Supporting Information

Unraveling the Factors Affecting the Electrochemical Performance of MoS_2–Carbon Composite Catalysts for Hydrogen Evolution Reaction: Surface Defect and Electrical Resistance of Carbon Supports

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1. Calculation of the number of active sites & turnover frequency (TOF)

To calculate the number of active sites of MoS_2 catalysts, cyclic voltammetry (CV) measurements were carried out in phosphate buffer solution (pH = 7). Before the measurements, phosphate buffer solution was deaerated by N_2 gas purging. The potential window was between -0.2 and 0.6 V versus reversible hydrogen electrode (RHE), and the scan rate was 50 mV/s for the CV measurements. The number of active sites of MoS_2 was calculated by equation (1).

$$n = Q/2F \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (1)$$

n; The number of active sites [mol]

Q; Voltammetric charges [C]

F; Faraday constant [96,485 C/mol]

First, the voltammetric charges obtained from the CVs in Figure 2e were divided by "2". The result was then divided by Faraday constant to get the total number of active sites of MoS_2 catalysts. Table S1 shows the total number of active sites and the number of active sites per area (0.25 cm^2).

When the number of active sites is known, the turnover frequencies can be calculated by equation (2).

$$TOF = I/2Fn \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (2)$$

I; Current obtained from polarization curve [A]

F; Faraday constant [96,485 C/mol)

n; The number of active sites [mol]

The current value should be divided by "2" since two electrons are involved in the formation of a H_2 molecule from two protons.

Table S1. The number of active sites (or divided by geometric area) calculated from CVs.

Sample	MoS_2/GCS@SiO_2 (G0)	MoS_2/GCS@SiO_2 (G1)	MoS_2/GCS@SiO_2 (G2)	MoS_2/GCS@SiO_2 (G5)
The number of active sites (mol)	1.46×10^{-8}	1.74×10^{-8}	3.34×10^{-8}	5.02×10^{-8}
The number of active sites per area (mol/cm^2)	5.83×10^{-8}	6.96×10^{-8}	1.33×10^{-7}	2.00×10^{-7}

2. Synthesis of MoS_2 NPs and preparation of working electrode using MoS_2 NPs

MoS_2 nanoaparticles (NPs) were prepared in the same manner as the synthesis of MoS_2 described in the main text except for the addition of GCS@SiO_2 NWs. To prepare the MoS_2 catalyst ink, MoS_2 NPs of 10 mg were well dispersed in a mixed solution of Nafion (60 μL) and isopropyl alcohol (800 μL). The catalyst ink solution was used to load the synthesized MoS_2 NPs on a Ti foil of 0.25 cm^2. After the deposited catalyst ink was sufficiently dried under air conditions, the Ti foil covered with MoS_2 NPs was used as a working electrode for the HER.

