Three-Dimensional Heterostructures of MoS$_2$ Nanosheets on Conducting MoO$_2$ as an Efficient Electrocatalyst To Enhance Hydrogen Evolution Reaction

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**ABSTRACT:** Molybdenum disulfide (MoS$_2$) is a promising catalyst for hydrogen evolution reaction (HER) because of its unique nature to supply active sites in the reaction. However, the low density of active sites and their poor electrical conductivity have limited the performance of MoS$_2$ in HER. In this work, we synthesized MoS$_2$ nanosheets on three-dimensional (3D) conductive MoO$_2$ via a two-step chemical vapor deposition (CVD) reaction. The 3D MoO$_2$ structure can create structural disorders in MoS$_2$ nanosheets (referred to as 3D MoS$_2$/MoO$_2$), which are responsible for providing the superior HER activity by exposing tremendous active sites of terminal disulfur of S$_2^−$ (in MoS$_2$) as well as the backbone conductive oxide layer (of MoO$_2$) to facilitate an interfacial charge transport for the proton reduction. In addition, the MoS$_2$ nanosheets could protect the inner MoO$_2$ core from the acidic electrolyte in the HER. The high activity of the as-synthesized 3D MoS$_2$/MoO$_2$ hybrid material in HER is attributed to the small onset overpotential of 142 mV, a largest cathodic current density of 85 mA cm$^{-2}$, a low Tafel slope of 35.6 mV dec$^{-1}$, and robust electrochemical durability.

**KEYWORDS:** CVD growth, 3D heterostructures, MoS$_2$ nanosheets, 3D MoO$_2$ conductive core, electrocatalyst, hydrogen evolution reaction

**1. INTRODUCTION**

Due to the massive demand of energy, hydrogen fuel has been proposed as a main future energy resource.$^1$–$^3$ Beyond the conventional hydrogen production, a lot of effort has been made recently to develop electrocatalytic and photocatalytic techniques to produce efficient hydrogen through the hydrogen evolution reaction (HER).$^4$–$^7$ However, the existence of high operating overpotential for HER limits the practical applications of these techniques; therefore, developing high-performance catalysts to drive HER with minimum external energy is highly desirable. Platinum (Pt) is well-known for its superior electrocatalytic property; nevertheless, large-scale application of Pt-based technology is hindered by high cost and low availability. Hence, intensive research has recently been directed to search for earth abundant, low-cost potential substitutes for the Pt catalyst. Among the newly discovered catalysts, two-dimensional layered transition metal dichalcogenides (TMDs) have emerged as promising electrocatalysts for HER.$^8$–$^{12}$

In TMDs, molybdenum disulfide (MoS$_2$) has shown to be an excellent HER catalyst.$^8$ The computational and experimental results confirmed that the active catalytic sites of layered MoS$_2$ crystals are located at the sulfur edge, while basal planes are catalytically inert.$^{13,14}$ Notwithstanding, due to high surface energy and strong interlayer $π−π$ interaction, the inherent layer stacking and agglomeration in MoS$_2$ decrease the number of active sites.$^{15}$ In addition, the very poor electrical conductivity between two stacked S$−$Mo$−$S interlayers are about 2 orders of magnitude lower than that of intralayers.$^{16,17}$ Therefore,
seeking advanced structural designs to engineer the morphological MoS2 of more active sites for higher conductivity to enhance the electrocatalytic efficiency of MoS2 in HER is highly demanded.

To overcome the conductivity barrier, MoS2 has been grown on various conductive carbon-based substrates in recent years, such as graphene nanosheets,18 N-doped graphene,19 carbon nanotube,20,21 carbon fiber,22 carbon cloth,23 three-dimensional (3D) hierarchical graphene oxide,24 and graphene protected 3D Ni foam.25,26 However, the direct deposition of MoS2 on nonactive HER substrates would block the active sites of MoS2, thus significantly decreasing the HER activity. Alternatively, enormous effort has been taken to create efficient active sites by using different nanostructures of MoS2, such as mesopores,27 chemically exfoliated 1T metallic nanosheets,28,29 amorphous nanosheets,30–34 nitrogen-doped nanosheets,35–37 defect-rich nanosheets,38,39 monolayer 3D porous gold,40 nanosheets on porous MoO2,41 nitrogen-doped nanosheets on MoO2 nanobelts,42 and nanoparticles on TCNQ.43 Among these, the recently developed phase-transfer synthesis of the 3D assembled structures acted as an excellent catalyst for HER. The 3D MoO2/MoS2 structure possesses a high specific active site by creating structural disorders in MoS2 nanosheets, which are responsible for exposing tremendous active sites of terminal S2− to facilitate the HER.

