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Supporting information (SI) for

$SnO_2/CoS_{1.097}$ heterojunction as a green electrocatalyst for hydrogen evolution linking to assistant glycerol oxidation

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Characterizations

The microstructure was observed by a Field-emission scanning electron microscope (FE-SEM, Sigma 500) with an energy dispersive spectrometer (EDS) and Transmission electron microscopy (TEM, JEM-2100) with selected area electron diffraction (SAED). The chemical properties were scanned by X-Ray Diffraction (XRD, X'PERT POWDER, scanning rate is 10° min^{-1}) and X-ray photoelectron spectroscopy (XPS, ThermoFisher Scientific ESCALAB 250, Al target). The H_2 reduction curve was tested by H_2-TPR (Xianquan TP-5080, heating rate and cooling rate are both 10°C min^{-1}). The contents of Co and S were measured by Inductive Coupled Plasma Emission Spectrometer Optical Emission Spectrometry (ICP-OES, Plasma 2000). The GOR product is characterized by ^{1}H NMR (Bruker Avance III HD, 400 MHz, solution is D_2O) and LC-MS (ThermoFisher U3000 liquid phase-QE mass spectrometry, flowing phase is water: methanol = 95:5).

The electrochemical measurements were performed by an electrochemical workstation (Chenhua, CHI 760E), tested programs include cyclic voltammetry (CV), linear sweep voltammetry (LSV), Chronopotentiometry (CP), electrochemical impedance spectroscopy (EIS), impedance–potential, and i-t curve.

For the three-electrode system, 2 mg of powder sample was dispersed in 200 μL of mixed solution (deionized water: ethanol: Nafion = 2:7:1) to form ink, and then 10 μL of this ink was dripped on a glass carbon electrode (GCE) and dried at room temperature, which was used as the working electrode, and Hg/HgO and graphite electrodes were used as the reference and counter electrodes, respectively. For the two-electrode system, the sample was mixed with acetylene black and polyvinylidene fluoride (PVDF) with a weight ratio of 8:1:1, and dispersed in N-methylpyrrolidone (NMP) to form slurry. The above slurry was coated on the nickel foam (1×1 cm) and dried. The electrolyte is 1 M KOH or 1 M KOH with organics.

The electrochemically active surface (ECSA) was calculated on the basis of the double-layer capacitance (C_{dl}) theory,[S1]

$$ECSA = C_{dl} / C_s$$

Where the slope in the plot of current densities to scan rates stands for $2C_{dl}$, and C_s

is 0.04 mF cm^{-2}.

The Mott-Schottky (M-S) plot was performed according to the equation: $^{1}/_{C^2} = \frac{2}{N_d e \varepsilon \varepsilon_0}(V - V_{FB} - \frac{KT}{e})$

where C is the capacitance at the interface between semiconductor and electrolyte (F cm^{-2}); e is the elementary charge (1.6×10^{-19} C); ε is the relative dielectric constant (F m^{-1}); ε_0 is the permittivity of the vacuum; N_d is the carrier density (cm^{-3}); V is the applied potential (V); V_{FB} is flat band potential; K is Boltzmann's constant (1.38×10^{-23} F m^{-1}); T is the absolute temperature (K).[S2]

In the above equation, the line plot of $1/C^2$ to V is named M-S plot. The flat band potential (E_{fb}) is the intercept by extrapolating the linear part of M-S plot to $1/C^2 = 0$.

Faradaic efficiency (FE) of GOR

The half-reaction formula for each product from GOR is listed as follows:

Product	Anode reaction formula	e^- (mol)
Glycerol acid	$CH_2OH\text{-}CHOH\text{-}CH_2OH + 5OH^- \rightarrow CH_2OH\text{-}CHOH\text{-}COO^- + 4H_2O + 4e^-$	4
Glyceraldehyde	$CH_2OH\text{-}CHOH\text{-}CH_2OH + 2OH^- \rightarrow CH_2OH\text{-}CHOH\text{-}CHO + 2H_2O + 2e^-$	2
Formic acid	$CH_2OH\text{-}CHOH\text{-}CH_2OH + 11OH^- \rightarrow 3CHOO^- + 8H_2O + 8e^-$	8/3

