Supporting Information for

**Monolayer-Precision Synthesis of Molybdenum Sulfide
Nanoparticles and Their Nanoscale Size Effects in the Hydrogen
Evolution Reaction**

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1. Experimental Section

1.1. Synthesis of SBA-15 Mesoporous Silica

The SBA-15 mesoporous silica template was synthesized by the previously reported method,^{S1,S2} with some modifications. 8.00 g of P123 (Sigma-Aldrich), 251.4 g of deionized (DI) water (18.2 MΩ), and 48.6 g of HCl (35%, Samchun) were mixed in a 500-mL polypropylene (PP) bottle, and the solution was stirred at 35 °C until P123 was completely dissolved. 17.0 g of tetraethyl orthosilicate (TEOS, 98%, Sigma-Aldrich) was immediately added to the P123 solution and was stirred for 5 min at 35 °C; the solution was kept at 35 °C overnight without stirring. The slurry was then transferred to a Teflon-lined stainless steel autoclave and aged at 150 °C for 24 h, and subsequently cooled to room temperature (RT). White precipitates were filtered and subsequently washed with DI water, and dried in an oven at 60 °C for 24 h. 250 mL of ethanol (EtOH, 94.5%, Samchun) and 5 g of HCl were mixed with the dried product, and the mixture was stirred for 30 min, followed by filtering and washing with EtOH, and then drying at 60 °C. Finally, the resulting powder was calcined in a box furnace at 550 °C for 5 h.

1.2. Synthesis of Mesoporous MoS₂ (Meso-MoS₂)

The ordered mesoporous material, composed of molybdenum disulfides (Meso-MoS₂), was prepared using SBA-15 mesoporous silica as a template, following the previously reported method.^{S3} First, 2 g of phosphomolybdic acid hydrate (PMA, Sigma-Aldrich) was dissolved in 7.5 mL of absolute ethanol (Samchun). Then, 0.5 g of SBA-15 was added to the solution. The mixture was stirred at 35 °C to evaporate the ethanol. The dried powder was sulfided by gradually heating to desired temperature (100, 200, 300, 400, 500 and 600 °C) at a heating rate of 2 °C min⁻¹, and was then maintained at each set temperature for 5 h under 10% H₂S (balanced with Ar) gas at a flow rate of 200 mL min⁻¹. Finally, in order to etch the silica template, the MoS₂-silica was mixed with 1:1=EtOH:10 wt% HF solution (J. T. Baker), stirred for 30 min, filtered, and washed with EtOH. The etching process was repeated once, and the product was dried. It was confirmed that 72 wt% of the PMA was converted to MoS₂. This percent yield for the MoS₂ product was used as a basis for calculating the amount of precursor for the preparation of metal disulfide nanoparticles embedded in the ordered mesoporous carbons, which will be described in detail below.

1.3. Synthesis of Sulfur-Doped OMC (S-OMC)

For comparative purposes, sulfur-doped OMC (S-OMC) was also prepared by synthesizing CMK-3 mesoporous carbon,^{S4} followed by sulfidation. 5.5 g of sucrose was dissolved in 20 g of DI water in a PP bottle, and 0.62 g of H₂SO₄ was added to the solution. Then, 4.0 g of SBA-15

was added to this solution, and a homogeneous paste was formed. The paste was then heated at 100 °C for 6 h, and subsequently heated at 160 °C for 2 h under air. The brownish composite was impregnated again with the solution comprising 3.3 g of sucrose, 20 g of DI water, and 0.37 g of H₂SO₄. The mixture was then heated to 100 °C then 160 °C under air, in the same manner as above. The brownish product was subsequently carbonized at 400 °C for 4 h, and continuously heated at 900 °C for 2 h under N₂ at a flow rate of 1 L min⁻¹. The OMC was obtained by etching the silica template, which entailed two consecutive 30-min washings with HF solution. Finally, the resulting OMC was sulfided at 600 °C to produce S-OMC, using the same sulfidation scheme as with the MS₂@OMC nanostructures.

1.4. Characterization Methods

Scanning electron microscopy (SEM) analysis was conducted on a field emission scanning electron microscope (Nanonova 230, FEI). High-resolution transmission electron microscopy (HRTEM) images, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images, and corresponding energy dispersive spectroscopy (EDS) mapping analyses were taken on a JEOL JEM-2100F field emission electron microscope at an acceleration voltage of 200 kV. Atomic resolution TEM images were taken by a low-voltage spherical aberration-corrected TEM (FEI Titan³ G2 60-300 with an image Cs corrector) with an acceleration voltage of 80 kV. X-ray powder diffraction (XRD) patterns were obtained with a high power X-ray diffractometer (Rigaku) equipped with Cu K_α radiation, and operated at 40 kV and 200 mA. Low-angle and wide-angle XRD patterns were measured in a 2θ range from 0.5° to 5° and from 10° to 90° with a scan rate of 0.5, and 4 ° min⁻¹, respectively. The metal content (Mo and Co) of each sample was analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) analyzer (Varian). The ICP-OES analysis results are summarized in Table S1. The porous and textural properties of the catalysts were examined using a nitrogen sorption analyzer (BEL BELSORP-MAX) at liquid-nitrogen temperatures. The total pore volume was determined at a relative pressure of 0.99, and specific surface area was calculated using the Brunauer–Emmett–Teller (BET) equation in a relative pressure range of 0.05–0.2. The pore size was determined from the adsorption branch using the Barrett–Joyner–Halenda (BJH) method. The textural data of the samples are summarized in Table S3. Chemical states of the samples were analyzed with an X-ray photoelectron spectrometer (XPS, K-alpha, ThermoScientific) equipped with a monochromatic Al K_α X-ray source (1486.6 eV). The curve fitting of the XPS spectra was performed using XPSpeak41 software. The baseline of the XPS spectra was corrected by the Shirley-type background with a zero slope. Peaks in the Mo 3d spectrum were deconvoluted using a Gaussian–Lorentzian mixed function (70% Gaussian and 30% Lorentzian). The respective peak for Mo 3d_{5/2} and Mo 3d_{3/2} spin–orbit couplings could be deconvoluted into

