as-grown MoS\(_2\) nanoflakes hybridized on exfoliated MoS\(_2\) and WS\(_2\) 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.

Received 10th April 2019
Accepted 9th June 2019
DOI: 10.1039/c9ra02673h
rsc.li/rsc-advances

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

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 MoS\(_2\)/exfoliated MoS\(_2\) and WS\(_2\). Such well-designed hetero-structural hybrids of MoS\(_2\)/exfoliated MoS\(_2\) and MoS\(_2\)/exfoliated WS\(_2\) exhibit dramatically promoted electrochemical activity and high stability. The as-grown MoS\(_2\) nanoflakes hybridized on exfoliated MoS\(_2\) and WS\(_2\) 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, and they are expected to have a prosperous future in catalysis, water splitting, opto-electronic performance and energy storage devices. 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 (MoS\(_2\)) and tungsten disulfide (WS\(_2\)) 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. 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. Hinnemann et al. simulated the Gibbs free energy (\(\Delta G\)) at the edge sites of MoS\(_2\) 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 \(\Delta G = 0\). A lower \(\Delta G\) will lead to very high surface coverage of \(H_{ads}\), while a higher \(\Delta G\) will make the proton bonding on the catalyst surface tremendously fragile, resulting in slow HER kinetics. 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. 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. Tailoring the electronic arrangement of TMD crystals by doping could significantly promote their catalytic activity.

Herein, defect-rich MoS\(_2\) nanoflakes are synthesized via a chemical hydrothermal approach of loading onto the surface of exfoliated MoS\(_2\)/WS\(_2\) layers to prepare extraordinary heterostructures. The exfoliated MoS\(_2\)/WS\(_2\) layers act as scaffolds. The Mo source is generated from \((NH_4)_6Mo_7O_{24}\cdot4H_2O\), and the S source is supplied by excessive thiourea triggering to obtain defect-rich MoS\(_2\), 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. The aim is to supply a platform for designing TMD-based heterostructures as alternatives for noble metal catalysts with increased catalytic properties.
2 Experiment

2.1 Exfoliation of layered MoS$_2$ and WS$_2$

Pristine MoS$_2$ (WS$_2$) 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 washed three times using ultrapure water to remove precursor residues and surface adsorption contamination. Finally, the exfoliated MoS$_2$ nanosheets are then uniformly dispersed into IPA, and dried at 60 °C in a vacuum. The supernatant solution removed, and the precipitate continuously centrifuged (12 000 rpm) at room temperature for 10 min, 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$_2$SO$_4$ solution,

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

Electrochemical performance. Before the electrochemical measurement, the electrolyte (0.5 M H$_2$SO$_4$) 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 H$_2$SO$_4$ solution. The potential scan rate is 50 mV s$^{-1}$ for the CV measurement. The Tafel plots are investigated by replotted the polarization curves as overpotential ($\eta$) 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 H$_2$SO$_4$ 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.

2.2 Preparation of hybrids of MoS$_2$ grown on exfoliated MoS$_2$ or WS$_2$ via a hydrothermal approach

Exfoliated MoS$_2$ (WS$_2$) dispersion: 20.00 mg of as-exfoliated MoS$_2$ (WS$_2$) is dissolved into 20.00 mL of IPA, sonicated for 30 min to obtain a homogeneous MoS$_2$ (WS$_2$)/IPA mixture (1 mg mL$^{-1}$). Precursor: prepare 0.03 mM mL$^{-1}$ (NH$_4$)$_6$Mo$_7$O$_24$·4H$_2$O and 0.1 mM mL$^{-1}$ thiourea solution. The synthesis of MoS$_2$ hybridized MoS$_2$ (WS$_2$) heterostructures: add 20 mL of ultrapure water into 5 mL of the above MoS$_2$ (WS$_2$)/IPA mixture (1 mg mL$^{-1}$), 0.5 mL of 0.03 mM mL$^{-1}$ (NH$_4$)$_6$Mo$_7$O$_24$·4H$_2$O solution, 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 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 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 H$_2$SO$_4$ solution,
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 nanosheets 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.† 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 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 active 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 3d₅/₂ and Mo 3d₃/₂, respectively, which indicates the valence of Mo⁴⁺. The binding energies of 161 eV and 163 eV contribute to S 2p₃/₂ and S 2p₁/₂, 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
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 MoS2 with a multi-layered morphology grown on exfoliated WS2 (Fig. 3G). The clear boundary between as-grown MoS2 and exfoliated WS2 is demonstrated in Fig. 3H and S4† due to the obvious lattice mismatch.

A morphological image of MoS2 grown on exfoliated WS2 hybrids is shown in Fig. 4A, indicating that the branch-like grafted MoS2 grows in situ on the surface of exfoliated WS2. 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 MoS2 layers, exfoliated WS2 layers and hybrids of MoS2 grown on exfoliated WS2 layers (MoS2/WS2), as shown as Fig. 4F. This indicates that the exfoliated WS2 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 MoS2/WS2 hybrids, XPS measurement is conducted, as shown as Fig. 4G. The peaks located at 33 eV and 38 eV are assigned to W 4f1/2 and W 4f3/2, respectively, indicating the valence state of W with +4. The binding energies of S 2p3/2 and S 2p1/2 negatively shift to 161.9 eV and 163.1 eV (compared to pure MoS2 layers with their binding energies of 162.7 eV and 163.9 eV for S 2p3/2 and S 2p1/2), illustrating the electron transfer from WS2 to MoS2 in MoS2/WS2 hybrids. And the typical peaks are located at 227 eV and 232 eV corresponding to Mo 3d5/2 and Mo 3d3/2, 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, CH104, Ø = 3 mm) in argon-saturated 0.5 M H2SO4 electrolyte (see ES† 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 MoS2/WS2 hybrids, MoS2/MoS2 hybrids, exfoliated MoS2, and exfoliated WS2 as investigated catalysts. Fig. 5A exhibits that the initial overpotentials of both MoS2/WS2 hybrids and MoS2/MoS2 hybrids are much lower than those of exfoliated MoS2, or exfoliated WS2, indicating that the electro-catalytic activities of MoS2 hybridized layered MoS2 and WS2 heterostructures are promoted significantly. Comparably, the catalytic performance of the hetero-structural MoS2/WS2 hybrids is superior to that of the MoS2/MoS2 hybrids, a possible reason being that the structure of MoS2 is not infected by MoS2 hybridization, the lattice structure and constants of synthesized MoS2 remain consistent with exfoliated MoS2 layers, and thus the electronic effect would not be varied. But in terms of MoS2/WS2 hybrids, the banding energy and electronic property of exfoliated WS2 are influenced dramatically after MoS2 hybridization.22
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 MoS$_2$ hybridized MoS$_2$ (WS$_2$) demonstrate superior catalytic performance compared with exfoliated MoS$_2$ (WS$_2$) layers. In order to further evaluate the durability of as-catalysts, the electrochemical activity of MoS$_2$ hybridized MoS$_2$ (WS$_2$) 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 MoS$_2$/exfoliated MoS$_2$ hybrids and MoS$_2$/exfoliated WS$_2$ hybrids.

4 Conclusions

In summary, we explored heterogeneous hybrids of MoS$_2$/exfoliated MoS$_2$ (WS$_2$) 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

The presented research was financially supported by Key International Science and Technology Cooperation Project (2015DFH50230), the Natural Science Foundation of China (51602195, 51502333), the Guangdong Natural Science Foundation of Research Team (2016A030312006), and the Science and Technology Program of Shenzhen (JCYJ20120615124830232, JCYJ20160429191503002).

Notes and references