# Electronic Supplementary Information

# Nickel Sulfide Nanocrystals for Electrochemical and

# **Photoelectrochemical Hydrogen Generation**

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References

### **Experimental Details**

*Characterization.* Scanning electron microscopy (SEM, Hitachi S-4700), field-emission transmission electron microscopy (FETEM, FEI TECNAI G<sup>2</sup>, 200 kV), high-voltage TEM (Jeol JEM ARM 1300S, 1.25 MV), and energy-dispersive X-ray fluorescence spectroscopy (EDX) The structure and composition of the products were analyzed by s. Fast Fourier transform (FFT) images were generated by inversion of the TEM images using Digital Micrograph GMS1.4 software (Gatan Inc.). A tilt holder (Dual Orientation Tomography Holder 927, Gatan Co.) was used for the TEM measurements. High-resolution X-ray diffraction (XRD) patterns were obtained using the 9B and 3D beamlines of the Pohang Light Source (PLS) with monochromatic radiation ( $\lambda = 1.54595$  Å). XRD pattern measurements were also carried out in a Rigaku D/MAX-2500 V/PC using Cu K<sub>a</sub> radiation ( $\lambda = 1.54056$  Å). X-ray photoelectron spectroscopy (XPS) data were collected using the 8A1 beam line of the PLS with a photon energy of 600 or 640 eV. XPS measurements were also performed using a laboratory-based spectrometer (Thermo Scientific Theta Probe) using a photon energy of 1486.6 eV (Al Ka). A UV-Vis-IR spectrometer (Agilent Cary 6000) was used to measure the diffuse reflectance spectrum of samples.

*Electrochemical Measurements of HER/OER*. Experiments were carried in a three-electrode cell connected to an electrochemical analyzer (CompactStat, Ivium Technologies). An Ag/AgCl electrode (saturated with 4 M KCl, Pine Co.) was used as reference electrode. A graphite rod (6 mm dia. × 102 mm long, 99.9995%, Pine Instrument) was used as counter electrode. The NiS<sub>x</sub> (2.5 mg cm<sup>-2</sup>)-deposited carbon cloth pieces were loaded in a polytetrafluoroethylene (PTFE) holder (Wizmac Co., Multifunctional Electrode Holder) as working electrode. For HER and OER electrocatalysis, H<sub>2</sub> and O<sub>2</sub> (ultrahigh grade purity) gas,

respectively, was bubbled with a flow rate of 20 sccm during the measurement. Linear sweeping voltammetry (LSV) of HER electrocatalysis was measured from 0 to -0.8 V (vs. RHE) with a scan rate of 5 mV s<sup>-1</sup>. LSV curves of OER electrocatalysis was measured from 1.0 to 1.8 V (vs. RHE) with a scan rate of 5 mV s<sup>-1</sup>. The electrolyte was purged with  $H_2$  or  $O_2$  (ultrahigh grade purity) gas during the measurement.

*Electrochemical impedance spectroscopy (EIS) and Mott-Schottky (MS) plot.* For the Sibased PEC cells, the EIS measurements were performed under dark and light irradiation (100 mW cm<sup>-2</sup>) by applying an AC voltage of 20 mV in the frequency range of 1 MHz–0.1 Hz. In the case of CC electrode, the EIS measurements were carried out in an electrolyte by applying an AC voltage of 10 mV in the frequency range of 100 kHz to 0.1 Hz. Mott-Schottky plots were obtained using 0.5, 1, and 2 kHz. The collected data were analyzed using the MS equation as follows:  $C^{-2} = 2(\varepsilon \varepsilon_0 A^2 e N_D)^{-1} (E - E_{fb} - e k_B T)$ , where *C* is the interfacial capacitance, *A* is the effective roughness factor (or interfacial area),  $\varepsilon$  is the dielectric constant of the sample,  $\varepsilon_0$  is the permittivity of free space (8.85 × 10<sup>-12</sup> J<sup>-1</sup> C<sup>2</sup> m<sup>-1</sup>), *e* is the electron charge (1.6 × 10<sup>-19</sup> C),  $N_D$  is the number of carriers, E is the applied voltage (V vs. RHE),  $E_{fb}$  is the flat-band potential,  $k_B$  is the Boltzmann constant (1.38 × 10<sup>-23</sup> J K<sup>-1</sup>), and T is the absolute temperature (K).

