Hydrogen Evolution Reaction Property of Molybdenum Disulfide/Nickel Phosphide Hybrids in Alkaline Solution

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Abstract: The hydrogen evolution reaction (HER) property of molybdenum disulfide (MoS$_2$) is undesirable because of the insufficient active edge sites and the poor conductivity. To enhance HER performance of MoS$_2$, nickel phosphide (Ni$_2$P) was combined with this catalyst and three MoS$_2$/Ni$_2$P hybrids (38 wt % Ni$_2$P addition for MoS$_2$/Ni$_2$P-38, 50 wt % Ni$_2$P addition for MoS$_2$/Ni$_2$P-50, and 58 wt % Ni$_2$P addition for MoS$_2$/Ni$_2$P-58) were fabricated via a hydrothermal synthesis process. Morphologies, crystallinities, chemical components, specific surface areas, and HER properties of the fabricated MoS$_2$/Ni$_2$P samples in an alkaline electrolyte were characterized and tested. In addition, the insight into the HER properties of as-prepared catalysts were revealed by the density functional theory (DFT) calculation. Additionally, the stabilities of pure MoS$_2$, Ni$_2$P, and MoS$_2$/Ni$_2$P-50 samples were evaluated. The results show that the addition of Ni$_2$P can enhance the HER property of the MoS$_2$ catalyst. Although HER properties of the above-mentioned three MoS$_2$/Ni$_2$P hybrids are inferior to that of pure Ni$_2$P, they are much higher than that of MoS$_2$. Among as-prepared three hybrids, MoS$_2$/Ni$_2$P-50 exhibits the best HER performance, which may be due to its uniform morphology, large specific surface area, and excellent stability. The MoS$_2$/Ni$_2$P-50 hybrid shows a high cathodic current density (70 mA/cm$^2$ at $-0.48$ V), small Tafel slope (~$58$ mV/decade), and a low charge transfer resistance (0.83 kΩ·cm$^2$).

Keywords: hydrogen evolution reaction; molybdenum disulfide; nickel phosphide; hydrothermal synthesis; density functional theory; alkaline electrolyte

1. Introduction

With growing concerns about environmental pollution and energy crises resulting from overconsumption of coal and fossil fuels, the exploitation of renewable clean energies, such as solar energy, wind energy, hydraulic power, biological energy, fuel cell, and hydrogen energy come to the forefront [1–3]. Among the clean energies mentioned above, hydrogen energy is attracting ever-growing attention due to the convenient production and effective cost [4,5]. Apart from the traditional method through steam from fossil fuels, the process of electrochemical water splitting is considered as an alternative to produce hydrogen through the HER [6–9]. Until the present, the well-known platinum and platinum-based alloys show the best electrocatalytic performance for HER [10–13]. However, their high-cost and scarcity impede their wide applications in practice [14–16].

To facilitate HER application, it is urgent to develop low-cost alternatives with Earth-abundant and cost-effective features to replace the noble metals [17,18]. Thus, various non-noble materials including transition metal sulfides [19], selenides [20], oxides [21], carbides [22], and nitrides [23],

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as well as phosphides [24], have been reported as electrocatalysts for HER. Among these catalysts, MoS$_2$-based materials have been researched as the promising substitutes owing to their low cost, Earth-abundance, and the relatively high activity [25,26]. However, the inert basal surface, poor intrinsic conductivity, and insufficient edged activity sites limit their HER performance [27]. In order to enhance the HER performance of this catalyst efficiently, a large number of efforts have been devoted and can be briefly classified as follows [4,28,29]: (1) increasing the density of active edge sites; (2) enhancing the inherent activity; (3) improving the electrical contact between active sites. Generally, intensive endeavors such as interlayer intercalation [30,31], phase transformation (from 2H-MoS$_2$ to 1T-MoS$_2$) [32], gentle oxidation [33], functional structural design [34], and stabilizing the edge layers with organic molecules [35] have been made to increase the active sites located at the edge, whereas the basal plane is still chemically inert.

Additionally, for the purpose of improving the electrical contact between active sites of MoS$_2$, various promoters, such as gold [30], platinum [36], palladium [37], carbon materials [38], core-shell MoO$_3$ [39], Co$_2$O$_4$ nanosheet array [40], graphene [41,42], graphene oxide [17,43], and nickel-phosphorus (Ni-P) powders [4], have been adopted as electrical conduction-enhancing supports. Of all the above-mentioned supports, the cost-effective Ni-P powder possesses superior electrical conductivity and outstanding HER performance [28,44,45]. Thus, this material is a suitable candidate employed to enhance the HER activity of MoS$_2$. In view of the fact that Ni-P incorporation is advantageous to the enhancement in the HER property of MoS$_2$ [4], herein, it should be worth noting that the coexistent nickel phosphate phases (i.e., Ni$_5$P$_2$, Ni$_2$P, Ni$_3$P, Ni$_{12}$P$_5$, NiP$_2$, Ni$_5$P$_4$, NiP, and Ni$_7$P$_3$) [46] will play a major role in HER feature of this catalyst. Among these nickel phosphides, Ni$_2$P demonstrates an excellent HER characteristic [14,47] and draws tremendous attention. Although the attempt of incorporation of Ni$_2$P on to the surface of nano-MoS$_2$ has been made in the hope of the increment in HER performance [16]; to the best of our knowledge so far, the effort of Ni$_2$P employed as a sublayer support to improve the HER property of MoS$_2$ is insufficient. In this sense, the role of Ni$_2$P as a layer support in pursuit of the increase in MoS$_2$ HER deserves to be investigated.

Unambiguously, the density functional theory (DFT) calculations as a major supplement to experimental techniques will be significantly valuable for revealing the intrinsic feature of HER [30,42,48–50]. Atomic details related to the adsorption and desorption of hydrogen atoms, as well as the immanent interaction between hydrogen atom and the catalyst can be perfectly interpreted. To date, some studies in HER process for MoS$_2$, Ni$_2$P, and MoS$_2$/graphene catalysts have been reported [42,49,50], but efforts related to that of MoS$_2$/graphene hybrid catalyst via the DFT simulation are insufficient.