2. EXPERIMENTAL SECTION

2.1. Synthesis of 3D MoS2/MoO2 Catalysts. The 3D MoS2/MoO2 heterostructures were synthesized in a low-pressure chemical vapor deposition (LPCVD) reaction. The distorted MoS2 nanosheets on metallic 3D MoO2 were produced by low-temperature sulfurization in a two-step CVD process as illustrated in Figure 1. The commercially available carbon cloth (CeTech, W0S1002) was used as a template to grow metallic 3D MoO2 cores. Before the synthesis, MoO2 powder (Sigma-Aldrich, 99.995% 10 mg) as a chemical precursor was placed in a quartz boat close to the central heating zone of a furnace, where a carbon cloth substrate of 2 × 2 cm2 was placed on top of the quartz boat containing the MoO2 powder. Before starting the growth, highly pure Ar gas was purged into the furnace for 30 min to make the reaction chamber oxygen-free. The furnace was then heated to 650 °C at a heating rate of 25 °C/min. During the growth, the chamber pressure was maintained at 5 Torr with an Ar flow rate of 100 sccm. To form distorted MoS2 nanosheets, the pregrown 3D MoO2 core supported by carbon cloth were sulfided by hydrogen sulfide (H2S) gas at 100 Torr in another furnace with various reaction temperatures (200–1000 °C) under a ramp rate of 25 °C/min in a mixture of H2S (4 sccm)/Ar(1000 sccm) for 60 min.

2.2. Structural Characterizations. Powder X-ray diffraction (XRD) patterns of the as-synthesized samples were recorded by a Bruker D8 X-ray diffractometer with Cu Kα (λ = 1.5406 Å) radiation in the 2θ range of 10–80°. Raman spectroscopy was used to identify the compositions of the samples with a confocal Raman microscope (NT-MDT, NTegra SPECTRA) and a liquid-nitrogen cooled charge-coupled device (CCD) camera. A laser at 488 nm with the spot size of ~1 μm, adjusted by a 100X objective lens, was used as an excitation source. To avoid sample damage and to gain better spectral resolution, the laser was adjusted to a medium power of 30 mW with the laser exposure time of 10 s. The Raman scattering signal of a silicon substrate at 520 cm−1 was used as a reference for calibration. The surface morphologies of the samples were examined by scanning electron microscopy (FEI, Nova 200) equipped with an energy dispersive X-ray (EDX) spectrometer. The microstructural analysis was carried out using high-resolution transmission electron microscope (HRTEM, Tecnai F30) equipped with X-ray energy dispersive spectroscopy (EDS).

2.3. Electrochemical Measurements. Electrochemical studies were carried out in a 3-electrode cell using an AUTOLAB potentiostat (PGSTAT, 302N), where the as-prepared 3D MoS2/MoO2 samples coated on a carbon cloth substrate served as the working electrode (WE), an Ag/AgCl (3.0 mol/kg KCl) was used as the reference electrode (RE), and a graphite rod worked as the counter electrode (CE). All of the electrochemical measurements were performed in 0.5 M H2SO4 electrolyte. Linear sweep voltammetry was employed to obtain polarization plots with a fixed scan rate of 5 mV/s. The obtained polarization data were calibrated with respect to the
reversible hydrogen electrode (RHE) by \( E_{\text{RHE}} = E_{\text{SCE}} + 0.28 \text{ V} \) and were reported with an \( iR \) compensation by \( V_{\text{corr}} = V - jR_i \), where \( V_{\text{corr}} \) is the corrected potential for \( iR \) drop, \( j \) is polarization current, and \( R_i \) is the series resistance. The electrochemical impedance spectra (EIS) were recorded in the frequency range of 102–105 Hz and at the applied amplitude of AC potential of 10 mV. The obtained experimental EIS data were fitted and deconvoluted to an equivalent circuit (2R-CPE circuit model using NOVA 1.9). The Nyquist and Bode plots were recorded from the fitted EIS results.

3. RESULTS AND DISCUSSION

The distorted Mo\(_2\) nanosheets on metallic 3D MoO\(_2\) were produced by low-temperature sulfurization in a two-step CVD process. Figure 1 illustrates the growth process and SEM images of the prepared 3D MoS\(_2\)/MoO\(_2\) hybrid structure, which involved two major steps. (A) Deposition of MoO\(_2\) cores on a carbon cloth substrate under an oxygen-free atmosphere to avoid the oxidation of MoO\(_2\). (B) Formation of distorted MoS\(_2\) nanosheets via the stepwise sulfurization of the predeposited 3D MoO\(_2\) by H\(_2\)S under an inert Ar atmosphere. For tests, different samples were prepared at various sulfurization temperatures. The SEM images to display the carbon cloth, MoO\(_2\) cores on carbon cloth, and 3D MoS\(_2\)/MoO\(_2\) hybrid structures are shown in Figure 1. Briefly, the formation mechanism of the layered MoS\(_2\)/MoO\(_2\) structures is based on a controlled reduction and sulfurization process. In this method, underlying MoO\(_2\) cores were first synthesized on the 3D carbon cloth by the thermal reduction of MoO\(_3\) powder in an inert Ar atmosphere at 650 °C. The surface sulfurization of crystalline MoO\(_2\) cores by H\(_2\)S produces the top MoS\(_2\) nanosheets at various temperatures, where the efficiency of sulfurization depends on the diffusion rate of H\(_2\)S gas. Therefore, the structures and sizes of the underlying MoO\(_2\) cores and MoS\(_2\) nanosheets can be controlled via the layer-by-layer sulfurization by adjusting the sulfurization conditions.