*Water-splitting PEC cell*. The backside of NW substrate was connected to a copper (Cu) wire (diameter = 1 mm) using Ga/In eutectic alloy ( $\geq$  99.99%, Sigma-Aldrich) and conductive silver paste (resistivity = < 50 µΩ·cm, Dotite D-500, Fujikura Kasei Co.), and then covered with epoxy glue (Hysol 1C, Loctite). The exposed area of the front side was usually 0.25 cm<sup>2</sup>. The PEC cells with a three-electrode system was characterized using an electrochemical analyzer (CompactStat, Ivium Technologies). A 450 W Xe lamp (EUROSEP Instruments) was used

with an AM1.5G filter, and the light intensity (100 mW cm<sup>-2</sup>) was calibrated using a Si solar cell (Abet Technologies, Model 15150 Reference Cell).

When the Si NW electrodes were used as photocathode in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte (pH 0), a saturated calomel electrode (SCE, saturated KCl, Basi Model RE-2BP) was used as the reference electrode, while a Pt wire (0.5 mm dia., Pine Instrument) was used as the counter electrode. In pH 14, an Ag/AgCl electrode (saturated with 4 M KCl, Pine Co.) was used as reference electrode. The potentials were referenced to the reversible hydrogen electrode (RHE). The potential (E), measured against the SCE electrode (used in pH 0), was converted to the potential versus the RHE: E (V vs. RHE) = E (V vs. SCE) +  $E_{SCE}$  (= 0.241 V) + 0.0592 pH = E (V vs. SCE) + 0.241 V. At pH 14, the potentials (E) versus RHE was E (vs. RHE) = E (vs. Ag/AgCl) +  $E_{Ag/AgCl}$  (= 0.197 V) + 0.0592 pH = E (vs. Ag/AgCl) + 1.0258 V.

The hydrogen (H<sub>2</sub>) and oxygen (O<sub>2</sub>) gas evolution in the PEC cells was monitored using gas chromatography (GC, Young Lin ACME 6100). The electrolyte was purged with helium gas ( $\geq$ 99.999%). A pulsed discharge detector (VICI, Valco Instruments Co., Inc.) and a GC column (SUPELCO Molecular Sieve 13X) were used. The quantities of H<sub>2</sub> were calibrated using standard H<sub>2</sub>/He and O<sub>2</sub>/He mixtures. The amount of H<sub>2</sub> was calibrated using standard H<sub>2</sub>/He mixtures, respectively. Faradaic efficiency (FE) for H<sub>2</sub> generation was calculated using the

equations:  $FE = \frac{2 \times N_{H_2} \times 96485}{Q}$ , where  $N_{H_2}$  is the amounts (in mol) of H<sub>2</sub>, and Q is the generated charge (= photocurrent × time) in Coulomb.

		HER at pH 0		HER at pH 14	
No.	Materials	η (mV)	Tafel slope	η (mV)	Tafel slope
		at 10 mA cm <sup>-2</sup>	$(mV dec^{-1})$	at 10 mA cm <sup>-2</sup>	$(mV dec^{-1})$
<b>S</b> 1	NiS <sub>2</sub> on glassy carbon		42		
S2	NiS <sub>2</sub> on graphite	150	41	200	80
S3	β-NiS (rhombohedral phase)	220			
S4	NiS <sub>2</sub> nanowires	450	83.5		
S5	Carbon-coated β-NiS	85	46	232	89
Our work	NiS and NiS <sub>1.97</sub> on carbon cloth	216 257	66 84	203 259	96 126

**Table S1**. Comparison of HER performance of NiS and NiS<sub>2</sub> in the literatures; overpotential  $(\eta)$  at current density of 10 cm<sup>2</sup> and Tafel slope.

