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**MoS_x-coated NbS₂ nanoflakes growth on glass carbon: an advanced
electrocatalyst for the hydrogen evolution reaction**

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Recent experimental and theoretical studies have demonstrated that two-dimensional (2D) transition metal dichalcogenide (TMDC) nanoflakes are one of the most promising candidates for non-noble metal electrocatalysts for hydrogen evolution reaction (HER). However, it is still demanding to optimize their conductivity and enrich active sites for the high efficient electrochemical performance. Herein, we report a chemical vapor deposition (CVD) and thermal annealing two-step strategy to controllably synthesize hybrid electrocatalysts consisting of metallic NbS₂ nanoflake backbones and highly catalytic active MoS_x nanocrystalline shell on polished commercial glass carbon (GC). In addition, the amounts of MoS_x in the hybrids can be easily adjusted, we first demonstrate that small amount of MoS_x obviously promotes the HER activity of 2D NbS₂ nanoflakes, which is in good consistence with the density functional theory (DFT) calculation results. Meanwhile, the optimized MoS_x@NbS₂/GC electrocatalyst displays a superior HER activity with an overpotential of -164 mV at -10 mA/cm², a small Tafel slope of 43.2 mV/dec, and prominent electrochemical stability. This study provides a new path for enhancing the HER performance of 2D TMDC nanoflakes.

Introduction

Hydrogen generated by water splitting is one of the most promising alternatives for sustainable and clean future energy source. Two key factors for improving the catalytic performance of hydrogen evolution reaction (HER) are the conductivity and effectively active sites of the catalysts.¹ Due to the good conductivity and high

catalytic activity, Pt-based catalysts are among the most efficient electrocatalysts for HER. In recent years, two-dimensional (2D) transition metal dichalcogenides (TMDCs) have received increasing research interest because of their unique properties and fascinating applications potentials.²⁻⁵ Mono- and few-layer nanosheets of 2D transition metal dichalcogenide (TMDC) materials including MoS₂, MoSe₂, WS₂, WSe₂, VS₂, TaS₂ and etc. display many unconventional physicochemical or electronic properties compared to their bulk counterparts making them hold great promise in the areas of electronic,^{6,7} optoelectronic,^{8,9} catalysis,¹⁰⁻¹⁴ and biology.¹⁵

Among the TMDC family, metallic niobium disulfide (NbS₂) shows unique anisotropic, optical, superconductivity, and magnetic properties.¹⁶⁻²⁰ NbS₂ has already been found as a promising material in several applications, such as battery,²¹ hydrotreating catalyst,²² and sensor.²³ At present, several effective approaches have been reported for synthesizing NbS₂ with different morphologies, for instance nanowires,²⁰ nanotubes,²⁴ nanobelt arrays,²⁵ and thin films.²⁶ However, the exploration of new applications for NbS₂ is still hampered by the lack of well-controlled sample preparation method. Chemical vapor deposition (CVD) is one of a feasible bottom-up way to synthesize 2D nanoflakes with high crystalline quality.^{27,28} Recently, Ago et al.¹⁹ successfully synthesized single-crystalline NbS₂ nanoflakes with controlled orientation (perpendicular and lateral) on Si and SiO₂ insulating substrates by CVD growth under the ambient pressure condition. However, for electrochemical application, the direct synthesis of NbS₂ on conductive substrate materials is essential for the HER application. Furthermore, more detailed research is

still needed to clearly reveal the macroscopic structure and physicochemical property of the 2D NbS₂ materials and extend its corresponding new applications.

Several excellent reviews on the catalytic application of 2D TMDCs toward high performance HER are available.²⁹⁻³² Most of the reported 2D TMDCs nanomaterials show higher HER performance comparing with their bulk form.^{29,30,32-34} Recently, both experimental and theoretical studies have demonstrated that 2D TMDCs nanoflakes or nanoparticles can be more catalytically active for water splitting.³⁵⁻³⁹ Remarkably, the metallic 1T-MoS₂ and 1T-Ws₂ nanoflakes have showed improved HER performance compared to their corresponding 2H phase semiconducting counterparts, i.e., 2H-MoS₂ and 2H-Ws₂.^{35,36} In all reported strategies,^{30,31,40} the hybridization of 2D TMDCs with other nanomaterials (e.g., noble metals, conductive materials) is one of the most effective methods for improving the electrocatalytic HER activity.^{31,40} Considering that NbS₂ is a metallic 2D TMDC material with good conductivity, there may be great promise for their HER catalytic activity and even with further enhanced performance by fabricating multidimensional NbS₂-based hybrids, which are awaiting thorough experimental confirmation.

