Supplementary Information

Integrated Cobalt Disulfide (CoS_2) Co-catalytic Passivation Layer on Silicon Microwires for Photoelectrochemical Hydrogen Evolution

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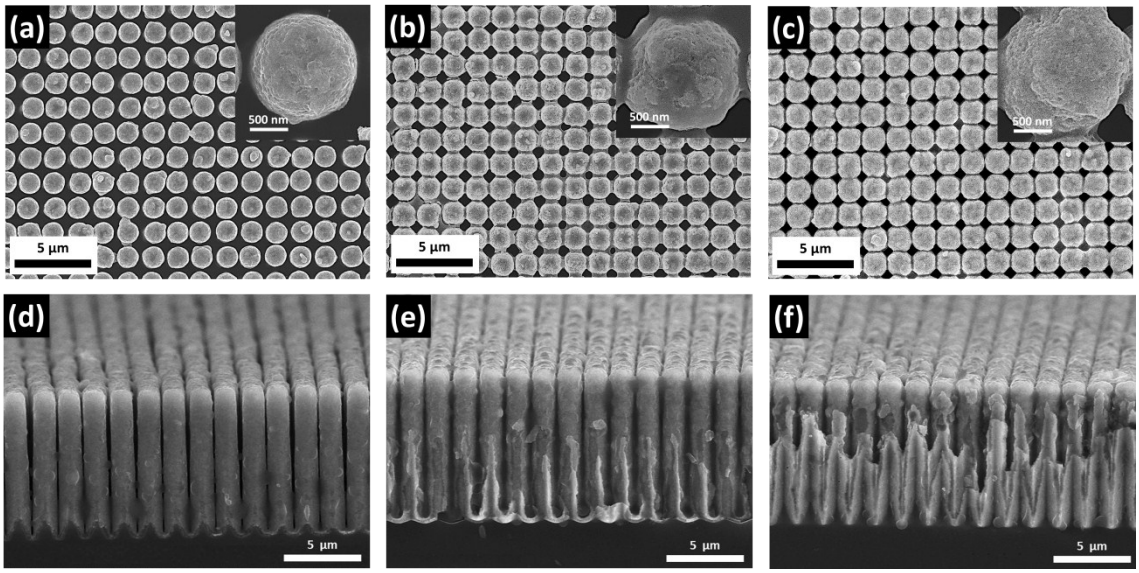

Fig. S1 (a–c) Top view and (d–f) cross-sectional SEM images of CoS_2-Si-200, CoS_2-Si-280, and CoS_2-Si-310 microwire arrays.

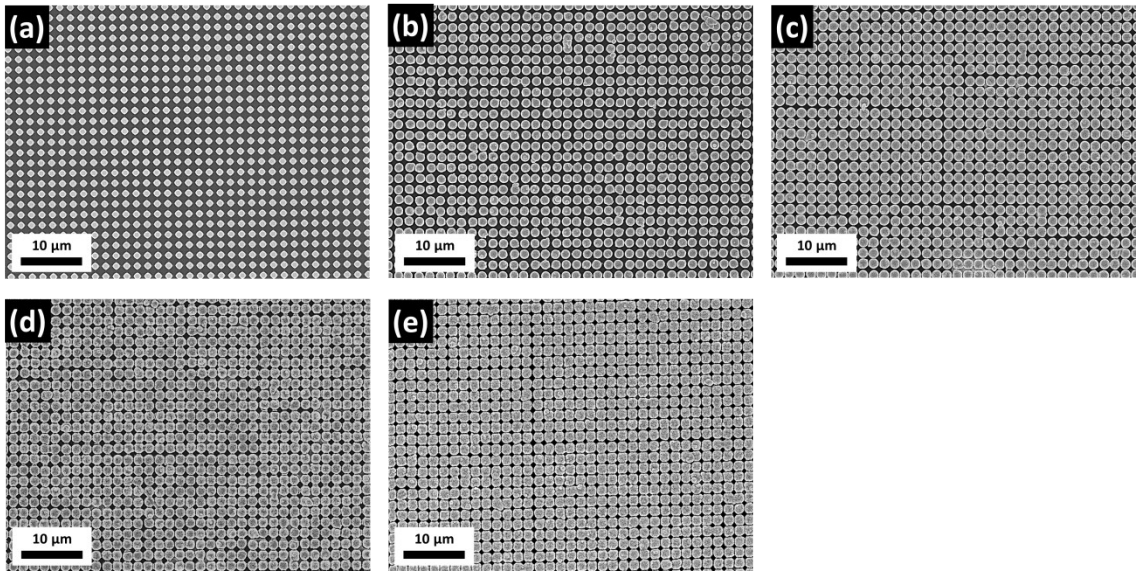

Fig. S2 Low-magnification top-view SEM images of (a) bare Si, (b) CoS_2-Si-200, (c) CoS_2-Si-250, (d) CoS_2-Si-280, and (e) CoS_2-Si-310 microwire arrays.