In this work, MoS$_2$ was anchored on the surface of the Ni$_2$P nanosheet via a hydrothermal synthesis process, and the three MoS$_2$/Ni$_2$P hybrids (38 wt % Ni$_2$P addition for MoS$_2$/Ni$_2$P-38, 50 wt % Ni$_2$P addition for MoS$_2$/Ni$_2$P-50, and 58 wt % Ni$_2$P addition for MoS$_2$/Ni$_2$P-58) were fabricated. The aim of this study is to offer an effective route to improve the HER property of MoS$_2$ by combining of this metal sulfide with Ni$_2$P. Morphologies, crystallinities, chemical components, and active areas of the prepared MoS$_2$/Ni$_2$P hybrids were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and the Brunauer-Emmett-Teller (BET) method. Techniques of linear sweep voltammetry (LSV), Tafel polarization, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) were employed to test HER properties of the above three hybrids; subsequently, the effect of Ni$_2$P as the bottom substrate was illustrated. Additionally, the adsorption energies ($\Delta E_{ads}$) and the Gibbs free energies of adsorption ($\Delta G_{ads}$) between the hydrogen atoms and the catalyst were calculated. Furthermore, the stability of the hybrid was evaluated.
2. Experimental Section

2.1. Material

Analytical grade reagents of ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, 99 wt %), thiourea (CH₄N₂S, 99 wt %), red phosphorus, nickel chloride hexahydrate (NiCl₂·6H₂O, 98 wt %), potassium hydroxide (KOH), and absolute ethanol were purchased from Jingchun Scientific Co. Ltd. (Shanghai, China). The 5 wt % of Nafion solution was offered by Alfa Aesar Chemicals Co. Ltd. (Shanghai, China). The Pt/C power (20 wt % Pt on Vulcan XC-72R) was supplied by Yu Bo Biotech Co. Ltd. (Shanghai, China). In this present study, all above reagents were used as received in the present study and without further purification.

2.2. Synthesis of the Ni₂P Nanosheet

Under vigorous stirring condition, 1.63 g red phosphorus and 1.25 g NiCl₂·6H₂O were dissolved in 15 mL deionized water for 30 min and a slurry-like mixture was obtained. Then this mixture solution was transferred into a 25 mL Teflon-lined stainless steel autoclave and followed by placed into a muffle furnace (WRN-010, Eurasian, Tianjin, China), which was preheated to 180 °C. The hydrothermal synthesis process was carried out at 180 °C for 24 h. When the temperature of the muffle furnace was cooled to room temperature naturally, the formed particles were separated by centrifugation and washed with ethanol twice and deionized water three times. Lastly, the fabricated gray-black Ni₂P powders were dried in a vacuum oven (DZF-6050, Boxun Industrial Co. Ltd., Shanghai, China) and retained for use.

2.3. Synthesis of the MoS₂/Ni₂P Hybrids

A total of 1.41 g (NH₄)₆Mo₇O₂₄·4H₂O, 0.26 g CH₄N₂S and three different amounts of Ni₂P (38 wt %, 50 wt %, and 58 wt %) were dispersed in 20 mL of distilled water. The mixture solution was vigorously stirred for 1 h at room temperature. After that, the solution was transferred into a 25 mL Teflon-lined stainless steel autoclave placed in a muffle furnace, and then reacted at 200 °C for 24 h. As the solution temperature was cooled to room temperature naturally, the resultant three black samples (MoS₂/Ni₂P-38, MoS₂/Ni₂P-50, and MoS₂/Ni₂P-58) were centrifuged and adequately washed with ethanol and deionized water. Finally, the as-synthesized samples were dried under a vacuum atmosphere at 60 °C for 12 h.

2.4. Characterization

Crystal structures of the synthesized MoS₂/Ni₂P samples were determined by an X-ray diffractometer (XRD, SmartLab, Tokyo, Japan) using Cu Kα radiation (λ = 1.5418 Å) from 5 to 100 angles at a scanning rate of 5°/min. The morphologies of the samples were obtained using a scanning electron microscope (SEM, S-4800, Hitachi, Tokyo, Japan) at an accelerating voltage of 5 kV. The elemental compositions and chemical states of these three MoS₂/Ni₂P samples were characterized by X-ray photoelectron spectra (XPS, ESCALAB MK II, Thermo Fisher Scientific, Waltham, MA, USA) using Mg Kα as the excitation source. The Brunauer-Emmett-Teller (BET) specific surface areas of the obtained samples were examined by N₂ adsorption/desorption measurement on a Nova 4000e analyzer (Quantachrome Instrument, Boynton Beach, FL, USA) at 77 K.

2.5. Electrochemical Measurements

Before preparing the working electrode, a glassy carbon electrode (GCE) of 3 mm in diameter was firstly polished with 1000# water sandpaper and cleaned with ethanol and deionized water. Typically, 5 mg of catalyst (Ni₂P, MoS₂, MoS₂/Ni₂P hybrids, and the commercial 20 wt % Pt/C) and 30 µL Nafion solution (5 wt %) were dispersed in 1 mL solution consisting of 250 µL absolute ethanol and 750 µL deionized water, and followed by sonication for 1 h to form a homogeneous ink. Then, 5 µL of the
dispersion solution was loaded onto the surface of the polished GCE and the electrode was dried at room temperature; herein, the excessive ethanol present in the slurry was removed as much as possible by extending the drying time. Prior to each electrochemical test, the electrolyte solution was degassed by bubbling pure nitrogen gas for 30 min to remove the dissolved oxygen.

All electrochemical tests were conducted in a typical three-electrode system attached to an electrochemical workstation (CHI 650C, Chenhua Co. Ltd., Shanghai, China) in 1.0 mol/L KOH electrolyte. The GCE modified by the MoS$_2$/Ni$_2$P hybrids (MoS$_2$, Ni$_2$P or Pt/C) acted as the working electrode, while a Ag/AgCl electrode and a platinum foil were employed as the reference and counter electrodes, respectively. The acquired potential values relevant to the Ag/AgCl electrode were converted to the reversible hydrogen electrode (RHE) scale: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{pH} + 0.209 \text{V}$, i.e., the value of potential throughout this manuscript is relative to RHE. Linear sweep voltammetry (LSV) was analyzed in the potential of $-0.8$ to $0.2 \text{V}$ at a scan rate of $2 \text{mV/s}$. Tafel polarization curves were measured in a potential window of $0.3$–$0.65 \text{V}$ with a scan rate of $2 \text{mV/s}$. Cyclic voltammetry (CV) tests were conducted in a potential window from $-0.6$ to $0.8 \text{V}$ at a scan rate of $10 \text{mV/s}$. The electrochemical impedance spectroscopy (EIS) measurements were carried out at a cathodic overpotential of $0.7 \text{V}$ by employing the sinusoidal signal amplitude of $5 \text{mV}$; the frequency ranged from $10^5$ to $0.01 \text{Hz}$.

