Bi-axial grown amorphous MoS$_x$ bridged with oxygen on r-GO as a superior stable and efficient nonprecious catalyst for hydrogen evolution

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Amorphous molybdenum sulfide (MoS$_x$) is covalently anchored to reduced graphene oxide (r-GO) via a simple one-pot reaction, thereby inducing the reduction of GO and simultaneous doping of heteroatoms on the GO. The oxygen atoms form a bridge between MoS$_x$ and GO and play a crucial role in the fine dispersion of the MoS$_x$ particles, control of planar MoS$_x$ growth, and increase of exposed active sulfur sites. This bridging leads to highly efficient (−157 mV overpotential and 41 mV/decade Tafel slope) and stable (95% versus initial activity after 1000 cycles) electrocatalyst for hydrogen evolution.

Hydrogen is becoming increasingly essential as an environmentally friendly energy carrier. Global warming and abnormal climate resulting from the anthropogenic use of petroleum and environmental pollution accelerated its importance. Hence, hydrogen should be produced renewably, using clean technologies rather than by the steam reforming of natural gas. Among the potential technologies, sustainable hydrogen production using an electrochemically driven water dissociation process has been intensively explored. Efficient catalysts for the electrochemical hydrogen evolution reaction (HER) are needed to reduce the overpotential and increase the efficiency of hydrogen production. Platinum (Pt) shows the best electrocatalytic activity for the HER in acidic media; however, Pt is too expensive to be used beyond a few specialized applications. Hence, replacing Pt with low-cost and earth abundant materials for electrocatalysts is a critical challenge. In-depth research seeking highly efficient and stable HER catalysts has become necessary, though various materials such as metal dichalcogenides, polymer-based carbon nitride, transition metal carbides, and nickel alloys have been proposed as promising catalysts.

Recently, a family of two-dimensional transition metal disulfides (TMDs) with MS$_2$ structure, where M is a transition metal such as molybdenum (Mo) or tungsten (W) and S is sulfur, has attracted much attention. These materials are a promising class of HER catalyst because they are one of the most efficient materials among the nonprecious catalysts. It is well known that the efficient electrochemical activity of the TMD stems from the S-terminated edge or strained metallic phase of MS$_2$ while the basal plane of semiconducting MS$_2$ is catalytically inert. Jaramillo et al. reported that only one in four atoms of MoS$_2$ edge sites could evolve H$_2$ molecules because of the atomic hydrogen coverage of only 25% on the edge in contrast to Pt (111) as calculated by Density Functional Theory. Hence, it is necessary either to synthesize nano-sized particles or to tune the electronic

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structure of the edges to improve the activity. However, unsupported nanoscale MoS2 with a large number of edge sites is thermodynamically unstable, leading to aggregation or transformation of the nanoparticles10. In addition, S-terminated edges are easily oxidized in acidic media11. These intrinsic properties induce the deactivation and instability of the materials when used for HER. There are two strategies to overcome these challenges: (1) controlling the morphology and (2) designing hybrid structure. Specific morphology control has been achieved using hard or soft templates such as MoO3/MoS2 (core/shell) nanowire, highly ordered double-gyroid MoS2, vertically aligned MoS2, and MoS2 flowers12–15. Although these methods could prevent the degradation of MoS2 electrochemical activity, the synthetic processes are unsuitable for the industrial scale because of their complexity and expense. Meanwhile, the hybrid structure consists of carbon supported MoS2, which has exhibited a strong interaction between the TMD and the carbon support, minimizing the thermodynamically unstable properties and improving the morphological and electrochemical stability. However, much remains to be studied regarding the origins of the interaction and the properties of the carbon supported amorphous molybdenum sulfide. Herein, we report a one-pot synthetic strategy to produce the highly-stable and efficient MoSx/r-GO catalyst via oxygen bridging between amorphous MoSx and r-GO. These features are induced by the functional coupling of oxygen bridges between molybdenum sulfide and graphene oxide as shown in Fig. 1a.