In this contribution, we report a two-step method via a facile CVD and thermal annealing process to synthesize the hybrid electrocatalysts comprising with NbS₂ and nanocrystalline MoS_x on polished commercial glass carbon (GC). Firstly, the NbS₂ nanosheets with 3R-type geometry were successfully grown by CVD tactics on the substrate of polished GC, as shown in Figure 1a (details are given in the Experimental Section). Then, ammonium thiomolybdates were drop-coated on the CVD-grown

samples, followed by thermal annealing to form polycrystalline MoS_x surrounding the NbS_2 nanoflakes. Controlled amount of MoS_x was well dispersed onto the surface of NbS_2 , and the obtained hybrid materials ($\text{MoS}_x@ \text{NbS}_2/\text{GC}$) not only displayed the metallic properties of NbS_2 , but also showed enhanced stability compared to pristine MoS_x . The obtained $\text{MoS}_{x-y}@ \text{NbS}_2/\text{GC}$ (y denotes the mass fraction of MoS_x in hybrid) hybrid samples were then evaluated the HER performance by using 0.5 M H_2SO_4 acidic electrolyte, exhibiting the highest HER activity (a small Tafel slope of 43.2 mV/dec, and -164 mV overpotential at -10 mA/cm^2 current density). We further show the results of density functional theory (DFT) calculations, consistently suggesting the improved HER catalytic activities derived from the smaller Gibbs free energy difference (ΔG_{H}). To the best of our knowledge, this is the first time that NbS_2 -based hybrids are reported to catalyze HER effectively.

Experimental

Materials

All chemical reagents including niobium (V) chloride ($\geq 99.99\%$), sulfur powder ($\geq 99.0\%$), ammonium tetrathiomolybdate ($(\text{NH}_4)_2\text{MoS}_4$, purity $\geq 99.97\%$ trace metals basis), dimethylformamide (DMF, 99.8%), sulfuric acid (H_2SO_4 , 95%-98%), and isopropanol (99.5%) were purchased from Sigma-Aldrich. The commercial Pt/C (20% for platinum) was purchased from Alfa Aesar. Glass carbon was purchased from Structure Probe, Inc. Water was purified through a Millipore system. All the chemicals were used as received without any further purification.

Synthesis method of NbS₂ nanoflakes

Niobium chloride (NbCl₅) was used as a precursor in the synthesis of NbS₂. As displayed in Figure 1a, a quartz boat with about 0.2 g NbCl₅ powder was placed in the upstream heating zone (Heating Chamber II) of the furnace. Polished glass carbon substrates with the size 0.5 cm×2.5 cm were put at the center of the Heating Chamber II. Before growth, the commercial glass carbon (GC) substrates were polished by aqueous alumina suspension on felt pads. Subsequently, the polished glass carbon substrates were consecutively washed with acetone, isopropanol, and deionized water under ultrasound sonication for 30 min in each solution respectively. The S powder was placed in a separated quartz boat at the upper stream side of the furnace (Heating Chamber I) and the temperature was maintained at 250 °C during the synthesis of NbS₂. A mixed Ar/H₂ gas (Ar=200 sccm, H₂=15 sccm) flowed to the growth chamber, while the pressure was kept at 250 Torr. The temperature of Heating Chamber II was first raised to 90 °C and kept for 10 min, then rising up to 850 °C. After reaching the desired growth temperature 850 °C and kept for 15 min, the furnace was cooled down to room temperature naturally. The averaged loadings of NbS₂ on GC substrates were about 0.8 mg/cm².