three peaks, which correspond to Mo^{4+} , Mo^{5+} , and Mo^{6+} from lower to higher binding energy, respectively. The full-width-at-half-maximum (FWHM) values for the peaks of Mo^{4+} , Mo^{5+} , and Mo^{6+} were constrained to 1.5, 2.0, and 2.5 eV, respectively. Peaks in the S 2p region were deconvoluted using a Gaussian–Lorentzian mixed function (70% Gaussian and 30% Lorentzian). The two doublets arising from S 2p_{3/2} and S 2p_{1/2} spin–orbit couplings corresponded to S^{2-} and S_2^{2-} from lower to higher binding energy, respectively. The FWHM values of the peaks in the S 2p spectrum were constrained to 1.5 eV. The local coordination structure of the samples was investigated with extended X-ray absorption fine structure (EXAFS) analysis, performed on the Beamline 10C of the Pohang Accelerator Laboratory (PAL) in South Korea, with a beam energy and current of 3 GeV and 200 mA, respectively. X-ray photon energy was monochromatized by a Si(1 1 1) double-crystal monochromator, which was detuned by around 30% to remove high-order harmonics. Background removal and normalization of the EXAFS spectra was carried out by using IFEFFIT (Athena) software. The EXAFS spectra were k^3 -weighted and Fourier transformed to a radial distribution function (RDF) over a k range of 3–14 Å⁻¹ and an R range of 1.5–3.4 Å (1.2–3.3 Å for CoMoS₂@OMC) using a Hanning window. The RDF was fitted with a known crystal structure of MoS₂ (space group: P6₃/mmc, a : 3.161, b : 3.161, c : 12.295, α : 90, β : 90, γ : 120), using IFEFFIT (Artemis) software. The resulting EXAFS fitting parameters are summarized in Table S4.

1.5. Electrochemical Measurements

All electrochemical measurements were performed on an IviumStat electrochemical analyzer at RT under atmospheric pressure using a three-compartment electrochemical cell. A graphite rod and Ag/AgCl (in 3 M NaCl solution) were used as a counter electrode and reference electrode, respectively. The Ag/AgCl reference electrode was calibrated with respect to reversible hydrogen electrode (RHE) before every use. For the calibration, a hydrogen reference electrode (Hydroflex[®], Gaskatel) and the Ag/AgCl electrode were immersed in 0.5 M H₂SO₄ for 30 min. The open circuit voltage (OCV) was recorded, resulting in $E(\text{RHE}) = E(\text{Ag/AgCl}) - \text{OCV}$. All potentials in this report were presented in the RHE scale. For electrochemical measurement, a rotating ring-disk electrode (RRDE) containing a glassy carbon (GC) as central disk (4-mm diameter, 0.126 cm² area) was used as a working electrode. The RRDE was polished with a 1.0-μm alumina suspension, and then with a 0.3-μm suspension to generate a mirror finish before use. Catalyst inks were prepared by mixing 8 mg of catalyst with 80 μL of Nafion (5 wt% in isopropanol, Sigma-Aldrich) in a solution of 800 μL DI water, 200 μL of EtOH (99.9%), and the mixture was sonicated for 30 min to produce homogeneous slurry. Afterwards, 5 μL of the catalyst ink was dropped onto the glassy carbon electrode, and dried at RT for 30 min with a rotation at 700 rpm. The resulting catalyst loading on GC was 300 μg·cm⁻². Before

electrochemical measurements, 0.5 M H₂SO₄ electrolyte was bubbled with N₂ for 20 min followed by conducting cyclic voltammetry (CV) for electrochemical cleaning; this consisted of 20 repetitions in a potential range of −0.3 to 0.6 V (vs. RHE) at a scan rate of 100 mV s^{−1}. Linear sweep voltammetry (LSV) for the hydrogen evolution reaction (HER) was conducted from 0.1 V to −0.4 V (vs. RHE) at a scan rate of 2 mV s^{−1} with a rotating speed of 1500 rpm in H₂-purged 0.5 M H₂SO₄. The LSV of each sample was measured five times, and the averages of these data were used. The electrochemical impedance spectroscopy (EIS) was performed on the same electrochemical system. After the electrochemical cleaning by CV, the Nyquist plots were measured in a frequency range of 100 kHz to 0.01 Hz at an overpotential of 100 mV. The resulting impedance spectra were fitted to a simplified equivalent Randles circuit model using the Zview software. A series resistance (R_s) arises from a combination of resistance in solution, resistance in the catalysts themselves, and resistance in the glassy carbon substrate, and the charge-transfer resistance results from the resistance in the catalyst–electrolyte interface.^{S5} The resulting series and charge transfer resistances of the samples are summarized in Table S6. The LSVs in this paper were plotted after compensating the ohmic drops with R_s values.