FE of GOR is calculated based on the following equation:

$$FE\ (\%) = \frac{4 \times Cglya + 2 \times Cglycd + \frac{8}{3} \times Cformic}{Q} \times V \times F \times 100\%$$

Where, C_{glya}, C_{glycd}, and C_{formic} are the concentration (mol L^{-1}) of glycerol acid, glyceraldhyde, and formic acid; V is the volume of tested electrolyte (10×10^{-3} L); F is the Faradaic constant (96485 C mol^{-1}); Q is the total charge (C) passed during electrochemical reaction.[S3]

DFT calculations

All the spin-polarized DFT calculations are performed by the Vienna Ab initio Simulation Package (VASP)[S4] with the projector augmented wave (PAW) method.[S5]

The exchange-function is treated using the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE)[S6] function. The energy cutoff for the plane wave basis expansion was set to 500 eV. Partial occupancies of the Kohn−Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV and the spin polarization was considered. For k-space sampling, k1 × k2 × k3 Γ-centered Monkhorst-Pack meshes were used, where kn (n = 1,2,3) was prepared as the mesh spacing near ($2\pi \times 0.04$ $Å^{-1}$) to each direction. The self-consistent calculations apply a convergence energy threshold of 10^{-4} eV, and the force convergency was set to 0.05 eV/Å.

Table S1. The contents of Co and S tested by ICP-OES

Element	Co	S
Content (mg L^{-1})	7.14	4.26

Table S2. The contents of component

Component	$C_3H_6O_3$	$C_3H_6O_4$	HCOOH
Content (mol L^{-1})	0.037	0.027	0.029

Table S3. Comparison with other electrocatalysts in electrolyte with organic additions by two-electrode method.

Electrocatalyst	Electrolyte	Cell voltage (V) at 10 mA cm^{-2}
Mn-$CoSe_2$/CFC) [S7]	1 M KOH + 0.1 M glycerol	1.45
Ni_3N-$Ni_{0.2}Mo_{0.8}N$ [S8]	1 M KOH + 0.1 M glycerol	1.40
PtSA-NiCo LDHs/ NF [S9]	1 M KOH + 0.1 M glycerol	1.21
CNs@CoPt [S10]	1 M KOH + 10 mM glycerol	1.50
W-NiS_2/MoO_2@CC [S11]	1 M KOH + 0.33 M urea	1.372
Core-corona Co/CoP [S12]	1 M KOH + 0.5 M glucose	1.42
Ni-MoS_2 [S13]	1 M KOH + 0.3 M glucose	1.67
0.5 SnO_2/0.5 $CoS_{1.097}$ (This work)	1 M KOH + 0.1 M glycerol	1.18

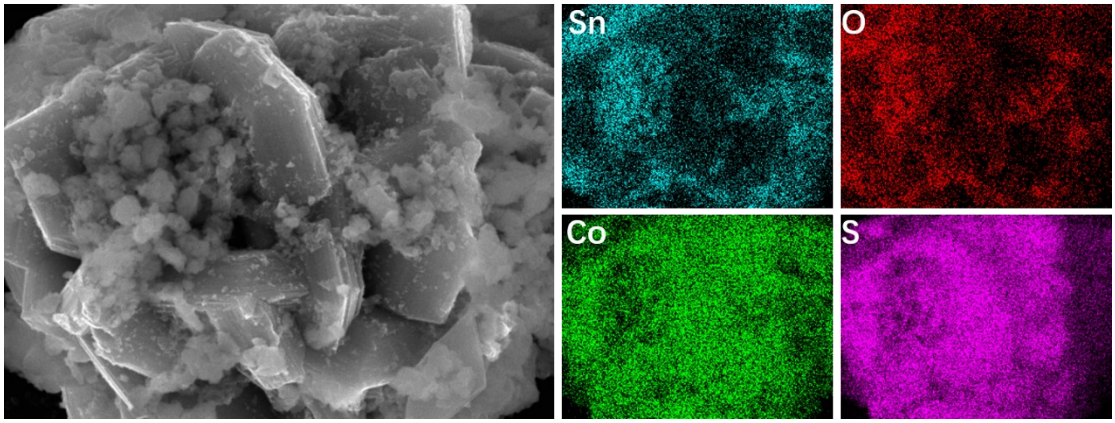

Figure S1 The elemental mapping of 0.7 SnO_2/0.3 $CoS_{1.097}$.