### 2.6. Computational Details

The calculations based on DFT were implemented in the Materials Studio DMol$^3$ (version 7.0, Accelrys Inc., San Diego, CA, USA) [50,51]. Pulay’s direct inversion in the iterative subspace (DIIS) technique, as well as double numerical plus polarization functions (DNP) and the revised Perdew-Burke-Ernzerhof (RPBE) functional were employed. The effective core potential was applied to treat the core electrons of nickel atoms. With respect to the aqueous HER process, a continuum solvation model (COSMO) was used and water with the dielectric constant of 78.54 as the solvent [52]. In addition, for the purpose of taking into account of the weak interactions (hydrogen bond and van der Waals force), the TS (Tkatchenko-Scheffler) method for DFT-D correction was employed [52].

As is well known, the basal plane of MoS$_2$ has been validated as chemically inert, thus, only the Mo edge-type structure of this catalyst was considered [30]. Three kinds of geometries for MoS$_2$, Ni$_2$P, and MoS$_2$/Ni$_2$P catalysts were employed: a $(4 \times 5 \times 1)$ supercell with two S-Mo-S trilayer for MoS$_2$, a $(2 \times 1 \times 1)$ supercell derived from Ni$_2$P (111) crystal surface with four layers, and a single $(4 \times 5 \times 1)$-sized trilayer MoS$_2$ combined by three $(2 \times 1 \times 1)$-sized Ni$_2$P layers for MoS$_2$/Ni$_2$P. A vacuum with the thickness of $15 \text{Å}$ in the z-direction was used to separate neighboring slabs and to minimize the interactions between them. During the calculations, only the first layers of MoS$_2$ and Ni$_2$P were relaxed in order to save time and computational cost.

### 3. Results and Discussion

#### 3.1. Characterization of Samples

##### 3.1.1. X-ray Diffraction (XRD) Analysis

The XRD patterns of MoS$_2$, Ni$_2$P, and three MoS$_2$/Ni$_2$P hybrids (MoS$_2$/Ni$_2$P-38, MoS$_2$/Ni$_2$P-50, and MoS$_2$/Ni$_2$P-58) are displayed in Figure 1. The characteristics peaks at $2\theta = 33.8^\circ$ and $57.1^\circ$ (curve 1) can be identified, corresponding to (100) and (110) crystal planes of MoS$_2$, respectively. Herein, it should be noted that the diffraction peak of (002) plane of MoS$_2$ is undetected. The absence of the (002) diffraction peak of MoS$_2$ indicates a low stacking height along this direction [53,55]. As demonstrated in curve 2, the diffraction peaks at $2\theta = 40.71^\circ$, $44.61^\circ$, $47.34^\circ$, $50.19^\circ$, $54.96^\circ$, $66.37^\circ$, $72.4^\circ$, $74.9^\circ$, $80.5^\circ$, and $88.6^\circ$ corresponding to (111), (201), (210), (300), (211), (310), (311), (400), (401), and (321) confirm the presence of hexagonal Ni$_2$P; besides the above-mentioned peaks, the detectable weak peaks ($2\theta = 30.36^\circ$, $31.58^\circ$) may be attributed to the coexistence of Ni$_2$P$_4$ phase [54], and another weak peak at
2θ = 35.4° can be assigned to the presence of Ni$_{12}$P$_3$ phase [55]. XRD patterns of the MoS$_2$/Ni$_2$P hybrids are presented in curves 3–5. The diffraction patterns of MoS$_2$/Ni$_2$P hybrids consist of very weak diffraction peak of MoS$_2$, which indicates that the MoS$_2$ is amorphous [5]. In addition, the diffraction peaks related to MoS$_2$ and Ni$_2$P are observed, thus suggesting the successful combination between MoS$_2$ and Ni$_2$P. It may be indexed to a proof of the fabrication of MoS$_2$/Ni$_2$P hybrid. Compared with pure Ni$_2$P, the diffraction intensity of Ni$_2$P crystal for three MoS$_2$/Ni$_2$P hybrids becomes weak. However, with the increase of Ni$_2$P addition, intensities of diffraction peaks attributed to Ni$_2$P become strong and those of MoS$_2$ show a descending trend, which indicates that Ni$_2$P plays a major role in the crystallinity of the hybrids.

Figure 1. XRD patterns of MoS$_2$, Ni$_2$P, and three MoS$_2$/Ni$_2$P hybrids.

3.1.2. Scanning Electron Microscope (SEM)

The morphologies of MoS$_2$, Ni$_2$P, and three MoS$_2$/Ni$_2$P hybrids are given in Figure 2. As shown in Figure 2a, the nanoflower-like structure of MoS$_2$ can be ascertained; of course, there are some nanosheets randomly stacking, which may lead to the decrease in active sites. The fabricated Ni$_2$P particle exhibits a nanosheet-type morphology (Figure 2b), which would be advantageous to electrochemical conduction among the active sites. Morphologies of the three hybrids are observed in Figure 2c (MoS$_2$/Ni$_2$P-38), 2d (MoS$_2$/Ni$_2$P-50) and 2e (MoS$_2$/Ni$_2$P-58). All of them exhibit a mixed morphology of flower-like and lamellar structures.