Figure 2A shows the XRD patterns of the as-prepared samples of MoO\(_2\), 3D MoS\(_2\)/MoO\(_2\), and MoS\(_2\). From the XRD patterns, it is clear that the sulfurization temperature has an important effect on the crystallinity of a catalyst. For the unsulfurized 3D MoO\(_2\) sample, Figure 2A(a) shows the pure crystalline MoO\(_2\) (JCPDS:32-0671, monoclinic) with the characteristic diffraction peaks at 40° (120), 43° (112), 58° (031), and 73° (131). As the sulfurization temperature was raised to 300 °C [Figure 2A(b)], in addition to MoO\(_2\) several medium-weak peaks appeared at 14.3°, 33.1°, and 60.4°, corresponding to MoS\(_2\) (003), (101), and (113), respectively (JCPDS: 65-3656, hexagonal). These results suggest that the 3D MoS\(_2\)/MoO\(_2\) hybrid structure could be formed at 300 °C. Figure 2A(c) further shows that pure MoS\(_2\) was obtained at 1000 °C, where only the diffraction peaks at 14.3° (003), 33.1° (101), and 60.4° (113) were observed, indicating the disappearance of the MoO\(_2\) core. These results demonstrate that the transition of 3D MoS\(_2\)/MoO\(_2\) to crystalline MoS\(_2\) can be adjusted by the sulfurization temperature.

The as-prepared samples were also characterized by Raman spectroscopy as shown in Figure 2B. Thermal deposition of MoO\(_3\) on the carbon cloth substrate leads to the formation of metallic MoO\(_2\) cores through the thermal reduction of MoO\(_3\). In Figure 2B(a), Raman signals of the unsulfurized 3D metallic MoO\(_2\) core comprise those of the reported rutile MoO\(_2\) crystal,\(^{42}\) where the peaks at 203–495 cm\(^{-1}\) are assigned to the stretching modes of the doubly coordinated oxygen (\(\text{Mo}–\text{O}–\text{Mo}\)) and the signals at 571, 589, and 741 cm\(^{-1}\) are due to the stretching modes of terminal oxygen (\(\text{M}–\text{O}\)). This Raman identification of the unsulfurized MoO\(_2\) sample suggests the presence of tetrahedral co-ordination on the Mo\(^{2+}\) (i.e., metallic 3D MoO\(_3\)) center, which is subjected to sulfurization by H\(_2\)S at various temperatures from 200 to 1000 °C. When the sulfurization temperature was increased to 300 °C [Figure 2B(b)], accompanying with the original signals of MoO\(_2\), new emerging peaks at ~384 and 405 cm\(^{-1}\), corresponding to the \(\text{E}_{1g}\) (the in-plane vibration of the S atoms) and \(\text{A}_{1g}\) (the out-of-plane vibration of the S atoms) modes of MoS\(_2\), respectively.\(^{43}\) This outcome confirms that the partial sulfurization of 3D MoO\(_2\) core occurred at 300 °C, leading to the formation of the 3D MoS\(_2\)/MoO\(_2\) hybrid structure. At higher sulfurization temperature of 1000 °C [Figure 2B(c)], all peaks of the MoO\(_2\) core disappeared, transforming to the complete formation of MoS\(_2\) on the carbon cloth substrate. The detailed spectral analyses of the observed Raman bands are listed in Table S1.