3. Structures of pristine Si NW and oxidized Si NW

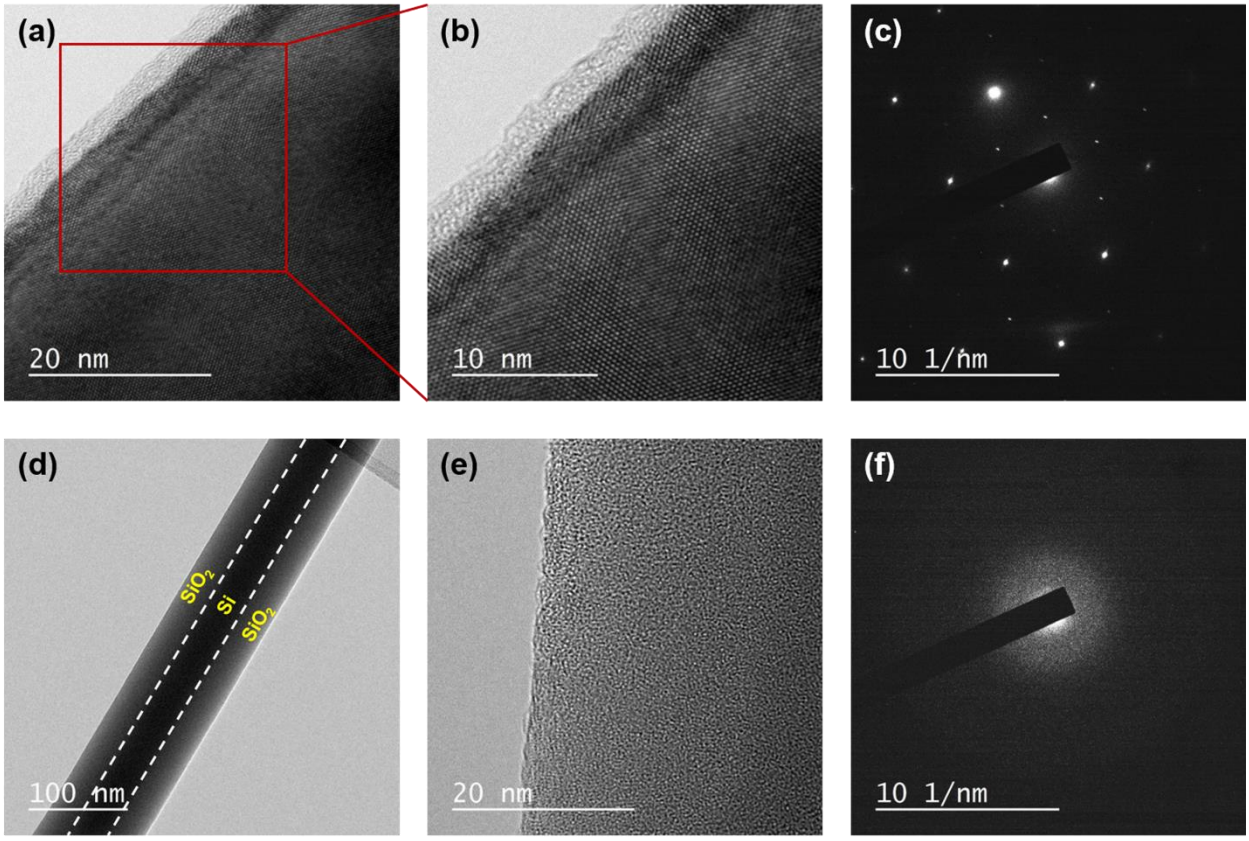

Figure S1. (a,b) TEM images of the pristine Si NW surface. (c) SAED pattern obtained at the position corresponding to the image of (b). (d) TEM image of oxidized Si NW having a thick SiO_2 layer formed by wet oxidation process. (e) Enlarged TEM image of the SiO_2 layer formed on the Si NW surface. (f) SAED pattern obtained from the SiO_2 layer.