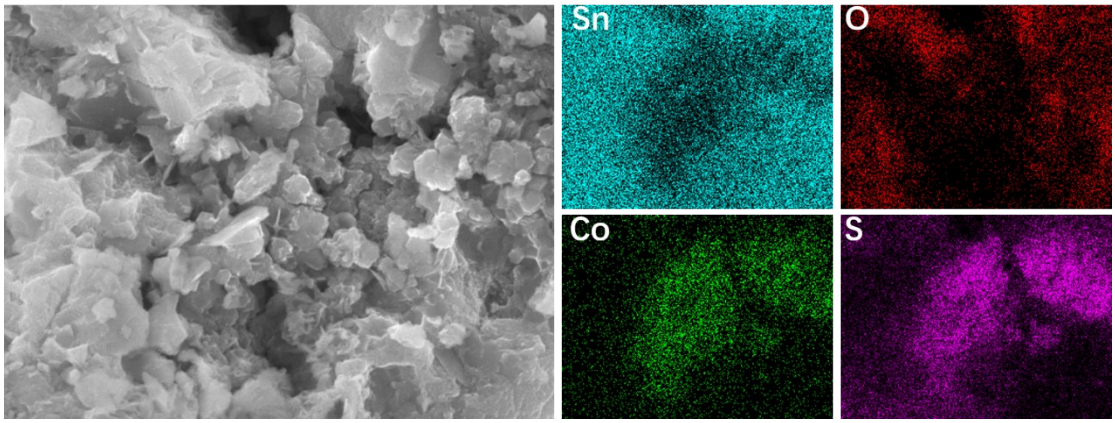

Figure S2 The elemental mapping of 0.3 SnO_2/0.7 $CoS_{1.097}$.

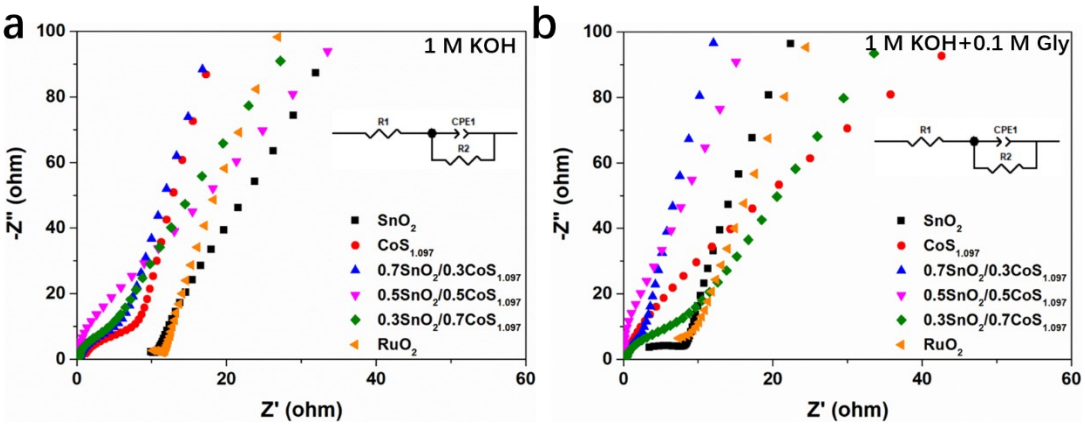

Figure S3 The EIS plots of SnO_2, $CoS_{1.097}$, 0.7 SnO_2/0.3 $CoS_{1.097}$, 0.5 SnO_2/0.5 $CoS_{1.097}$, 0.3 SnO_2/0.7 $CoS_{1.097}$, and RuO_2 in 1 M KOH (a) and 1 M KOH + 0.1 M glycerol (b). (All the EIS test at Amplitude = 0.005 V from 1 HZ to 10^5 HZ.)