The surface morphologies of MoO\(_2\), 3D MoS\(_2\)/MoO\(_2\), and MoS\(_2\) on carbon cloth were further investigated by scanning electron microscopy (SEM). Figure 3A shows the high- and low-magnification SEM images of 3D MoO\(_2\) cores, indicating that the entire surface of the carbon cloth was uniformly covered with MoO\(_2\) cores of ~100 nm in thickness. After the sulfurization temperature was increased to 300 °C, it can be seen from Figure 3B that the MoO\(_2\) surfaces were decorated with MoS\(_2\) nanosheets of ~22 nm in thickness and ~50 nm in length. This result provides a strong evidence of forming distorted MoS\(_2\) nanosheets on the 3D MoO\(_2\) core. As revealed from Figure 3C, the distorted MoS\(_2\) nanosheets were converted into continuous MoS\(_2\) layers by raising the sulfurization temperature to 1000 °C and the MoO\(_2\) cores also turned completely into MoS\(_2\) layers. In Figure 3D, the SEM image and EDX elemental mappings of the as-prepared 3D MoS\(_2\)/MoO\(_2\) hybrid structure obtained at 300 °C reveal uniform distributions of the Mo, O, and S elements. In comparison, while the EDX mapping of the unsulfurized MoO\(_2\) in Figure S1 contains the elements of Mo and O, the MoS\(_2\) sample was obtained only at 1000 °C as shown in Figure S2. The results from EDX elemental mapping are consistent with those
The layer spacings can be determined to be ∼0.347 nm for MoO2 (011), which are in good agreement with 0.620 nm for MoS2 and MoO2 crystals.37 To provide a further insight into the structural and morphological features of the obtained 3D MoO2 core, transmission electron microscopic characterization of the 3D MoS2/MoO2 heterostructures was performed. Figure 3E displays an HRTEM image taken in the middle of this 3D MoS2/MoO2 heterostructure. Several sheet-like MoS2 layers of ∼20 nm in length and several nanometers in width were observed to be closely packed on the top of MoO2 layers. The HRTEM image of a selected MoS2 region (Figure 3E) reveals the individual atomic planes ordered in the S\(2_\text{p}^\text{3/2}\) sequence for the layer of MoS2 and MoO2 crystals.37 To provide a further insight into the structural and morphological features of the obtained 3D MoO2 core, transmission electron microscopic (TEM) characterizations were performed. Figure S3A and S3B show the low-magnification TEM images for the detached catalysts grown on carbon cloth. In the S\(2_\text{p}^\text{3/2}\) region, the doublet A, corresponding to the apical S\(2_\text{p}^\text{3/2}\) at the lower-energy side (162.1–163.3 eV), partially overlap the doublet B, attributed to the bridging S\(2_\text{p}^\text{3/2}\) at the higher-energy side (163.7–164.9 eV). In the Mo 3d\((2_\text{d}^5/2\)−3/2\) region, the doublet C is due to the Mo\(^{6+}\) in MoO3 (229.8–233.04 eV), doublet D is Mo\(^{10+}\) in MoS2 (231.9–234.6 eV), doublet E is Mo\(^{4+}\) in MoO5 (235.4–238.7 eV), and doublet F is Mo\(^{4+}\) in MoS2 (229.6–232.8 eV).

It is well-known that the apical divalent sulfide ions (S\(2^-\)) in MoS2 act as active sites in HERi,44 moreover, recent studies reported that the presence of terminal S\(2^-\) in addition to S\(2^-\), boosts the HER activity. In XPS spectra, the S\(2_\text{p}^\text{3/2}\) and 2p\(1/2\) signals of terminal S\(2^-\) (denoted by doublet B) at 163.7–164.9 eV are located at higher binding energies than those of apical S\(2^-\) (represented as doublet A) at 162.1–163.3 eV.14,45 In Figure 4, the MoO2 core to facilitate the formation of apical S\(2^-\) ions is confirmed by the presence of doublet A in XPS spectra, where the signals were deconvoluted. The analysis from Figure 4 shows that 3D MoS2/MoO2 has both terminal S\(2^-\) (doublet B) and apical S\(2^-\) (doublet A). It is interesting to observe that the signals of S\(2^-\) (doublet B) almost disappeared in MoS2 because of the high crystalline phase of MoS2. Also in Figure 4, the unsulfated MoO2 sample does not possess S\(2^-\) and S\(2^-\). The ratios of apical S\(2^-\) to terminal S\(2^-\) for MoO2, 3D MoS2/MoO2, and MoS2 are summarized in Table S2. These XPS results suggest that the presence of terminal S\(2^-\) could be the main cause to enhance the HER activity in 3D MoS2/MoO2.

In the XPS analysis, the Mo 3d orbital splits into 3d\(3/2\) (higher energy) and 3d\(1/2\) (lower energy) due to the spin–orbit splitting. In MoO2, the doublets are at 229.8 eV for Mo\(^{4+}\) 3d\(3/2\) and at 233.04 eV for Mo\(^{4+}\) 3d\(1/2\). After the complete reduction of MoO2, the characteristic doublets at 235.4–238.7 eV for MoO2 were not observed; however, due to the slight surface oxidation of the metastable MoO2 in air, doublets for the Mo\(^{6+}\) (235.4–238.7 eV) of MoO3 were detected.47,48 In the 3d regions of the Mo ions, the main 3d\(3/2\) and 3d\(1/2\) peaks were further analyzed with several doublets of Mo\(^{4+}\) (peak C, at 229.8–233.04 eV) for MoO2, Mo\(^{10+}\) (peak D, at 231.9–234.6 eV) for MoO3, Mo\(^{4+}\) (peak E, at 229.6–232.8 eV) for MoS2, and Mo\(^{4+}\) (peak F, at 229.4–232.8 eV) for MoO3. Each doublet was deconvoluted with a fixed peak.
separation of 3.2 eV, intensity ratio (3d5/2:3d3/2) of 3:2, and the same full width at half-maximum (FWHM).