Results
The molybdenum sulfide catalysts were easily synthesized by the wet-chemical reaction of (NH4)2MoS4 and HCl in an aqueous dispersion of graphene oxide (GO) at room-temperature. The precursor was reduced to molybdenum sulfide (MoSx, sulfur content (x) changed from 1 to 3) on the graphene supports. To investigate the effects of the amount of deposited MoSx particles on electrochemical hydrogen production, we synthesized the MoSx/r-GO catalysts with the amount of MoSx precursor varying from 0.1 to 0.7 g. (Hereafter, a catalyst prepared using y g of MoSx precursor and a fixed amount of GO is denoted as y MoSx/r-GO sample.) For comparison, unsupported MoS3 particles were also prepared in the absence of GO using the same process.

High-resolution transmission electron microscopy (HR-TEM) images show that both the size and the amount of MoSx particles on thin graphene flake depend strongly on the weight of precursor used as shown in Fig. 1b–e. For 0.5 MoSx/r-GO, the particles are uniformly deposited on the GO surface with full coverage, whereas catalysts synthesized with either less or more than 0.5 MoSx/r-GO exhibited insufficient or aggregated particle features, respectively. However, the particle size of MoSx/r-GO is relatively smaller than for unsupported MoS3 (see Supplementary Figure S1). Elemental mapping was conducted using energy dispersive spectroscopy (EDS) to confirm the origin of the particles deposited on the r-GO sheets. For all MoSx/r-GO composite samples, the positions of Mo atoms are highly correlated with the positions of S atoms, and MoSx particles are considered to have been successfully synthesized on the r-GO sheets (see Supplementary Figure S2).

We further investigated the morphological features of as-synthesized MoSx/r-GO composites using atomic force microscopy (AFM) as shown in Fig. 2. Each GO sheet has a thickness of ~1.1 nm consistent with double- or triple-layered GO. Similar to the TEM results for the MoSx/r-GO composites, the width and height of MoSx on the r-GO composites depend on the amount of MoSx precursor. The average width of the MoSx particles on r-GO were increased from 50.2 nm to 58.8, 66.8, and 87.6 nm for 0.1, 0.3, 0.5, and 0.7 MoSx/r-GO, respectively. Average
thickness also gradually increased from 2.9 nm to 4.3, 5.6, and 7.7 nm for 0.1, 0.3, 0.5, and 0.7 MoSx/r-GO respectively. The unsupported MoS3 particles synthesized using the same method show a larger average particle width of 117.8 nm and height of 22.3 nm (see Supplementary Figure S3). Interestingly, all the MoSx/r-GO composites show a very high aspect ratio—above 10, in contrast to the unsupported MoS3. This result indicates that MoSx particles were biaxially grown on the r-GO surface in a planar or coin shape. Thus, we believed that interaction between the precursor and the GO might affect the growth and morphology of the particles, which are closely related to the catalytically active edge sites.

Figure 2. AFM images of as-synthesized MoSx/r-GO composites by added amount of (NH4)2MoS4 precursor. (a) 0.1, (b) 0.3, (c) 0.5, and (d) 0.7 g, and corresponding height spectra along with dashed rectangles in AFM images indicating that MoSx on r-GO has a planar shape with a high aspect ratio.
The structural composition and interaction between the MoSx and r-GO were investigated using X-ray photoelectron spectroscopy (XPS) as shown in Fig. 3. The XPS spectra of all composite samples exhibited predominant C1s, Mo3d, and S2p peaks. The peak intensities of oxygen functional groups on the GO, such as epoxy, carbonyl, and carboxyl groups, which are observed at binding energies (BE) of 286.7, 288.4, and 289.5 eV, respectively, gradually decreased with increasing precursor concentrations (Fig. 3a). Thus, it is believed that the insulating GO substrate can be spontaneously reduced to the conductive r-GO by the hydrazine or ammonium chloride species generated during the growth reaction of MoSx particles17. Similar trends were observed in the X-ray diffraction (XRD) patterns of the GO and MoSx/r-GO composites as shown in Figure S4. The sharp (001) peak of GO at 10.8 degrees, which represents the wider interlayer distance between the graphitic layers compared to graphite, was shifted into the (002) plane at 22.0 degrees for the composites.