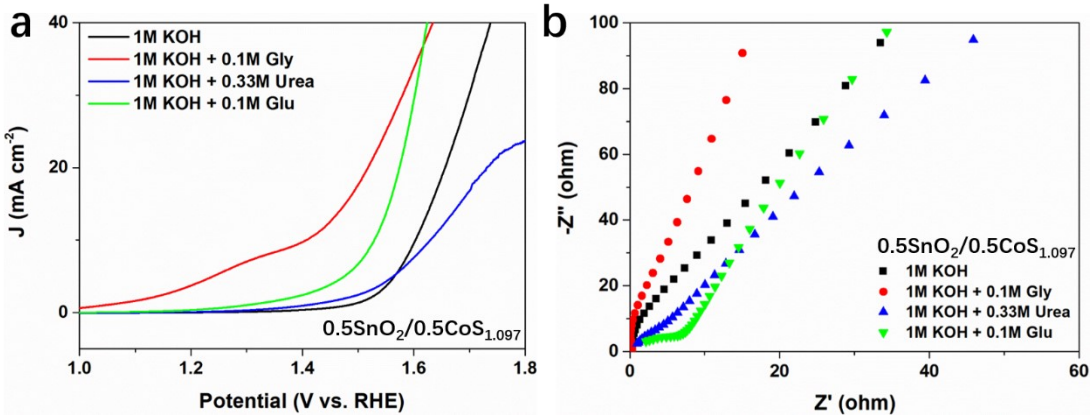

Figure S4 The OER LSV curves (a) and EIS plots (b) of 0.5 SnO_2/0.5 $CoS_{1.097}$ in the different electrolytes.

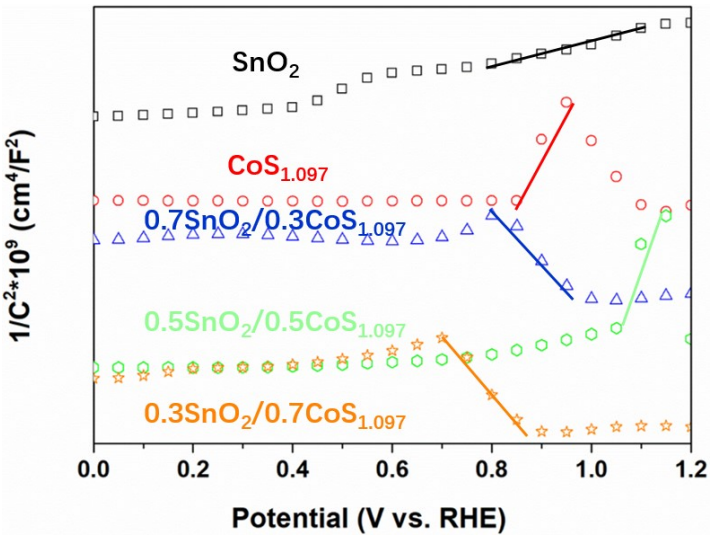

Figure S5 The M-S plots of SnO_2, $CoS_{1.097}$, 0.7 SnO_2/0.3 $CoS_{1.097}$, 0.5 SnO_2/0.5 $CoS_{1.097}$, 0.3 SnO_2/0.7 $CoS_{1.097}$ in 1 M KOH.

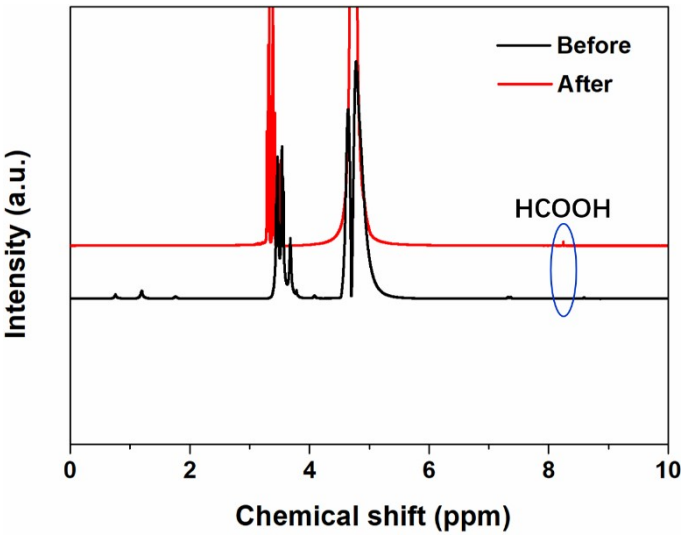

Figure S6 The ^{1}H NMR of electrolyte of 0.5 SnO_2/0.5 $CoS_{1.097}$ before and after GOR.