The XPS results for the unsulfurized MoO2 sample (Figure 4) clearly show that peak intensities for the reduced states of Mo4+ 3d3/2 and 3d5/2 from MoO2 (peak C) and of Mo10+ 3d3/2 and 3d5/2 from MoO5 (peak D) are much higher than those of Mo6+ 3d3/2 and 3d5/2 of MoO3 (peak E), suggesting a complete reduction of MoO3 to MoO2. Similarly, Figure 4 also presents the 3d Mo regions for 3D MoS2/MoO2 and MoS2. In both spectra, the new S 2s peak at 226.7 eV (peak F) belongs to MoS2, indicating the formation of MoS2. For 3D MoS2/MoO2 sample, fractional percentages of the oxidation states of +4 (MoO2), +10 (MoO5), +4 (MoS2), and +6 (MoO3) were measured to be 8.04%, 61.89%, 18.3%, and 8.31%, respectively, which confirmed the formation of the MoS2/MoO2 core. In the formation of MoS2, while the fractional percentages of +4 (MoO2), +10 (MoO5), and +6 (MoO3) reduced to 0%, 0%, and 16.09%, respectively, the intensity of +4 (MoS2) increased to 68.73%. In Table S3, the ratios of Mo4+ (MoO2)/Mo10+ (MoO5) and of Mo4+ (MoO2)/Mo6+ (MoO3) were estimated for all samples. Additionally, the results obtained from the XPS analysis are summarized in Figure S4 and are also correlated with the results collected from the EDX spectral analysis in Figure S5. The results obtained from XPS, consistent well with those of EDX, clearly show that the formation of MoS2 on the 3D MoO2 core through sulfurization was carried out at 300 °C, of which the as-prepared samples possess high percentage of active sites of apical S2− and terminal S2−. Additionally, the structure and composition of the 3D MoS2/MoO2 prepared at 300 °C were investigated by SEM, EDX, and XPS. The observed SEM (Figure S6A) shows that the part of the sample peeled off from the original substrate due to the high sulfurization rate and reveals that almost all of the underlying MoO2 was converted to MoS2. The XPS analyses (Figure S6, F−G) on both Mo 3d and S 2p regions indicate that this sample contains +10 (MoO5), +4 (MoS2), and apical S2−, which are consistent with the EDX examination (Figures S6, B−D).

The electrocatalytic HER activities for the samples prepared above were conducted in a 3-electrode cell containing 0.5 M H2SO4. Figure 5A shows the polarization curve of the HER between −0.4 and 0.0 V vs RHE (iR corrected) at the scan rate of 5 mV/s for MoO2, 3D MoS2/MoO2, and MoS2, which were deposited on the carbon cloth with the same loading of ∼0.30 mg/cm2. While the unsulfurized MoO2 and the completely sulfurized MoS2 exhibited poor catalytic activity for HER (with small cathodic currents at η = 300 mV), the as-prepared 3D MoS2/MoO2 (at 300 °C) hybrid electrode could provide an extremely large cathodic current density of 85 mA cm−2 at η = 300 mV. As shown in Figure S7, compared with MoO2 and MoS2, 3D MoS2/MoO2 holds a much lower onset potential of 142 mV. This small onset potential and higher cathodic current density yield a superior HER activity, which can be attributed to the distorted structures of MoS2 nanosheets assembled on the metallic 3D MoO2 core. It is widely accepted that the HER active sites are located on the edge planes; therefore, the HER activity can be greatly enhance by tailoring the MoS2 microstructures to obtain highly exposed edge planes.49,50 In the present case, the distorted MoS2 nanosheets assembled on the 3D MoO2 core possess much more exposed edge planes than pure MoS2, hence significantly improving the HER activity. However, the sulfurization temperature plays an important role in determining the intrinsic structures and sizes of the MoO2 core. As shown in Figure 5A, as the sulfurization temperature increases, the HER activity of MoO2 samples increases first (from 200 to 300 °C), reaches a
The exchange current density for 3D MoS2/MoO2 was determined by extrapolating the Tafel plot as shown in Figure 5B. The Tafel slope was estimated to be 86.4 mV/dec, which is the Tafel slope. The Tafel slope was estimated to be 86.4 mV/dec, and MoS2 was determined to be 9.0 × 10^−7 mA cm^−2, which is remarkably higher than those of MoO2 (1.69 × 10^−7 mA cm^−2) and MoS2 (5.4 × 10^−7 mA cm^−2).