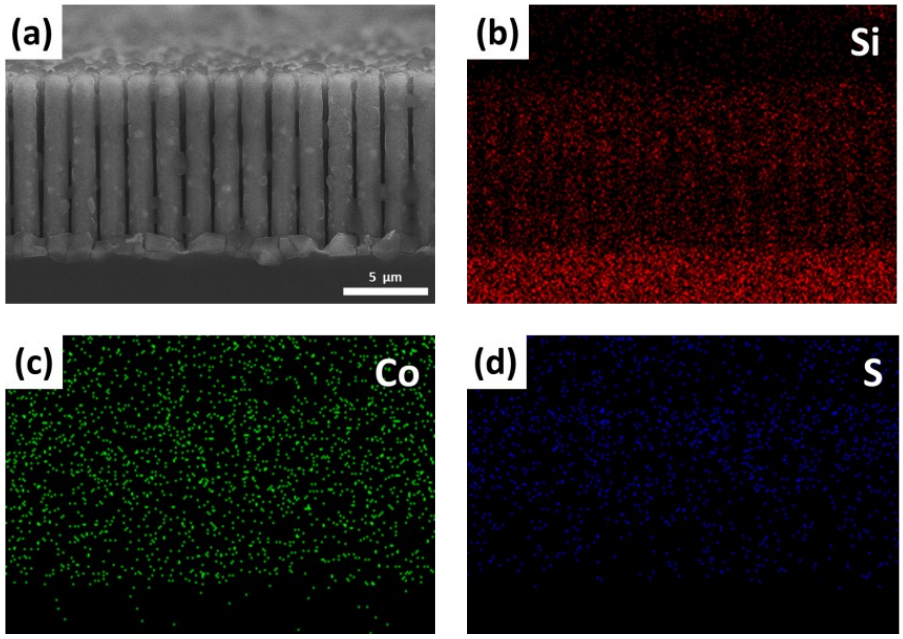

Fig. S3 (a) Cross-sectional SEM images of CoS_2-Si-250 electrode and its elemental mapping of (b) Si, (c) Co, and (d) S.

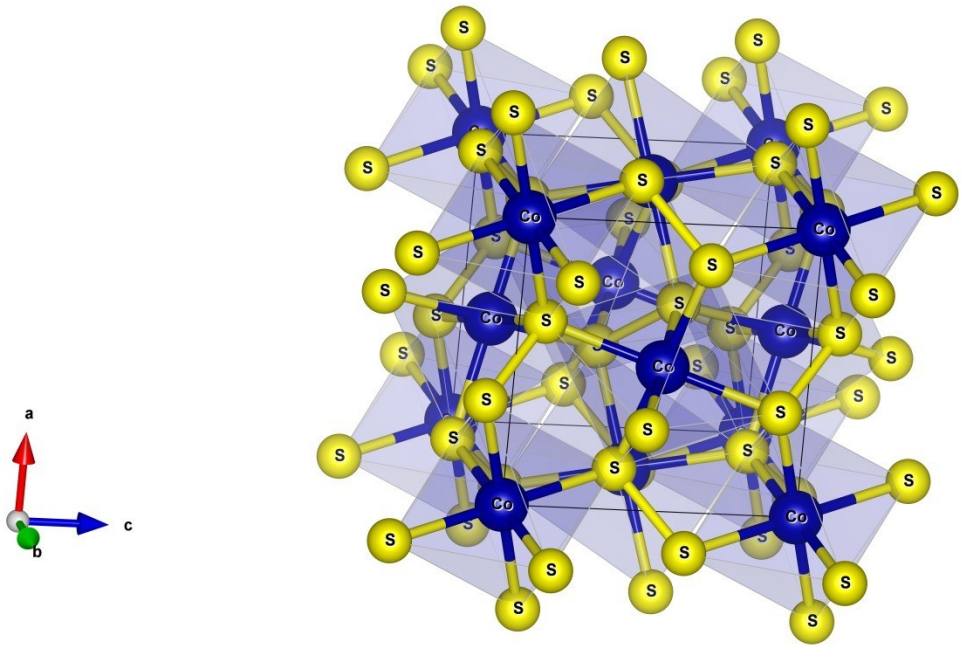

Fig. S4 Schematic illustration of the crystal structures for CoS_2.

