

Three-Dimensional Hierarchical Frameworks Based on MoS₂ Nanosheets Self-Assembled on Graphene Oxide for Efficient Electrocatalytic Hydrogen Evolution

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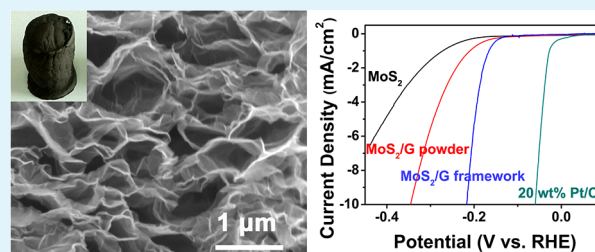
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Supporting Information

ABSTRACT: Advanced materials for electrocatalytic water splitting are central to renewable energy research. In this work, three-dimensional (3D) hierarchical frameworks based on the self-assembly of MoS₂ nanosheets on graphene oxide were produced via a simple one-step hydrothermal process. The structures of the resulting 3D frameworks were characterized by using a variety of microscopic and spectroscopic tools, including scanning and transmission electron microscopies, X-ray diffraction, X-ray photoelectron spectroscopy, and Raman scattering. Importantly, the three-dimensional MoS₂/graphene frameworks might be used directly as working electrodes which exhibited apparent and stable electrocatalytic activity in hydrogen evolution reaction (HER), as manifested by a large cathodic current density with a small overpotential of -107 mV (-121 mV when loaded on a glassy-carbon electrode) and a Tafel slope of 86.3 mV/dec (46.3 mV/dec when loaded on a glassy-carbon electrode). The remarkable performance might be ascribed to the good mechanical strength and high electrical conductivity of the 3D frameworks for fast charge transport and collection, where graphene oxide provided abundant nucleation sites for MoS₂ deposition and oxygen incorporation led to the formation of defect-rich MoS₂ nanosheets with active sites for HER.

KEYWORDS: MoS₂ nanosheet, graphene oxide, hydrothermal, three-dimensional framework, electrocatalytic, hydrogen evolution reaction



INTRODUCTION

Hydrogen has been hailed as a promising alternative and renewable energy source that may replace fossil fuels in the future. Toward this end, one effective approach to hydrogen production is based on environmentally friendly electrochemical water-splitting.^{1–3} In these studies, advanced catalysts for the hydrogen evolution reaction (HER) are generally needed to reduce overpotential and increase energy efficiency.^{4,5} To date, the most effective electrocatalysts for HER are based on Pt-group metals, which are capable of catalyzing HER at a significant rate with almost no overpotential.^{6,7} However, their scarcity and high costs have inhibited large-scale applications, and it remains a great challenge to develop highly active HER catalysts based on earth-abundant materials with a low overpotential. Since the report by Hinnemann et al.⁸ that MoS₂ nanoparticles were active HER catalysts, the interest in using MoS₂ and related metal sulfides as water-splitting

electrocatalysts has been intensified, and extensive research efforts have been devoted toward the enhancement of the catalytic activity by, for instance, loading catalysts on conductive substrates (e.g., graphene-protected 3D Ni foams and graphene nanosheets)^{9–12} and enhanced exposure of active edges.^{13–15} For instance, MoS₂ nanoparticles have been grown on reduced graphene oxide nanosheets (MoS₂/G) via a facile solvothermal procedure and the resulting composites exhibited excellent HER activity with a small overpotential of -100 mV, large cathodic currents, and a Tafel slope as small as 41 mV/dec.¹⁰

In fact, a large surface area and high electrical conductivity of the MoS₂-based HER electrocatalysts represent two important

Received: September 23, 2014

Accepted: October 27, 2014

Published: October 27, 2014

factors that are the key to the enhancement and optimization of the catalytic activity. 3D graphene frameworks with a high surface area and good electrical conductivity are good support materials for HER electrodes, which have been prepared previously by chemical vapor deposition (CVD),^{16,17} hydrothermal processes,^{18–21} and thermolysis.²² However, it remains a great challenge to prepare highly efficient and low-cost composite 3D graphene frameworks and, in particular, to use them directly as binder-free HER electrodes, in contrast to the conventional methods^{11,21} where Nafion is used as a binder to immobilize catalysts on an electrode surface. This is the primary motivation of the present study.

Within this context, herein we described the preparation of 3D hierarchical frameworks by the self-assembly of MoS₂ nanosheets on graphene oxide via a simple one-step hydrothermal process. The defect-rich MoS₂ nanosheets possessed an enlarged interlayer spacing due to oxygen incorporation from graphene oxides nanosheets. The resulting hierarchical frameworks might be used directly as binder-free working electrodes that exhibited efficient and stable electrocatalytic activity in HER, as manifested by a large cathodic current density with a small overpotential as low as -107 mV and a Tafel slope of 86.3 mV/dec.

EXPERIMENTAL SECTION

Materials. All reagents were of analytical grade and used without further purification. Ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O), thioacetamide (C₂H₅NS, TAA), graphite powders, sulfuric acid (H₂SO₄), sodium nitrate (NaNO₃), and potassium permanganate (KMnO₄) were obtained from Sinopharm Chemical Reagents Beijing Co. Water was supplied with a Barnstead Nanopure Water System (18.3 MΩ·cm).

Synthesis of Graphene Oxide. Graphene oxide was prepared by acid oxidation of graphite powders according to the modified Hummers' method.²³ Briefly, graphite (3.0 g) was added to concentrated sulfuric acid (70 mL) under magnetic stirring at room temperature, into which was added sodium nitrate (1.5 g) and the mixture was cooled to 0 °C. Under vigorous agitation, potassium permanganate (9.0 g) was added slowly while the temperature of the solution was kept below 20 °C. The reaction mixture was then incubated in a 40 °C water bath for 30 min, forming a thick paste. Then, 140 mL of Nanopure water was added, and the solution was stirred for another 15 min. An additional 500 mL of water was added, followed by a slow addition of 20 mL of H₂O₂ (30%), turning the color of the solution from brown to yellow. The mixture was filtered and washed with a 1:10 HCl aqueous solution (250 mL) to remove metal ions, followed by repeated washing with water and centrifugation to remove excessive acid. The resulting solids were dispersed in water by ultrasonication for 1 h at a concentration of 10 mg/mL.