The Tafel slope, the inherent property of an electrocatalyst, can be determined by the rate-limiting step of HER. In Figure 5B, the Tafel slope was calculated from the linear portion of the Tafel plots by fitting the experimental data to the Tafel equation of \( \eta = b \log j + a \), where \( j \) is the current density and \( b \) is the Tafel slope. The Tafel slope was estimated to be 86.4 mV/dec, and 101.8 mV/dec for MoO2, 3D MoS2/MoO2 (at 300 °C), and MoS2, respectively. It should be noted that in an acidic medium, three principal steps have been proposed for the conversion of H^+ to H_2, commonly referred to as the Volmer, Heyrovsky, and Tafel reactions with the corresponding Tafel slopes of 120, 40, and 30 mV/dec, respectively. The Tafel slope of 35.6 mV/dec for MoS2/MoO2 suggests that the HER mechanism proceeds through the Heyrovsky-Tafel reaction. The exchange current density (\( j_0 \)) is another important HER parameter, which is the intrinsic property of a catalyst to split a water molecule into hydrogen atoms without any external potential. The exchange current densities for MoO2, 3D MoS2/MoO2, and MoS2 were determined by extrapolating the Tafel plot as shown in Figure S8. The exchange current density for 3D MoS2/MoO2 was determined to be 9.0 × 10^−4 mA cm^−2, which is remarkably higher than those of MoO2 (1.69 × 10^−7 mA cm^−2) and MoS2 (5.4 × 10^−7 mA cm^−2). This role of MoO2 stems from the conductive underlying MoO2, which partially hinders the HER process. From our experiments, this decrease of HER activity can be eliminated by refreshing electrolyte and thoroughly releasing the H2 bubbles on the electrode. As shown in the inset of Figure 5D, the current density decreased slightly even after 1000 cycles, clearly indicating the superior stability. To further probe the stability of 3D MoS2/MoO2 in acidic environment, a continuous HER process was performed at −0.2 V (vs HER). The time-dependent current response for the 3D MoS2/MoO2 was measured as presented in the inset of Figure 5D. From the \( i-t \) curve, it can be seen that a negligible loss in current density was measured after the continuous operation for 3000 s. As tabulated in Table S4, the remarkable performance metrics of 3D MoS2/MoO2 in HER are compared with other previously reported MoS2-based electrocatalysts. Additionally, the data before and after the \( iR \) correction are also provided for comparison in Figure S10.

4. CONCLUSION

In this study, we have developed distorted MoS2 nanosheets on a 3D MoO2 metallic core by a two-step CVD process. Such a novel hybrid structure acts as an active catalyst effectively in HER and exhibits an excellent long-term stability with a small overpotential of ~0.1 V, large cathodic current density (85 mA cm^−2 at \( \eta = 300 \text{ mV} \)), and small Tafel slope of 35.6 mV/dec. The metallic 3D MoO2 core, formed by the partial reduction of MoO3, serves as a highly conductive layer, which facilitates the fast charge transport and collection; meanwhile, the distorted MoS2 nanosheets play the role of an HER catalyst with tremendous amount of exposed active sites and also protect the inner MoO2 core from an acidic electrolyte. The excellent electrocatalytic performance of 3D MoS2/MoO2 potentially enables this hybrid structure to replace the high-cost Pt catalyst.
Research Article

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Notes
The authors declare no competing financial interest.

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REFERENCES

(33) Xie, J.; Zhang, J.; Li, S.; Grote, F.; Zhang, X.; Zhang, H.; Wang, R.; Lei, Y.; Pan, B.; Xie, Y. Controllable Disorder Engineering in...


Supporting Information

Three-Dimensional Heterostructures of MoS\textsubscript{2} Nanosheets on Conducting MoO\textsubscript{2} as an Efficient Electrocatalyst to Enhance Hydrogen Evolution Reaction

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**Figure S1.** EDX elemental mapping images of Mo, S, and O in the unsulfidized MoO$_2$.
Figure S2. EDX elemental mapping images of Mo, S, and O in the MoS$_2$ nanosheets prepared at 1000 °C.
Figure S3. (A–B) TEM images of the detached MoO\textsubscript{2} core from a carbon cloth substrate by sonication show the spiral-like morphology of MoO\textsubscript{2} nanosheets.
**Figure S4.** Fractional percentage compositions of different specimens calculated from the XPS spectral data of (A) Mo 3d$_{5/2-3/2}$ and (B) S 2p$_{3/2-1/2}$ for MoO$_2$, 3D MoS$_2$/MoO$_2$, and MoS$_2$. 
Figure S5. Elemental analyses of the (A) MoO$_2$, (B) 3D MoS$_2$/MoO$_2$, and (c) MoS$_2$ samples by EDX spectroscopy indicate the presence of Mo, O, and S.
Figure S6. Structural and compositional analyses for the 3D MoS$_2$/MoO$_2$ sample prepared at 500 °C. (A) SEM image of the 3D MoS$_2$/MoO$_2$. (B–D) Selected-area elemental mappings by EDX for (B) S, (C) Mo, and (D) O. (E) Selected-area EDX spectrum of Mo, O, and S. (F) High-resolution XPS spectrum of Mo 3d$_{5/2}$–3d$_{3/2}$. (G) High-resolution XPS spectrum of S 2p$_{3/2}$–1/2.
Figure S7. Calculation of the onset potential ($\eta$). The Tafel plot of the 3D MoS$_2$/MoO$_2$ recorded in the region of low current densities. The onset potential for HER was determined from the semi-log plot. The semi-log plot of 3D MoS$_2$/MoO$_2$ in the region of low current densities is shown in Figure S8. The linear relationship is below -0.142 V, but starts to deviate above -0.166 V. Therefore, -0.142 V was chosen as the onset potential for 3D MoS$_2$/MoO$_2$. The same method was applied to determine the onset potentials for other samples.
Figure S8. Calculation of the exchange current density ($j_0$). Tafel plots were used for calculating the exchange current density ($j_0$) of the 3D MoS$_2$/MoO$_2$ with an extrapolation method. A linear fit of the Tafel plots to zero overpotential gives the value of $j_0$. Based on the above calculation, log ($j$) at zero overpotential for 3D MoS$_2$/MoO$_2$ is -3.07 and $j_0$ was calculated to be $9.0 \times 10^{-4}$ mA cm$^{-2}$. The same methods were applied to determine the exchange current densities of other samples.
Figure S9. The samples were prepared at the same sulfurization temperature (300 °C) but with different sulfurization times of 30 min, 1 hr, and 2 hr, respectively. (A) Polarization curves, (B) Tafel plots, and (C) Raman spectra of the as-obtained samples prepared at various sulfurization times.
Figure S10. (A) The polarization curves with and without the $iR$ correction. (B) The Tafel slopes with and without the $iR$ correction.
Table S1. The observed Raman scattering bands in MoO$_2$, 3D MoS$_2$/MoO$_2$, and MoS$_2$