Remarkably, the stoichiometric S/Mo ratios of the composite gradually increased from 1.5 to 2.3, 2.6, and 3.3 for 0.1, 0.3, 0.5, and 0.7 MoSx/r-GO, respectively, while the ratio of unsupported MoS3 particles was approximately ~3.0, indicating the MoS3 structure. The Mo 3d spectrum with Mo 3d3/2 and Mo 3d5/2 doublets indicates that the Mo metal in all composite samples had the 4+ oxidation state. In particular, Mo3d 3/2 (233.2 eV) and Mo3d5/2 (230.0 eV) in the composite samples were observed at higher BE than in unsupported MoS3 (231.5 eV and 228.4 eV for Mo3d3/2 and Mo3d5/2, respectively). These values can be attributed to the presence of Mo5+ and indicate that each of the Mo atoms in the composites was randomly bonded with 2 ~ 3S atoms as indicated in the stoichiometric S/Mo ratio. Wang et al. reported that MoSx was a fundamentally and thermodynamically amorphous structure with many active edge sites, in contrast to crystalline MoS2, when the stoichiometric ratio of S atoms to Mo atoms is above 218. There are broad diffraction peaks in all our MoSx and MoS3 particles in XRD patterns of Figure S4. Thus, the resulting MoSx particles have an amorphous structure irrespective of the GO, which is expected to expose more active edge sites of MoSx.

The S 2p spectrum consists of two doublets. One doublet with higher BE (S2p3/2 = 163.2 eV and S2p1/2 = 164.6 eV) is attributed to the existence of both bridging S2− and/or apical S2− ligands. The other doublet with relatively lower BE (S2p3/2 = 162.0 eV and S2p1/2 = 163.2 eV) stems from the existence of the terminal S2− and/or S−19. Considering the previous reports that the HER activity of MoSx is highly correlated to the amount of terminated S-edge sites, it can be expected that the abundance of catalytic edge sites estimated from the deconvolution of S peaks (area ratio of edged versus bridged S = −5/4) has a beneficial effect on the hydrogen evolution efficiency.

Importantly, new peaks related to molybdenum-oxygen (Mo-O) bonding (235.6 eV) and sulfur-oxygen (S-O) bonding (169.2 and 170.5 eV) are observed only for the MoSx/r-GO composite in the presence of graphene oxide. The amount of S-O bonding, both the strong SO2 and weak SO3 configurations, significantly decreases with increasing precursor concentration, while Mo-O bonding (MoO) increases slightly with precursor concentration. In particular, in the case of 0.5 MoSx/r-GO, 12.4 and 7.3 atomic percent of the molybdenum and sulfur atoms, respectively, in the edge area of MoSx particles are covalently bonded to oxygen functional groups on r-GO sheets19. Therefore, we believe that most of the epoxide among the oxygen functional groups plays a crucial role in the anchoring or bridging between MoSx and GO. From the XPS analysis, we can conclude that the novel oxygen-bridged structure could induce the modulation of particle growth, Mo/S stoichiometry, and an amorphous configuration with more exposed active sites, which are expected to improve catalytic activity for hydrogen evolution.