Preparation of MoS_{x-y}@NbS₂/GC electrocatalysts

To prepare the MoS_x-decorated NbS₂, the NbS₂/GC was drop-coated with an ammonium thiomolybdate solution (1.5 wt% of (NH₄)₂MoS₄ in DMF), followed by drying on a hot-plate at 60 °C for 30 min. It was then subsequently annealed at 120 °C for 1 hour in a mixed H₂/Ar (Ar=96 sccm, H₂=24 sccm) environment to obtain

MoS_x@NbS₂/GC hybrid. In this hybrid material, the mass fraction of MoS_x is 15.8% (0.15 mg/cm², it was calculated by the drop-coating volume of ammonium thiomolybdate solution), which can be simply regulated by modifying the drop-coating volume of ammonium thiomolybdate solution. The obtained samples were named as MoS_x-y@NbS₂/GC (y represents the mass fraction of MoS_x in hybrid MoS_x@NbS₂/GC). We have also prepared the sample MoS_x/GC (0.15 mg/cm²) for comparison by drop-coating an ammonium thiomolybdate solution (1.5 wt% of (NH₄)₂MoS₄ in N,N-dimethylformamide (DMF)) on GC, followed by the same thermal annealing process. To make the discussion more brief and convenient, we used MoS_x@NbS₂/GC to represent MoS_x-15.8%@NbS₂/GC in the manuscript.

Electrochemical measurements

The electrochemical measurements were performed in a PGSTAT 302N Autolab Potentiostat/Galvanostat (Metrohm) at room temperature. Graphite rod and Ag/AgCl (in a saturated KCl solution) electrodes were used as the counter and reference electrodes, respectively. The HER activities of studied catalysts were evaluated by measuring polarization curves with linear sweep voltammetry (LSV) at a scan rate of 0.5 mV/s in 0.5 M H₂SO₄ (pH=0.34) solutions. Potentials were referenced to a reversible hydrogen electrode (RHE) by adding a value of 0.217 V (0.197+0.0591×pH). The commercial Pt/C (20 wt% Pt on Vulcan carbon black) of the same loading as MoS_x-15.8%@NbS₂/GC (0.95 mg/cm²) supported by GC was prepared by mixing the Pt/C and isopropanol, followed by sonicating for 30 min, and then drop-casting on the GC. In addition, 10 μL Nafion (0.5 wt%) solution in

isopropanol was added to the surfaces of all the studied electrocatalysts to fix the catalysts. The stability test for the studied catalyst was performed with the time dependent current density measurement, where a constant overpotential (vs. RHE; after internal resistance compensation) was provided. All data have been corrected for a small ohmic drop based on impedance spectroscopy. It is noted that we use a graphite rod as the anode for evaluating the HER performance since conventionally used Pt anode may dissolve in electrolytes and contaminate the cathode, leading to overestimation of HER currents.

Characterizations

The crystalline structures of the samples were analyzed by X-ray diffraction (XRD, Bruker D8 Discover diffractometer, using Cu K α radiation, $\lambda=1.540598$ Å). The morphologies of the catalysts were determined by field-emission scanning electron microscopy (FESEM, FEI Quanta 600) and transmission electron microscopy (FEI Titan ST, operated at 300 kV). X-ray photoelectron spectroscopy (XPS) studies were carried out in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al K α X-ray source ($h\nu=1486.6$ eV) under a vacuum of 1×10^{-9} mbar. The spectra were collected at fixed analyzer pass energies of 160 eV and 20 eV. The binding energies in XPS analysis were corrected by referencing C 1s peak at 284.8 eV.

Results and discussion

Figure 1. a) A schematic illustration of the growth setup for NbS₂ nanoflakes. NbCl₅ was employed as the precursor of NbS₂ growth and polished glass carbon was adopted as the growth substrate. b) XRD patterns of bare GC, MoS_x/GC, NbS₂/GC, and MoS_x@NbS₂/GC samples. The standard PDF database of NbS₂ (PDF #38-1367) and MoS₂ (PDF#37-1492) were added for as the references. c-e) SEM images of MoS_x/GC (c), NbS₂/GC (d), and MoS_x@NbS₂/GC (e), the inset in each image is the corresponding higher-magnification SEM image.