			HER		OER at pH 14		
No.	Materials	nH	η (mV) at 10	Tafel slope	η (mV) at 10	Tafel slope	
		РП	mA cm <sup>-2</sup>	(mV dec <sup>-1</sup> )	mA cm <sup>-2</sup>	(mV dec <sup>-1</sup> )	
	NiS		474	124			
S6	NiS <sub>2</sub>	14	454	128			
	Ni <sub>3</sub> S <sub>2</sub>		355	97			
	NiS <sub>2</sub>	0	174	63			
S7		14	148	82			
	NiS	14			320	59	
<b>S</b> 8	V-doped NiS <sub>2</sub>	14	110	90	290	45	
S9	NiS <sub>2</sub>	14	165	136	246	94.5	
S10	Ni <sub>3</sub> S <sub>2</sub> /CdS	14	121	110	270	174	
S11	$Ni_2P/Ni_3S_2$	14	80	65	210	62	
S12	$Ni_3S_2/MoS_2$	14	99	71	185	46	
	NiS		190	142.3	548	255.3	
<b>G12</b>	NiS <sub>2</sub>	14	150	119.5	449	183.8	
515	NiS/NiS <sub>2</sub>	14	100	95.1	416 for 100	156.5	
					mA cm <sup>-2</sup>		
S14	Ni <sub>3</sub> S <sub>2</sub>	14	300	100	400	112	
\$15	CoS <sub>x</sub> /Ni <sub>3</sub> S <sub>2</sub>	14	204	122.22	280 for 20	105 /	
515	@carbon	14	204	155.52	mA cm <sup>-2</sup>	103.4	
\$16	CdS@Ni <sub>3</sub> S <sub>2</sub>	14	142	129.6	310 for 20	176 0	
510	@Ni foam	14	142	138.0	mA cm <sup>-2</sup>	1/0.8	
	NiS		160	93	357	92	
S17	NiS <sub>2</sub>	14	227	110	375	138	
	$Ni_3S_2$		112	67	295	52	
	NiS		220	145	322	108	
S18	NiS <sub>2</sub>	14	147	105	241	65	
	Ni <sub>3</sub> S <sub>4</sub>		187	124	270	72	
Our	NiS	14	203	96	338	114	
work	NiS <sub>1.97</sub>	14	259	126	383	142	

**Table S2**. Comparison of HER/OER performance (in pH 14) of NiS<sub>x</sub> in the literatures; overpotential ( $\eta$ ) at current density of 10 cm<sup>2</sup>, Tafel slope, and turn-of-frequency (TOF).