1.6. Calculation of Turnover Frequency (TOF)

The turnover frequency (TOF, s^{−1}), defined as the hydrogen evolution reaction (HER) rate per active site and per time, was derived from the following equation (1).

$$TOF(s^{-1}) = \left\{ j(A\text{ cm}^{-2}) \times S(\text{cm}^2) \times \frac{1H_2}{2e^-} \times \frac{1e^-}{q_e} \right\} / N_{active} \quad (1)$$

Here, the current density (j) was derived from the current generated during HER, S is the geometric surface area of working electrode (0.126 cm² in our case), and q_e is the electron charge of 1.602×10^{-19} C. N_{active} is the number of Mo atoms at the Mo-edges, which were assumed as active sites. For counting N_{active} , we suggest two possible geometric models based on Gibbs free energy (Fig. 5d) and binding energy (Supporting Information Fig. S18a) calculations. Complying with the geometric models, N_{active} was obtained by the following equation:

$$N_{active} = \left\{ \frac{m \times S(\text{cm}^2) \times (\text{wt}\% \text{ of } MoS_2) \times N_A}{MW \text{ of } MoS_2} \right\} \times F_{active} \quad (2)$$

Here, m is the loading of catalyst on the electrode. In our case, 300 μg cm^{−2} of catalyst was deposited on the GC. The wt% of MoS₂ was estimated by ICP-OES analysis, as summarized in

Table S1. F_{active} is the fraction of active sites versus total Mo atoms in a MoS₂ sheet. The F_{active} was calculated by the following equation:

$$F_{active} = \frac{n_{Mo}}{n_{Mo,total}} \quad (3)$$

Here, n_{Mo} and $n_{Mo,total}$ are the number of Mo atoms at the Mo-edges (50% S) and the total Mo atoms in a MoS₂ sheet, respectively. The n_{Mo} and $n_{Mo,total}$ were obtained using the crystallite sizes for the (002) plane determined from TEM analysis (Table S2). These crystallite sizes correspond to the diagonal length of the basal plane. The number of S atoms in the diagonal line was readily obtained by dividing this length with the S–S bond length, which is 0.315 nm.^{S5} From that, the number of S atoms in one edge (equal to half of the number of S atoms in the diagonal line) in a MoS₂ sheet was obtained, which was designated as a in the following equations and used to calculate the n_{Mo} , $n_{Mo,total}$, and F_{active} as follows.

$$n_{Mo} = 3a \quad (4)$$

$$n_{Mo,total} = 3a + 3(a-1)^2 + 3(a-1) \quad (5)$$

$$F_{active} = \frac{n_{Mo}}{n_{Mo,total}} = \frac{3a}{[3a] + [3(a-1)^2 + 3(a-1)]} \quad (6)$$

Equation (6) was based on the structural models, which were generated using density functional theory calculations of the Gibbs free energy and the binding energy of hydrogen on the MoS₂. The resulting fraction was integrated into Equation (2), thus affording the number of active sites (N_{active}) of each sample. Finally, the TOFs were calculated by inserting the result into the Equation (1).

The TOFs for the HER were also calculated in an alternative way assuming S atoms on the Mo-edges as the active sites, as the HER is initiated by the adsorption of H atoms on such unsaturated S atoms. In this case, the equations for N_{active} and F_{active} were modified as follows.

$$N_{active} = \left\{ \frac{m \times S (cm^2) \times (wt\% \text{ of } MoS_2) \times N_A}{MW \text{ of } MoS_2} \times 2 \right\} \times F_{active} \quad (7)$$

$$F_{active} = \frac{n_{S,H-adsorb}}{n_{S,total}} \quad (8)$$

Here, $n_{S,H-adsorb}$ and $n_{S,total}$ are the number of S atoms at the Mo-edges and the total S atoms in a MoS_2 sheet, respectively. The $n_{S,H-adsorb}$ and $n_{S,total}$ can be determined by the following equations.

$$n_{S,H-adsorb} = 3a - 3 \quad (9)$$

$$F_{active} = \frac{n_{S,H-adsorb}}{n_{S,total}} = \frac{3a - 3}{7.5a - 3 + 6(a - 1)^2 + 6(a - 1)} \quad (10)$$

$$F_{active} = \frac{n_{S,H-adsorb}}{n_{S,total}} = \frac{3a - 3}{9a - 3 + 6(a - 1)^2 + 6(a - 1)} \quad (11)$$

Equation (10) and (11) were based on the structural models, which were generated using density functional theory calculations of the Gibbs free energy and the binding energy of hydrogen on the MoS_2 , respectively. The resulting fraction was integrated into Equation (8), thus affording the number of active sites (N_{active}) of each sample. Finally, the TOFs were calculated by inserting the result into the Equation (7).