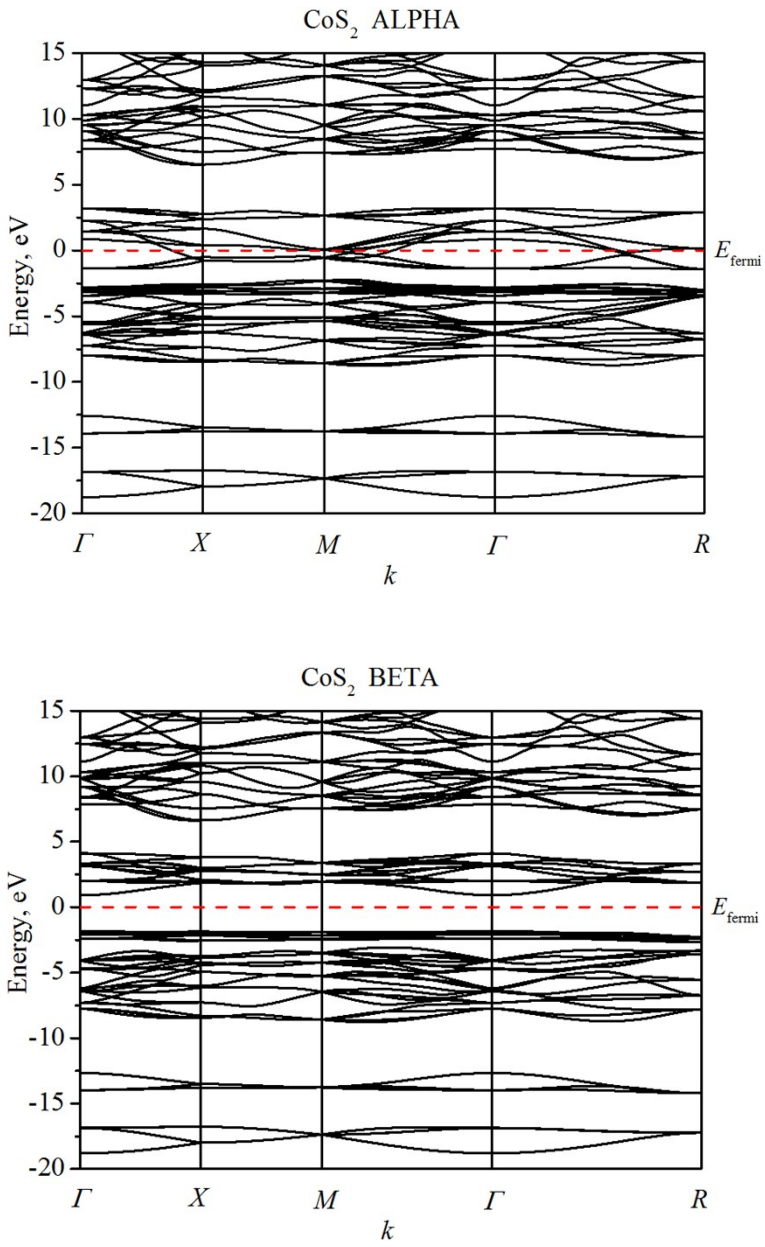

Fig. S5 The red horizontal dashed line denotes the Fermi level position, and the letters *Γ*, *X*, *M*, and *R* represent the high-symmetry *k* points: (0,0,0), (0,1/2,0), (1/2,1/2,0), and (1/2,1/2,1/2), respectively.

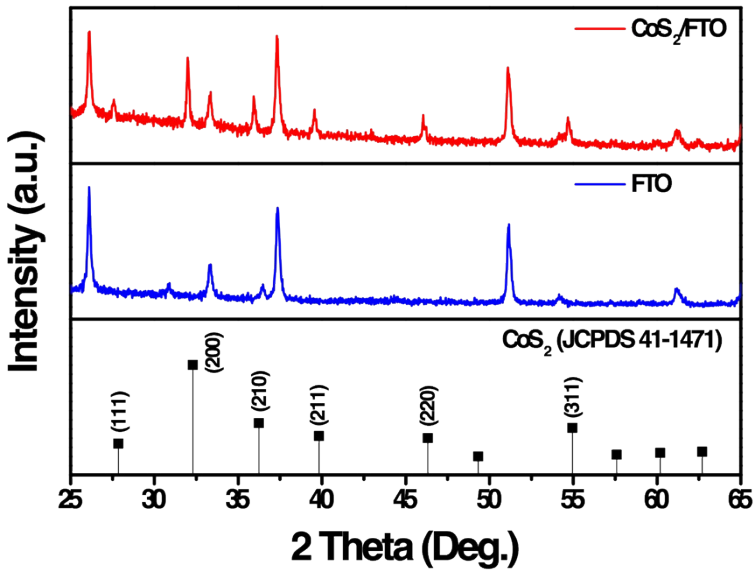

Fig. S6 XRD spectra of CoS_2/FTO electrode and FTO substrate. All diffraction peaks match well with the standard pattern of pyrite phase CoS_2 (JCPDS No. 41-1471).