<table>
<thead>
<tr>
<th>Peak number</th>
<th>Raman shift (cm$^{-2}$)</th>
<th>Mode &amp; assignment</th>
<th>Parent material</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>203</td>
<td>stretching of the Mo-O-Mo bridge</td>
<td>MoO$_2$</td>
</tr>
<tr>
<td>2</td>
<td>228</td>
<td>stretching of the Mo-O-Mo bridge</td>
<td>MoO$_2$</td>
</tr>
<tr>
<td>3</td>
<td>286</td>
<td>$E_{1g}$-mode of S atoms in the basal plane</td>
<td>MoS$_2$</td>
</tr>
<tr>
<td>4</td>
<td>345</td>
<td>antisymmetric stretching of the Mo-O-Mo bridge</td>
<td>MoO$_2$</td>
</tr>
<tr>
<td>5</td>
<td>363</td>
<td>stretching of the Mo-O-Mo bridge</td>
<td>MoO$_2$</td>
</tr>
<tr>
<td>6</td>
<td>384</td>
<td>$E_{2g}$-mode of Mo + S atoms in the basal plane</td>
<td>MoS$_2$</td>
</tr>
<tr>
<td>7</td>
<td>405</td>
<td>$A_{1g}$-mode of S atoms along the c axis</td>
<td>MoS$_2$</td>
</tr>
<tr>
<td>8</td>
<td>461</td>
<td>$B_{2g}$-antisymmetric stretching of the Mo-O-Mo bridge</td>
<td>MoO$_2$</td>
</tr>
<tr>
<td>9</td>
<td>495</td>
<td>$B_{3g}$-antisymmetric stretching of the Mo-O-Mo bridge</td>
<td>MoO$_2$</td>
</tr>
<tr>
<td>10</td>
<td>571</td>
<td>oxygen stretching in O-Mo-O terminal</td>
<td>MoO$_2$</td>
</tr>
<tr>
<td>11</td>
<td>589</td>
<td>$B_{1g}$-mode oxygen stretching in O-Mo-O terminal</td>
<td>MoO$_2$</td>
</tr>
<tr>
<td>12</td>
<td>741</td>
<td>$A_{g}$-mode oxygen stretching in O-Mo-O terminal</td>
<td>MoO$_2$</td>
</tr>
</tbody>
</table>
Table S2. Analyses from the XPS spectra in the S 2p region of MoO₂, 3D MoS₂/MoO₂, and MoS₂

<table>
<thead>
<tr>
<th>Region</th>
<th>MoO₂</th>
<th>3D MoS₂/MoO₂</th>
<th>MoS₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Position (eV)</td>
<td>FWHM (eV)</td>
<td>Fraction (%)</td>
</tr>
<tr>
<td>Apical S²⁻ 2p₃/₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Apical S²⁻ 2p₁/₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Terminal S₂⁻ 2p₃/₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Terminal S₂⁻ 2p₁/₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Polysulphide S-O</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

# Fractional % of S²⁻ is calculated from % S²⁻ = (the peak area under ( S²⁻ 2p₃/₂ + S²⁻ 2p₁/₂ )/the sensitivity factor of S²⁻ ) × 100. The same method was applied to calculate the fractional % of S₂⁻ and S-O.
Table S3. Analyses from the XPS spectra in the Mo 3d region of MoO$_2$, 3D MoS$_2$/MoO$_2$, and MoS$_2$