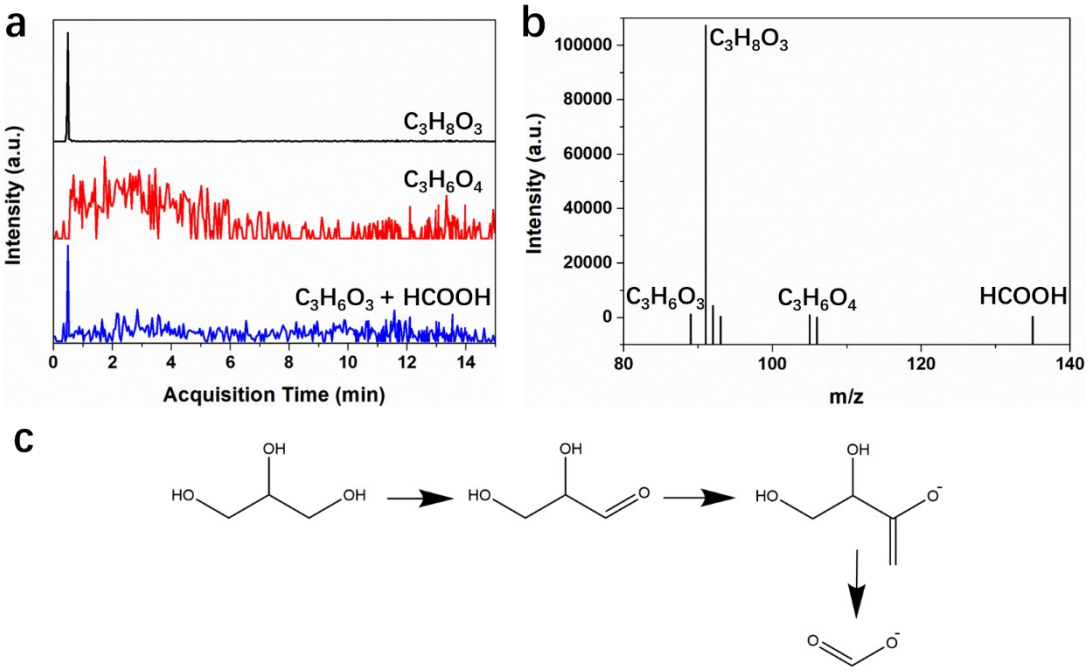

Figure S7 (a, b) LS-MS of product after GOR of 0.5 SnO_2/0.5 $CoS_{1.097}$. (c) GOR formula of 0.5 SnO_2/0.5 $CoS_{1.097}$.

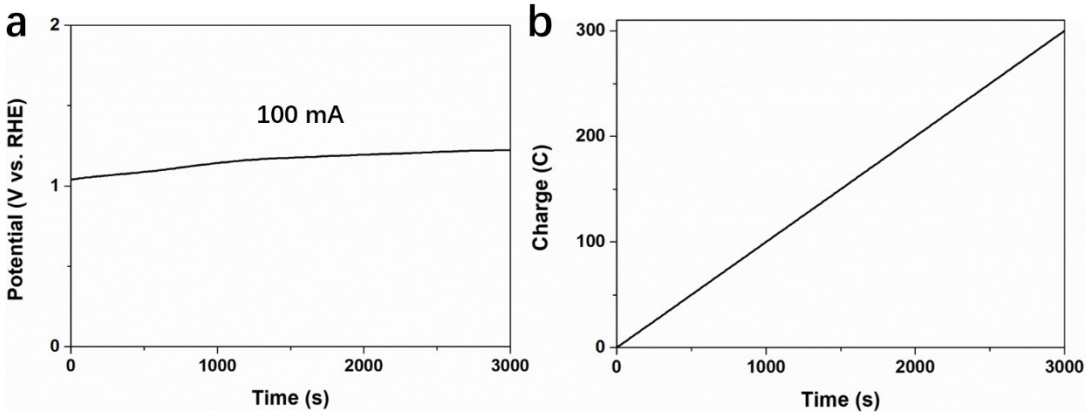

Figure S8 (a) Chronopotentiometry curve of the 0.5 SnO_2/0.5 $CoS_{1.097}$ at a constant current of 100 mA. (b) The plot of corresponding charge to time.