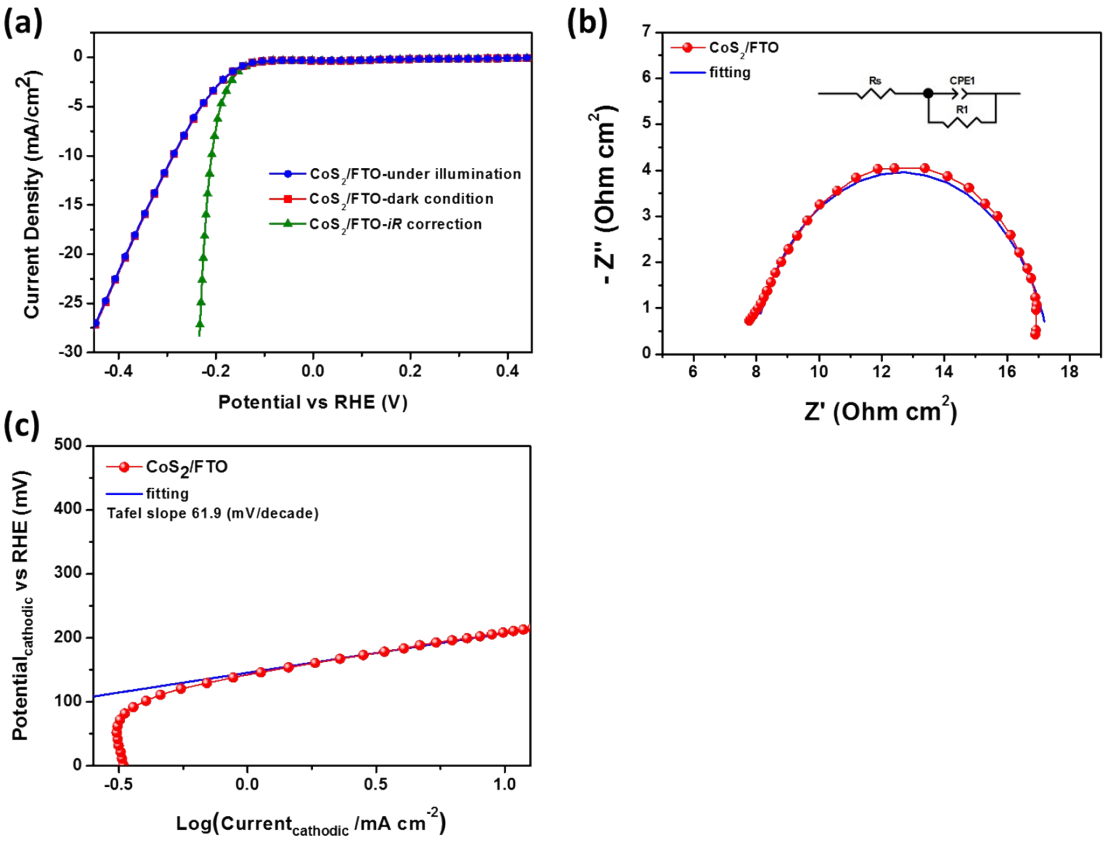

Fig. S7 (a) Linear sweep voltammograms, (b) electrochemical impedance spectroscopy, and (c) Tafel plot of CoS_2/FTO electrode.