Synthesis of 3D MoS₂ Nanosheets/Graphene Frameworks. 3D MoS₂ nanosheets/graphene hydrogels were prepared by a simple one-step hydrothermal process by adopting the procedures for the preparation of graphene hydrogels¹⁸ and MoS₂ nanosheets.¹⁷ Briefly, to prepare MoS₂ nanosheets/graphene (MoS₂/G) hydrogel at a mass ratio of 2:5, 26.5 mg of ammonium molybdate and 60 mg of thioacetamide were dissolved in 20 mL of a 3 mg/mL graphene oxide aqueous dispersion to form a homogeneous solution. The solution was transferred to a 25 mL Teflon-lined stainless steel autoclave and then heated in an electric oven at 200 °C for 24 h. The autoclave was naturally cooled to room temperature and the as-prepared 3D MoS₂ nanosheets/graphene hydrogels were removed with a pair of tweezers, washed with distilled water, and freeze-dried into an aerogel for further use. The 3D MoS₂ nanosheets/graphene frameworks at other MoS₂ loadings (mass ratio of MoS₂ and graphene at 1:4, 2:5, 11:20, 7:10, and 1:1) were synthesized in a similar manner. For comparison, MoS₂/G (2:5) nanopowders were also prepared via the same hydrothermal

process except that the concentration of the aqueous dispersion of graphene oxide was only 0.2 mg/mL such that no 3D framework was formed. In addition, pure MoS₂ nanosheets were synthesized under the same conditions but without the addition of graphene oxide.

Characterizations. Field-emission scanning electron microscopic (FESEM, Model JSM-7600F) measurements were employed to characterize the morphologies of the obtained samples. Transmission electron microscopic (TEM) measurements were carried out with a JEOL JEM 2100F microscope. Powder X-ray diffraction (XRD) patterns of the samples were recorded with a Bruker D8 Advance powder X-ray diffractometer with Cu Kα ($\lambda = 0.15406$ nm) radiation. X-ray photoelectron spectroscopic (XPS) measurements were performed using an ESCALAB 250 spectrometer. Raman spectra were recorded on a RENISHAW inVia instrument with an Ar laser source of 488 nm in a macroscopic configuration. BET surface areas were characterized by Micromeritics ASAP 2010 with nitrogen adsorption at 77 K and the Barrett–Joyner–Halenda (BJH) method.

Electrochemistry. Electrochemical measurements were performed with an electrochemical workstation (Solartron Analytical 1287 + 1260) in a 0.5 M H₂SO₄ aqueous solution. A saturated calomel electrode (Hg/HgCl₂ in saturated KCl) and a platinum wire were used as the reference and counter electrode, respectively. The MoS₂/G 3D frameworks were cut into small pieces and used as working electrodes. The current densities were evaluated in terms of the total mass of the MoS₂/G electrodes.

Comparative studies were also carried out by loading the catalysts, such as MoS₂/G 3D frameworks, MoS₂/G (2:5) powders, graphene oxide, and 20 wt % Pt/C, on a glassy carbon electrode. Experimentally, 4 mg of the respective catalyst powders was dispersed in 1 mL of 4:1 (v/v) water/ethanol mixed solvents with 40 μL of a Nafion solution under ultrasonication for 30 min. A 4 μL portion of the resulting solution was dropcast onto the glassy-carbon disk by a microliter syringe and dried at room temperature. The catalyst loadings were all 0.22 mg/cm².

The polarization curves were obtained by sweeping the potential from 0 to -0.8 V (vs SCE) at a potential sweep rate of 5 mV/s. The accelerated stability tests were performed in 0.5 M H₂SO₄ at room temperature by potential cycling between $+0.1$ and -0.5 V (vs SCE) at a sweep rate of 100 mV/s for a given number of cycles. Current–time responses were monitored by chronoamperometric measurements for up to 8 h. Hydrogen production at the electrodes was carried out at -0.4 V (vs SCE), and the rate of hydrogen gas production was quantified by gas chromatographic measurements (GC-2060F, LuNan Analytical Instruments, LTD, China). Experimentally, the gas generated from the sealed electrolytic cell was injected into the gas chromatography instrument by the continuous sample inlet system (with N₂ as the carrier gas) at a sampling interval of 1 point per 10 min. The hydrogen production rate was quantified by calibration of the integrated peak areas against the standard value of 1 mL of 99.999% H₂.

In all measurements, the SCE reference electrode was calibrated with respect to a reversible hydrogen electrode (RHE). The calibration was performed in a high purity H₂ (99.999%) saturated electrolyte with two Pt wires as the working electrode and counter electrode, respectively. Cyclic voltammograms (CVs) were acquired at the scan rate of 1 mV/s, and the average of the two potentials at which the current crossed zero was taken as the thermodynamic potential for the hydrogen electrode reactions. In 0.5 M H₂SO₄, $E(\text{SCE}) = E(\text{RHE}) + 0.164$ V (Figure S1).

RESULTS AND DISCUSSION

The MoS₂/G hierarchical framework hydrogels were prepared by simple one-step hydrothermal heating of a homogeneous aqueous dispersion containing graphene oxide, ammonium molybdate, and thioacetamide at 200 °C for 24 h (Figure 1a). As shown in Figure 1b and c, the MoS₂/G freeze-dried aerogel exhibit a well-defined and interconnected porous network. The pore diameters range from submicrometers to several micrometers, and the pore walls consist of stacked graphene oxide

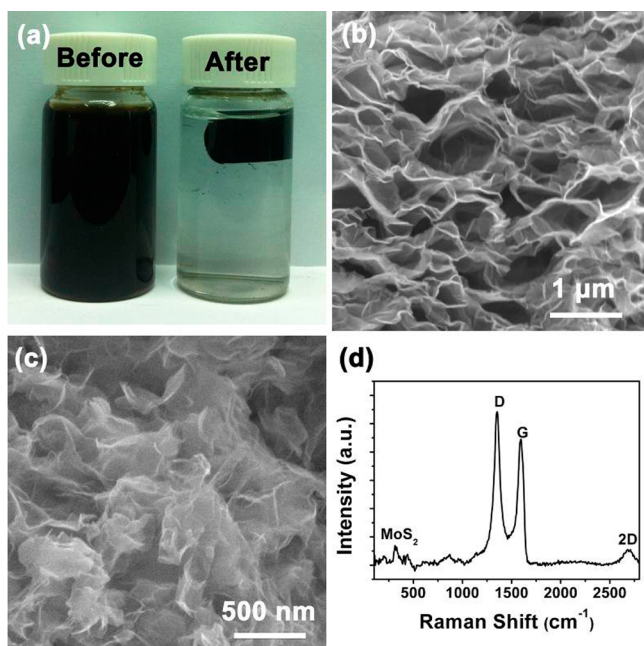


Figure 1. (a) Photographs of a homogeneous aqueous dispersion containing graphene oxide, ammonium molybdate, and thioacetamide (left) before and (right) after hydrothermal reduction at 200 °C for 24 h. (b, c) SEM images and (d) Raman spectrum of the resulting MoS₂/G (2:5) hierarchical framework.