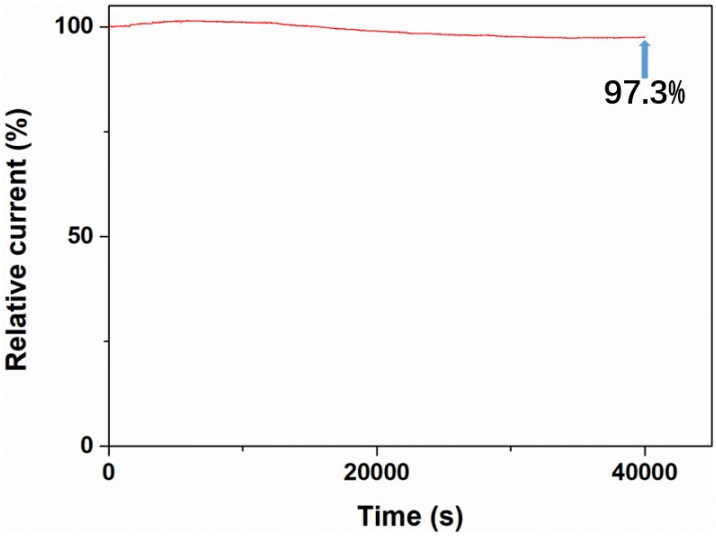

Figure S9 I-t plot of 0.5 SnO_2/0.5 $CoS_{1.097}$ in 1 M KOH + 0.1 M glycerol.