The third method for TOF calculations assumed that the S atoms in both the Mo- and S-edges were involved in the HER, as the S-edges can also be involved in the HER. In this case, the calculations for $n_{S,H-adsorb}$ and F_{active} were modified as follows.

$$n_{S,H-adsorb} = 6a - 3 \quad (12)$$

$$F_{active} = \frac{n_{S,H-adsorb}}{n_{S,total}} = \frac{6a-3}{[7.5a-3]+[6(a-1)^2+6(a-1)]} \quad (13)$$

$$F_{active} = \frac{n_{S,H-adsorb}}{n_{S,total}} = \frac{6a-3}{[9a-3]+[6(a-1)^2+6(a-1)]} \quad (14)$$

Equation (13) and (14) were based on the structural models, which were generated using density functional theory calculations of the Gibbs free energy and the binding energy of hydrogen on the MoS₂, respectively. The resulting fraction was integrated into Equation (8), thus affording the number of active sites (N_{active}) of each sample. Finally, the TOFs were calculated by inserting the result into the Equation (7).

2. Computational Section

2.1. Calculation Methods

We used density functional theory (DFT) calculation using DMol³ (Ref. S6,S7), under the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional.^{S8} The semi-empirical DFT-D method for dispersion correction^{S9} was included to accommodate van der Waals (vdW) interactions in the multi-layer structure. Unrestricted spin-polarized calculations were performed with the Brillouin-zone integration of a $4 \times 1 \times 1$ Monkhorst-Pack k-point grid^{S10} and basis set of DNP 4.4. The convergence criteria for the geometry optimization were 2.0×10^{-5} Ha for energy, 0.004 Ha/Å for force, and 0.005 Å for displacement. The self-consistent field convergence was less than 1.0×10^{-5} Ha and the electron smearing value was set to 0.005 Ha. The relativistic effect of all electrons on core electrons was also included in our DFT calculation. To dissect the HER process on the MoS₂ layers, the detailed elementary step energetics for the hydrogen adsorption and the desorption (Heyrovsky reaction) processes of H₂ were calculated: the first by energy calculation and the second by estimating the reaction path.

2.2. Energy Calculation

The hydrogen adsorption process was studied in terms of both the binding energy (ΔE_H) and the change of Gibbs free energy (ΔG_H°), which predict the structural stability of H adsorbed on MoS₂ and probabilities of adsorption and desorption of hydrogen, respectively. The binding energy, which represents the adsorption energy of hydrogen, is calculated by

$$\Delta E_H = E_{\text{MoS}_2+n\text{H}} - E_{\text{MoS}_2+(n-1)\text{H}} - \frac{1}{2} E_{\text{H}_2} \quad (15)$$

where n is the number of hydrogens; $E_{\text{MoS}_2+n\text{H}}$ is the total electronic energy of the $n\text{H-MoS}_2$ system, with n hydrogens adsorbed on an optimized MoS₂; $E_{\text{MoS}_2+(n-1)\text{H}}$ is the total electronic energy of the $(n-1)\text{H-MoS}_2$ system, with $(n-1)$ hydrogens adsorbed on an optimized MoS₂; and E_{H_2} is the electronic energy of a hydrogen molecule. The adsorption for hydrogen here is chemisorption, which is assumed only to occur on the edges because of energetically unfavorable adsorption on the basal plane. For ΔG_H° , a prior study^{S11} used a uniform energy value as a sum of the zero-point energy and the half value of the entropy of a gaseous H₂ at the standard condition (°), regardless of sulfur coverage. It is assumed that the change of the vibrational frequency as a function of sulfur coverage is negligible in their treatment. However, we have calculated the enthalpy and entropy of the reaction of a hydrogen with MoS₂ at 298 K, with

varying sulfur coverage, to precisely predict the adsorption and desorption of hydrogen. The formalism is expressed as follows,

$$\Delta G_H^\circ = \Delta H_H^\circ - T \Delta S_H^\circ \quad (16)$$

where ΔH_H° and ΔS_H° are the changes of enthalpy and entropy in the adsorption process, respectively, at $T = 298$ K. The notion and derivation of Eq.(16) are presented in detail below, and ΔG_H° can be expanded as

$$\begin{aligned} \Delta G_H^\circ &= H_2^\circ - H_1^\circ - T(S_2^\circ - S_1^\circ) \\ &= (U_2 + P_2 V_2) - (U_1 + P_1 V_1) - T(S_2^\circ - S_1^\circ) \end{aligned} \quad (17)$$

where U is molar internal energy, P is pressure, V is molar volume, and the subscripts 1 and 2 represent pre- and post-adsorptions of hydrogen, respectively. By introducing motional degrees of freedom (i.e. vibration, rotation, and translation) and ΔE_H , equation (17) can be rewritten as follows,

$$\Delta G_H^\circ = \Delta E_H + U_2' - U_1' - P_1 V_1 - T(S_2^\circ - S_1^\circ) \quad (18)$$