No.	Materials (electrolyte)	Onset potential (V) vs. RHE	J <sub>0</sub> (mA cm <sup>-2</sup> )	J <sub>max</sub> (mA cm <sup>-2</sup> )	ABPC (%)	η <sub>H2</sub> (%)
S19	SrTiO <sub>3</sub> /Si (0.5 M H <sub>2</sub> SO <sub>4</sub> )	0.45	25	35 at -0.1 V	4.9	
S20	MoS <sub>3</sub> @Si nanowires	0.37	25	35 at -0.4 V	2.26	
S21	Si nanohole	0	5	30 at -0.3 V		
S22	CoP/Si microwires (0.5 M H <sub>2</sub> SO <sub>4</sub> )	0.48	16	17 at -0.2 V	1.9	
S23	CoSe <sub>2</sub> /Si microwires (0.5 M H <sub>2</sub> SO <sub>4</sub> )	0.3	9	14 at -0.15 V		
S24	FeP <sub>2</sub> /Si nanowires (0.5 M H <sub>2</sub> SO <sub>4</sub> /0.5 M K <sub>2</sub> SO <sub>4</sub> )	0.43	14	15 at 0.1 V	2.64	
S25	MoS <sub>x</sub> Cl <sub>y</sub> /n <sup>+</sup> pp <sup>+</sup> Si pyramid (0.5 M H <sub>2</sub> SO <sub>4</sub> )	0.41	43	43 at 0 V	6.17	100
S26	NiCoSe <sub>x</sub> /p-Si nanopillar (0.5 M H <sub>2</sub> SO <sub>4</sub> )	0.25	37.5	37.5 at 0 V		
S27	Co-doped MoS <sub>2</sub> /p-Si (0.5 M H <sub>2</sub> SO <sub>4</sub> )	0.192	17.2	30 at -0.2 V		
S28	NiMo/NiSi/p-Si Microwire (1 M KOH)	0.551	29.8	29.8 at 0 V	10.1	
S29	NiSe <sub>2</sub> @Si nanowires (0.5 M H <sub>2</sub> SO <sub>4</sub> )	0.2	6.7	10 at -0.5 V		
S30	Ni–Mo/Ni/Si/n <sup>+</sup> np <sup>+</sup> - Si (1 M KOH)	0.5	36.3	36.3 at 0 V	7	
S31	MoS <sub>2</sub> on Si NWs	0.26	16.5	35 at 0.3 V		
S32	Ag@MoS <sub>2</sub> on Si Naboshere	0.11	5	33.2 at -0.4 V		
Our	NiS@Si nanowires (0.5 M H <sub>2</sub> SO <sub>4</sub> )	0.2	10	30 at -0.25 V		90
work	(1 M KOH)	0.2	11	23 at -0.3 V		

**Table S3**. Comparison of PEC performance of Si nanostructure photocathode in the literatures; onset potential (vs. RHE), current density at 0 V ( $J_0$ ), maximum applied bias photon-to-current (ABPC) or photon-to-H<sub>2</sub> (or O<sub>2</sub>) efficiency, and faradic efficiency for H<sub>2</sub> evolution ( $\eta_{H2}$ )



**Figure S1**. (a) TEM images and (b) XRD patterns of Ni(OH)<sub>2</sub> nanosheets. (a = 3.08 Å and c = 23.41 Å)

The Ni(OH)<sub>2</sub> exhibits a morphology of flower-like thin nanosheets. The XRD peaks were matched to those of rhombohedral phase  $\alpha$ -Ni(OH)<sub>2</sub> with JCPDS Card No. 38-0715 (a = 3.439 and c = 5.324 Å).



**Figure S2.** XRD pattern of NiS and NiS<sub>1.97</sub> NCs as free-standing form and deposited form on CC (CC-NiS and CC-NiS<sub>1.97</sub>), before/after the stability test of HER in 0.5 M  $H_2SO_4$ .

The peaks of the samples were referenced to those of hexagonal phase NiS with JCPDS Card No. 77-1624 (P6<sub>3</sub>/mmc, a = 3.439 and c = 5.324 Å) and cubic phase NiS<sub>1.97</sub> with JCPDS Card No. 83-0574 (Pa, a = 5.686 Å). All XRD peaks of NiS and NiS<sub>1.97</sub> NCs were matched to those of the references. The same crystal phase maintained during the HER.



**Figure S3**. XRD pattern of Si-NiS and Si-NiS $_{1.97}$  before/after the PEC test in 0.5M H<sub>2</sub>SO<sub>4</sub>. The reference peaks of JCPDS Card were shown.

The XRD peaks of Si-NiS and Si-NiS<sub>1.97</sub> were matched to those of hexagonal phase NiS with JCPDS Card No. 77-1624 (P6<sub>3</sub>/mmc, a = 3.439 and c = 5.324 Å) and cubic phase NiS<sub>1.97</sub> with JCPDS Card No. 83-0574 (Pa, a = 5.686 Å), respectively. The peaks at  $2\theta = 47.7^{\circ}$  and 56.6° are assigned to Si (220) and Si (311), respectively, because they are matched with the reference value of cubic phase Si (JCPDS Card No. 80-0018, F3m, a = 5.392 Å). The crystal phase of NCs maintained before/after the PEC test.



