Electronic Supplementary Information

Amorphous MoS_xCl_y Electrocatalyst Supported by Vertical Graphene for Efficient Electrochemical and Photoelectrochemical Hydrogen Generation

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I. Experimental Section 1. Chemicals and Materials

Sulfur powder (99.5%), MoCl₅ (95%), and other chemicals were purchased from Sigma-Aldrich and used without further purification. Graphite rods (6.0 mm diameter) were purchased from Ultra Carbon Corp. with Ultra "F" Purity.

2. Preparation of Graphite Disk Electrode Supports

The graphite rods were cut into thin disks (6 mm diameter; ~0.4 mm thick) with a geometric area of 0.2826 cm², which were polished to a near-mirror finish using abrasive cloths. They were sonicated subsequently in 18 M Ω deionized water for 10 min and dried in an oven at 120 °C for 20 min before usage.

3. Synthesis of Vertical Graphene

The vertical graphene on graphite disks was synthesized following a procedure previously reported^[S1] using a dc plasma-enhanced chemical vapor deposition system (PECVD). In a typical procedure, Ar and CH₄ flows were introduced into the reactor with two separate flows: a dry Ar flow (0.9 lpm) and a wet Ar/CH₄ flow through a water bubbler flask (Ar: 0.1 lpm, CH₄: 0.1 lpm). The plasma reactor was designed with a tungsten pin cathode (-3.5 kV) pointing toward the graphite disc (grounded) with a distance of 0.8-1.0 cm. Prior to the growth, the graphite disc was brought to 700 °C and held at that temperature for 10 minutes in an Ar/H₂ flow (0.5 lpm, 10% H₂). Throughout the deposition process, the reactor pressure was maintained at one atmosphere (101,325 Pa) and the reactor temperature was at 700 °C. The discharge duration (*i.e.*, growth time) was 10 minutes.

4. Synthesis of Crystalline MoS₂ and Amorphous MoS_xCl_y on VG or GT

The MoS₂ and MoS_xCl_y grown on VG or GT were synthesized using a chemical vapor deposition (CVD) method modified from the synthesis we previously developed.^[S2,3] In a

typical reaction, a quartz tube (1 inch I.D.) was first treated with a Zerostat gun for 2 min to remove the electrostatically absorbed water on the wall. It was then connected to Ar gas inlets and a vacuum pump, and placed in a tube furnace (Thermal Fisher, Linderberg Blue). Graphite disks or graphite disks covered with VG were placed inside parallel to the tube at the center of the furnace. Two alumina boats containing 25 mg MoCl₅ and 0.5 g sulfur powder, respectively, were placed side by side near the entrance of the tube furnace with the MoCl₅ boat sitting at more upstream position just outside the heating zone and the boat of sulfur sitting just inside the furnace. The MoCl₅ must be weighed in a glove box and rapidly sealed into the tube reactor to avoid hydrolysis in the air. The tube was first evacuated to a base pressure of 10 mTorr and flushed three times with Ar. Then the reaction zone was heated to 175–435 °C under an Ar flow of 125 sccm at 780 Torr, then both boats were moved into the heating zone to initiate the reaction, where the MoCl₅ boat was at about 120 °C and sulfur at about 150 °C. After reaction for 12 minutes, the temperature was brought down to 100 °C while maintaining the Ar flow at 125 sccm for another 10 min to remove the possible residual sulfur on the growth substrates. Finally the tube was cooled naturally to room temperature.

MoS_xCl_y on *p*-Si was also synthesized under the same conditions as above. Si wafers with resistivity of 1-2.5 Ω -cm (*p*-type, B doped, (100) orientation, prime grade, 525 μ m thickness, 100 mm diameter, native silicon oxide) were obtained from Silicon Inc. The Si wafers were cut into 7×7 mm pieces for photocathode fabrication and MoS_xCl_y growth. Si substrates were first etched with aqueous buffered HF solution (Buffer HF Improved, Transene Inc.) for 30 s to remove the native oxide layer and subsequently rinsed with deionized water and dried with a stream of N₂, and then placed at the center of the tube furnace before the reactor was immediately evacuated.