where $U_2' = E_{2,vib}$, $U_1' = E_{1,vib} + E_{1,trans}$, $S_2^\circ = S_{2,vib}^\circ$, $S_1^\circ = S_{1,vib}^\circ + S_{1,trans}^\circ$, and $P_1 V_1 = RT$ (where R is the ideal gas constant). Note that the following thermodynamic values are neglected: $E_{2,trans}$, $E_{2,rot}$, and $S_{2,trans}^\circ$, $S_{2,rot}^\circ$ of adsorbed H atoms on MoS₂; $E_{1,rot}$, $E_{1,trans}$, and $S_{1,trans}^\circ$ of MoS₂; $E_{1,rot}$, $E_{1,vib}$, and $S_{1,vib}^\circ$ of H; and P_2 . With the assumption of ideal H atoms, the translation energy and entropy can be obtained by

$$E_{trans} = \frac{3}{2} RT \quad (19)$$

$$S_{trans} = \frac{5}{2} R \ln T + \frac{3}{2} R \ln M_w - R \ln P - 2.31482 \quad (20)$$

where M_w is molecular weight.^{S12} By using Eq.(18), the enthalpy and entropy contribution in hydrogen adsorption at 298 K has been calculated, and it was observed that ΔG_H° without adsorption energy showed differences of around 0.36~0.49 eV for the systems of interest, unlike the uniform value of 0.29 eV found in previous work.^{S11}

2.3. Estimation of an Energy Diagram and Reaction Coordinates

The desorption (Heyrovsky reaction) process of H₂ was studied with the edge configurations of Mo-edge(50% S) and S-edge(75% S) in 1L, 2L, and 3L models, with adsorbed hydrogen(s). To study the effect of the energetics of the desorption process depending on hydrogen coverage, 1L, 2L, 3L with Mo-edge(50%S), where one or two hydrogen(s) are attached at the edge site, was

used. The implicit water environment is applied at the model system by conductor-like screening model (COSMO) calculation.^{S13} The reaction path was investigated by linear and quadratic synchronous transit (LST/QST) methods, combined with the conjugated gradient (CG) refinement.^{S14} The former was used to approximate the transition state and the latter was iteratively applied where the position of hydrogen was adjusted so that the minimum-energy structure emerged at a stationary point for each reaction coordinate.

3. Supporting Tables S1-S7

Table S1. The contents of metals and MoS₂ in MoS₂@OMC and CoMoS₂@OMC nanostructures, determined by ICP-OES analysis.

Sample	Co (wt%)	Mo (wt%) ^a	MoS ₂ (wt%) ^b
1L-MoS ₂ @OMC		2.66	4.43
2L-MoS ₂ @OMC		6.71	11.2
3L-MoS ₂ @OMC		9.11	15.2
4L-MoS ₂ @OMC		12.7	21.2
2.5L-CoMoS ₂ @OMC	0.45	6.95	11.6
3.5L-CoMoS ₂ @OMC	0.98	12.1	20.2

^a The content of Mo was obtained by averaging four ICP-OES results.

^b The contents of MoS₂ were calculated by assuming that all Mo exist in the form of MoS₂.

Table S2. Crystallite sizes in the (100) and (002) directions, and number of layers of the MoS₂@OMC, Meso-MoS₂ and CoMoS₂@OMC nanostructures, determined by TEM images.

Sample	Crystallite size in (100) direction ^a	Crystallite size in (002) direction ^a	Number of layers ^a
1L-MoS ₂ @OMC	3.85	0.80	1.23
2L-MoS ₂ @OMC	4.49	1.27	2.01
3L-MoS ₂ @OMC	4.22	1.86	2.91
4L-MoS ₂ @OMC	4.36	2.50	3.93
Meso-MoS ₂	5.12	3.45	5.37
2.5L-CoMoS ₂ @OMC	4.01	1.55	2.45
3.5L-CoMoS ₂ @OMC	4.27	2.24	3.51

^a Crystallite sizes and number of layers were measured on the particles in TEM images. The values were obtained by averaging the measured sizes over one hundred of particles.

Table S3. BET surface areas, total pore volumes, and pore sizes obtained from nitrogen adsorption–desorption analyses.

Sample	BET surface area ^a (m ² g ⁻¹)	Pore volume ^b (cm ³ g ⁻¹)	Pore size ^c (nm)
SBA-15	388	1.02	14
1L-MoS ₂ @OMC	1089	1.59	5.5, 28.1
2L-MoS ₂ @OMC	951	1.40	5.5, 24.4
3L-MoS ₂ @OMC	1004	1.48	5.5, 21.3
4L-MoS ₂ @OMC	972	1.42	5.5, 21.3
Meso-MoS ₂	105	0.19	6.3
S-OMC	1192	1.79	5.5, 24.4
2.5L-CoMoS ₂ @OMC	1092	1.63	5.5, 18.5
3.5L-CoMoS ₂ @OMC	1052	1.42	5.5, 18.5

^a BET surface area was obtained in the relative pressure range of 0.05-0.2.

^b Pore volume was determined at the relative pressure of 0.98-0.99.

^c Pore size was obtained by using BJH method from the adsorption branch.