**Figure 3.** XPS spectra and fitted peaks of MoSx/r-GO composites. (a) C1s spectra shows reduction of GO with increasing precursor. (b) Fitted Mo3d peaks indicate Mo with both 4+ and 5+ oxidation states. (c) Deconvolution of S2p consisting of both terminal S and bridging S.
We investigated the electrochemical HER performance of MoSx/r-GO composites deposited on a glassy carbon electrode in 0.5 M H2SO4 aqueous electrolyte using a typical three electrode setup as shown in the polarization curves (J-V) of current density (J) plotted against potential (V) of Fig. 4a. The overpotentials of all MoSx/r-GO composites at 10 mA/cm² were −240, −204, −157, and −176 mV for 0.1, 0.3, 0.5, and 0.7 MoSx/r-GO respectively. The activity of composite catalysts in the precursor range from 0.1 to 0.5 g dramatically improved from J = −1.5 to −59.7 mA/cm² at 190 mV (vs RHE). On the other hand, the HER activity of the 0.7 MoSx/r-GO catalyst was comparatively decreased, probably due to decreased electrical conductivity and reduced catalytically active sites. The conductivity of 0.5 MoSx/r-GO (5.7 × 10⁻² S/cm) measured by the 4-point probe resistivity measurement was three and two orders higher in magnitude than the conductivity of 0.1 and 0.3 MoSx/r-GO, respectively. The increased conductivity would be originated from the reduction of GO. At the same time, 0.7 MoSx/r-GO had a 44% lower value of 3.2 × 10⁻² S/cm, with respect to the relatively low amount of r-GO even though the high degree of reduction. Therefore, we concluded that the current density for the HER is closely related to the conductivity as shown in Fig. 4b; and thus high electrical conductivity would mainly affect the improvement of electrochemical HER activity.

To confirm the quantitative catalytic activity and rate determining step (RDS), we fitted a Tafel plot based on the HER polarization curves as shown in Fig. 4c. The calculated Tafel slopes were 54, 53, 42, and 41 mV/decade for 0.1, 0.3, 0.5, and 0.7 MoSx/r-GO, and unsupported MoS₃, respectively. The possible HER process in acidic electrolyte generally consists of three steps; Volmer (H⁺ + e⁻ → H_ads <120 mV/decade), Heyrovsky (H_ads + H⁺ + e⁻ → H₂, >40 mV/decade), and Tafel (H_ads + H_ads → H₂, <30 mV/decade). Considering the Tafel slopes of the catalysts, both the unsupported MoS₃ and the MoS₃/r-GO in this study might favor an electrochemical desorption mechanism, in which electrochemical desorption is the RDS, although the inherent mechanism of Mo sulfide based catalysts has been inconclusive to date. However, the resulting Tafel slope of 0.5 MoS₃/r-GO is the smallest among the catalysts. Previous studies have reported that the major factors affecting the HER activity are the surface energy for hydrogen desorption and the rate of electron transfer. It is well-known that MoS₃ itself is a semiconducting material, while the surface energy of MoS₃ is theoretically limited to desorbing the hydrogen. Thus, it can be concluded that obvious differences in the HER activity of the catalysts attributed to the electron transfer are evident in the electrochemical impedance spectra at 0.2 V (vs RHE). The MoS₃/r-GO catalysts, especially 0.5 (−14.6 Ω), show far lower charge-transfer impedance than unsupported MoS₃ (−432.6 Ω), leading to higher HER activity (Fig. 4d). In addition, calculated active site number and turnover frequency (TOF) of 0.5 MoS₃/r-GO at 0.1 V were 2.11 × 10⁻¹⁴ Mo atoms/cm² and 4.8 s⁻¹, respectively. The values of MoS₃/r-GO are similar value compared to other studies. The resulting overpotential and Tafel slope of 0.5 MoS₃/r-GO are among of the best values among the recently published studies on materials such as highly conductive molybdenum sulfides (1T-MoS₂, MoS₃/N-CNT, solvothermal MoS₃, and [Mo₅S₄]²⁻) and conventional molybdenum sulfides with no conductive substrate (double gyroid MoS₃, vertically aligned MoS₃, MoO₃-MoS₂ nanowire (NW), amorphous MoS₂, and [Mo₅S₄]²⁻) as shown in Fig. 4e. The achieved performance for hydrogen production is significantly useful compared to the materials for solar hydrogen production.