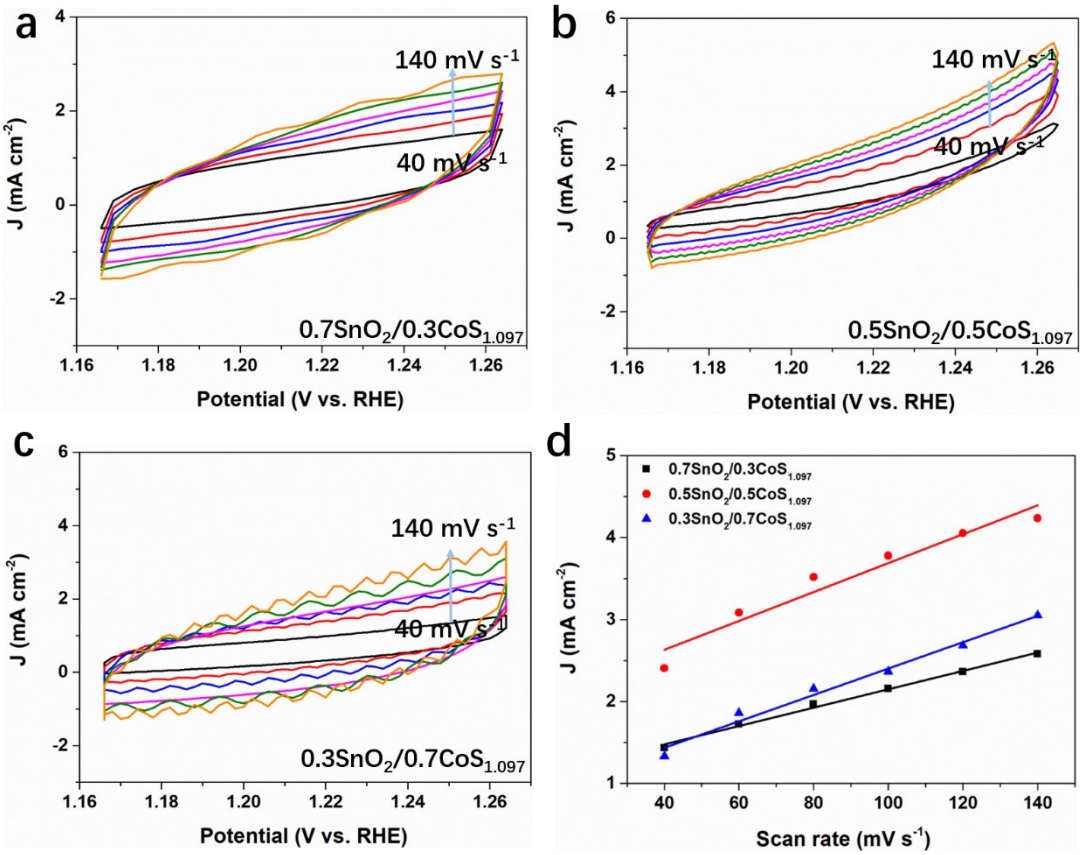

Figure S10 The CV curves at different scan rates of (a) 0.7 SnO_2/0.3 $CoS_{1.097}$, (b) 0.5 SnO_2/0.5 $CoS_{1.097}$, and (c) 0.3 SnO_2/0.7 $CoS_{1.097}$. (d) The plots of current density to scan rates.

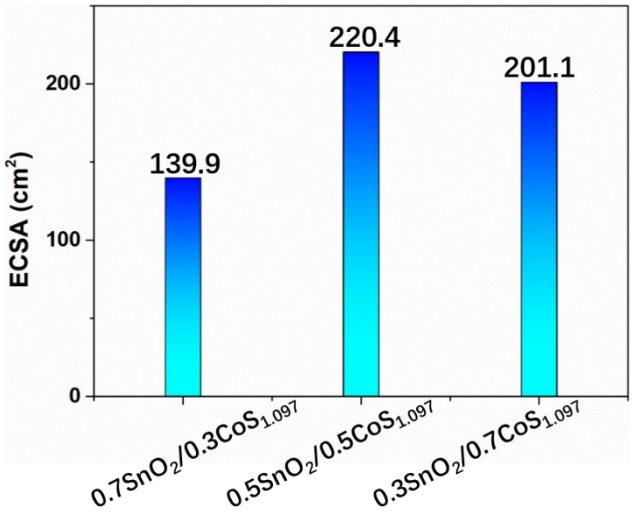

Figure S11 The ECSA of 0.7 SnO_2/0.3 $CoS_{1.097}$, 0.5 SnO_2/0.5 $CoS_{1.097}$, and 0.3 SnO_2/0.7 $CoS_{1.097}$.

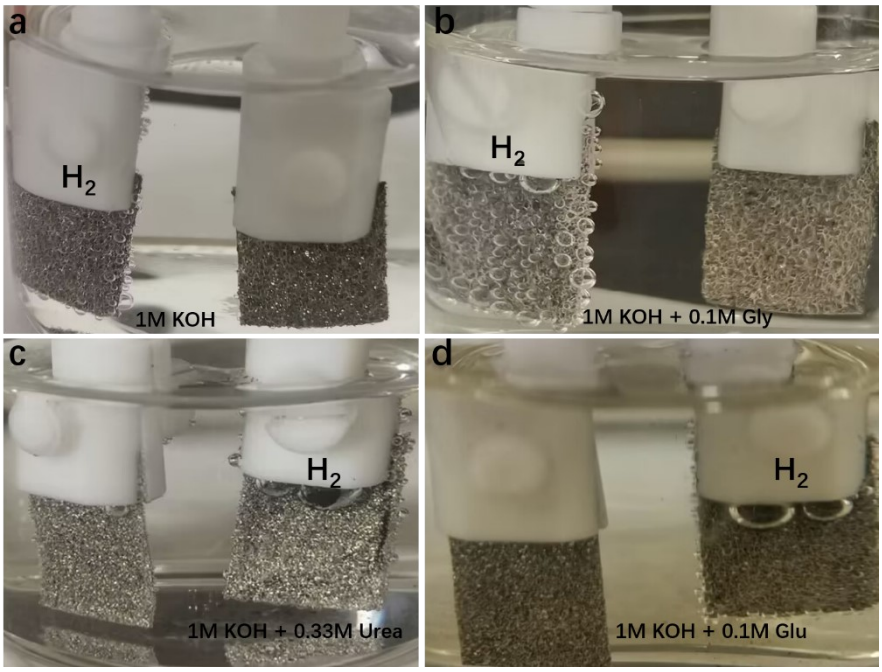

Figure S12 The photos of overall water splitting of 0.5 SnO_2/0.5 $CoS_{1.097}$ in (a) 1 M KOH, (b) 1 M KOH + 0.1 M gly, (c) 1 M KOH + 0.33 M urea, and (d) 1 M KOH + 0.1 M glu.

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