Table S4. Fitting parameters obtained by EXAFS analysis.^a

Sample	Pair	Distance (Å)	Coordination number (CN)	Debye-Waller factor (σ^2) (10^{-3} Å^2)	ΔE_0 (eV)	N_s/N_{Mo}^b
1L-MoS ₂ @OMC	Mo-S	2.41	5.71	4.1	2.08	1.45
	Mo-Mo	3.16	3.93	4.2		
2L-MoS ₂ @OMC	Mo-S	2.41	5.82	3.8	1.24	1.31
	Mo-Mo	3.16	4.44	4.3		
3L-MoS ₂ @OMC	Mo-S	2.41	5.81	3.7	1.43	1.33
	Mo-Mo	3.16	4.36	4.0		
4L-MoS ₂ @OMC	Mo-S	2.41	5.83	3.6	1.37	1.29
	Mo-Mo	3.17	4.53	4.0		
Meso-MoS ₂	Mo-S	2.41	5.64	3.6	1.57	1.28
	Mo-Mo	3.16	4.42	4.0		
Bulk-MoS ₂	Mo-S	2.41	6.05	3.3	2.17	0.94
	Mo-Mo	3.17	6.41	3.5		
2.5L-CoMoS ₂ @OMC	Mo-S	2.40	5.30	3.4	0.33	1.24
	Mo-Mo	3.16	4.29	4.4		
3.5L-CoMoS ₂ @OMC	Mo-S	2.41	5.57	3.3	1.02	1.19
	Mo-Mo	3.17	4.69	4.3		

^aUncertainties in fitting parameters : $< \pm 0.003 \text{ Å}$ for distance, $< \pm 8\%$ for CN, $< \pm 0.5 \times 10^{-3} \text{ Å}^2$ for σ^2 for undoped MoS₂(@OMC) / $< \pm 0.005 \text{ Å}$ for distance, $< \pm 20\%$ for CN, $< \pm 0.9 \times 10^{-3} \text{ Å}^2$ for σ^2 for Co-doped MoS₂@OMC

^bN_s: CN of Mo-S, N_{Mo}: CN of Mo-Mo.

Table S5. The binding energy and Gibbs free energy for hydrogen adsorption on Mo-edge and S-edge in 1L, 2L, 3L(2nd), and 3L(3rd) models. ‘H coverage’ indicates the coverage of hydrogen with respect to the number of available S atoms on the edge. Our model has four rows in the x-direction and thus it has four possible binding sites. Each hydrogen atom corresponds to 0.25 H coverage. ‘-’ indicates where Gibbs free energy was not calculated because the models are far from a thermo-neutral state. ‘0.50 (far)’ denotes the case when two protons are separately adsorbed on the active edge site at a distance. ‘0.50 (near)’ denotes the case when two protons are closely adsorbed on the active edge site.

H coverage		1L		2L			3L(2nd)			3L(3rd)		
		ΔE_H	ΔG_H°	Model	ΔE_H	ΔG_H°	Model	ΔE_H	ΔG_H°	Model	ΔE_H	ΔG_H°
Mo-edge (50%S) A	0.25	-0.66	-0.22	BA	-0.48	-0.12	BAB	-0.43	-0.06	ABA	-0.49	-0.13
				B'A	-0.62	-0.16	B'AB'	-0.59	-0.12	AB'A	-0.63	-0.17
				-			B'AB	-0.49	-0.08	A'BA	-0.48	-0.12
	0.50 (far)	-0.18	0.12	BA	-0.19	0.14	BAB	-0.16	0.17	ABA	-0.20	0.15
	0.50 (near)	0.30	0.59	BA	0.29	0.60	BAB	0.29	-	ABA	0.28	-
Mo-edge (100%S) A'	0.25	-0.09	0.31	BA'	-0.07	0.33	-			-		
				B'A'	-0.1	0.32						
S-edge (75%S) B	0.25	-0.31	0.05	AB	-0.33	0.03	ABA	-0.33	0.04	BAB	-0.34	0.02
				A'B	-0.45	-0.1	A'BA'	-0.48	-0.03	BA'B	-0.41	-0.06
				-			A'BA	-0.4	0.03	B'AB	-0.36	0.02
	0.50 (far)	-0.61	-0.32	AB	-0.67	-0.34	ABA	-0.72	-0.40	BAB	-0.65	-0.36
	0.50 (near)	0.26	0.53	AB	0.33	0.66	ABA	0.23	-	BAB	0.30	-
S-edge (100%S) B'	0.25	-0.68	-0.31	AB'	-0.67	-0.3	-			-		
				A'B'	-0.72	-0.36						
Mo-edge (0%S)	0.25	-0.67	-0.29	-			-			-		
S-edge (50%S)	0.25	0.35	-	-			-			-		

Table S6. Series and charge-transfer resistances obtained from electrochemical impedance spectroscopy analysis.

Sample	Series resistance (Ω) ^a	Charge transfer resistance ($\Omega \text{ cm}^2$) ^b
1L-MoS ₂ @OMC	8	1816
2L-MoS ₂ @OMC	11	1133
3L-MoS ₂ @OMC	10	917
4L-MoS ₂ @OMC	9	896
2.5L-CoMoS ₂ @OMC	11.5	36
3.5L-CoMoS ₂ @OMC	13.6	27

^{a,b} The series and charge transfer resistances were determined by fitting the numerical data obtained from Nyquist plots, using Zview software.