XRD analysis (Figure 1b) was conducted to determine the crystalline structure of the synthesized NbS₂ nanosheets. The black line (Figure 1b) displays the XRD spectra

of a bare glass carbon (GC) substrate. Several new peaks are clearly observed from the NbS₂/GC sample that can be assigned to NbS₂ with 3R phase, matching well with the PDF database (PDF #38-1367). The diffraction peaks are also in good agreement with the model structures based on the inorganic crystal structure data file²⁰ and other's report.¹⁹ For the MoS_x/GC sample, besides the peaks of GC substrates no obvious crystalline peaks can be observed, suggesting the obtained MoS_x is either amorphous or nanocrystalline by the preparation method. The XRD pattern for the MoS_x-decorated NbS₂ (MoS_x@NbS₂/GC) displays peaks ascribed to NbS₂, suggesting that the NbS₂ crystals can be well kept after the decoration of MoS_x. Note that in this hybrid catalyst, the mass fraction of MoS_x was 15.8%. The morphologies of thermal annealed MoS_x/GC, CVD-grown NbS₂/GC crystals, and hybrid sample of MoS_x@NbS₂/GC are shown in Figure 1c-e, respectively. The scanning electron microscopy (SEM) image and the corresponding inset in Figure S1 show that the surface of the pure and polished GC is relatively smooth. For the morphology of MoS_x grown on GC (Figure 1c and inset), the coating is rather non-uniform, micro-scale clumps were formed on the surface of GC. In Figure 1d and inset, large amounts of NbS₂ nanoflakes structures with different orientations are exhibited, most of them show a clear polygonous shape with the lateral dimension ranging from several micrometers to 10 μm. The SEM image of MoS_x@NbS₂/GC in Figure 1e and the inset reveal that the MoS_x nanoparticles are well dispersed on the surface of NbS₂ nanoflakes. The SEM element mapping in Figure S2 shows that the Nb, Mo, and S signals are uniformly distributed over the whole image area, indicating the MoS_x is

well dispersed on the surfaces of NbS₂ nanoflakes.

Figure 2. a) Low-magnification TEM image of a transferred NbS₂ nanoflake. It shows a hexagonal morphology with an angle of 120 °C between two edge lines. b) HRTEM image of the transferred NbS₂ nanoflake. c) TEM image of the hybrid MoS_x@NbS₂/GC sample. d) HRTEM image of the hybrid MoS_x@NbS₂/GC sample. The boundary between NbS₂ (core) and MoS_x (shell) and the film and nanoparticle shape of MoS_x can be clearly observed. Insets of b) and d) show the FFT data of the corresponding TEM images b) and d), respectively. The inner sets of orientation-matched hexagonal patterns are identified as {10} diffraction spots from NbS₂.

Transmission electron microscope (TEM) was performed to determine the microstructures of the synthesized NbS₂/GC, MoS_x/GC, and MoS_x@NbS₂/GC

samples. The low-magnification TEM image of NbS₂ nanoflake exhibits the typical hexagon (Figure 2a). High-resolution TEM (HRTEM) image and the corresponding regular hexagonal pattern seen in Fast Fourier Transform (FFT) of the TEM image (Figure 2b and inset) along the c-axis (the out-of-plane axis) of a nanoflake were also obtained. From the HRTEM image (Figure 2b), the atomic spacing is around 2.88 Å, which matches with the (010) or (100) lattice plane distance¹⁹ and the lattice parameters of NbS₂ (a=b=3.335 and c=17.867, PDF #38-1367). The inset of Figure 2b indicates the single crystallinity of the NbS₂ nanoflake. The well-defined hexagonal pattern shows the hexagonal structure of NbS₂ nanoflakes basal planes. The TEM images and the corresponding electron diffraction patterns in Figure S3 further confirm that MoS_x obtained by the annealing method was in polycrystalline phases. Figure 2 c and d display the TEM images of hybrid sample MoS_x@NbS₂/GC, the images prove that a thin shell (film) of amorphous MoS_x with about 5 nm was formed on the surface NbS₂ crystals. Meanwhile, small MoS_x nanoparticles with various particle sizes were also observed on the surface of NbS₂ nanoflake, which in good consistency with the SEM measurements (Figure 1e). More TEM representative images of MoS_x@NbS₂/GC given in Figure S4 further confirm the above conclusions. In addition, after the drop-coating of MoS_x, the polycrystalline electron diffraction ring (the inset of Figure 2d) of MoS_x was also clearly seen from the FFT of the HRTEM image (Figure 2d).