sheets and MoS₂ nanosheets, as revealed in EDS studies where the MoS₂/G hierarchical framework was found to be composed of C, Mo, and S elements (Figure S2). Such a 3D hierarchical framework was found to possess a high specific surface area and electrical conductivity. The corresponding BET results (Figure S3) show that there are similar BET values between the MoS₂/G (2:5) hierarchical framework and pure graphene hydrogel at 149.3 and 147.5 m²/g, respectively. This is probably because the ultrathin MoS₂ nanosheets possess a high surface area and limit the restacking of graphene sheets by π - π interactions.^{24,25} Raman spectroscopic studies further confirmed the formation of a hierarchical nanocomposite framework. From Figure 1d, one can see that the D, G, and 2D vibrational bands of graphene oxide can be clearly identified at 1351, 1598, and 2698 cm⁻¹ respectively; and the vibrational band at 313.5 cm⁻¹ is characteristic of MoS₂.¹⁰

Further structural insights were obtained in TEM studies, as depicted in Figure 2. One can see that ripples and corrugations are rather well-defined, revealing the ultrathin nature of the graphene and MoS₂ nanosheets (Figure 2a and b) with MoS₂ represented by the dark-contrast objects whereas graphene oxide by the gray background; and the layered structures can be clearly seen in high-resolution TEM studies with an interlayer spacing of about 0.8 nm (Figure 2c), which is somewhat larger than 0.6 nm between the (002) crystal planes of pure MoS₂ (JCPDS No. 73-1508). This is possibly due to the incorporation of oxygen from graphene oxide nanosheets into MoS₂ that weakened the interlayer interactions and steric contributions of the three-dimensional graphene frameworks.¹⁵ Furthermore, on the surface of the MoS₂ nanosheets one can see a defect-rich structure with nanodomains of short-range ordering, with an interlayer spacing of 0.27 nm that corresponds to the (100) crystal planes of MoS₂ (Figure 2e). The exposed molybdenum edges are likely the active sites for

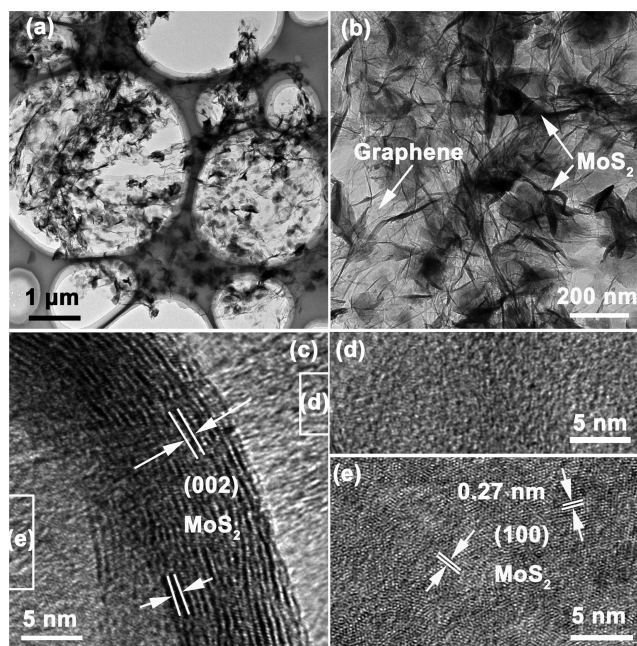


Figure 2. Representative TEM images of (a–c) the MoS₂/G (2:5) frameworks, (d) graphene nanosheets, and (e) MoS₂ nanosheets.

HER (vide infra).^{15,26,27} In contrast, no lattice phases were observed with the graphene nanosheets (Figure 2d).

X-ray photoelectron spectroscopic (XPS) measurements were then carried out to further investigate the chemical composition and valence states of the MoS₂/G nanocomposite frameworks. From the survey spectrum in panel a of Figure 3,

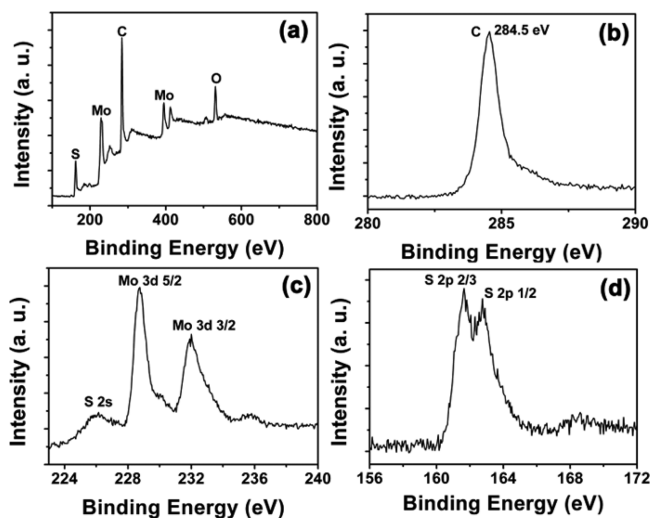


Figure 3. (a) XPS survey spectrum and high-resolution scans for (b) C 1s, (c) Mo 3d, and (d) S 2p electrons of MoS₂/G (2:5).

the elements of Mo, C, O, and S can be clearly identified. Figure 3b shows the C 1s characteristic peak at 284.5 eV which is consistent with the sp² carbon of the graphene (oxide) scaffold. Figure 3c and d depicts the high-resolution scans of the Mo 3d, S 2p, and S 2s electrons, with the characteristic peaks for Mo⁴⁺ at 228.7 and 232 eV and those for S²⁻ at 161.6, 162.7, and 226 eV, again, signifying the formation of MoS₂ in the 3D frameworks.

Note that during hydrothermal treatments, three-dimensional random stacking between flexible graphene sheets most likely occurred because of the hydrophobic and π -interactions between the graphene oxide nanosheets;¹⁸ concurrently, MoS₂ nanosheets were produced from ammonium molybdate and thioacetamide and self-assembled onto the graphene oxide surfaces. Stable MoS₂/G aerogels were obtained after the freeze-dried process, as shown in Figure 4a. The corresponding

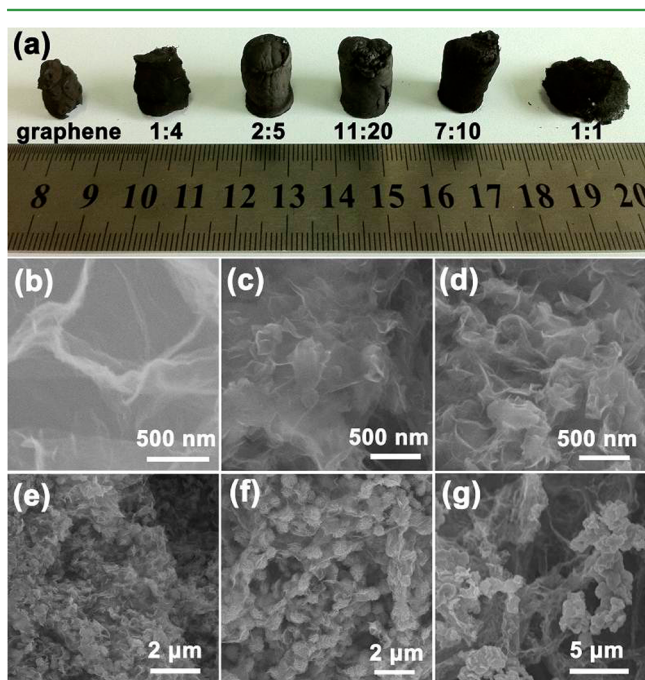


Figure 4. (a) Photographs and SEM images of MoS₂/G hierarchical frameworks at different MoS₂ loadings: (b) pure graphene frameworks, (c) 1:4, (d) 2:5, (e) 11:20, (f) 7:10, and (g) 1:1.