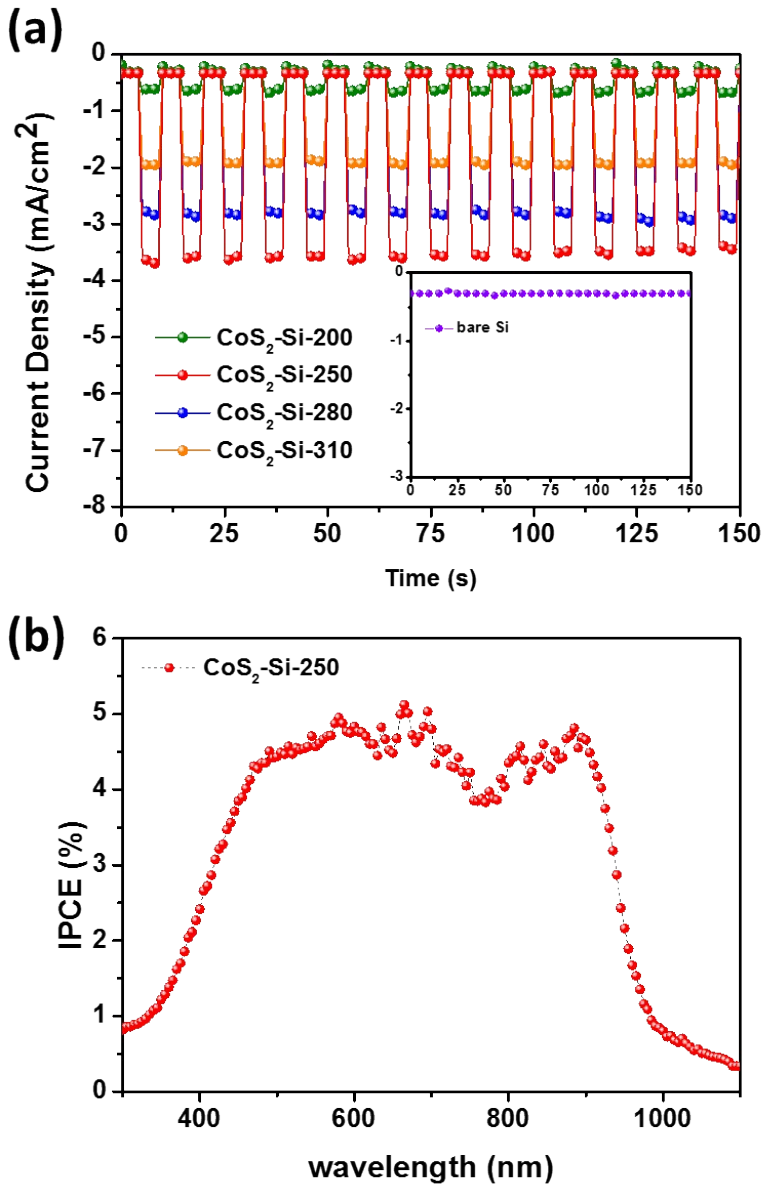

Fig. S8 (a) Transient photocurrent density of CoS_2-Si electrodes with various CoS_2 thicknesses at 0 V. (b) IPCE of CoS_2-Si-250 electrode under different wavelengths of illumination at 0 V.

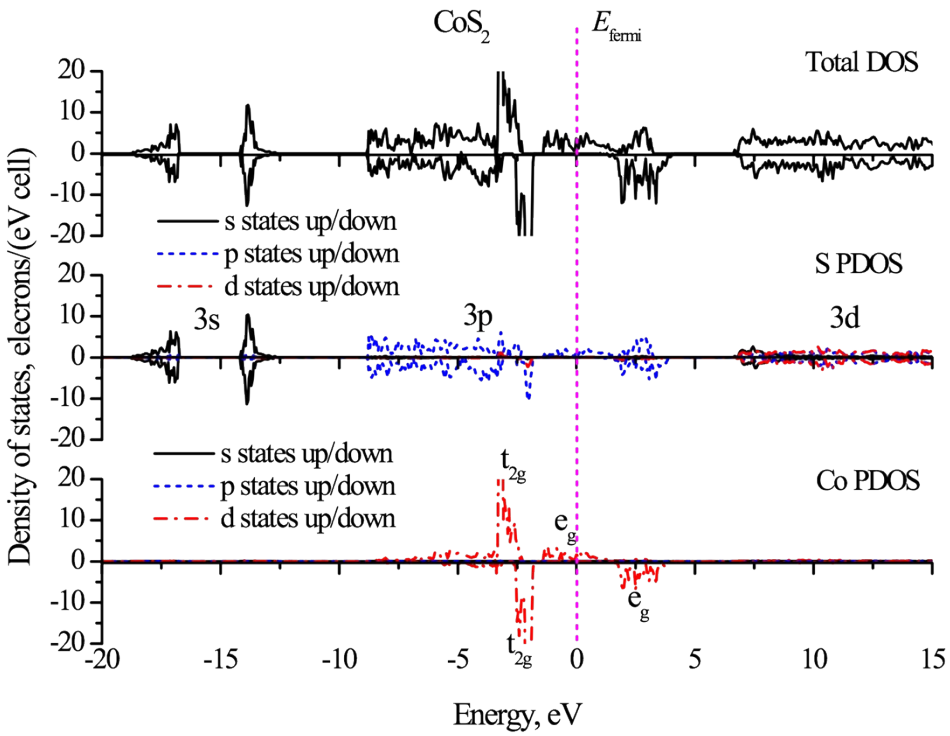

Fig. S9 Calculated PDOS/DOS diagrams for CoS_2. The purple vertical dashed line denotes the Fermi level position.