The surface electronic state and composition of MoS_x@NbS₂/GC were further investigated by X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum

in Figure S5 exhibits that the $\text{MoS}_x\text{@NbS}_2/\text{GC}$ comprises Mo, Nb, S, C, and O elements. Figure 3(a) exhibits a high-resolution spectrum of Nb 3d of the hybrid $\text{MoS}_x\text{@NbS}_2/\text{GC}$ catalyst, the two peaks at 203.3 and 206.1 eV can be assigned to $\text{Nb}^{4+} 3d_{5/2}$ and $\text{Nb}^{4+} 3d_{3/2}$.^{41,42} For Mo 3d peaks, as shown in Figure 3(b), can be de-convoluted in to two Mo doublets ($\text{Mo}^{5+} 3d_{3/2}$, $\text{Mo}^{5+} 3d_{5/2}$, $\text{Mo}^{4+} 3d_{3/2}$, and $\text{Mo}^{4+} 3d_{5/2}$) with the existence of overlapping S 2s peak, which is consistent well with our previous study.⁴³ In the high-resolution S 2p region (Figure 3(c)), the main spectrum peaks between 161 and 166 eV clearly split into two doublets ($\text{S}_1^{2-} 2p_{3/2}$, $\text{S}_1^{2-} 2p_{1/2}$ and $\text{S}_2^{2-} 2p_{3/2}$, $\text{S}_2^{2-} 2p_{1/2}$) suggest the existence of both S_1^{2-} and S_2^{2-} ligands, in accordance with the formation of MoS_x .^{43,44} The other two $\text{S}_2^{2-} 2p$ peaks at 160.8 and 161.8 eV are attributed to the S $2p_{3/2}$ and S $2p_{1/2}$ (the similar binding energy with $\text{S}_1^{2-} 2p_{3/2}$ of MoS_x) binding energies of Nb-S bondings, respectively.²⁶ Compared to the XPS spectra of pure MoS_x (230.2 and 233.3 eV, Figure 3(d)), the binding energie of Mo 3d shifts to a lower banding energy i.e., 229.8 and 232.9 eV, respectively, suggesting the existence of a strong interaction between the NbS_2 and MoS_x . And the electron transfer phenomenon from NbS_2 to MoS_x by intermediate sulfur atoms may occur when they form the hybrid crystals.⁴⁵⁻⁴⁷ In addition, due to the surface oxidation, we also observed a Nb doublet at 207.3 and 210.2 eV corresponding to $\text{Nb}^{5+} 3d_{5/2}$ and $\text{Nb}^{5+} 3d_{3/2}$ of Nb_2O_5 (Figure 5(a))^{41,42} and the S 2p in S-O bonds at 168.9 eV, respectively.

Figure 3. Nb 3d (a), Mo 3d (b), and S 2p (c) XPS spectra for the $\text{MoS}_x@\text{NbS}_2/\text{GC}$ sample; obvious binding energy shifts in the XPS spectra of (d) Mo 3d for the MoS_x/GC and $\text{MoS}_x@\text{NbS}_2/\text{GC}$ samples.

Figure 4. a) Polarization curves after iR correction in bare GC, MoS_x/GC , NbS_2/GC ,

MoS_x@NbS₂/GC, and commercial Pt/C/GC (20 wt%) samples. The loadings for MoS_x/GC, NbS₂/GC, and MoS_x@NbS₂/GC are 0.15 mg/cm², 0.8 mg/cm², and 0.95 mg/cm², respectively. Sweep rate: 0.5 mV/s. b) Tafel slopes extracted from the polarization curves in a). c) Time-dependent HER performance (at a low working current density of 50 mA/cm²) of the MoS_x/GC, NbS₂/GC, and MoS_x@NbS₂/GC conducted in 0.5 M H₂SO₄ solution for 12 h. A hydrogen atom is absorbed at the defect site of a defected MoS₂ layer on top of NbS₂ layer: d) side view and e) top view. (hydrogen: white, Mo: purple, Nb: green, S: yellow).