morphologies, structures, and composition of the 3D hierarchical frameworks at different MoS₂ loadings were examined by SEM and EDS studies (Figure 4b–g and Figure S4), where one can see that the eventual MoS₂ loadings were in good agreement with the initial feed ratios and the aerogel structures depend strongly on the mass ratio between graphene oxide and MoS₂. For instance, at the MoS₂ loadings up to 7:10, mechanically robust MoS₂/G hierarchical frameworks were obtained; and in the intermediate range of MoS₂ loadings (2:5 and 11:20), the resulting MoS₂/G 3D frameworks exhibited a more rigid structure than those at lower MoS₂ contents (pure graphene and 1:4). This is possibly due to the bonding interactions between cations and graphene oxide nanosheets. Similar results have been reported previously where Fe³⁺ ions were found to induce the self-assembly of graphene oxide.²⁸ We also observed the condensation of graphene oxide sheets and ammonium molybdate in aqueous solutions into hydrogel at room temperature after 24 h (Figure S5). In contrast, when the MoS₂ content was increased to 1:1, no cross-linking of graphene oxide occurred because of blocking by the large-sized MoS₂ nanoparticles (Figure 4g), such that MoS₂/G hydrogels could not be produced (Figure 4a). In fact, MoS₂/G (1:1) exhibits a small BET specific surface area of only 28.4 m²/g (Figure S6), much lower than that (149.3 m²/g) of MoS₂/G (2:5), as a result of the large-size MoS₂ nanoparticles and the collapse of the 3D frameworks.

XRD studies were then carried out to examine the crystalline characteristics of the MoS₂/G hierarchical frameworks at different MoS₂ loadings. As depicted in panel a of Figure 5,

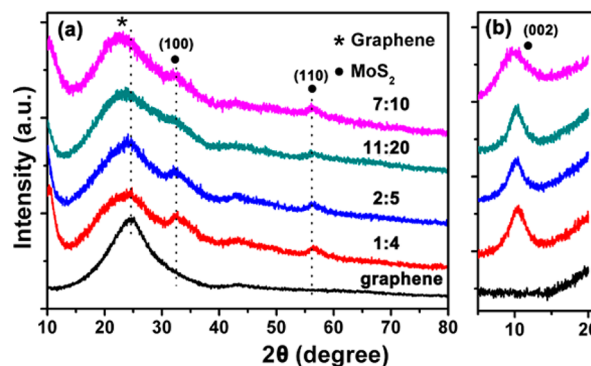


Figure 5. (a) XRD patterns of the MoS₂/G hierarchical frameworks at different MoS₂ loadings. (b) Zoom-in of the low-angle region of the XRD profiles.

for pure graphene oxide (black curve), a broad diffraction peak can be identified at 24.5°, corresponding to an interlayer spacing of 0.364 nm that is somewhat larger than that of the graphite (002) crystal planes. This indicates poor ordering of the graphene sheets along their stacking direction with only a few layers in the graphene oxide sheets. Interestingly, this peak position exhibited a clear decrease with increasing MoS₂ contents: 23.8° for 1:4 (red curve), 23.5° for 2:5 (blue curve), 22.9° for 11:20 (green curve), and 22.5° for 7:10 (magenta curve), suggesting increasing interlayer separation of the graphene (oxide) sheets likely because of the steric effect of MoS₂ nanosheets and/or effect of S-doping. Similar results have been reported where the interlayer spacings of graphene increased when the graphene was functionalized with oxygen or phosphate.^{29,30} With the loading of various amounts of MoS₂, the MoS₂/G 3D frameworks exhibited three additional diffraction peaks at ca. 10.4°, 32.7°, and 56.5°, which may be assigned to the (002), (100), and (110) crystal planes of MoS₂, respectively. Note that the (002) diffraction of MoS₂ in the MoS₂/G 3D frameworks actually occurred at a somewhat smaller angle than pure MoS₂ (JCPDS No. 73-1508), signifying an enlarged interlayer spacing. In addition, detailed analysis in panel b shows that the (002) diffraction of all MoS₂/G 3D frameworks actually shifts to a lower angle. The calculated *d* spacings (0.85–0.90 nm) of MoS₂/G at various MoS₂ loadings are clearly greater than that of pristine 2H-MoS₂ (0.61 nm), suggesting the formation of a new lamellar structure. In fact, these XRD results suggested an enlarged (002) interlayer spacing which was consistent with the TEM data presented in Figure 2, likely due to the incorporation of oxygen from graphene oxides nanosheets and weakened interlayer interactions. Similar results have been reported by Xie et al.¹⁵ where MoS₂ with an enlarged interlayer spacing of the (002) lattice planes was observed and oxygen incorporation was found to effectively regulate the electronic structures of the MoS₂ nanosheets. Moreover, two almost invariant diffractions at 32.7° and 56.5° for the MoS₂ (100) and (110) crystal planes indicates consistent atomic arrangements along the basal planes among the series of MoS₂/G nanocomposite frameworks.

The MoS₂/G hierarchical frameworks obtained above were then cut into small slices with a knife, and were used directly as electrodes without a binding agent and/or conducting additives

because of its high porosity, good conductivity, and excellent mechanical strength. Linear sweep voltammograms of the MoS₂/G electrodes are shown in Figure 6a. As can be seen,

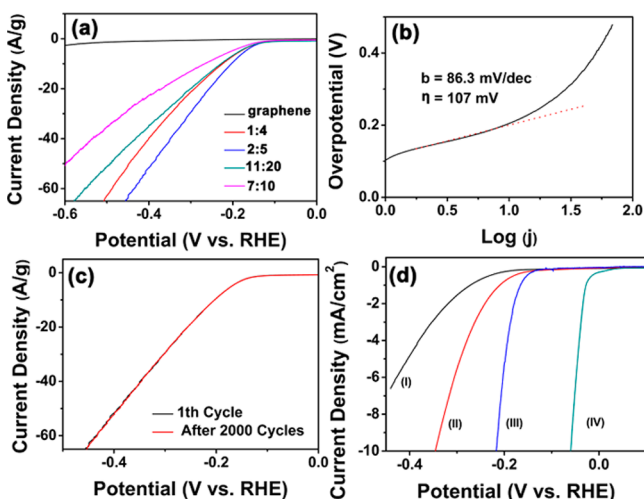
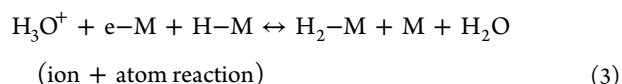
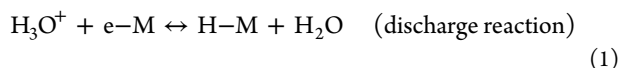