**Figure S4**. Fine-scanned Ni  $2p_{3/2}$  and  $2p_{1/2}$  peaks of NiO and Ni<sub>3</sub>S<sub>2</sub> powders. The position of the neural element (Ni<sup>0</sup>) peaks ( $2p_{3/2}$  at 852.7 eV and  $2p_{3/2}$  at 870.0 eV) is marked by a dotted line to delineate the shift.

NiO (99.99% trace metal basis) powders were purchased from Sigma-Aldrich. The  $2p_{3/2}$  peak consisted of three bands at 853.7, 855.4, and 860.7 eV. They were blue shifted by 1.0, 2.3, and 8.0 eV from the peak position of neutral Ni<sup>0</sup> (852.7 eV), respectively. The first and second bands were assigned to the Ni-O bonding structures of Ni<sup>2+</sup> and Ni<sup>3+</sup> ions, respectively. The third peak corresponds to a shake-up satellite peak of Ni<sup>3+</sup> ions.

Ni<sub>3</sub>S<sub>2</sub> (99.7% trace metal basis) powders were purchased from Sigma-Aldrich. The  $2p_{3/2}$  peaks show the bands at 852.5 and 855.4 eV. The position of first band is almost the same as that of neutral Ni<sup>0</sup> and the second band is blue shifted by 2.3 eV from the peak position of neutral Ni<sup>0</sup>. The first and second bands were assigned to the metallic Ni of Ni-S and the Ni<sup>3+</sup> ions of Ni-O bonding structures, respectively. The shake-up satellite peak appears at 860.7 eV due to the Ni<sup>3+</sup> ions.



**Figure S5**. XPS of CC-NiS and CC-NiS<sub>1.97</sub> NCs. Fine-scanned (a) Ni 2*p* and (b) S 2*p* peaks of as-grown samples; (c) Ni 2*p* and (d) S 2*p* peaks after the stability test of HER in 0.5 M H<sub>2</sub>SO<sub>4</sub> The data points (open circles) are fitted by Voigt functions, and the sum of the resolved bands is represented by black lines. The position of the neutral peak (Ni<sup>0</sup> and S<sup>0</sup>) is marked by a dotted line to delineate the shift.

(a) The Ni  $2p_{3/2}$  peak of NiS is resolved into three bands: Ni-S (N1) at 852.7 (0) eV, Ni(III)-O (N2) at 855.5 (2.8) eV, and satellite at 860.8 (8.1) eV. The peak of NiS<sub>1.97</sub> consisted of Ni-S (N1) at 853.7 (1.0) eV, N(III)-O (N2) at 857.5 (4.8) eV, and satellite at 862.4 (9.7) eV. The number in parentheses represents the blue shift relative to neutral Ni (Ni<sup>0</sup>) at 852.7 eV. The NiS NCs exhibit the N1 band at the position of the neural Ni (marked by magenta dotted line), while the NiS<sub>1.97</sub> NCs exhibit the 1 eV blue-shifted N1 band from the neural Ni, indicating

more metallic phase of NiS. NiS has stronger peak intensities in the N2 and N3 bands compared to the  $NiS_{1.97}$ , indicating it contains a higher fraction of surface oxide layers.