To evaluate the electrochemical catalytic performance over different electrocatalysts, Figure 4a compares the HER activities of bare GC, MoS_x/GC, NbS₂/GC, and MoS_x@NbS₂/GC (the mass fraction of MoS_x is 15.8%). The bare GC electrode displayed a negligible background activity for H₂ evolution. As a comparison, the commercial Pt/C catalyst (20 wt% Pt on Vulcan carbon black) was also evaluated, which exhibited the best HER catalytic performance with a near zero overpotential for initializing hydrogen evolution at low current density values. The reference samples i.e., pure MoS_x/GC and NbS₂/GC, both of them exhibited poor HER performance (Figure 4a). For the above two catalysts, at a current density of -10 mA/cm² the overpotential (vs. RHE) were -442 mV and -221 mV (Figure 4a), with corresponding Tafel slope 79.2 mV/dec and 161.9 mV/dec, respectively (Figure 4b). Remarkably, for the hybrid MoS_x@NbS₂/GC sample, the overpotential at current density of 10 mA/cm² was -164 mV, drastically smaller than its constituent MoS_x/GC

and NbS₂/GC. Meanwhile, the Tafel slope of MoS_x@NbS₂/GC sample was 43.2 mV/dec, which was much lower than MoS_x/GC and NbS₂/GC, and close to the value of 31.2 mV/dec for Pt/C/GC, demonstrating the outstanding intrinsic HER kinetics of the MoS_x@NbS₂/GC. This specific overpotential (at 10 mA/cm²) and Tafel slope of MoS_x@NbS₂/GC catalyst is lower than (or comparable) to other reported TMDCs such as 1T-, 2H-MoS₂,^{34,35,48,49} 1T, 2H-WS₂,^{36,50} WS₂(1-x)Se_{2x},¹¹ MoS₂/WS₂,⁵¹ and other similar materials (Table S1). Moreover, it only requires an overpotential value of -233 mV to achieve -200 mA/cm², suggesting a better HER performance than the commercial Pt/C catalyst (-274 mV at -200 mA/cm²) at the high current density. In addition, the HER activities of a series of MoS_x-y@NbS₂/GC catalysts with different MoS_x mass fractions from 0 to 23.8% (details in Figure S6) and MoS_x@NbS₂/GC prepared under different annealing temperature (details in Figure S7) were also evaluated. Meanwhile, a simple cyclic voltammetry (CV) method i.e., measuring the double layer capacitance was used to estimate electrochemical active surface area (ESCA).^{52,53} In our study, CV in the potential region from 0.08 to 0.225 V (vs. RHE) at different scan rates (10~60 mV s⁻¹) were recorded (details in Figure S8). The double layer capacitances (C_{dl}) for three studied samples, which should be directly proportional to the surface area, are extracted by plotting the Δj at a given potential (0.152 V vs. RHE) against the CV scan rates (Figure S8b). The measured C_{dl} for NbS₂/GC, MoS_x/GC, and MoS_x@NbS₂/GC samples were summarized in Figure S8b, from which we conclude that the catalyst MoS_x@NbS₂/GC exhibits to a higher double-layer capacitance i.e., 7.13 mF cm⁻² (large than 3.3 times for MoS_x/GC, large

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than 64 times for NbS₂/GC), this demonstrating that the greatly increase in active sites after hybridization.