Figure 6. (a) Polarization curves of MoS₂/G 3D framework at different MoS₂ loadings. The currents were normalized to the total mass of the MoS₂/G catalysts. (b) Tafel plot for the MoS₂/G (2:5) framework electrode; (c) HER polarization curves for the MoS₂/G (2:5) framework electrode before and after 2000 cycles in the stability test. (d) Polarization curves for HER on a glassy-carbon electrode modified with (I) pure MoS₂, (II) MoS₂/G (2:5) powders, (III) MoS₂/G (2:5) frameworks, and (IV) 20 wt % Pt/C, respectively.

pure graphene oxide frameworks (black curve) showed poor catalytic activity for HER, with virtually no cathodic currents even at potentials up to -0.6 V. In contrast, the MoS₂/G framework electrodes exhibited apparent cathodic currents at potentials more negative than about -0.107 V. This small overpotential (η) of 107 mV suggests superior HER activity, which is close to leading literature results, such as MoS₂ nanoparticles/graphene (100 mV),¹⁰ MoS₂/graphene/Ni-foam (109 mV),⁹ and defect-rich MoS₂ nanosheets (120 mV).¹⁴ In addition, one can see from Figure 6a that at -0.4 V, the MoS₂/G electrode (2:5) exhibits the largest cathodic current density of 52.4 A/g, as compared to 40.4 A/g for 1:4, 34.9 A/g for 11:20, 24.0 A/g for 7:10, and 1.1 A/g for pure graphene. Moreover, the linear portion of the Tafel plots (Figure 6b) were fit to the Tafel equation ($\eta = b \log j + a$, where j is the current density and b is the Tafel slope). The Tafel slope was estimated to be 86.3 mV/dec for MoS₂/G (2:5). Note that this is close to or better than the records of MoS₂-based electrocatalysts (Table S1), such as MoS₂/graphene/Ni-foam (42.8 mV/dec),⁹ MoS₂ films with vertically aligned layers (105–120 mV/dec),¹³ and 3D MoS₂ sponges (175 mV/dec).³¹

It should be noted that in acidic media, three principal steps have been proposed for the conversion of H⁺ to H₂, commonly referred to as the Volmer, Heyrovsky, and Tafel reactions, where the corresponding Tafel slopes are 120, 40, and 30 mV/dec, respectively.^{9,13,32} The mechanism typically involves three major reactions,^{32,33}



where $e-\text{M}$ denotes metal-bound electrons and $\text{H}-\text{M}$ and H_2-M represent a hydrogen atom and molecule adsorbed on to a surface metal atom, respectively. The Tafel slope of 86.3 mV/dec observed herein suggests that both the Volmer reaction, a discharge step that converted protons into adsorbed hydrogen atoms on the catalyst surface, and the Heyrovsky reaction that involved the formation of surface-bound hydrogen molecules, played a significant role in determining the HER rate at the MoS₂/G (2:5) framework electrode.

In addition to good catalytic activity, the MoS₂/G electrodes also exhibited good stability for HER in acidic environments. Figure 6c shows that even after 2000 potential cycles, the j - V curve of the MoS₂/G (2:5) electrode remained almost invariant. The reverse scans between -0.34 and $+0.26$ V also confirmed good stability and high electrochemical area of the MoS₂/G electrode (Figure S7). This suggests strong bonding interactions between the MoS₂ nanosheets and the graphene oxide in the one-step hydrothermal procedure, which enabled fast electron transfer and collection.

Comparative studies were also carried out with other catalysts, where a calculated amount of the MoS₂/G framework nanocomposites, MoS₂/G powders, pure MoS₂, and 20 wt % Pt/C were cast onto a glassy-carbon electrode and subjected to voltammetric sweeps in 0.5 M H₂SO₄, as depicted in Figure 6d. One can see that the MoS₂/G (2:5) frameworks-modified electrode (curve III) exhibited a markedly higher cathodic current and lower overpotential than pure MoS₂ (curve I) and MoS₂/G (2:5) powders (curve II), although the overall performance was subpar as compared to that of 20 wt % Pt/C (curve IV). For instance, the overpotentials are 193.2, 154.1, 121.4, and 8.4 mV for pure MoS₂, MoS₂/G powders, MoS₂/G framework, and 20 wt % Pt/C, respectively. The corresponding Tafel slopes for pure MoS₂, MoS₂/G (2:5) powders, MoS₂/G (2:5) framework, and 20 wt % Pt/C were estimated to be 152.8, 58.1, 46.3, and 31.2 mV/dec, respectively (Figure S8). In comparison with the MoS₂/G powders, the enhanced HER performance of the MoS₂/G frameworks is likely due to the 3D framework structure, which exhibited a high electrochemical area for the diffusion of electrolyte ions. In fact, SEM studies showed a much rougher surface of the MoS₂/G frameworks-modified glassy-carbon electrode than that modified by MoS₂/G powders (Figure S9). This suggests a higher contact area of the MoS₂/G frameworks with electrolyte ions and thus a shorter ion diffusion path and faster charge transport. In additions, with a maximal loading of only 0.22 mg/cm² of the catalysts on the glassy carbon electrode surface (Figure S10), it is not ideal for practical applications. These results also highlight the significance of using the 3D MoS₂/G frameworks directly as working electrodes in enhancing the HER catalytic performance.

To further investigate the stability of the MoS₂/G hierarchical frameworks in HER, the cathodic currents of the MoS₂/G framework electrodes at the applied potential of -0.236 V were monitored for up to 1 h, as presented in Figure 7a. It can be seen that the MoS₂/G hierarchical framework (2:5) electrode exhibited the largest HER current of about 17.2 A/g among the series (in comparison, 15.1 A/g for 1:4, 11.4 A/g for 11:20, 8.3 A/g for 7:10, and 2.5 A/g for pure graphene); and the currents remained largely unchanged (similar behaviors

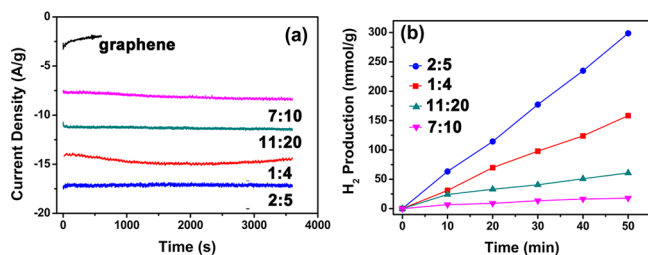


Figure 7. (a) Current–time responses of the MoS₂/G hierarchical frameworks at different MoS₂ loading at the applied potential of -0.236 V. (b) Production of hydrogen gas normalized by the weight of the MoS₂/G framework electrodes at different reaction times.