5. Structural Characterization

Scanning electron microscopy (SEM) was performed using a LEO SUPRA 55 VP

field-emission scanning electron microscope operated at 5 kV. To prepare the specimen for transmission electron microscope (TEM) and scanning transmission electron microscopy (STEM) imaging, the as-grown substrates were immersed in 2 mL of ethanol and sonicated for 1 min. The resulting suspension was drop casted onto a piece of TEM grid (Ted Pella, lacey carbon type-A support film, 300-mesh, copper, #01890-F). TEM and STEM-EDS mapping were carried out on a FEI Titan scanning transmission electron microscope at an accelerating voltage of 200 kV. The Raman spectra of the samples were collected with an Aramis Confocal Raman Microscope using a 532 nm laser source and CCD detector with a 1800 l/mm grating and a 100 µm aperture. The spatial resolution was about 1 µm. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was measured on Optima 2000 DV (PerkinElmer Inc.) to estimate the loading density of MoS_xCl_y on VG. X-ray photoelectron spectroscopy (XPS) was taken on a custom-built XPS system (Phi Electronics, Eden Prairie, MN) that included a model 10-610 Al K α x-ray source (1486.6 eV photon energy) and a model 10-420 toroidal monochromator. A model 10-360 hemispherical analyzer with a 16-channel detector array was used, which under effective operating conditions had an analyzer resolution of 0.4 eV. Electrons were collected at an emission angle of 45° from the surface normal of the sample. High resolution data was collected for Mo3d, S2p, and Cl2p. All X-ray photoelectron spectra are shifted so that the adventitious carbon C1s peak is at 284.8 eV to make sure the data across samples are aligned and that the samples are not experiencing differential charging effects that may convolute the data. Because the Mo and S peaks are overlapped in the EDS spectra, the stoichiometry of the MoS_xCl_y sample grown at 275 °C was determined with Electron Probe Micro-Analysis by X-ray Wavelength Dispersive Spectroscopy (EPMA-WDS) using Cameca SX51 with Probe for Windows software, operated at 15 kV. Ultraviolet photoelectron spectroscopy (UPS) was conducted with a custom-built system (Phi Electronics Inc., Eden Prairie, MN), complete with a model 10-360 hemispherical analyzer and a UV light source of a He I discharge lamp (21.2 eV photon energy). Electrons were collected at a 0° take-off angle from the surface normal with analyzer resolution of 0.09 eV. The location of the Fermi level was determined using platinum by setting the valence band maximum of platinum to zero. All data reported contains a Fermi level that has been set to 0 eV.

6. Electrochemical Characterization

Electrochemical measurements were performed using a rotating disk electrode (BASi, RDE-2) in a three-electrode electrochemical cell using a Bio-Logic SP-200 potentiostat. All measurements were performed in 25 mL of 0.5 M H₂SO₄(aq) electrolyte (pH = 0.16) prepared using 18 M Ω deionized water and constantly purged with H₂ gas (99.999%), with graphite disks covered with MoS₂, MoS_xCl_y, MoS₂-VG, or MoS_xCl_y-VG as the working electrode, a graphite rod as a counter electrode, and a saturated calomel (SCE) reference electrode.

To allow potentials to be referenced against the reversible hydrogen electrode (RHE), the SCE was calibrated against the reversible hydrogen potential using platinum wire (Kurt J. Lesker, 99.99%; 0.50 mm diameter) as both the working and counter electrodes after each measurement. Linear sweep or cyclic voltammograms of samples were measured from +0.25 V to -0.45 V vs. RHE at a scan rate of 3 mV s⁻¹ in both the forward and reverse directions while rotating the working electrode at 2000 RPM. Electrochemical impedance spectroscopy (EIS) was performed in potentiostatic mode at -0.5 V vs. SCE, applying a sinusoidal voltage with an amplitude of 10 mV and scanning frequency from 200 kHz to 50 mHz. The main arc in each EIS spectrum was modeled using a simplified Randles equivalent circuit shown below, which consists of a resistor (R_s) in series with a parallel arrangement of a resistor (R_{ct}) and a constant phase element (CPE), with the fitting parameters obtained through application of the Levenberg-Marquardt minimization procedure.