4. XPS spectra of MoS_2/GCS@SiO_2 (G0)

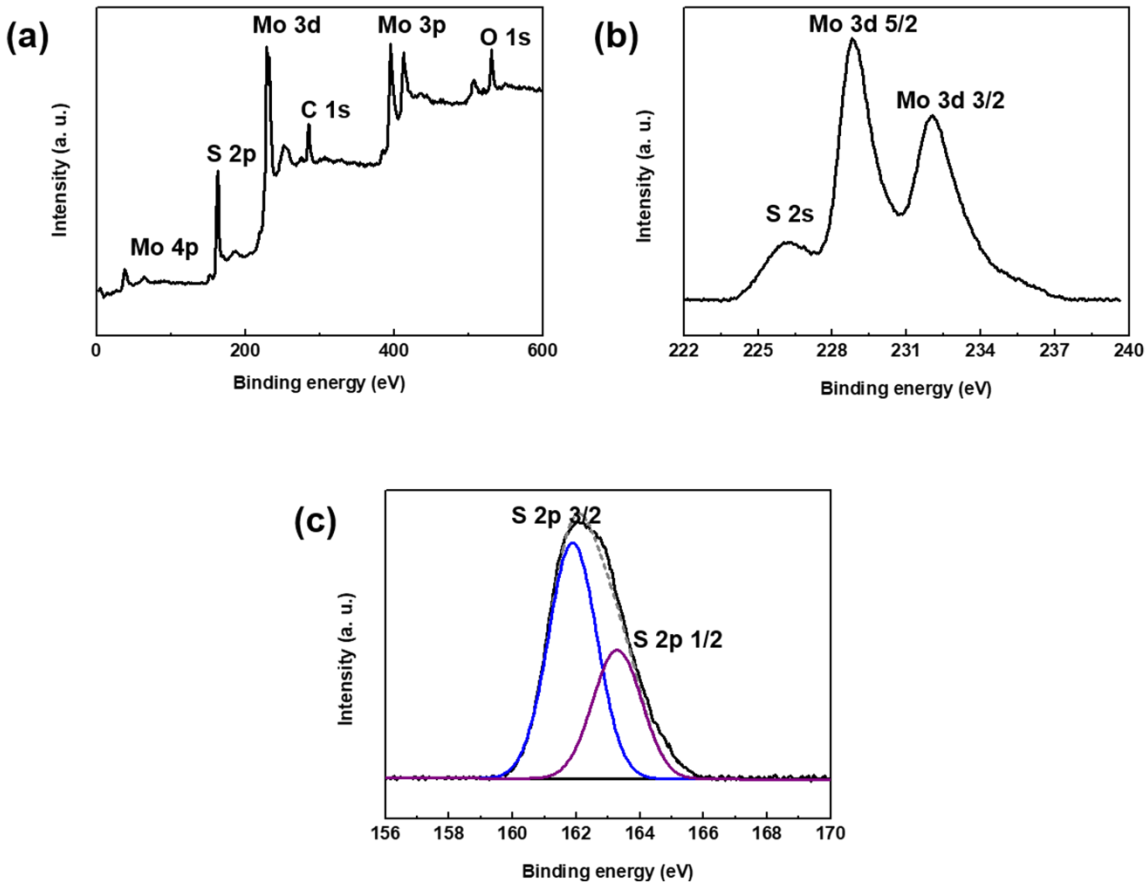

Figure S2. (a) Wide scan, (b) Mo 3d, and (c) S 2p XPS spectra for MoS_2/GCS@SiO_2 (G0)

5. Micro-device structure for resistance measurement of GCS@SiO_2 NWs

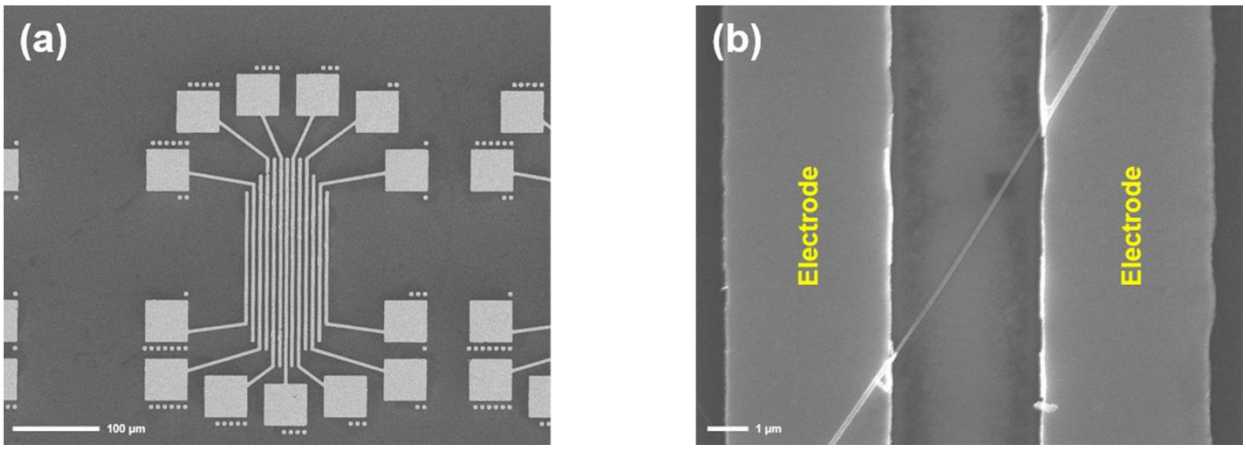

Figure S3. SEM images of (a) micro-device patterned for the resistance mesaurement of GCS@SiO_2 NWs and (b) a single GCS@SiO_2 NW loaded between two electrodes.