were observed even for over 8 h of continuous operation, Figure S11), suggesting excellent durability of the MoS₂/G hierarchical framework electrodes for HER. A number of bubbles were also observed on the surface of the MoS₂/G hierarchical framework electrode (Figure S12). The gas was confirmed to be hydrogen by gas chromatography measurements, and the amounts of hydrogen produced at the MoS₂/G hierarchical framework electrodes at different MoS₂ loadings are shown in Figure 7b. Linear regressions of the experimental data yield the corresponding hydrogen production rates which decrease in the order of 2:5 (358.2 mmol/g h) > 1:4 (189.5 mmol/g h) > 11:20 (72.7 mmol/g h) > 7:10 (21.5 mmol/g h). Again, this suggests that the MoS₂/G (2:5) 3D frameworks represent the best electrocatalysts for HER among the series. It is worth noting that stable MoS₂/G hydrogel (1:1) could not be produced and cut into small pieces as working electrodes. Thus, no HER data were obtained.

The high HER activity as well as good stability of the MoS₂/G hierarchical frameworks can be attributed to at least three factors. (i) Large conjugated structures of the graphene (oxide) 3D frameworks with continuously interconnected pores and a high surface-to-volume ratio provide abundant nucleation sites to form strong bindings with MoS₂ nanosheets, leading to fast interdomain electron transport. (ii) Good conductivity of the 3D graphene frameworks allows for effective charge collection and transfer, as revealed in electrochemical impedance spectroscopy (EIS) studies (Figure S13). More detailed analyses were carried out by fitting the impedance data to an equivalent circuit consisting of a series of a resistor and a capacitor. The internal resistances of the MoS₂/G hierarchical framework electrodes were found to be all very small within the narrow range of 1.78–2.46 Ω . The charge transfer resistance (R_{ct}) for the MoS₂/G hierarchical frameworks (2:5) was also very small at 2.52 Ω , close to that of pure graphene framework (1.85 Ω). At increasing loading of MoS₂, the R_{ct} values increased somewhat to, for example, 14.3 Ω for 11:20 and 18.7 Ω for 7:10. Additionally, in the low frequency region, a vertical straight line was evident suggesting that the 3D graphene frameworks (MoS₂ loading up to 11:20) exhibited facile ion diffusion. This confirms that the incorporation of the 3D graphene frameworks greatly enhanced charge transport, resulting in significant improvement of the HER performances. (iii) MoS₂ nanosheets that were grown on the surface of graphene oxide exhibited a high defect density due to the incorporation of oxygen from graphene oxide nanosheets that produced increasing molybdenum-edge catalyst sites. Because of the synergistic structural and electronic interactions, the MoS₂/G hierarchical frameworks displayed both rich active

sites and high electrical conductivity, leading to enhanced HER activity.

CONCLUSIONS

Mechanically robust and electrically conductive MoS₂/G 3D hierarchical frameworks were prepared by a one-step hydrothermal process with an aqueous dispersion of graphene oxide, ammonium molybdate, and thioacetamide. The formation of nanocomposite frameworks was confirmed in SEM, TEM, XRD, XPS, and Raman measurements. The defect-rich MoS₂ nanosheets possessed an enlarged interlayer spacing due to the incorporation of oxygen from graphene oxides nanosheets that led to weakened interlayer interactions. Interestingly, blocks of the MoS₂/G hierarchical frameworks might be used directly as working electrodes and exhibited apparent and stable HER electrocatalytic activity. The best performance was observed with the frameworks at a MoS₂/G ratio of 2:5 that featured an overpotential of only -107 mV (in comparison to -121 mV when loaded on a GC electrode), a Tafel slope of 86.3 mV/dec (46.3 mV/dec when loaded on a GC electrode), and almost no change of the cathodic currents in HER for up to 8 h of continuous operation. This study highlights the significance of the formation of three-dimensional hierarchical frameworks based on the self-assembly of MoS₂ nanosheets on graphene oxide in the enhancement of HER electrocatalytic activity.

ASSOCIATED CONTENT

Supporting Information

EDS results, nitrogen adsorption/desorption isotherms, cyclic voltammograms, Tafel plots, SEM images, current–time plots, Nyquist plots, XRD data, and comparison of HER activity. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Recruitment Program of Global Experts, the PhD Start-up Funds of the Natural Science Foundation of Guangdong Province (S2013040016465), Zhujiang New Stars of Science & Technology (2014J2200061), and the Fundamental Research Funds for Central Universities (x2hjD2131690).

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**Three-Dimensional Hierarchical Frameworks Based on MoS₂ nanosheets
Self-Assembled on Graphene Oxide for Efficient Electrocatalytic Hydrogen Evolution**

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Table S1. Comparison of the HER activity between the MoS₂/G hierarchical frameworks and literature data

Types	Samples	η (V)	Tafel slope (mV/dec)	Current Density	Ref.
3D blocks used directly as working electrodes	① MoS ₂ /G hierarchical framework	0.107 (0.121 when the catalysts were loaded on a GC electrode)	86.3 (46.3 when the catalysts were loaded on a GC electrode)	51.6 A/g ($\eta = 0.4$ V)	this study
	② MoS ₂ /Graphene/Ni-foam	0.109	42.8	44 mA/cm ² ($\eta = 0.2$ V)	<i>Adv. Mater.</i> 2013, 25, 756
	③ MoS ₂ Films with Vertically Aligned Layers	~0.21	105–120	8 mA/cm ² ($\eta = 0.4$ V)	<i>Nano Lett.</i> 2013, 13, 1341
	④ 3D MoS ₂ Sponges	unknown	185	72 mA/cm ³ ($\eta = 0.2$ V)	<i>Small</i> 2014, 10, 895
Electrocatalyst powders loaded on a glassy carbon electrode	⑤ MoS ₂ nanoparticles/graphene	0.10	41	48 mA/cm ² ($\eta = 0.2$ V)	<i>JACS</i> , 2011, 133, 7296.
	⑥ Defect-Rich MoS ₂ Nanosheets	0.12	50	13 mA/cm ² ($\eta = 0.2$ V)	<i>Adv. Mater.</i> 2013, 25, 5807
	⑦ Amorphous MoS ₂ /Nanoporous Metal	125 (onset)	41	5.7 mA/cm ² ($\eta = 0.2$ V)	<i>Adv. Mater.</i> 2014, 26, 3100
	⑧ MoS ₂ Formed on mesoporous Graphene	0.1	42	30–40 mA/cm ² ($\eta = 0.2$ V)	<i>Adv. Funct. Mater.</i> 2013, 23, 5326.
	⑨ MoS ₂ /nitrogen-doped graphene nanosheet aerogels	0.236	230	10 mA/cm ² ($\eta = 0.261$ V)	<i>J. Mater. Chem. A</i> , 2014, 2, 13795