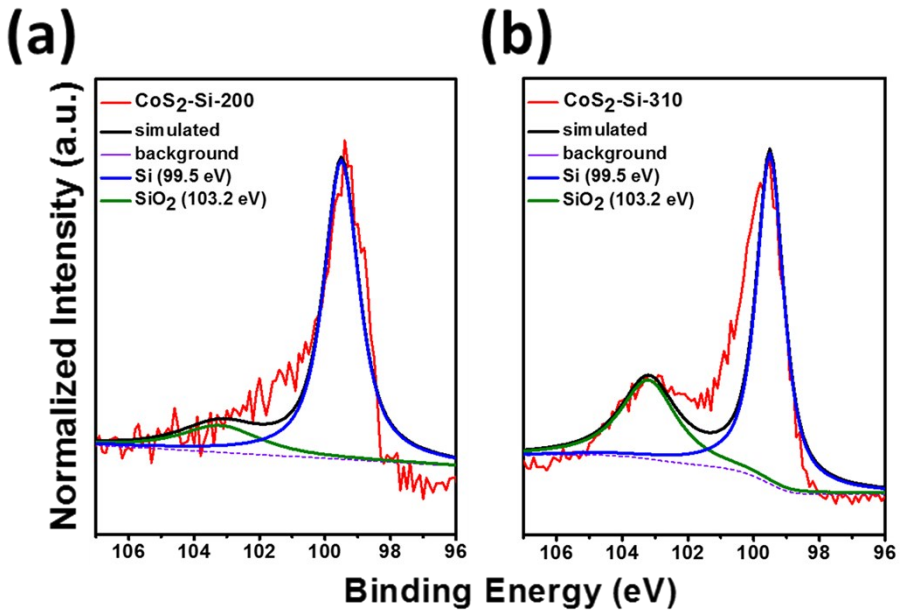

Fig. S10 High-resolution Si 2p spectra of (a) CoS_2-Si-200 and (b) CoS_2-Si-310 electrodes with different coordination conditions.

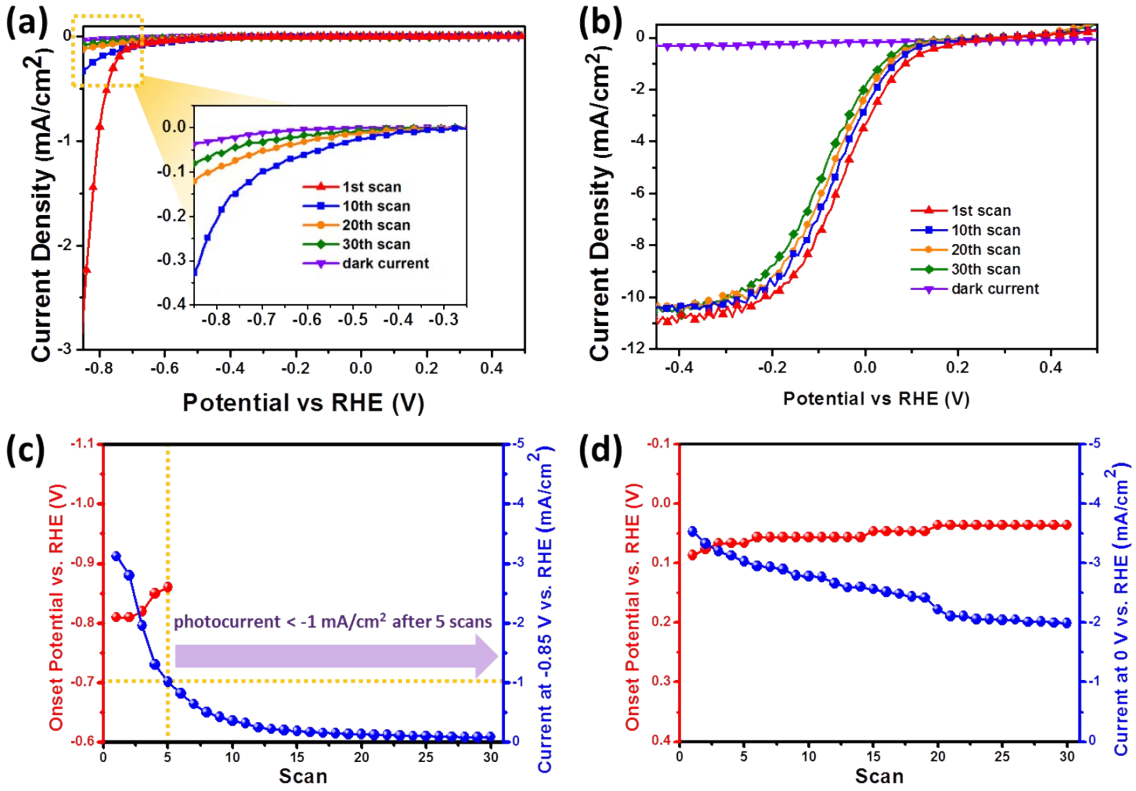

Fig. S11 Linear sweep voltammograms of (a) bare Si and (b) Pt-Si electrodes scanned for 30 times. Onset potential and photocurrent of (c) bare Si and (d) Pt-Si electrodes versus scan times.