Figure 2. SEM images of MoS$_2$, Ni$_2$P, and three MoS$_2$/Ni$_2$P hybrids: (a) MoS$_2$; (b) Ni$_2$P; (c) MoS$_2$/Ni$_2$P-38; (d) MoS$_2$/Ni$_2$P-50; and (e) MoS$_2$/Ni$_2$P-58.
As for the SEM pictures of hybrids, with the increasing addition of Ni$_2$P, the flower-shaped structure can be more easily observed, the presence of the Ni$_2$P nanosheet will be helpful for the fabrication of MoS$_2$ nanoflowers. For the sample of MoS$_2$/Ni$_2$P-38, the small amount of Ni$_2$P cannot provide an abundant depositing area, thereby resulting in the serious agglomeration of MoS$_2$ (Figure 2c). For MoS$_2$/Ni$_2$P-50 sample (the mass ratio of MoS$_2$ and Ni$_2$P is 1:1), it can be observed that the petal structure and the plate-type structure uniformly coexist (Figure 2d), and more well-proportioned nanoflower-like MoS$_2$ particles distribute on the surface of Ni$_2$P. Whereas, for MoS$_2$/Ni$_2$P-58 (Figure 2e), with the large addition of Ni$_2$P, it is explicit that the dense MoS$_2$ flower structure can be obtained, showing a resemblance to that of MoS$_2$ (Figure 2a). By a comparison of morphologies of the three hybrids, for the MoS$_2$/Ni$_2$P-50 sample, the MoS$_2$ nanoparticles evenly disperses on the surface of the Ni$_2$P nanosheet.

3.1.3. X-ray Photoelectron Spectroscopy (XPS)

The elemental compositions and their valences of three MoS$_2$/Ni$_2$P hybrids were measured by XPS. The Mo 3d, S 2p, Ni 2p, P 2p and O 1s high-resolution spectra of three MoS$_2$/Ni$_2$P hybrids are respectively presented in Figure 3, and the corresponding bond energies and assignments are given in Table 1. As shown in Figure 3a, the characteristic peaks located at 229.0 eV and 231.9 eV (take MoS$_2$/Ni$_2$P-38 as an example, the following is the same) can be assigned to Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ respectively, suggesting the existence of Mo$^{4+}$. The two peaks at 232.9 eV and 236.0 eV are ascribed to the compounds MoO$_3$ or MoO$_4$$^{2-}$ (Mo$^{6+}$) due to the oxidation of the samples. In addition, the weak peak appearing at 226.4 eV corresponds to S 2s of MoS$_2$ [56]. For S 2p spectra, which is shown in Figure 3b, the two peaks at 161.8 eV and 163.3 eV are attributed to the 2p$_{3/2}$ and 2p$_{1/2}$ orbitals of divalent sulfide ion (S$^{2-}$), while the other two peaks at 168.9 eV and 170.0 eV represent the existence of tetravalent sulfur in the form of SO$_3$$^{2-}$ (S$^{4+}$). Generally, the sulphur atom with a +4 state locates at the edge of MoS$_2$ layered structure due to the oxidation of MoS$_2$ particle [57].

![Figure 3. XPS spectra of three MoS$_2$/Ni$_2$P hybrids: (a) Mo 3d; (b) S 2p; (c) Ni 2p; (d) P 2p; and (e) O 1s.](image-url)
As shown in Figure 3c, the three peaks observed at 857.2 eV, 858.9 eV and 862.8 eV may be assigned to Ni$^{δ+}$ (0 < $δ$ < 2) in Ni$_2$P, oxidized Ni species (Ni$^{2+}$) and the satellite of Ni 2p$_{3/2}$, respectively, while the other three peaks at 875.0 eV, 876.8 eV, and 881.2 eV can be indexed to Ni$^{δ+}$ in Ni$_2$P, oxidized Ni species, and the satellite of Ni 2p$_{1/2}$ [58]. As for the P 2p spectra (Figure 3d), the peak at 130.2 eV is mark of metal-P bonds in metal phosphides, the peak at 133.7 eV can be assumed to the oxidized P species because the samples are exposed to the air [59].

Additionally, the O 1s peak (Figure 3e), with the binding energies of 532.0 eV, indicates the existence of Mo(IV)-O bond [60]. Thus, to some extent, it is also confirmed that the three hybrids were oxidized during the preparation process.

Table 1. Bond energies and assignments of Mo 3d, S 2p, Ni 2p, P 2p, and O 1s photoelectron peaks of three MoS$_2$/Ni$_2$P hybrids.

| Bond Energies/(eV) | MoS$_2$/Ni$_2$P-38 | MoS$_2$/Ni$_2$P-50 | MoS$_2$/Ni$_2$P-58 | Assignments | References |
|-------------------|---------------------|---------------------|---------------------|-------------|------------|
| Mo 3d             | 229.0               | 229.1               | 228.9               | Mo$^{4+}$   | [56]       |
|                   | 231.9               | 232.0               | 232.1               | Mo$^{4+}$   |            |
|                   | 232.9               | 233.1               | 233.0               | Mo$^{6+}$   |            |
|                   | 236.0               | 236.1               | 236.0               | Ni 2p$_{3/2}$ |            |
|                   | 226.4               | 226.4               | 226.3               | S 2s        |            |
| S 2p              | 161.8               | 162.0               | 162.0               | S$^{2−}$    | [57]       |
|                   | 163.3               | 163.4               | 163.4               | S$^{2−}$    |            |
|                   | 168.9               | 169.4               | 169.1               | S$^{4+}$    |            |
|                   | 170.0               | 170.5               | 170.0               | S$^{4+}$    |            |
| Ni 2p             | 857.2               | 857.7               | 857.5               | Ni$^{δ+}$ (0 < $δ$ < 2) | [58]       |
|                   | 858.9               | 859.7               | 859.3               | Ni$^{2+}$   |            |
|                   | 862.8               | 863.2               | 863.3               | Ni 2p$_{3/2}$ |            |
|                   | 875.0               | 875.5               | 875.3               | Ni$^{δ+}$ (0 < $δ$ < 2) | [58]       |
|                   | 876.8               | 877.4               | 877.3               | Ni$^{2+}$   |            |
|                   | 881.2               | 881.3               | 881.8               | Ni 2p$_{1/2}$ |            |
| P 2p              | 130.2               | 129.9               | 129.9               | Metal-P     | [59]       |
|                   | 133.7               | 133.9               | 133.7               | P-O         |            |
| O 1s              | 532.0               | 531.8               | 532.0               | Mo(IV)-O    | [60]       |