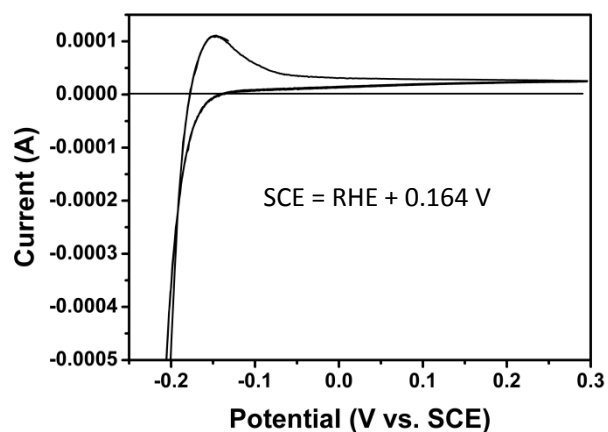


Figure S1. Calibration of the SCE electrode against a reversible hydrogen electrode (RHE).

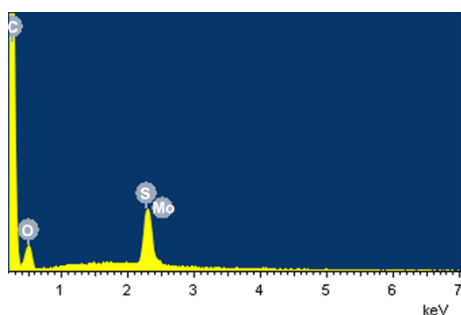


Figure S2. EDS results of the MoS₂/G (2:5) frameworks. It is noted that the peaks of Mo and S are overlapped.

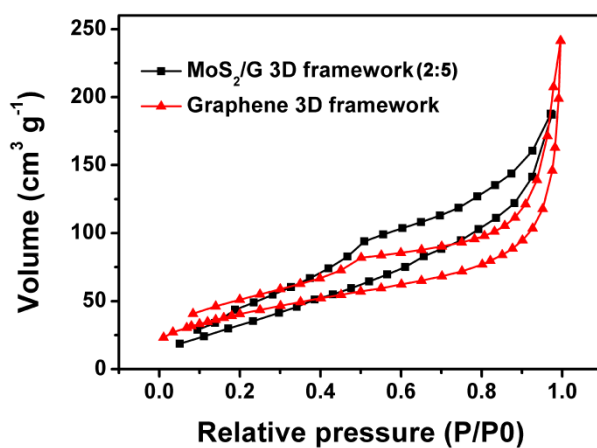


Figure S3. Nitrogen adsorption/desorption isotherms of 3D frameworks of MoS₂/G (2:5) and graphene hydrogel.

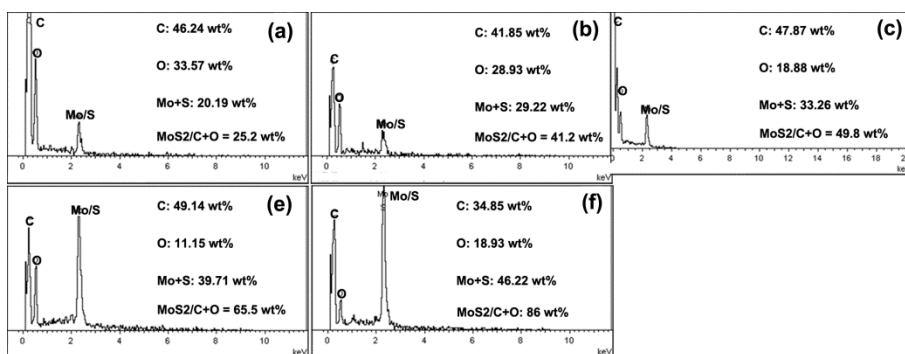


Figure S4. EDS results of the MoS₂/G 3D frameworks at different MoS₂ loading: (a) 1:4, (b) 2:5, (c) 11:20, (d) 7:10, (e) 1:1. One can see that there was almost no difference between the initial feed ratios and measured values at lower MoS₂ loadings (1:4, 2:5 and 11:20). At high MoS₂ loadings, the measured value was somewhat less than the initial feed ratio (7:10 vs 6.5:10, 1:1 vs 0.86:1), suggesting a limited loading of MoS₂ on the graphene frameworks. In fact, in the last two samples, powders were also observed at the bottom of the hydrothermal reactors.



Figure S5. (left) Formation of graphene hydrogel 24 hours after the addition of ammonium molybdate at room temperature. (right) Pure graphene oxide sheets in solution without ammonium molybdate.

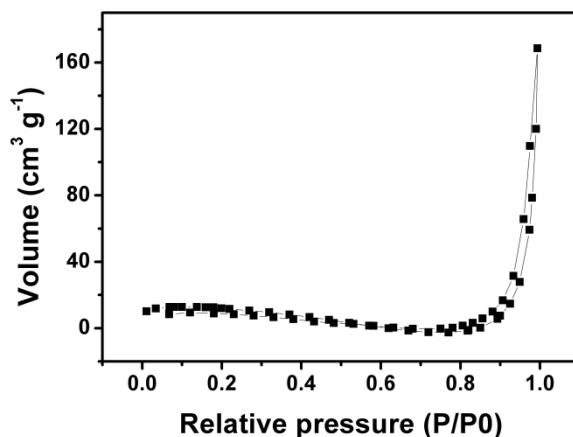


Figure S6. The nitrogen adsorption/desorption isotherms of MoS₂/G (1:1).

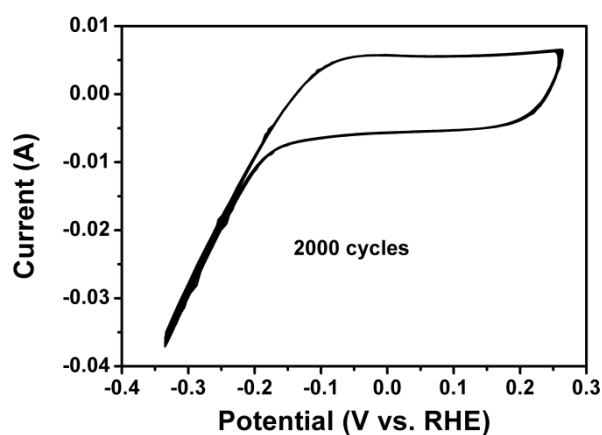


Figure S7. Cyclic voltammograms of the MoS₂/G framework (2:5) electrode within the potential range of -0.34 V and +0.26 V (vs. RHE) at a constant scan rate of 100 mV/s for 2000 cycles. The large current envelope between -0.15 V and +0.25 V is due to the double-layer charging of the framework electrode, suggesting a high electrochemical area.