6. Resistivity of GCS@SiO_2 nanowires

To systematically analyze the electrical property of GCS@SiO_2 nanowires, the electrical resistances of "single" nanowires were measured using a micro-device consisting of two electrodes widely used in carbon nanomaterials research. For example, after a single GCS@SiO_2 nanowire is loaded between the electrodes, an I-V curve is measured and a resistance is calculated using Ohm's law. Meanwhile, the resistance is affected by dimensions such as the length and cross-sectional area of the nanowire as shown in equation (3).

$$R = \rho \frac{l}{A} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (3)$$

R: resistance [Ω]

ρ: resistivity [Ω·m]

l: length of conductive channel [m]

A: cross-sectional area of conductive channel [m^2]

Therefore, high resistance values (24 ~ 94 kΩ) for the single GCS@SiO_2 nanowires are obtained since the graphitic carbon shells (GCS) with very small thickness (2 ~ 10 nm) have extremely small cross-sectional areas compared to the length (several μm) of the nanowires.

To help your understanding, we have calculated the resistivity (ρ) of the nanowires through following assumptions.

1. GCS@SiO_2 nanowire has a perfect cylinder shape. (**Figure S4a**)
2. The diameter of the SiO_2 nanowire is 100 nm (**Figure S1d**), and the thickness of the GCS are estimated from TEM images. (**Figure 1b**)
3. Nanowire lies between two electrodes, and its channel length is 4 μm.

For example, in case of GCS@SiO_2 (G0), the thickness of GCS (G0) estimated from TEM image is 10 nm.

$$R = \rho \frac{l}{A}$$

$$2.4 \times 10^4\ \Omega = \rho \times \frac{4 \times 10^{-6}\ m}{\pi\ (60^2 - 50^2) \times 10^{-18}\ m^2}$$

$$\rho = 2.07 \times 10^{-5}\ \Omega \cdot m$$

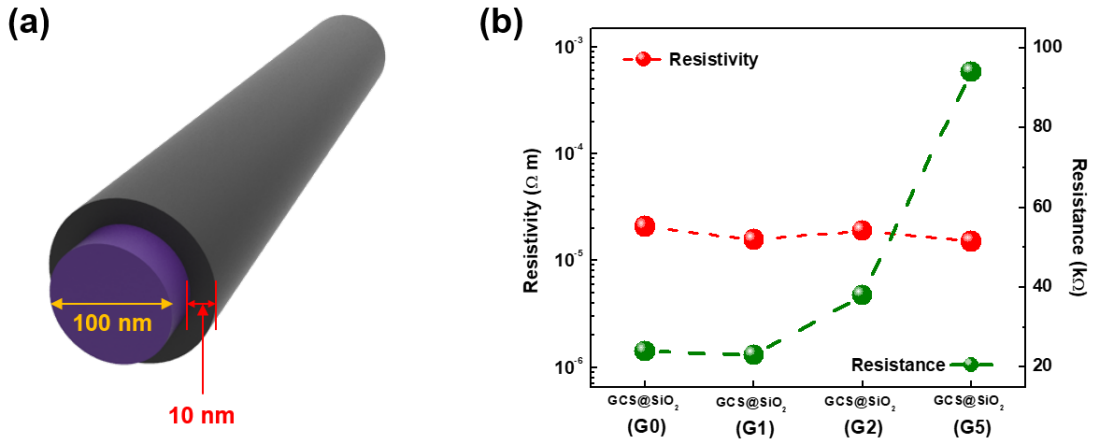

Figure S4. (a) Illustration of GCS@SiO_2 (G0) nanowire. (b) Resistivity and resistance values of GCS@SiO_2 (G0, G1, G2, and G5) nanowires.