3.1.4. N$_2$ Adsorption/Desorption Isotherm Measurement

The specific surface areas of the as-synthesized pure MoS$_2$, Ni$_2$P, and three MoS$_2$/Ni$_2$P hybrids were characterized by N$_2$ adsorption/desorption isotherm measurement (Figure 4). All curves reveal a type IV isotherm with a distinct hysteresis loop, indicating the mesoporous structures of the above samples. The specific surface areas of aforementioned three hybrids are in a trend: MoS$_2$/Ni$_2$P-50 (2.42 m$^2$/g) > MoS$_2$/Ni$_2$P-58 (1.95 m$^2$/g) > MoS$_2$/Ni$_2$P-38 (1.86 m$^2$/g). The specific surface areas of these three hybrids are smaller than that of pure Ni$_2$P (4.62 m$^2$/g). For pure MoS$_2$, although its specific surface area (7.04 m$^2$/g) is larger than the other four samples, its basal surface is HER inert, so it cannot provide abundant active sites for hydrogen adsorption, which means an inferior HER property. Among the three hybrids, MoS$_2$/Ni$_2$P-50 possess the largest specific surface area, the HER performance of this hybrid will be more outstanding than the other two hybrids. However, its HER characteristic cannot be comparable to that of Ni$_2$P, because of its smaller determined specific surface area (ca. 52.4% of that of Ni$_2$P).
The obtained onset overpotentials ($\eta_{\text{onset}}$) are tabulated in Table 2. All samples were measured within the potential window of $-0.8$ to $0.2$ V. The pure MoS$_2$ shows the lower HER activity which is attributed to its inert basal surface and inferior conductivity [28]. By contrast, HER performances of the three hybrids are higher than pure MoS$_2$ because of the excellent conductivity and affordable active sites. Although the catalytic performances of three MoS$_2$/Ni$_2$P hybrids are lower than those of Ni$_2$P and commercial Pt/C, they can still raise attention in hydrogen evolution reaction. When the potential was kept at $-0.1$ V, the cathodic current density of HER for tested samples is in the following sequence: MoS$_2$ (1.56 mA/cm$^2$) < MoS$_2$/Ni$_2$P-38 (1.86 mA/cm$^2$) < MoS$_2$/Ni$_2$P-58 (2.52 mA/cm$^2$) < MoS$_2$/Ni$_2$P-50 (3.53 mA/cm$^2$) < Ni$_2$P (5.71 mA/cm$^2$) < Pt/C (8.57 mA/cm$^2$). Herein, it should be mentioned that although Ni$_2$P shows a better HER feature than the produced three hybrids, its stability will be worse in an alkaline solution [14]. Among the three hybrids, MoS$_2$/Ni$_2$P-50 shows a high cathodic current density (70 mA/cm$^2$ at $-0.48$ V), thus exhibiting the best HER performance. The HER performance of this hybrid might be due to the excellent conductivity, as well as the coexistence of nanosheet-type Ni$_2$P crystal on the bottom and nanoflower-like MoS$_2$ on the surface. Without doubt, the incorporation of Ni$_2$P brings a great enhancement in HER performance of MoS$_2$.

3.2. Electrochemical Analysis of HER

3.2.1. Linear Sweep Voltammetry (LSV)

The LSV curves of all samples in 1.0 mol/L KOH at a scan rate of 2 mV/s are depicted in Figure 5. All samples were measured within the potential window of $-0.8$ to $0.2$ V. The pure MoS$_2$ shows the lower HER activity which is attributed to its inert basal surface and inferior conductivity [28]. By contrast, HER performances of the three hybrids are higher than pure MoS$_2$ because of the excellent conductivity and affordable active sites. Although the catalytic performances of three MoS$_2$/Ni$_2$P hybrids are lower than those of Ni$_2$P and commercial Pt/C, they can still raise attention in hydrogen evolution reaction. When the potential was kept at $-0.1$ V, the cathodic current density of HER for tested samples is in the following sequence: MoS$_2$ (1.56 mA/cm$^2$) < MoS$_2$/Ni$_2$P-38 (1.86 mA/cm$^2$) < MoS$_2$/Ni$_2$P-58 (2.52 mA/cm$^2$) < MoS$_2$/Ni$_2$P-50 (3.53 mA/cm$^2$) < Ni$_2$P (5.71 mA/cm$^2$) < Pt/C (8.57 mA/cm$^2$). Herein, it should be mentioned that although Ni$_2$P shows a better HER feature than the produced three hybrids, its stability will be worse in an alkaline solution [14]. Among the three hybrids, MoS$_2$/Ni$_2$P-50 shows a high cathodic current density (70 mA/cm$^2$ at $-0.48$ V), thus exhibiting the best HER performance. The HER performance of this hybrid might be due to the excellent conductivity, as well as the coexistence of nanosheet-type Ni$_2$P crystal on the bottom and nanoflower-like MoS$_2$ on the surface. Without doubt, the incorporation of Ni$_2$P brings a great enhancement in HER performance of MoS$_2$. 

Figure 4. N$_2$ adsorption/desorption curves of the samples: (a) MoS$_2$/Ni$_2$P-38, MoS$_2$/Ni$_2$P-50, and MoS$_2$/Ni$_2$P-58; (b) MoS$_2$/Ni$_2$P-50, Ni$_2$P, and MoS$_2$.

Figure 5. LSV curves of the pure MoS$_2$, Ni$_2$P, three MoS$_2$/Ni$_2$P hybrids, and commercial 20 wt % Pt/C. Scan rate: 2 mV/s, potential window: $-0.8$ to $0.2$ V (vs. RHE).
Table 2. The obtained values of onset overpotentials (\(\eta_{\text{onset}}\)), Tafel slope (\(b\)), and charge transfer coefficient (\(\alpha\)).

| Samples                  | \(\eta_{\text{onset}}\)/(mV) | \(b\)/(mV/Decade) | \(\alpha\) |
|--------------------------|-------------------------------|-------------------|-----------|
| MoS\(_2\)                | −245                          | 128               | 0.46      |
| Ni\(_2\)P                | −48                           | 49                | 1.21      |
| 20 wt % Pt/C             | −25                           | 35                | 1.69      |
| MoS\(_2\)/Ni\(_2\)P-38  | −124                          | 102               | 0.58      |
| MoS\(_2\)/Ni\(_2\)P-50  | −86                           | 58                | 1.02      |
| MoS\(_2\)/Ni\(_2\)P-58  | −111                          | 70                | 0.84      |