In order to accurately represent the catalytic activity of various samples, it is necessary correct the measurements of current density (*J*) vs. applied voltage (*E*) for all ohmic losses throughout the system, which include the wiring, substrate, catalyst material, and solution resistances. Together, these resistances constitute the series resistance (R_s) of the measurement, which can be obtained from an EIS Nyquist plot as the first intercept of the main arc (corresponding to the electrode–electrolyte interface) with the real axis. Then, for each measured value of current, the potential loss can be calculated using R_s and Ohm's Law and subtracted from the raw data to give the *i*R-corrected data.

Cyclic voltammograms taken with various scan rates (4, 8, 16, 32, 64, 128 mV/s) were collected in the region of 0.1–0.2 V vs. RHE for various samples and were used to estimate the double-layer capacitance (C_{dl}).

7. Photoelectrochemical Characterization

The photoelectrochemical characteristics of MoS_xCl_y/p -Si photocathodes were measured in a three-electrode configuration under simulated 1 sun irradiation (100 mW/cm²) supplied by 1 kW Xe short arc lamp solar simulator (Newport Corp., Model 91191; AM1.5G filter) using a Bio-Logic SP-200 potentiostat. The light intensity was calibrated with a Si photodiode (Thorlabs) to generate a photocurrent equal to that at 100 mW/cm² light intensity. All measurements were performed in 0.5 M sulfuric acid electrolyte, using a graphite rod (National Carbon Co., AGKSP Spectroscopic Electrode) as the counter electrode and Ag/AgCl/1 M KCl (BASi) as the reference electrode, which was calibrated against the reversible hydrogen electrode (RHE) in hydrogen saturated electrolyte with a platinum wire (Kurt J. Lesker, 99.99%; 0.50 mm diameter) as the working electrode. The electrolyte was rapidly stirred to minimize mass transport limitations and remove accumulated hydrogen gas bubbles on the electrode surface, and constantly purged with research-grade H₂ gas (99.999%) to maintain a constant Nernst potential for H^+/H_2 redox couple. The current density versus potential (*J*–*E*) data were measured with a scan rate of 10 mV/s, and were not corrected for any uncompensated resistance losses or any other extrinsic losses.



II. SEM Images of the Original Vertical Graphene Sample

Figure S1. Typical SEM images of the original vertical graphene samples on graphite disks.

III. STEM-EDS Analysis of MoS₂-VG Samples at 435 °C



Figure S2. (A) STEM-EDS mapping of MoS₂-VG samples at 435 °C showing the absence of

Cl element and the crystallinity of the MoS₂ deposited. Lower right inset shows a typical SAED pattern of crystalline 2H-MoS₂. The orange box indicates the region where the EDS elemental mapping shown on the right was performed. (B) A typical SEM image of MoS₂-VG samples at 435 °C.

IV. EDAX Spectra of the MoS_xCl_y-VG Sample Grown at 275 °C and MoS₂-VG at 435 °C

Figure S3. EDAX spectra of the MoS_xCl_y -VG sample grown at 275 °C shown in Figure 1 and the MoS_2 -VG sample grown at 435 °C shown in Figure S2.

V. SEM Images of the MoS_xCl_y -GT Sample at 275 °C and the MoS_2 -GT Sample at 435 °C

Figure S4. SEM images of the MoS_xCl_y -GT sample grown at 275 °C (A) and the MoS_2 -GT sample grown at 435 °C (B). The major features seen in the images come from the rough graphite disk substrates.

VI. Summary of Electrochemical Performance for All Samples

Figure S5. Polarization curves all samples synthesized from 435 °C to 175 °C onto either vertical graphene (VG) or graphite (GT) substrates. Figure 3A in the main text displays the data for selective samples for clarity.

Figure S6. Polarization curves in the potential range of 0 V to - 0.25 V vs. RHE for all samples synthesized from 435 °C to 175 °C onto either vertical graphene (VG) or graphite (GT) substrates. Figure 3B in the main text displays the data for selective samples for clarity.

Figure S7. Tafel analysis of the data for all samples presented in Figure S5 and S6.