Table S7. HER activity of MoS₂@OMC and CoMoS₂@OMC nanostructures, expressed in terms of overpotentials at 10 mA cm⁻², Tafel slopes, exchange current densities, and TOF values.

Sample	Overpotential at 10 mA cm ⁻² (V)	Tafel slope ^a (mV dec ⁻¹)	Exchange current density ^b (A cm ⁻²)	TOF (s ⁻¹) ^c
1L-MoS ₂ @OMC	0.215	65	4.82 x 10 ⁻⁶	2.32
2L-MoS ₂ @OMC	0.189	61	7.14 x 10 ⁻⁶	2.32
3L-MoS ₂ @OMC	0.182	60	8.04 x 10 ⁻⁶	1.95
4L-MoS ₂ @OMC	0.182	60	8.07 x 10 ⁻⁶	1.45
2.5L-CoMoS ₂ @OMC	0.166	60	1.70 x 10 ⁻⁵	5.13
3.5L-CoMoS ₂ @OMC	0.170	73	4.69 x 10 ⁻⁵	2.30

^{a,b} The Tafel slopes and exchange current densities were derived from the linear portion of the corresponding Tafel plots.

^c The TOFs were determined with current densities at overpotential of 200 mV. The TOF (s⁻¹) per Mo atom in Mo-edges(50% S coverage) was calculated using the structural model based on theoretically calculated Gibbs free energy, the details of which has been described in the Supporting Information Section 1.6.

4. Supporting Figures S1-S24

Figure S1. SEM images of (a) SBA-15, (b) 1L-MoS₂@OMC, (c) 2L-MoS₂@OMC, (d) 3L-MoS₂@OMC, (e) 4L-MoS₂@OMC, (f) Meso-MoS₂, and (g) S-OMC.

Figure S2. EDS elemental mapping images of (a) 1L-MoS₂@OMC, (b) 2L-MoS₂@OMC, (c) 3L-MoS₂@OMC, (d) 4L-MoS₂@OMC, and (e) Meso-MoS₂.

Figure S3. HRTEM images of (a) 1L-MoS₂@OMC, (b) 2L-MoS₂@OMC, (c) 3L-MoS₂@OMC, (d) 4L-MoS₂@OMC, and (e) Meso-MoS₂.

Figure S4. Small-angle XRD patterns of SBA-15, MoS₂@OMCs, Meso-MoS₂, and S-OMC.

Figure S5. (a) Nitrogen adsorption-desorption isotherms of SBA-15 and MoS₂@OMC samples. Filled circles and empty circles represent adsorption and desorption branches, respectively. The isotherms of the 2L-, 3L-, and 4L-MoS₂@OMC were offset by 350, 650, and 1000 cm³ g⁻¹, respectively, for clarity. (b) BJH pore size distribution of SBA-15 and MoS₂@OMC samples obtained from the adsorption branches of their isotherms.

Figure S6. (a) Nitrogen adsorption-desorption isotherms for Meso-MoS₂ and S-OMC samples. Filled circles and empty circles represent adsorption and desorption branches, respectively. The isotherm of the Meso-MoS₂ was offset by 1100 cm³ g⁻¹ for clarity. (b) BJH pore size distribution of Meso-MoS₂ and S-OMC samples obtained from the adsorption branches of their isotherms.

Figure S7. N_s/N_{Mo} ratio of $MoS_2@OMC$ nanostructures with respect to number of layers (N_s : CN of Mo-S, N_{Mo} : CN of Mo-Mo, obtained from EXAFS analysis).

Figure S8. All structural models for 1L, 2L, 3L(2nd), and 3L(3rd) MoS₂ under our consideration. The terms, A, A', B, and B' represent Mo-edge(50% S), Mo-edge(100% S), S-edge(75% S), and S-edge(100% S), respectively. Black spheres represent the stably adsorbed hydrogen. The red letters indicate the location of the layers at which hydrogen adsorption occurs.

Figure S9. Comparative energetics for different configurations of unsaturated S atoms in the S-edge(100% S) model: (a) no S₂ dimer, (b) four S₂ dimer (zig-zag), (c) two S₂ dimer, and (d) two S₂ dimer (zig-zag) on the edge. The presented energies are relative those calculated for the model (a). The models (a) through (c) were previously studied by references S15 and S16. The most stable model is (d), which is found from our calculations.

	1L	2L	3L(2nd)	3L(3rd)
H coverage : 25%	E_{rxn} : 22.1 E_a : 32.3	E_{rxn} : 28.9 E_a : 34.2	E_{rxn} : 31.0 E_a : 56.5	E_{rxn} : 31.5 E_a : 38.9
H coverage : 50%	E_{rxn} : 12.7 E_{rxn} : 13.3 E_a : 17.7 E_a : 18.3	E_{rxn} : 18.9 E_{rxn} : 20.7 E_a : 25.8 E_a : 25.8	E_{rxn} : 22.7 E_{rxn} : 24.4 E_a : 55.3 E_a : 55.0	E_{rxn} : 22.8 E_{rxn} : 24.2 E_a : 29.6 E_a : 33.1

Figure S10. DFT calculations of the energetics on Mo-edge layer models depending on the hydrogen coverage during the Heyrovsky reaction. The term E_a denotes the activation energy of the transition states and E_{rxn} denotes the heat of reaction. The label ‘near’ represents the case in which two hydrogen atoms located closely together are adsorbed and the label ‘far’ represents the case in which two hydrogen atoms located further apart are separately adsorbed.