3.2.2. Tafel Polarization

Equation (1) was employed to describe the relationship of overpotential (\(\eta\), V) and current density (\(j\), mA/cm\(^2\)); the charge transfer coefficient (\(\alpha\)) can be obtained by Equation (2) [62]:

\[
\eta = b \times \log j + A
\]

\[
b = \frac{2.303RT}{n_e\alpha F}
\]

where \(b\) and \(R\) are the Tafel slope (mV/decade) and gas constant (8.314 J/(K·mol)), respectively. \(A\) is an analyzed constant, \(T\) is the absolute temperature, \(n_e\) is number of electrons transferred, and \(F\) is the Faraday constant (96,485 C/mol). According to published studies [12,13], the HER in alkaline solutions is typically considered as the Volmer-Heyrovsky process or Volmer-Tafel pathways, they are depicted as follows:

Volmer reaction: \(H_2O + e \rightarrow H_{\text{ads}} + OH^-\);  
Heyrovsky reaction: \(H_{\text{ads}} + H_2O + e \rightarrow H_2 + OH^-\);  
Tafel reaction: \(H_{\text{ads}} + H_{\text{ads}} \rightarrow H_2\)

The kinetic mechanism in the HER process is determined by the rate-determining step (rds) of a multi-step reaction. The Tafel equation can play an important role in estimating the kinetic mechanism. The parameter of \(\alpha\) corresponds to the rds for multi-step reactions, this is depicted as follows: the value of \(\alpha\) is ~0.5 when the rds is Volmer reaction step, the value of \(\alpha\) is ~1.5 when the rds is Heyrovsky reaction step, and the value of \(\alpha\) will be close to 2 when the rds is step Tafel reaction [63,64]. Additionally, the Tafel slope is an important factor to describe the HER rate by examining the change of current density with overpotential. Generally, a small Tafel slope is desirable to drive a large catalytic current density at low overpotentials [65]. The Tafel plots of these samples derived from the polarization curves are shown in Figure 6. The HER performance of MoS\(_2\) is inferior due to its large Tafel slope (~128 mV/decade) and small \(\alpha\) (0.46). Within three MoS\(_2\)/Ni\(_2\)P hybrids, MoS\(_2\)/Ni\(_2\)P-50 has a minimum Tafel slope (~58 mV/decade), indicative of the excellent HER performance. It might be a substitute to noble metals in HER application.
For the three hybrids, cathodic reduction potentials of them are as follows: $-0.21 \text{ V}$ for MoS$_2$/Ni$_2$P-38, $-0.11 \text{ V}$ for MoS$_2$/Ni$_2$P-50, and $-0.15 \text{ V}$ for MoS$_2$/Ni$_2$P-58. In addition, the current density follows the same tendency. Thus, a positive potential and the large current density for MoS$_2$/Ni$_2$P-50 composite can be validated, inferring its higher HER property than those of the other two hybrids.

3.2.3. Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) measurement (in a potential window of $-0.6$~$0.8 \text{ V}$) can be helpful to reveal the reversibility of the electrochemical reaction. CV curves of MoS$_2$/Ni$_2$P-38, MoS$_2$/Ni$_2$P-50 and MoS$_2$/Ni$_2$P-58 samples are exhibited in Figure 7; the inset shows those of MoS$_2$/Ni$_2$P-50, pure MoS$_2$, pure Ni$_2$P and Pt/C. It can be seen from the determined CV curves that each of them is composed of an anodic oxidation and a cathodic reduction peak. The quasi-reversible redox peaks may be related to the processes of electrochemical hydrogen adsorption and electrochemical hydrogen desorption [28]. For the three hybrids, cathodic reduction potentials of them are as follows: $-0.21 \text{ V}$ for MoS$_2$/Ni$_2$P-38, $-0.11 \text{ V}$ for MoS$_2$/Ni$_2$P-50, and $-0.15 \text{ V}$ for MoS$_2$/Ni$_2$P-58. In addition, the current density follows the same tendency. Thus, a positive potential and the large current density for MoS$_2$/Ni$_2$P-50 composite can be validated, inferring its higher HER property than those of the other two hybrids.

Figure 6. Tafel plots of MoS$_2$, Ni$_2$P, three MoS$_2$/Ni$_2$P hybrids, and commercial 20 wt % Pt/C. Scan rate: 10 mV/s, potential window: $0.3$~$0.65 \text{ V}$.

Figure 7. CV curves of pure MoS$_2$, Ni$_2$P, three MoS$_2$/Ni$_2$P hybrids and commercial 20 wt % Pt/C. Scan rate: 10 mV/s, potential window: $-0.6$~$0.8 \text{ V}$ (vs. RHE).
3.2.4. Electrochemical Impedance Spectroscopy (EIS)

The obtained Nyquist plots for the pure MoS$_2$, Ni$_2$P and three MoS$_2$/Ni$_2$P samples are shown in Figure 8. The $R_s$ (CPE) equivalent circuit was adopted to analyze the obtained EIS data by use of Zsimpwin software. Where $R_s$ (Ω·cm$^2$) and $R_{ct}$ (kΩ·cm$^2$) are the solution resistance and charge transfer resistance. The double layer capacitance ($C_{dl}$) and the exchange current density ($j_0$) of the electrode are calculated by Equations (6) and (7) [6,66,67]:

$$C_{dl} = \left[ \frac{Q}{R_s^{-1} + R_{ct}^{-1}} \right]^{\frac{1}{n}}$$

$$j_0 = \frac{RT}{m_eR_{ct}}$$

Herein, $Q$ is the capacitance coefficient (Ω$^{-1}$·s$^n$·cm$^{-2}$) of constant phase element (CPE), and $n$ is the phase angle of constant phase element. $R$ is the gas constant (J/(K·mol)), $T$ is the absolute temperature (K), $m_e$ is the number of switched electrons (the parameter of $m_e$ is the same as that in Equation (2)) and $F$ is the Faraday constant. The calculated values of them are also reported in Table 3.

Of all the tested samples, it is no doubt that Pt/C, with the feature of the largest $C_{dl}$ and $j_0$, exhibits the best HER performance. Apart from the commercial Pt/C specimen, among other five lab-made samples, pure Ni$_2$P has the largest $C_{dl}$ and $j_0$, followed by the three hybrids and, lastly, by the pure MoS$_2$. From the above results, it seems that Ni$_2$P is an ideal HER catalyst, however, the demerit of its instability in alkaline solution will retard its application. Although $C_{dl}$ and $j_0$ of the three hybrids are smaller than Ni$_2$P, they are much larger than that of MoS$_2$. Among these catalysts, the HER performance of MoS$_2$/Ni$_2$P-50 is remarkable.