When MoS_x was coated to NbS₂, a new structure of MoS_x@NbS₂ nanointerfaces was formed by the directly contacting regions between the NbS₂ core and the MoS_x shell, which likely creates open latent vacancy sites between Nb and Mo atoms and the formation of direct Nb-S-Mo bonds, which is similar with the system of Co₉S₈@MoS₂.^{46,47,54} And the strong electron transfer from Nb to Mo by intermediate sulfur atoms bonded to both metals may occur when they form the hybrid crystals, as proved from our XPS results, may result in more negatively charged S sites in MoS_x which are become more active for the interaction of the H⁺ in HER.^{45,46} Because the value of ΔG_H is broadly used as a reasonable index of HER performance for a wide variety of catalysts,^{47,55-57} we modeled hybrid materials (MoS_x@NbS₂) with a layer of defected MoS₂ with single S vacancy defects onto a layer of NbS₂, and calculate the corresponding hydrogen adsorption free energy difference ΔG_H at the S vacancy sites. An optimum HER activity is generally suggested to be obtained if ΔG_H is closer to zero.^{56,58} Because from the HER activity evaluation (Figure 4a&b, Figure S6, and Figure S7) results, we could draw the conclusion that the MoS_x is the main performance contributor for the hybrid catalyst. We performed first-principles calculations using Vienna ab-initio simulation package (VASP) (The calculation details are in the Supporting Information), and calculated 4×4 supercells of MoS_x and MoS_x@NbS₂, using the same lattice constant of NbS₂. We considered 1, 2, 3, and 4 single S vacancy defects and the full hydrogen coverage at all defect sites on the 4×4

MoS₂ (Figure S9), and found that, for MoS_x ($x = 1.9375, 1.875, 1.8125, \text{ and } 1.75$, respectively), $\Delta G_H = -0.30, -0.25, -0.36, -0.28$ eV for 1-4 defects respectively. When the defected MoS_x is placed onto NbS₂, $\Delta G_H = -0.20, -0.25, -0.36 -0.25$ eV for 1-4 defects of MoS₂ (Figure S10). Figure 4d and e show the optimized structures that a hydrogen atom is absorbed at the defect site of a defected MoS₂ layer on top of NbS₂ layer. Compared with pure MoS_x, all ΔG_H values obtained in different defects are closer to zero, suggesting that the hybrid materials (MoS_x@NbS₂) render better HER performance. On the other hand, the Mo-edge is also catalytically active for HER.⁵⁹ We thus considered the HER at Mo-edge of (1) a 4×2 flake of MoS₂, and (2) a 4×2 flake of MoS₂ on a 10×2 supercell of NbS₂. We obtained $\Delta G_H = -0.48$ eV for (1), and $\Delta G_H = -0.16$ eV for (2). The much reduced ΔG_H for the hybrid system corresponds to a better HER performance than the pristine MoS₂ flake. Therefore, our density functional calculations suggested that MoS_x@NbS₂ offer better HER performance than MoS_x, consistent with our experimental findings.

In addition to the HER efficiency, the stability is another critical factor for evaluating a catalyst. Figure 4c displays the time dependent measurement for MoS_x/GC, NbS₂/GC, and MoS_x@NbS₂/GC at a low working current density (about 50 mA/cm²). It was observed that the decay of the HER current for MoS_x/GC was about 32%, in comparison the decay is around 4% for NbS₂/GC and 20% for hybrid MoS_x@NbS₂/GC under HER for 12 h. This difference may be closely related to the density of defects in the catalysts. Markovic and co-works found that less active crystalline materials are more stable than their counterparts by approximately a factor

of ten.⁶⁰ Therefore, the amorphous MoS_x with many defects shows weak stability, while less active NbS₂ with well crystalline phase displays the highest stability.

Conclusions

In conclusion, we have developed a facile two-step method (CVD and thermal annealing) to synthesize a new hybrid NbS₂ nanoflakes coated with MoS_x on a glass carbon substrate, where the amounts of MoS_x in the hybrid MoS_x@NbS₂/GC catalyst can be well controlled by the drop-coating amounts of ammonium thiomolybdate solution. The hexagonal 3R crystalline structures of NbS₂ and the corresponding hybrid MoS_x@NbS₂ materials have been well determined by using SEM, XRD, and TEM informative tools. The produced hybrid catalyst MoS_x@NbS₂/GC (15.8 wt% of MoS_x) exhibits an excellent activity (-164 mV at -10 mA/cm²; Tafel slope 43.2 mV/dec) and the better HER performance (-233 mV at -200 mA/cm²) than the commercial Pt/C catalyst at the high current density values, demonstrating promising application as a non-noble metal HER catalyst. The high HER activity of the MoS_x@NbS₂/GC can be attributed to the smaller Gibbs free energy difference (ΔG_H). These findings broaden our vision on how to improve the HER performance of 2D TMDCs nanoflakes.

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Graphical Abstract