Figure S8. EIS Nyquist plots collected under catalytic HER operating conditions at -0.5 V vs. SCE for samples synthesized from 435 °C to 175 °C onto both vertical graphene (VG) or graphite (GT) substrates.

Figure S9. Plots showing the extraction of the double layer capacitance (C_{dl}) for all samples

synthesized from 435 °C to 175 °C onto both vertical graphene (VG) or graphite (GT) substrates.

VII. CV of the MoS₂Cl-VG Sample Grown at 275 °C

Figure S10. An example of the CV scans for the MoS_2Cl-VG sample grown at 275 °C to allow the construction of the plots shown in Figure S9 to obtain the double layer capacitance.

VIII. EDS Spectrum of the MoS₂Cl/p-Si Heterostructure Grown at 275 °C

Figure S11. EDS spectrum of the MoS₂Cl/p-Si heterostructure grown at 275 °C.

IX. Elemental Compositions of MoS_xCl_y Samples Grown at 275 °C Determined by

EPMA-WDS

Table S1. Composition analysis of MoS_xCl_y samples grown at 275 °C on various substrates determined by EPMA-WDS.

sample		mass ratio (%)	molar ratio (%)	relative molar ratio
	Mo	49.8	0.519	1
MoS _x Cl _y -VG	S	33.7	1.051	2.02
	Cl	16.5	0.465	0.90
MoS _x Cl _y -GT	Мо	48.6	0.507	1
	S	31.5	0.982	1.94
	Cl	19.8	0.558	1.10
MoS _x Cl _y /p-Si	Мо	48.6	0.507	1
	S	33	1.029	2.03
	Cl	18.4	0.519	1.02
Average	Мо			1
	S			1.998
	Cl			1.008

sample	Tafel slope	R _{ct}	$C_{\rm dl}$
	(mV decade ¹)	$(\Omega \text{ cm}^2)$	$(mF cm^{-2})$
435 VG	122	623	7.2
375 VG	64	9.1	5.4
375 GT	67	8.4	3.1
325 VG	50	2.4	21.1
325 GT	51	3.1	18.6
300 VG	50	2.4	27.7
300 GT	57	3.3	16.8
275 VG	46	2.3	24.2
275 GT	50	3.8	12.8
250 VG	54	2.1	35.1
250 GT	52	3.6	14.7
225 VG	50	3.8	12.7
225 GT	48	4.1	17.2
175 VG	54	4.1	24.9
175 GT	65	7.5	16.9
Pt wire	30	-	-

X. Summary of Electrochemical Data for All Samples

Table S2. Summary of the electrochemical properties for all samples synthesized different temperatures onto both vertical graphene (VG) and graphite (GT) substrates.

Figure S12. XPS spectra of the MoS₂Cl (275 °C) and MoS₂ (435 °C) samples after the HER tests for (A) Cl 2p, (B) S 2p, and (C) Mo 3d peaks, showing that there is little change, specifically the Cl peak remained after the HER test. Note that the new S peaks around 168 eV in panel B come from sulfate species from the H_2SO_4 electrolyte used during the HER test.

XII. UPS results of MoS₂ single crystal, amorphous MoS₂Cl (275 °C) and crystalline MoS₂ nanoflakes (435 °C)

Figure S13. UPS spectra of different molybdenum sulfides. (A) Overall UP spectra and (B) zoom-in of the low binding energy edge of the UP spectra showing the valence band maxima with respect to the Fermi level for an MoS₂ single crystal, amorphous MoS₂Cl (275 °C) and crystalline MoS₂ nanoflakes (435 °C).

XIII. References:

(S1) Z. Bo, K. Yu, G. Lu, P. Wang, S. Mao, J. Chen, Carbon 2011, 49, 1849-1858.

(S2) M. A. Lukowski, A. S. Daniel, F. Meng, A. Forticaux, L. S. Li, S. Jin, J. Am. Chem. Soc. 2013, 135, 10274-10277.

(S3) X.W. Zhang, F. Meng, J. R. Christianson, A. Christian, M. A. Lukowski, L. Dong, J. R. Schmidt, S. Jin, *Nano Lett.* 2014, 14, 3047-3054.