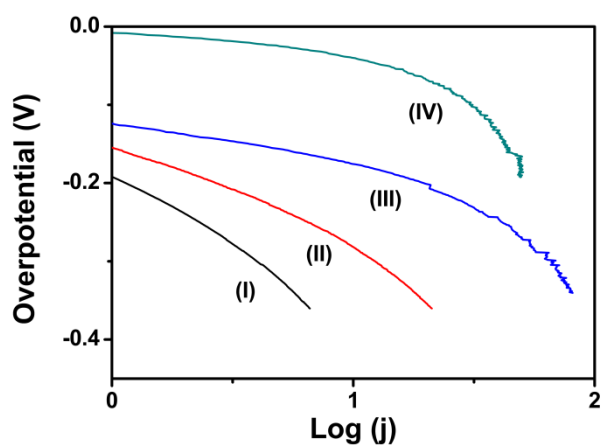


Figure S8. Tafel plot of glassy-carbon electrodes modified with (I) pure MoS₂, (II) MoS₂/G powder (2:5), (III) MoS₂/G framework (2:5), and (IV) 20 wt% Pt/C, respectively

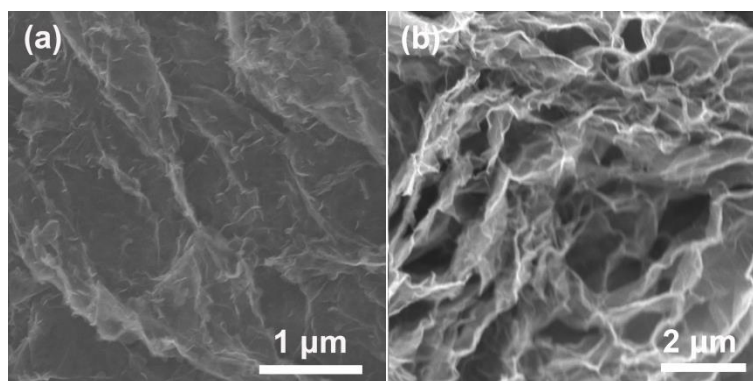


Figure S9. SEM images of (a) MoS₂/G powders and (b) MoS₂/G(2:5) 3D frameworks loaded on the surface of a glassy-carbon electrodes.

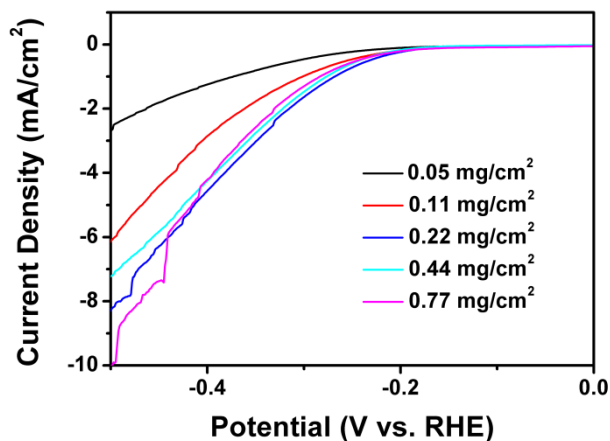


Figure S10. Loading capacity of MoS₂/G powders on the surface of a glassy-carbon electrodes. The HER current densities increased with increasing catalyst loading and reached a plateau at the loading of 0.22 mg/cm².

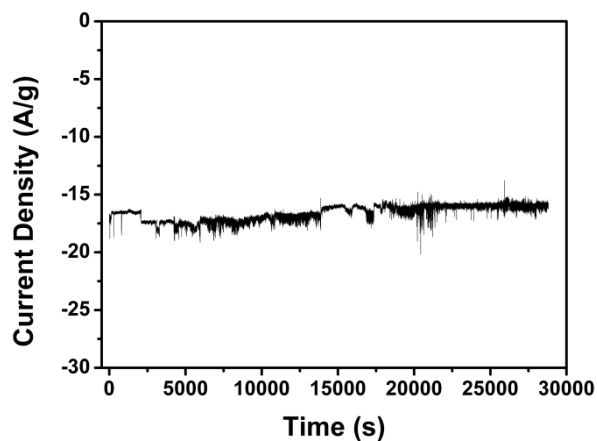


Figure S11. Current-time plot of the MoS₂/G framework electrode (2:5) at the applied potential of -0.236 V (vs. RHE) for 8 h.

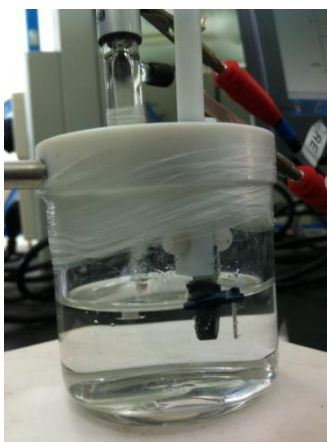


Figure S12. Bubble formation on the MoS₂/G framework electrode (2:5) at the applied potential of -0.236 V (vs. RHE).

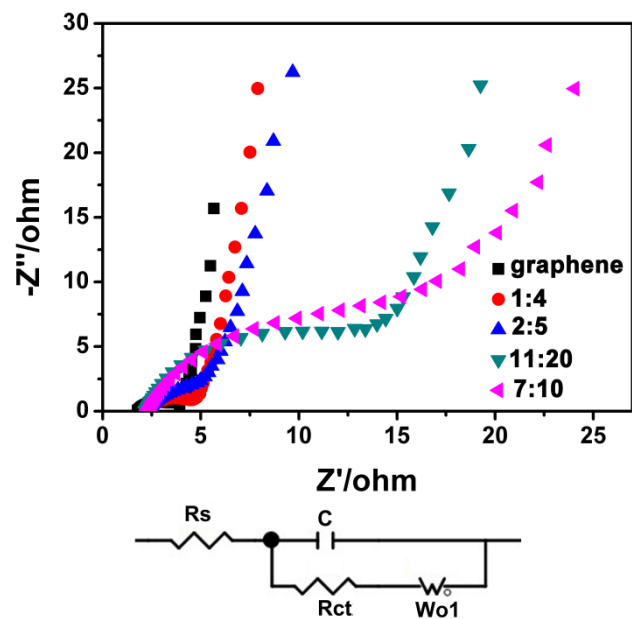


Figure S13. Nyquist plots and the equivalent circuit model of MoS₂/G framework electrodes with the different MoS₂ loading. Capacitance C1 and resistance R2 corresponds to MoS₂ nanosheets; Capacitance C2 and charge-transfer resistance R3 are attributed to 3D graphene framework; R1 represents the internal resistance of the electrochemical workstation. Wo1 is associated with the Warburg impedance.