The catalytic stability of 0.5 MoS₃/r-GO over 3,000 cycles was measured by cyclic voltammetry with a potential range from −0.3 to 0.2 V as shown in Fig. 5a. After 3,000 cycles, there is no significant change in HER performance except for a slight potential shift. Kibsgaard reported that the slight potential shift caused by not the decline of electrocatalytic activity but rigorous H₂ bubble formation in structure of electrodes, which ultimately results in fewer active sites for HER. In contrast, unsupported MoS₃ showed a considerable decrease in current.

**Figure 4.** (a) Polarized curves of each MoS₃/r-GO catalysts and unsupported MoS₃, (b) relationship between electrical conductivity and HER activity, (c) corresponding Tafel plot obtained from polarized curve, (d) Nyquist plots measured at 0.2 V, (e) Overpotential and Tafel slope of various molybdenum sulfide catalysts.
density from 14.5 to 5.6 mA/cm² after 1,000 cycles. It is believed that the excellent durability of MoSx/r-GO originated from the functional coupling of oxygen bridges between MoSx and r-GO, leading to thermodynamic stability of the MoSx particles. The XPS analysis was conducted to investigate the structural changes before and after the durability test. The atomic ratio of S to Mo after the durability test was converted from 2.6 to 2.0 based on the XPS spectrum as shown in Figure S6. Further, the BE of the deconvoluted S 2p peaks was also shifted to lower positions, as in MoS2. Previous studies reported that MoS3 is electrochemically reduced to MoS2 as the active species for HER31. However, covalent S-O and Mo-O bonds are retained after 1,000 cycles, indicating that MoSx particles could be anchored on the r-GO. Therefore, we believe that the oxygen bridges might improve the stability of HER compared to MoS3 on multi walled carbon nanotubes with no functional coupling between the MoS3 and the support (88% after 500 cycles vs initial activity)32.

The functional coupling between MoSx and r-GO was also significantly effective in preventing oxidation from affecting catalytic stability. The electrochemical oxidation test was conducted in 0.5 M H2SO4 electrolyte at positive potential. Unsupported MoS3 initially shows two dominant oxidation peaks at approximately 0.50 and 0.95 V as depicted in Fig. 5b. Thermodynamically unstable sulfur atoms located at edge sites are oxidized first at 0.5 V, and the rest of sulfur atoms in the basal plane are then oxidized later at nearly 0.95 V33. However, the oxidation potential of 0.5 MoSx/r-GO is positively shifted to 0.65 V (black arrow in Fig. 5c), indicating high oxidation resistance that is closely related to the stability. In addition, after electrochemical oxidation at 0.65 V, 0.5 MoSx/r-GO exhibits a negligible potential shift, whereas the current density of unsupported MoS3 decreases significantly as shown in Fig. 5d. Therefore, the novel functional coupling of oxygen could induce anchoring and oxidation-resistance effects through the strong interaction between MoSx and r-GO, leading to the realization of Mo sulfide based catalysts with tremendous activity and durability.

Discussion
In summary, we synthesized MoSx anchored r-GO composite catalysts by a simple one-pot solution process at room temperature. MoSx particles were covalently bonded to r-GO through oxygen functional groups, and GO was simultaneously reduced to conductive r-GO. The oxygen atoms bridged between MoSx and GO play substantial roles in the fine dispersion of MoSx particles, control of planar MoSx growth, and increase of exposed active sulfur sites, leading to highly efficient and stable electrocatalysts for hydrogen evolution. Therefore, biaxially grown MoSx anchored with r-GO could act as promising nonprecious electrocatalysts for the future hydrogen-based energy world.
Methods

The preparation of GO. The GO was prepared via a modified Hummers method as described in a previous report. First, graphite was dispersed in sulfuric acid (133 mg/ml) by sonication and stirring. Then, KMnO₄ was slowly added to suspension at low temperature, which was kept at 45 °C for 6 h. Then, 100 mL of distilled water and 20 mL of H₂O₂ were added to remove any residual oxidizing agent. The brownish mixture was washed by centrifugation. The resulting gel-like GO was freeze-dried at −45 °C for 24 h and used for the preparation of the MoSₓ/r-GO composite materials.