![Figure 8. EIS spectra of pure MoS$_2$, Ni$_2$P, three MoS$_2$/Ni$_2$P hybrids, and commercial 20 wt % Pt/C.](image)

**Table 3.** Parameters of solution resistance ($R_s$), charge transfer resistance ($R_{ct}$), double-layer capacitance ($C_{dl}$), the dimensionless CPE exponent ($n$), and exchange current density ($j_0$) analyzed from the EIS spectra.

| Samples          | $R_s$ (Ω·cm$^2$) | $R_{ct}$ (kΩ·cm$^2$) | $n$  | $C_{dl}$ (×10$^{-5}$ F/cm$^2$) | $j_0$ (×10$^{-5}$ A/cm$^2$) |
|------------------|------------------|----------------------|------|-----------------------------|-----------------------------|
| MoS$_2$          | 0.66             | 55.6                 | 0.844| 0.726                       | 0.02                        |
| Ni$_2$P          | 0.74             | 0.41                 | 0.793| 7.452                       | 3.11                        |
| 20 wt % Pt/C     | 2.27             | 0.056                | 0.670| 51.306                      | 22.90                       |
| MoS$_2$/Ni$_2$P-38 | 0.73             | 2.01                 | 0.816| 1.864                       | 0.64                        |
| MoS$_2$/Ni$_2$P-50 | 0.75             | 0.83                 | 0.784| 6.246                       | 1.55                        |
| MoS$_2$/Ni$_2$P-58 | 0.71             | 1.82                 | 0.837| 2.614                       | 0.71                        |
3.3. DFT Calculations

The optimized structures of the three catalysts of MoS$_2$, Ni$_2$P, and MoS$_2$/Ni$_2$P without hydrogen adsorption, as well as those with one and two adsorbed hydrogen atoms are shown in Figure 9. The adsorption energy ($\Delta E_{\text{ads}}$) and Gibbs free energy of adsorption ($\Delta G_{\text{ads}}$) for the uptake of hydrogen by the catalyst at 298 K were calculated using Equations (8) and (9) [30].

\[
\Delta E_{\text{ads}} = E(\text{catalyst} + x\text{H}) - E(\text{catalyst} + (x - 1)\text{H}) - \frac{1}{2}E(\text{H}_2)
\]

\[
\Delta G_{\text{ads}} = \Delta E_{\text{ads}} + G_{298}(\text{catalyst} + x\text{H}) - G_{298}(\text{catalyst} + (x - 1)\text{H}) - \frac{1}{2}G_{298}(\text{H}_2)
\]

where $E(\text{catalyst} + x\text{H}, x = 1$ or 2) is the COSMO-corrected total energy for the system containing the catalyst support and $x$ adsorbed hydrogen atoms, $E(\text{catalyst} + (x - 1)\text{H})$ is that of for $(x - 1)$ adsorbed hydrogen atoms-including system, and $E(\text{H}_2)$ is the energy of an isolated hydrogen molecule. $G(X)$ is the computed temperature-corrected free energy of the aforesaid species (X) at 298 K. $\Delta E_{\text{ads}}$ shows the absorption capability catalyst toward the hydrogen atom; the more negative value of $\Delta E_{\text{ads}}$ suggests the stronger interaction between them, and the geometry with the most negative $\Delta E_{\text{ads}}$ will be more stable. The negative value of $\Delta G_{\text{ads}}$ convinces the spontaneous characteristic of the adsorption interaction process.

As for pristine MoS$_2$, there are six edge sites (identified by numbers in Figure 9a) that can absorb the hydrogen atom. After one hydrogen atom capture, $\Delta E_{\text{ads}}$(MoS$_2$ + H) values are as follows: $-16.12$ kcal/mol for site 1, $-16.07$ for site 2, $-16.08$ for site 3, $-12.91$ for site 4, $-12.98$ for site 5, and $-12.97$ kcal/mol for site 6. Therefore, among these six sites, site 1 is more suitable than others for the uptake of hydrogen atom (Figure 9b). When one hydrogen atom is absorbed, the negative $\Delta G_{\text{ads}}$ of all six hydrogen-containing configurations ($-13.47$, $-13.34$, $-13.35$, $-9.55$, $-9.67$, and $-9.61$ kcal/mol for hydrogen atom at sites 1–6) indicates the spontaneous characteristic of the hydrogen uptake. After one hydrogen atom adsorption, there are only five edge sites (2–6) for trapping another hydrogen atom. Among geometries for the two hydrogen atoms, the structure with $\Delta E_{\text{ads}}$ of $-14.78$ kcal/mol for MoS$_2$ with sites 1 and 3 for the capture of hydrogen atoms (Figure 9c) is most stable; $\Delta E_{\text{ads}}$ for others are: $-13.52$ kcal/mol for sites 1 and 2, $-2.45$ kcal/mol for sites 1 and 4, $-12.37$ kcal/mol for sites 1 and 5, and $-13.19$ kcal/mol for sites 1 and 6. The values of $\Delta G_{\text{ads}}$ of these five compounds are negative, also inferring the easy uptake of the second hydrogen atom. Of course, by comparison of $\Delta E_{\text{ads}}$, the capture of the first hydrogen atom is easier than that of the second one.

For the case of hydrogen adsorption by Ni$_2$P, all four sites (labeled by numbers in Figure 9d) are employed to trap hydrogen atoms. Site 3 is desirable for the capture of the first hydrogen atom (Figure 9e), and the value $\Delta E_{\text{ads}}$ for the hydrogen-capturing compound is $-6.095$ kcal/mol; those for the other three compounds are $-1.658$ kcal/mol at site 1, $-4.889$ kcal/mol at site 2, and $-4.898$ kcal/mol at site 4. Values of $\Delta G_{\text{ads}}$ for hydrogen trapper at sites 1–4 are $-0.235$ kcal/mol, $-4.037$ kcal/mol, $-4.045$ kcal/mol and $-4.036$ kcal/mol, respectively. As for the three systems containing two hydrogens, $\Delta E_{\text{ads}}$ and $\Delta G_{\text{ads}}$ of them are $-0.31$ and $1.74$ kcal/mol for sites 1 and 1, $1.78$ and $0.33$ kcal/mol for sites 1 and 2, and $-4.19$ and $-2.23$ kcal/mol for sites 1 and 4. Therefore, the Ni$_2$P catalyst tends to use sites 3 and 4 to trap hydrogen atoms (Figure 9f).