(b) The S  $2p_{3/2}$  and S  $2p_{1/2}$  peaks are separated by about 1.2 eV. The NiS shows the S  $2p_{3/2}$  and S  $2p_{1/2}$  peaks at 161.3 and 162.5 eV, respectively, which are 2.7 eV red-shifted with respect to the S<sup>0</sup> ( $2p_{3/2}$  at 164.0 eV marked by magenta dotted line). These peaks were resolved into four bands; two each for the Ni-S (S1 band at 161.3 and 162.5 eV, red) and the S vacancies/defects (e.g.,  $S_2^{2-}$  anions, S2 bands at 163.7 and 165 eV, green). Another peak (S3 band, blue) at 168.2 eV is assigned mainly to the S-O bond of surface oxide. For NiS<sub>1.97</sub>, the peaks (S1 band) appear at 162.5 and 163.7 eV, which are 1.5 eV red-shifted with respect to the signal of S<sup>0</sup>, corresponding to the S anions bonded with the Ni cations. The larger red shift of NiS than that of NiS<sub>1.97</sub> (2.7 vs. 1.5 eV) corresponds to more negative charged S atoms due to their metallic nature. The NiS has the stronger S-O bands compared to the NiS<sub>1.97</sub>, indicating more surface oxide layers.

(c) The Ni  $2p_{3/2}$  peak of CC-NiS (after HER) is resolved into three bands: Ni-S (N1) at 852.9 eV, Ni(III)-O (N2) at 856.7 eV, and satellite at 861.8 eV. The peak of NiS<sub>1.97</sub> consisted of Ni-S (N1) at 853.7 eV, N(III)-O (N2) at 857.9 eV, and satellite at 862.5 eV. The more metallic N1 band of NiS NCs than that of NiS<sub>1.97</sub> NCs maintains after HER. The fraction of N1 band decreases while that of N2 and N3 bands increases during the HER.

(d) For NiS, the S 2*p* peak was resolved into four bands; two each for the Ni-S (S1 bands at 161.0 and 162.1 eV) and the S vacancies/defects (e.g.,  $S_2^{2-}$  anions, S2 bands at 163.2 and 165.4 eV). The S-O peak (S3 bands) appears at 168.8 eV. For NiS<sub>1.97</sub>, the S 2*p* peak were resolved into Ni-S (S1 bands at 162.5 and 163.6 eV), S vacancies/defects (e.g.,  $S_2^{2-}$  anions, S2 bands at 163.7 and 164.8 eV), and S-O peak (S3 bands) at 169.0 eV. The S-O peak becomes more significant after the HER (see the XPS data before HER, Figure S10). The larger red shift of NiS than that of NiS<sub>1.97</sub> (3.0 vs. 1.5 eV) due to their metallic nature persists after HER.



**Figure S6.** (a) XPS valence band (VB) spectra of Si-NiS and Si-NiS<sub>1.97</sub> showing the valence band position. (b) UV–visible-IR diffuse reflectance spectra (plotted in absorption mode) of NiS and NiS<sub>1.97</sub> NCs (as freestanding form), and Tauc plot of  $[F(v)hv]^{1/2}$  of NiS NCs as a function of photon energy (hv).

The positions of the valence band maximum (VBM) (vs. vacuum level) were evaluated by linear extrapolation of the onset in the XPS VB spectra. Owing to the short probe depth of photoelectrons (<1 nm at ~630 eV), the XPS peak probably originated from the surface region, which means that the VB data cannot provide information about NiS or NS<sub>1.97</sub>. The onset of NiS and NiS<sub>1.97</sub> appears at 2.1 and -0.5 eV, respectively. The higher VBM position of NiS is due to the more surface oxide layers. The onset at 0 eV is ascribed to the VBM of NiS.

We estimated the band gap from the UV-visible-IR diffuse reflectance spectra, F(v) in absorption mode, as displayed in (b). The absorption starts below 0.5 eV (inset), indicating that the band gap is lower than 0.5 eV. Based on the Kubelka–Munk (K–M) transformation, the Tauc plot of  $[F(v)hv]^{1/2}$  vs. photon energy (hv) allowed linear interpolation of the indirect band gap. For NiS, the shoulder at ~2 eV is correlated with the surface oxide, and consistent with the XPS VB spectrum.