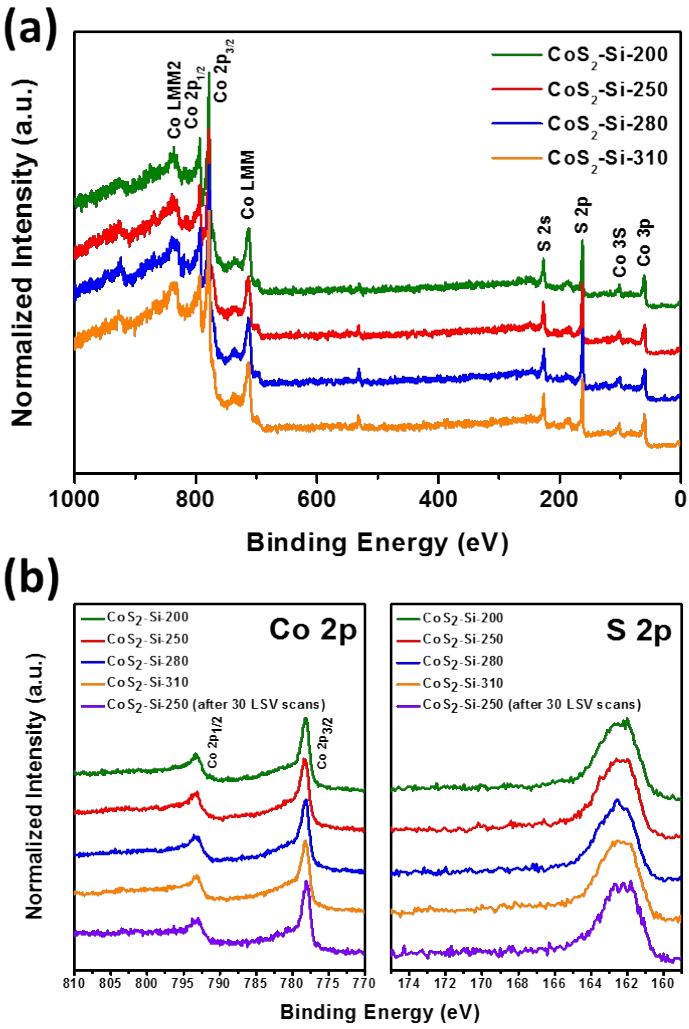

Fig. S12 (a) XPS spectra and (b) high-resolution Co 2p and S 2p XPS spectra of CoS_2-Si electrodes with various CoS_2 thicknesses.

