Supporting information (SI) for

SnO$_2$/CoS$_{1.097}$ heterojunction as a green electrocatalyst for hydrogen evolution linking to assistant glycerol oxidation

Xinjie Xie$^a$, Chunyong Zhang$^a$, Meng Xiang$^a$, Chengbin Yu$^b$, Wangxi Fan$^{a,*}$, Shuang Dong$^{c,*}$, and Zhou Yang$^{a,*}$

a. Department of Chemistry and Chemical Engineering, Jiangsu University of Technology, Changzhou 213001, China.
b. Research Institute of Advanced Materials (RIAM), Department of Materials Science and Engineering, Seoul National University, Seoul 08826, Republic of Korea.
c. School of Chemical Engineering and Materials, Changzhou Institute of Technology, Changzhou 213032, China.

*Correspondences: Wangxi Fan, fwx@jsut.edu.cn; Shuang Dong, dongs@czu.cn; Zhou Yang, zhouyang@jsut.edu.cn.
**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\(_2\)O) 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,

\[
\text{ECSA} = \frac{C_{dl}}{C_s}
\]

Where the slope in the plot of current densities to scan rates stands for \(2C_{dl}\), and \(C_s\) stands for the double-layer capacitance at zero scan rate.
is 0.04 mF cm$^{-2}$.

The Mott-Schottky (M-S) plot was performed according to the equation:

$$\frac{2}{N_a e \varepsilon_0} \left( V - V_{FB} - \frac{KT}{e} \right)$$

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); $\varepsilon$ is the relative dielectric constant (F m$^{-1}$); $\varepsilon_0$ is the permittivity of the vacuum; $N_a$ 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).

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:

<table>
<thead>
<tr>
<th>Product</th>
<th>Anode reaction formula</th>
<th>$e^-$ (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol acid</td>
<td>CH$_2$OH-CHOH-CH$_2$OH + 5OH$^-$ → CH$_2$OH-CHOH-COO$^-$ + 4H$_2$O + 4e$^-$</td>
<td>4</td>
</tr>
<tr>
<td>Glyceraldehyde</td>
<td>CH$_2$OH-CHOH-CH$_2$OH + 2OH$^-$ → CH$_2$OH-CHOH-CHO + 2H$_2$O + 2e$^-$</td>
<td>2</td>
</tr>
<tr>
<td>Formic acid</td>
<td>CH$_2$OH-CHOH-CH$_2$OH + 11OH$^-$ → 3CHOO$^-$ + 8H$_2$O + 8e$^-$</td>
<td>8/3</td>
</tr>
</tbody>
</table>

FE of GOR is calculated based on the following equation:

$$FE \text{ (%) } = \frac{4 \times C_{glya} + 2 \times C_{glycd} + \frac{8}{3} \times C_{formic}}{Q} \times V \times F \times 100\%$$

Where, $C_{glya}$, $C_{glycd}$, and $C_{formic}$ are the concentration (mol L$^{-1}$) of glycerol acid, glyceraldehyde, 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)\textsuperscript{56} 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, $k_1 \times k_2 \times k_3$ Γ-centered Monkhorst-Pack meshes were used, where $k_n$ ($n = 1, 2, 3$) was prepared as the mesh spacing near $(2\pi \times 0.04 \text{ Å}^{-1})$ 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

<table>
<thead>
<tr>
<th>Element</th>
<th>Co (mg L⁻¹)</th>
<th>S (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (mg L⁻¹)</td>
<td>7.14</td>
<td>4.26</td>
</tr>
</tbody>
</table>

Table S2. The contents of component

<table>
<thead>
<tr>
<th>Component</th>
<th>C₃H₆O₃ (mol L⁻¹)</th>
<th>C₃H₆O₄ (mol L⁻¹)</th>
<th>HCOOH (mol L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (mol L⁻¹)</td>
<td>0.037</td>
<td>0.027</td>
<td>0.029</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>Electrolyte</th>
<th>Cell voltage (V) at 10 mA cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-CoSe₂/CFC) S⁷</td>
<td>1 M KOH + 0.1 M glycerol</td>
<td>1.45</td>
</tr>
<tr>
<td>Ni₃N-Ni₀.₂Mo₀.₈N S⁸</td>
<td>1 M KOH + 0.1 M glycerol</td>
<td>1.40</td>
</tr>
<tr>
<td>PtSA-NiCo LDHs/ NF S⁹</td>
<td>1 M KOH + 0.1 M glycerol</td>
<td>1.21</td>
</tr>
<tr>
<td>CNs@CoPt S¹⁰</td>
<td>1 M KOH + 10 mM glycerol</td>
<td>1.50</td>
</tr>
<tr>
<td>W-NiS₂/MoO₂@CC S¹¹</td>
<td>1 M KOH + 0.33 M urea</td>
<td>1.372</td>
</tr>
<tr>
<td>Core-corona Co/CoP S¹²</td>
<td>1 M KOH + 0.5 M glucose</td>
<td>1.42</td>
</tr>
<tr>
<td>Ni-MoS₂ S¹³</td>
<td>1 M KOH + 0.3 M glucose</td>
<td>1.67</td>
</tr>
<tr>
<td>0.5 SnO₂/0.5 CoS₁.₀97 (This work)</td>
<td>1 M KOH + 0.1 M glycerol</td>
<td>1.18</td>
</tr>
</tbody>
</table>
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.
References