Figure S11. DFT calculations of reaction paths on the S-edge layer models during the Heyrovsky reaction. The energy diagrams of the reaction paths on the S-edge (75%S) for a hydrogen coverage of 25% in (a) 1L, (b) 2L, (c) 3L(2nd), and (d) 3L(3rd) models with respect to the reaction coordinate. The acronyms IS, TS, and FS represent the initial, transition, and final states, respectively. The numbers represent the relative energies at each state based on that of the IS. The black spheres represent either adsorbed H or desorbed H₂. The pink letter represents the layer with adsorbed H.

Figure S12. Raw data for LSV curves of (a) 1L-MoS₂@OMC, (b) 2L-MoS₂@OMC, (c) 3L-MoS₂@OMC, (d) 4L-MoS₂@OMC, (e) Meso-MoS₂, (f) Bulk-MoS₂, and (g) S-OMC.

Figure S13. Nyquist plots for impedance spectra of MoS₂@OMC nanostructures at $\eta = 100$ mV (vs RHE). The empty circles and the solid lines represent numerical raw data and fitting results, respectively. The tendency of the charge transfer resistance to decrease with the number of layers is correlated with the increase in the current density with the number of layers (Figure 5) due to increasing MoS₂ content in the MoS₂@OMC composite.

Figure S14. TOF calculations on MoS₂@OMC and Meso-MoS₂ nanostructures using the structural model based on the Gibbs free energy calculations (see Fig. 5d). (a-b) TOF calculations assuming H-binding sites at the Mo-edge as active sites: (a) TOFs with respect to potential and (b) TOFs at -200 mV (vs RHE) with respect to the number of layers. (c-d) TOF calculations assuming H-binding sites at both the Mo- and S-edges as active sites: (c) TOFs with respect to potential and (d) TOFs at -200 mV (vs RHE) with respect to the number of layers.

Figure S15. TOF calculations on MoS₂@OMC and Meso-MoS₂ nanostructures using the structural model based on the binding energy calculations (a). (b-c) TOF calculations assuming Mo atoms at the Mo-edge as active sites: (b) TOFs with respect to potential and (c) TOFs at -200 mV (vs RHE) with respect to the number of layers. (d-e) TOF calculations assuming H-binding sites at the Mo-edge as active sites: (d) TOFs with respect to potential and (e) TOFs at -200 mV (vs RHE) with respect to the number of layers. f-g, TOF calculations assuming H-binding sites at both the Mo- and S-edges as active sites: (f) TOFs with respect to potential and (g) TOFs at -200 mV (vs RHE) with respect to the number of layers.

Figure S16. SEM images of (a) 2.5L- and (b) 3.5L-CoMoS₂@OMC nanostructures.

Figure S17. EDS elemental mapping images of (a) 2.5L- and (b) 3.5L-CoMoS₂@OMC nanostructures.

Figure S18. (a) Wide-angle and (b) small-angle XRD patterns of CoMoS₂@OMC nanostructures.

Figure S19. (a) Nitrogen adsorption/desorption isotherms of CoMoS₂@OMC nanostructures. Filled circles and empty circles represent adsorption and desorption branches, respectively. The isotherm of the 3.5L-CoMoS₂ was offset by 400 cm³ g⁻¹, for clarity. (b) BJH pore size distribution of CoMoS₂@OMC samples obtained from the adsorption branches of their isotherms.

Figure S20. Layer number distribution of (a) 2.5L- and (b) 3.5L-CoMoS₂@OMC nanostructures.

Figure S21. (a) Mo K-edge and (b) Co K-edge EXAFS spectra of CoMoS₂@OMC nanostructures. Empty circles are raw data and solid lines are fitting results. c, The resulting N_s/N_{Mo} ratios plotted as vertical bars with respect to the composition (N_s: coordination number of Mo–S, N_{Mo}: coordination number of Mo–Mo).

Figure S22. XPS spectra of CoMoS₂@OMC nanostructures: (a) Survey, (b) Mo 3d, (c) Co 2p, and (d) S 2s spectra. Peak intensities are normalized by setting the maximum intensity to one and the minimum intensity to zero.

Figure S23. Nyquist plots for the impedance spectra of CoMoS₂@OMC at $\eta = 100$ mV (vs RHE). The empty triangles and the solid lines represent numerical raw data and fitting results, respectively.

Figure S24. Durability test of 2.5L-CoMoS₂@OMC for the HER over 1000 cycles of potential scans from -0.3 V to 0.1 V (vs RHE) in 0.5 M H₂SO₄ at a scan rate of 50 mV/s. The LSV curves were not iR-corrected.

5. References for Supporting Information

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