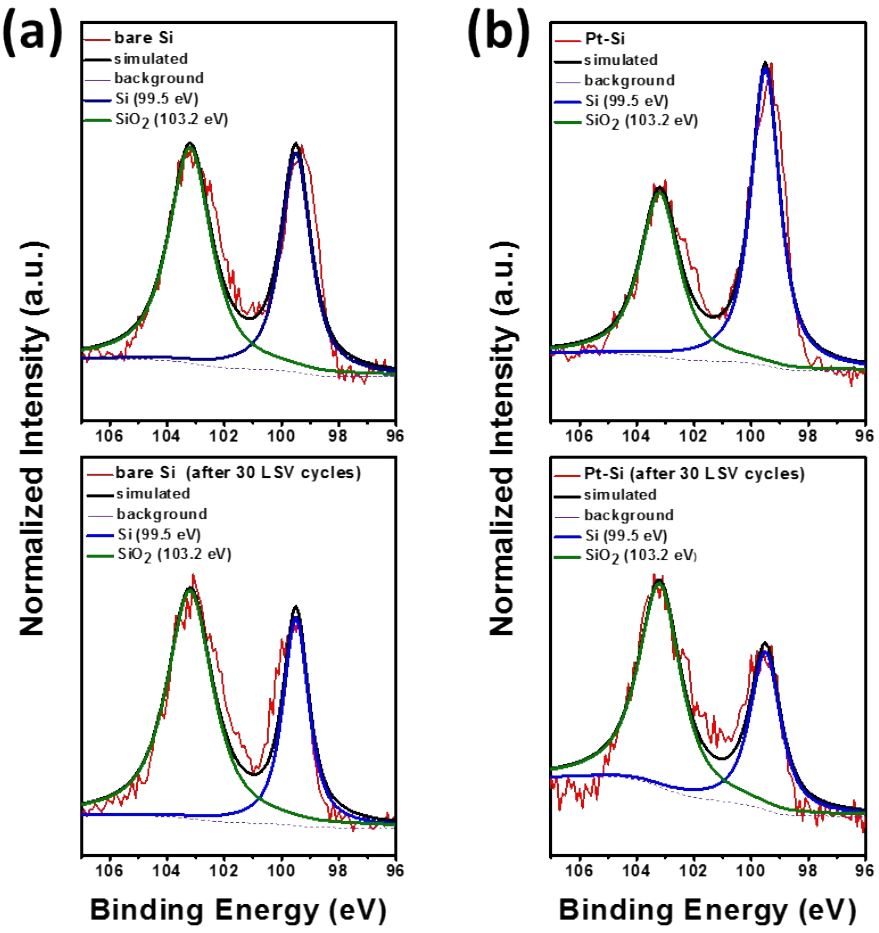

Fig. S13 High-resolution Si 2p spectra of the (a) as-prepared Si electrode and Si electrode after 30 LSV scans, and (b) as-prepared Pt-Si electrode and Pt-Si electrode after 30 LSV scans with different coordination conditions.

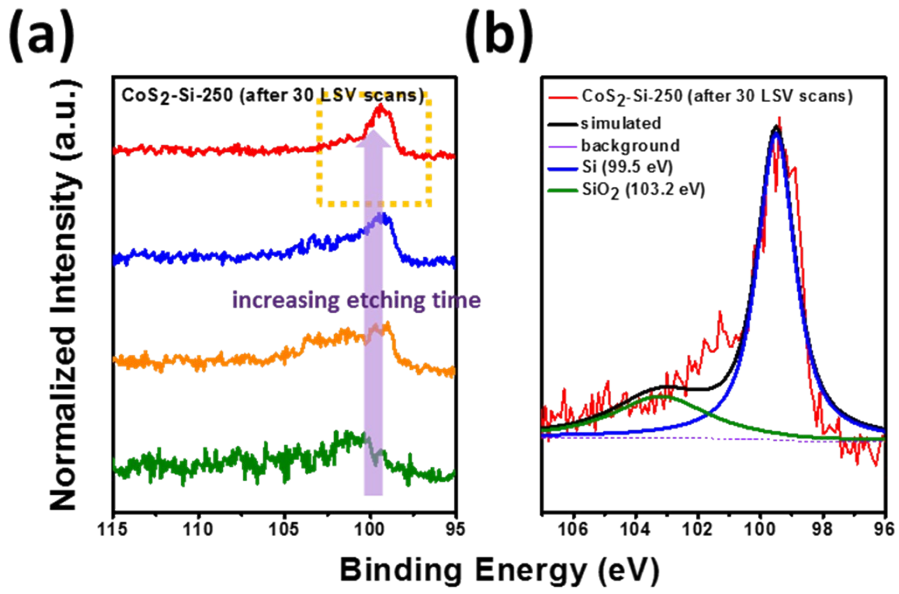

Fig. S14 High-resolution Si 2p spectra of CoS_2-Si-250 electrode after 30 LSV scans (b) with increasing Ar ion etching time and (c) different coordination conditions.

Table. S1 Summary of structural and electronic data for CoS_2.

	CoS_2	
	Exp.[a]	Calc.
a, Å	5.5385	5.5286
b, Å	5.5385	5.5286
c, Å	5.5385	5.5286
$\alpha=\beta=\gamma$, °	90	90
Co	0	0
	0	0
	0	0
X	0.38988	0.38811
	0.38988	0.38811
	0.38988	0.38811
R(Co-X) , Å	2.3252	2.3172
R(X-X) , Å	2.1128	2.1428
$Q(Co^{2+})$, e	-	1.094
$Q(X^{-})$, e	-	−0.547
$\mu(Co^{2+})$, μ_B	0.85[b]	1.117 (~1[c])
$\mu(X^{-})$, μ_B		−0.058(~0 [c])
E_g, eV		2.7261($\Gamma\rightarrow\Gamma$)

Notes: Coordinates of the crystallographic positions (in units of the lattice constants, (*x*, *y*, *z*) from top to bottom) of all ions and the Co-*X* and *X*-*X* chemical bond lengths (*R*) are also given. The electronic data contain the effective Mulliken charge (*Q*) and magnetic moment (μ) of individual ion, as well as the band gap (E_g) for beta electrons.

[a] Ref. [E. Nowack, D. Schwarzenbach, T. Hahn, Acta Crystallogr., Sect. B: Struct. Sci. 47 (1991) 650]; [b] Ref. [V.N. Antonov, O.V. Andryushchenko, A.P. Shpak, A.N. Yaresko, O. Jepsen, Phys. Rev. B 78 (2008) 094409]; [c]Other calculation result [S. Saha, M. De Raychaudhury, T. Saha-Dasgupta, Phys. Rev. B 77 (2008) 155428.]