<table>
<thead>
<tr>
<th>Region</th>
<th>MoO$_2$</th>
<th>3D MoS$_2$/MoO$_2$</th>
<th>MoS$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Position (eV)</td>
<td>FWHM (eV)</td>
<td>Fraction# (%)</td>
</tr>
<tr>
<td>Mo$^{+4}$ 3d$_{5/2}$ (MoO$_2$)</td>
<td>229.8</td>
<td>0.85</td>
<td>13.62</td>
</tr>
<tr>
<td>Mo$^{+4}$ 3d$_{3/2}$ (MoO$_2$)</td>
<td>233.0</td>
<td>0.85</td>
<td>8.41</td>
</tr>
<tr>
<td>Mo$^{+10}$ 3d$_{5/2}$ (MoO$_5$)</td>
<td>231.9</td>
<td>3.52</td>
<td>42.86</td>
</tr>
<tr>
<td>Mo$^{+10}$ 3d$_{3/2}$ (MoO$_5$)</td>
<td>234.6</td>
<td>3.52</td>
<td>11.19</td>
</tr>
<tr>
<td>Mo$^{+6}$ 3d$_{5/2}$ (MoO$_3$)</td>
<td>235.4</td>
<td>3.04</td>
<td>19.25</td>
</tr>
<tr>
<td>Mo$^{+6}$ 3d$_{3/2}$ (MoO$_3$)</td>
<td>238.7</td>
<td>3.04</td>
<td>4.64</td>
</tr>
<tr>
<td>Mo$^{+4}$ 3d$_{5/2}$ (MoS$_2$)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mo$^{+4}$ 3d$_{3/2}$ (MoS$_2$)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2s (MoS$_2$)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

#Fractional % of Mo$^{+6}$ is calculated as % Mo$^{+6}$ = (the peak area under (Mo$^{+6}$ 3d$_{5/2}$ + Mo$^{+6}$ 3d$_{3/2}$)/the sensitivity factor of Mo$^{+6}$) × 100. The same method was applied to calculate the fractional % of other element.
Table S4. Comparison of HER performances of 3D MoS$_2$/MoO$_2$ and other MoS$_2$ catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loading mass (mg/cm$^2$)</th>
<th>$\eta$ (mV)</th>
<th>Current density (mA/cm$^2$) at ($\eta = 0.2 \ V$)</th>
<th>Tafel slope (mA/dec)</th>
<th>Exchange current density (mA/cm$^2$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D MoS$_2$/MoO$_2$ on carbon cloth *</td>
<td>0.30</td>
<td>-142</td>
<td>-85</td>
<td>35.6</td>
<td>$9.0 \times 10^{-4}$</td>
<td>This work</td>
</tr>
<tr>
<td>MoS$_2$ nanoparticulate on Au (111)</td>
<td>-</td>
<td>-150</td>
<td>-0.67</td>
<td>55–60</td>
<td>$1.3 \times 10^{-4}$</td>
<td>Science, 2007, 317, 100</td>
</tr>
<tr>
<td>MoO$_3$-MoS$_2$ on FTO *</td>
<td>-</td>
<td>-150</td>
<td>-10</td>
<td>50–60</td>
<td>$8.2 \times 10^{-4}$</td>
<td>Nano Lett. 2011, 11, 4168</td>
</tr>
<tr>
<td>1T MoS$_2$ on graphite *</td>
<td>-</td>
<td>-187</td>
<td>-10</td>
<td>43</td>
<td>-</td>
<td>JACS, 2013, 135, 10274.</td>
</tr>
<tr>
<td>Monolayer MoS$_2$ on 3D nanoporous gold</td>
<td>-</td>
<td>-118</td>
<td>-1.5</td>
<td>46</td>
<td>$6.9 \times 10^{-4}$</td>
<td>Adv. Mater., 2014, 26, 8023</td>
</tr>
<tr>
<td>double-gyroid MoS$_2$ on FTO *</td>
<td>0.06</td>
<td>-150-200</td>
<td>-2</td>
<td>50</td>
<td>$6.9 \times 10^{-4}$</td>
<td>Nat. Mater., 2012, 11, 963</td>
</tr>
<tr>
<td>MoS$_2$ nanoparticulate on graphene *</td>
<td>0.28</td>
<td>0.10</td>
<td>-48</td>
<td>41</td>
<td>-</td>
<td>JACS, 2011, 133, 7296.</td>
</tr>
<tr>
<td>MoS$_2$ on graphene/Ni foam</td>
<td>11.7</td>
<td>-</td>
<td>-44</td>
<td>42.8</td>
<td>-</td>
<td>Adv. Mater. 2013, 25, 756</td>
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<tr>
<td>MoS$_2$ on Ti *</td>
<td>0.12</td>
<td>250</td>
<td>-30</td>
<td>51</td>
<td>$3.87 \times 10^{-4}$</td>
<td>Adv. Mater. 2014, 26, 2683</td>
</tr>
<tr>
<td>MoS$_2$ on TCNQ on carbon cloth</td>
<td>3.41</td>
<td>-209</td>
<td>40</td>
<td></td>
<td></td>
<td>Appl Mater Int., 2014, 85, 17679</td>
</tr>
<tr>
<td>MoO$_2$ on N-doped MoS$_2$</td>
<td>0.285</td>
<td>-156</td>
<td>47.5</td>
<td>-</td>
<td></td>
<td>J. Mater. Chem. A, 2014, 2, 11358</td>
</tr>
</tbody>
</table>

Note: The data calculated after the $iR$ correction are marked by *.