**Figure S7**. Nyquist plots of CC-NiS and CC-NiS<sub>1.97</sub> for EIS experiments in the frequency range from 1 MHz to 0.1 Hz. The applied potential is 0 V (vs. RHE) for (a) HER in 0.5 M  $H_2SO_4$  (pH 0) and (b) HER in 1 M KOH (pH 14), and (c) 1.23 V (vs. RHE) for OER in 1 M KOH (pH 14). (d) Equivalent circuit for the fitting curves represented by the solid lines. The fitting parameters are summarized in Table S4.

**Table S4.** Impedance fitting parameter  $R_e$  represents the internal resistance of the electrolyte,  $R_{ct}$  is associated with the charge transfer resistance between the electrode and electrolyte, and CPE represents the constant-phase element related to the double-layer capacitance.

	Samples	$R_{e}\left(\Omega ight)$	CPE (mF)	$R_{ct}(\Omega)$
HFR (nH 0)	NiS	3.01	2.99	13.8
fill(pff 0)	NiS <sub>1.97</sub>	3.12	2.85	27.3
HFR $(nH 14)$	NiS	4.34	3.50	9.05
merc (pri 14)	NiS <sub>1.97</sub>	5.01	3.02	50.96
OFR (pH 14)	NiS	4.15	3.42	9.87
OLK (pi 14)	NiS <sub>1.97</sub>	4.14	3.28	16.4



Figure S8. HAADF STEM image, EDX elemental mapping of Ni (L-shell), S (L-shell), and O (K-shell), and EDX spectrum of (a) CC-NiS and (b) CC-NiS<sub>1.97</sub> after the HER 2h in 0.5 M  $H_2SO_4$ .

After the HER, the oxide shell of NiS NCs remains the same as that of before. In contrast, the  $NiS_{1.97}$  NCs have the less oxide shell before/after the PEC, compared to the NiS NCs. The atomic ratio of Ni:S is about 1:1 and 1:2, for NiS and NiS<sub>1.97</sub>, respectively, which is similar to the ratio before HER.



**Figure S9**. XPS of the Si photocathode after 2h PEC (under the irradiation of AM1.5G, 100 mW cm<sup>-2</sup>) in 0.5 M H<sub>2</sub>SO<sub>4</sub>; fine-scanned (a) Ni 2*p* and (b) S 2*p* peaks of Si-NiS and Si-NiS<sub>1.97</sub>. The data points (open circles) are fitted by Voigt functions, and the sum of the resolved bands is represented by black lines. The position of the neutral peak (Ni<sup>0</sup> and S<sup>0</sup>) is marked by a dotted line to delineate the shift.

The Ni  $2p_{3/2}$  peak of Si-NiS was resolved into three bands: Ni-S (N1) at 852.3 eV, N(III)-O (N2) at 855.2 eV, and satellite at 860.8 eV. The peak of Si-NiS<sub>1.97</sub> consisted of Ni-S (N1) at 852.7 eV, N(III)-O (N2) at 854.7 eV, and satellite at 858.2 eV. The fraction of N1 band decreases while that of N2 and N3 bands increases during the PEC (see Figure 3 in text). The peak feature of S 2p shows that the Ni-S bonding structures is almost the same as that before PEC. However, the intensity of S-O peak at 169 eV increases during the PEC. We conclude that the metallic nature of NiS and the semiconducting nature of NiS<sub>1.97</sub> persist during the PEC, although the surface oxidation occurs.



(c) Si-NiS







**Figure S10**. HAADF STEM image, EDX elemental mapping (Ni L-shell, S L-shell, O K-shell, and Si K-shell, peaks), and EDX spectrum of (a) Si-NiS and (b) Si-NiS<sub>1.97</sub> after 2h PEC. HAADF STEM image and EDX elemental mapping of individual (c) NiS and (d) NiS<sub>1.97</sub> NCs deposited on Si NWs, before/after the PEC.