The resistivity of other GCS@SiO_2 nanowires with 8, 6, and 2 nm thickness can be calculated in the same way. As a result, it is confirmed that the GCS@SiO_2 nanowires exhibit quite good electrical properties since a graphite generally has the resistivity value between 2.5×10^{-6} and 5×10^{-6} Ω·m.[1] Furthermore, in case of reduced graphene oxide (rGO), which has been widely used as support materials of MoS_2, rGO films have the electrical conductivity of 20 ~ 100 S/cm, and the electrical resistance of the individual rGO sheet is about 6×10^6 Ω when the gate voltage is zero.[2,3] Therefore, the resistances of the GCS@SiO_2 nanowires are comparable to those of general carbon materials, but they are properly controlled within an acceptable range by changing the thickness of the GCS coated on SiO_2 nanowire.

7. Electrochemical impedance spectroscopy (EIS) measurements of MoS_2/GCS@SiO_2

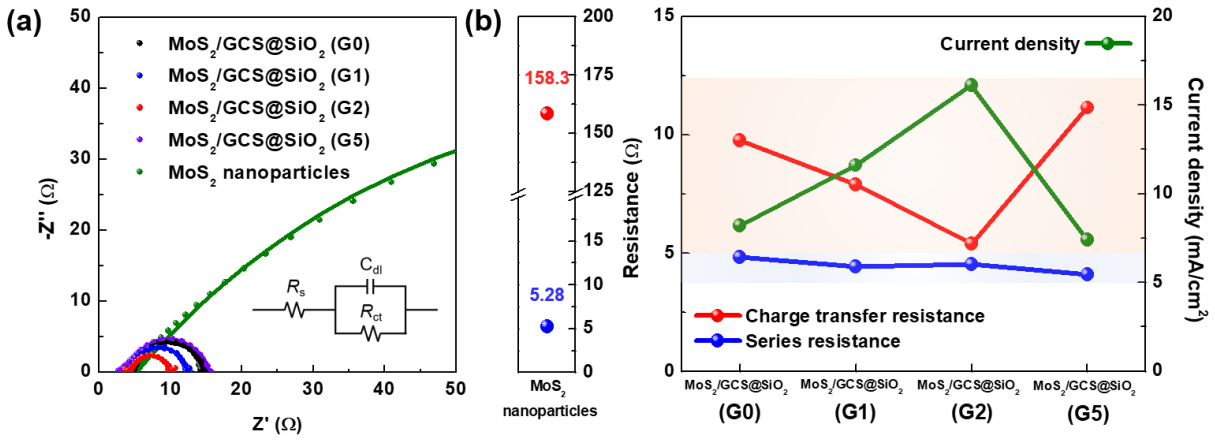

Figure S5. Nyquist plots of (a) MoS_2/GCS@SiO_2 (G0, G1, G2, and G5) and MoS_2 nanoparticles (Inset: equivalent circuit model; R_s: series resistance, R_{ct}: charge transfer resistance, C_{dl}: double layer capacitance). (b) Correlation among R_{ct}, Rs, and current density measured at -0.2 V for the samples.

Table S2. Comparison of series resistance (R_s) and charge transfer resistance (R_{ct}).

Materials	Series resistance (Ω)	Charge transfer resistance (Ω)
MoS_2/GCS@SiO_2 (G0)	4.83	9.76
MoS_2/GCS@SiO_2 (G1)	4.43	7.9
MoS_2/GCS@SiO_2 (G2)	4.53	5.39
MoS_2/GCS@SiO_2 (G5)	4.1	11.15
MoS_2 nanoparticles	5.28	158.3

REFERENCES

(1) Pierson, H. O. Handbook of Carbon, Graphite, Diamond, and Fullerenes: Properties, Processing, and Applications, p. 61, William Andrew, **1993**.

(2) Mohan, V. B.; Brown, R.; Jayaraman, K.; Bhattacharyya, D. Characterisation of Reduced Graphene Oxide: Effects of Reduction Variables on Electrical Conductivity. Mater. Sci. Eng. B **2015**, 193, 49-60.

(3) Gomez-Navarro, C.; Weitz, R. T.; Bittner, A. M.; Scolari, M.; Mews, A.; Burghard, M.; Kern, K. Electronic Transport Properties of Individual Chemically Reduced Graphene Oxide Sheets. Nano Lett. **2007**, 7, 3499-3503.