Lastly, for the hydrogen capture by the MoS$_2$/Ni$_2$P hybrid, among the six edge sites of top MoS$_2$ layer (Figure 9g), which is dissimilar to that of the pure MoS$_2$, site 5 is more competent for trapping the first hydrogen atom (Figure 9h), in view of $\Delta E_{\text{ads}}$ and $\Delta G_{\text{ads}}$ as follows: $-4.79$ and $-3.57$ kcal/mol for site 1, 9.15 and 11.25 kcal/mol for site 2, $-4.89$ and $-4.83$ kcal/mol for site 3, $-4.99$ and $-4.64$ kcal/mol for site 4, $-6.78$ and $-8.36$ kcal/mol for site 5, and $-5.2$ and $-6.87$ kcal/mol for site 6. Additionally, for the adsorption of two hydrogen atoms, sites 5 and 3 (Figure 9i) are the most acceptable, because of the following values of $\Delta E_{\text{ads}}$ and $\Delta G_{\text{ads}}$ for the second hydrogen uptake: $-3.81$ and $-1.88$ kcal/mol for site 1, $-3.56$ and $-1.77$ kcal/mol for site 2, $-6.30$ and $-2.73$ kcal/mol for site 3, $-6.29$ and $-2.58$ kcal/mol for site 4, 7.32 and 11.90 kcal/mol for site 6. Furthermore, it should be...
mentioned that for S atoms at the sites 4 and 6, the distances between which and the second hydrogen atom are extended, and this hydrogen atom tends to close to the S atoms at sites 3 and 5.

In terms of the DFT calculations results, for the first and second hydrogen uptakes, $\Delta E_{\text{ads}}$ and $\Delta G_{\text{ads}}$ of MoS$_2$ are the most negative, followed by MoS$_2$/Ni$_2$P and Ni$_2$P. Compared with that of MoS$_2$, affinities of MoS$_2$/Ni$_2$P and Ni$_2$P to hydrogen neither too strong nor too weak, indicating its excellent HER performance [51,68]. In addition, the $\Delta G_{\text{ads}}$ of Ni$_2$P that capturing hydrogen atoms is more close to zero than those of the other two systems, it is sure that the HER property of Ni$_2$P is higher than those of MoS$_2$ and MoS$_2$/Ni$_2$P hybrids [51,69]. Thus, it can be concluded that the HER performances for these catalysts are in an order of Ni$_2$P > MoS$_2$/Ni$_2$P > MoS$_2$. This deduction is consistent with the experimental tests. Herein, the combination between MoS$_2$ and Ni$_2$P, and the role of Ni$_2$P in the enhancement of MoS$_2$ HER property will be investigated in a further study.

![Figure 9](image-url)

**Figure 9.** The optimized structures of MoS$_2$, Ni$_2$P, and MoS$_2$/Ni$_2$P three catalysts without hydrogen adsorption, as well as those with one and two adsorbed hydrogen atoms. (a) MoS$_2$; (b) MoS$_2$-1H; (c) MoS$_2$-2H; (d) Ni$_2$P; (e) Ni$_2$P-1H; (f) Ni$_2$P-2H; (g) MoS$_2$/Ni$_2$P; (h) MoS$_2$/Ni$_2$P-1H; and (i) MoS$_2$/Ni$_2$P-2H.

### 3.4. HER Stability of the MoS$_2$/Ni$_2$P Hybrids

For practical applications, in addition to the HER activity mentioned above, the stability of electrocatalysts is another important criterion to evaluate the catalytic activity. To assess the durability of pure MoS$_2$, Ni$_2$P, and the MoS$_2$/Ni$_2$P-50 hybrid, continuous CV tests for 1000 cycles with the potential in range of −1.0 to 0.4 V were conducted at a scan rate of 50 mV/s in 1.0 mol/L KOH (Figure 10). By comparison of polarization curves of these three samples before and after 1000 cycles, the cathodic current densities of them decrease somewhat after tests. Compared with electrocatalytic
behaviors of pure MoS\textsubscript{2} and Ni\textsubscript{2}P, the MoS\textsubscript{2}/Ni\textsubscript{2}P-50 hybrid just shows a slight decay, and thereby exhibits an excellent durability in the HER process.

![Figure 10. Stability tests for the pure MoS\textsubscript{2}, Ni\textsubscript{2}P, and MoS\textsubscript{2}/Ni\textsubscript{2}P-50 hybrid. Scan rate: 50 mV/s, potential window: −1.0 to 0.4 V (vs. RHE).](image)

4. Conclusions

In this work, morphologies, crystallinities, and chemical components of pure MoS\textsubscript{2}, Ni\textsubscript{2}P, and three MoS\textsubscript{2}/Ni\textsubscript{2}P hybrids obtained via a hydrothermal synthesis process were characterized. Then, HER performances of them in 1.0 mol/L KOH solution were evaluated. The main conclusions are summarized as follows:

1. The result of DFT calculation is in consistence with that of experimental test. The incorporated Ni\textsubscript{2}P observably enhances the HER property of MoS\textsubscript{2}. Among the three fabricated kinds of catalysts, the HER performance of them follows the trend: Ni\textsubscript{2}P > MoS\textsubscript{2}/Ni\textsubscript{2}P > MoS\textsubscript{2}.

2. The MoS\textsubscript{2}/Ni\textsubscript{2}P-50 shows a large cathodic current density (70 mA/cm\textsuperscript{2} at −0.48 V) and small Tafel slope (−58 mV/decade), thus exhibiting the higher HER activity than other two MoS\textsubscript{2}/Ni\textsubscript{2}P hybrids.

3. The excellent HER performance of MoS\textsubscript{2}/Ni\textsubscript{2}P-50 hybrid can be due to the desirable conductivity, the uniform morphology, large specific surface area, and favorable stability.

**Author Contributions:** F.Y. and N.K. prepared the manuscript. L.S. designed this work and gave the guidance for HER evaluation. F.Y., J.Y., N.K., and S.H. performed the experiments and the measurement of HER. J.H., X.W., and F.Y. analyzed the data and reviewed the manuscript. All authors read and approved the manuscript.

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