After the PEC, the NCs remain on the Si NWs and the ratio of Ni:S is about 1:1 and 1:2, respectively, for Si-NiS and Si-NiS<sub>1.97</sub>, which are nearly the same as those of before sample. The EDX mapping of individual NCs before/after the PEC shows that the NiS NCs consisted of the NiS core and the oxide shell, and the core-shell structures are persistent during the PEC reaction. In contrast, the NiS<sub>1.97</sub> NCs have the less oxide layers for before/after the PEC, compared to the NiS NCs. The atomic ratio of Ni:S decreases slightly after the PEC due to the surface oxidation, which is consistent with the XPS shown in Figure S9.



**Figure S11**. Nyquist plots of Si-NiS and Si-NiS<sub>1.97</sub> in 0.5 M H<sub>2</sub>SO<sub>4</sub> (pH 0) measured for EIS in the frequency range from 1 MHz to 0.1 Hz, under (a) dark and (b) AM1.5G irradiation (100 mW cm<sup>-2</sup>). The applied potential is 0 V (vs. RHE) for HER. The equivalent circuit is shown in the inset of (a), and the fitting curves are represented by the solid lines.

Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range of 1 MHz-0.1 Hz and an AC amplitude of 20 mV. In the high-frequency limit and under non-Faradaic conditions, the electrochemical system is approximated by the modified Randles circuit as shown in the inset of (a), where  $R_e$  denotes the internal resistance of the electrolyte, CPE is a constant-phase element related to the double-layer capacitance, and  $R_{ct}$  is the charge-transfer resistance from any residual Faradaic processes. A semicircle in the low-frequency region of the Nyquist plots represents the charge transfer process, with the diameter of the semicircle reflecting the charge-transfer resistance. The real (Z') and negative imaginary (-Z'') components of the impedance are plotted on the x and y axes, respectively. Simulating the EIS spectra using an equivalent circuit model allowed us to determine  $R_{ct}$ , which is a key parameter for characterizing the catalyst-electrolyte charge transfer process. Two semicircles appear for both samples. The simulation of EIS spectra (fitted lines) using an equivalent circuit model yielded the  $R_{ct}$  values ( $R_{ct1}$  and  $R_{ct2}$ ), with the corresponding CPE (CPE<sub>1</sub> and CPE<sub>2</sub>). Under dark, the value of  $R_{ct}$  (=  $R_{ct1}$  +  $R_{ct2}$ ) is 294.7 and 498.2  $\Omega$ , respectively, for Si-NiS and Si-NiS<sub>1.97</sub>. The smaller  $R_{ct}$  value of Si-NiS than that of Si-NiS<sub>1.97</sub> indicates more

efficient charge transfer at the electrode-electrolyte interface. Under light irradiation, the  $R_{ct}$  value reduced to 45.2 and 168.9  $\Omega$ , respectively, suggesting that the photoinduced charge transfer at the electrode-electrolyte interface is greatly enhanced. The fitting parameters are summarized in Table S5.

		$R_{e}(\Omega)$	$R_{ct1}(\Omega)$	$R_{ct2}(\Omega)$	R <sub>ct-tot</sub>
Dark	Si-NiS	0.0001	81.7	213.0	294.7 Ω
Durk	Si-NiS <sub>1.97</sub>	2.95	176.5	321.7	498.2 Ω
Light	Si-NiS	0.0001	28.1	17.1	45.2 Ω
Eight	Si-NiS <sub>1.97</sub>	1.19	128.2	40.7	168.9 Ω

 Table S5. Impedance fitting parameters.



**Figure S12**. Mott-Schottky plots at 0.5, 1, and 2 kHz for Si-NiS and Si-NiS<sub>1.97</sub> in 0.5 M H<sub>2</sub>SO<sub>4</sub> (pH 0). The flat-band potentials are obtained from the intercepts of the extrapolated lines; 0.40 V for Si-NiS and 0.16 V for Si-NiS<sub>1.97</sub>. The reciprocal of the slope in the MS plots gives information for the carrier concentrations in the samples (see Experimental details), which are much larger by 170 times in the Si-NiS than in the Si-NiS<sub>1.97</sub>.

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