The preparation of MoSₓ/r-GO composite materials. First, GO was dispersed in deionized water at a concentration of 3 mg/ml with a brief bath-sonication. Then, a specific amount of ammonium thiomolybdate (0.1, 0.3, 0.5, or 0.7 g) as a MoSₓ precursor was separately added in 100 ml of GO dispersion with constant stirring at room temperature. Hydrochloric acid (5 ml) was slowly added to the homogeneous mixture. After gas evolution was completed, the product was centrifuged at 7000 rpm for 10 min, followed by washing using ethanol and water to remove acidic residues. Finally, the resulting gel-like MoSₓ/r-GO was freeze-dried at −45 °C for 24 h and used as the hydrogen evolution catalyst.

Sample characterization. The crystal structure was investigated using XRD equipment (Smartlab 3, Rigaku) with a scan rate of 2 degree/min from 5 to 70 degrees. The morphologies of the prepared materials were analyzed using atomic force microscopy (AFM, Veeco, Digital Instruments Nanoscope IIIA). A sample for AFM measurement was prepared by spin-coating the catalyst dispersed in DMF at a concentration of ~1 mg/ml onto a Si wafer. The surface morphology and atomic contents of Mo, S, and C in the catalysts were analyzed using a field emission transmission electron microscope (FETEM, JEOL, JEM-2200FS) and X-ray photoelectron spectroscopy (XPS, Thermo Fisher, Multilab 2000), respectively. The TEM specimens were prepared by mixing the products in ethanol using an ultrasonic bath for 5 min, and then a drop of the suspension was placed on a copper grid. The XPS data were recorded using Al Kα radiation (hν = 1000 eV). The electrical conductivity was investigated using a four-point probe instrument (FPP-RS8, Dasol Eng.) and the film thickness of each catalyst was analyzed using a surface profiler (AlphaStep IQ, KLA Tencor).

Electrochemical analysis. First, 15 mg of each MoSₓ/r-GO composite powder was dispersed in a mixture of 1000 μL of DMF and 100 μL of Nafion with a brief sonication. Then, 8 μL of the prepared sample was deposited on glassy carbon electrode stand tried at at 50 °C. Linear sweep voltammetry using a potentiostat with a scan rate of 5 mV/s was conducted in 0.5 M H₂SO₄ electrolyte using an Ag/AgCl electrode as the reference electrode and a platinum wire as the counter electrode.

Calculation of electrochemical active sites and TOF. The oxidation peak at lower potential indicated the oxidation potential of edge area of MoSₓ to MoO₂ as shown in Fig. 5c. Thus, total current of edge oxidation peak was used to calculate the electrochemical active sites. The following equations were used to calculate the active sites and TOF.

\[
\text{Total hydrogen turnover} = \frac{(\text{current density, A/cm}^2) \times (96485.3 \text{C/mol} \text{e}^-)}{(2 \text{ mole} / \text{H}) \times (6.022 \times 10^{23} \text{ molecules of H}_2 / 1 \text{ mol H}_2)} \quad (1)
\]

\[
\text{Electrochemical active sites} = \frac{(\text{area of edge oxidation peak, C/cm}^2) \times (6.24 \times 10^{18} \text{ electrons})}{(8.9 \text{ electrons/Mo})} \quad (2)
\]

\[
\text{TOF} = \frac{(\text{total hydrogen turnover})}{(\text{electrochemical active sites})} \quad (3)
\]

we assumed that the average number of electrons for each Mo oxidation is approximately 8.9 electrons.

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Author Contributions
C.-H. Lee, J.-M. Yun and H.-I. Joh wrote the main manuscript text. C.-H. Lee, J.-M. Yun and K. S. Eom prepared and characterized all samples in this manuscript. T. F. Fuller, D. Lee and S. Lee discussed and advised the experimental results. All authors reviewed the manuscript.

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