

Supporting Information:

Electrochemical Reduction of CO₂ at Thiolated Au Electrodes

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I: Statistics

The results were replicated at least 3 times.

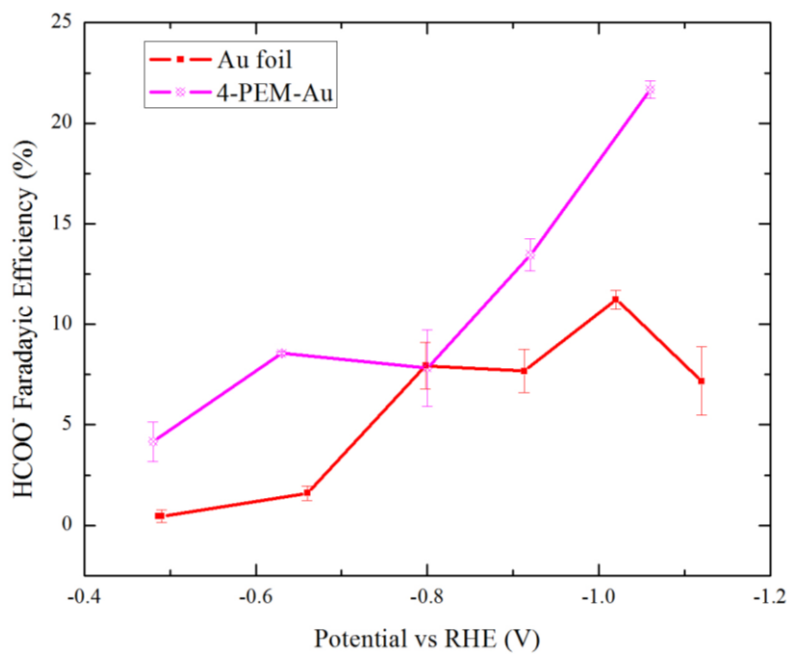


Figure S1: The example of error bar included formate faradaic efficiency vs potential the significance level is above 99% (except at -0.8V, 90%)

II: Onset Potential

Example of determining onset potential from Tafel plot.¹⁻² We pick the transition point from the thermodynamic controlled region to the kinetic controlled region to be the onset potential. The onset potential here is referring to the experimental equilibrium potential.³

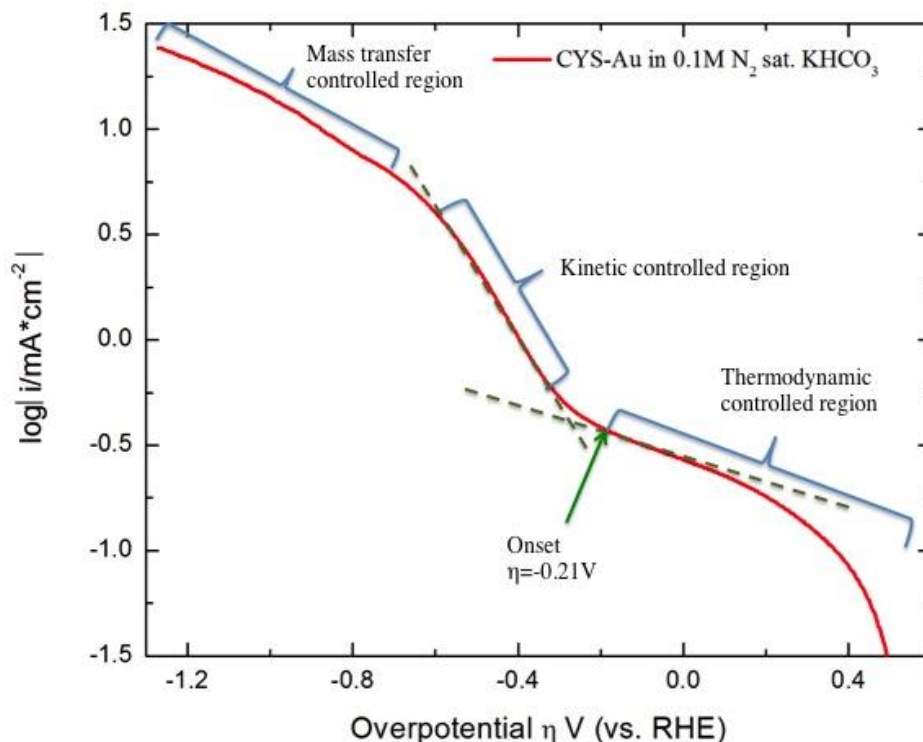


Figure S2: showing the way to determine the onset potential for HER on CYS-Au is -0.21V. vs RHE

For a 2e⁻ electron transfer process, the current density –potential characteristic can be written as Equation S1, where F is the Faraday's constant, k_0 is the standard kinetic rate constant, $C_O(0,t)$ is the concentration of oxidized species (in this case proton for HER and CO₂ for CO₂ reduction.) on the electrode at any time, C_R is the concentration of the reduced species (in this case H₂ for HER and CO/HCOOH for CO₂ reduction.), α is the transfer coefficient (in most case, α lies between 0.3 to 0.7, 0.5 is the usual approximate in lack of measurement. Thus we assume α is the same value in both reaction. , f is F/RT , E is the applied potential and E^0 is the equilibrium potential. The reverse reaction can be neglected in this system since the concentration of the reactant is much higher, thus the equation can be reduced to Equation S2.² The selectivity of HER over CO₂ reduction can be defined as S in Equation S3.⁴ The selectivity change expressed in S_1/S_2 (sample 1 selectivity / Sample 2 selectivity) is derived in Equation S4 with the substitution of

Equation S2 into Equation S3. Assuming the exact same experiment condition (same T, P, C_o, t and E), Equation S4 can be simplified into Equation S5.

$$j = 2Fk_0[C_o(0, t)e^{-2\alpha f(E-E^0)} - C_R(0, t)e^{(1-\alpha)2f(E-E^0)}] \quad \text{Equation S1}$$

$$j = 2Fk_0[C_o(0, t)e^{-2\alpha f(E-E^0)}] \quad \text{Equation S2}$$

$$S = \frac{FE_{HER}}{FE_{CO_2}} = \frac{i_{HER}}{i_{CO_2}} \quad \text{Equation S3}$$

$$\frac{S_1}{S_2} = \frac{C_{H1}(0, t) * C_{C2}(0, t)}{C_{H2}(0, t) * C_{C1}(0, t)} e^{-2\alpha f[(E_{2, HER}^0 - E_{2, CO_2}^0) - (E_{1, HER}^0 - E_{1, CO_2}^0)]} \quad \text{Equation S4}$$

$$\frac{S_1}{S_2} = e^{-2\alpha f[(E_{2, HER}^0 - E_{2, CO_2}^0) - (E_{1, HER}^0 - E_{1, CO_2}^0)]} \quad \text{Equation S5}$$

$$\text{if } \Delta E_2^0 > \Delta E_1^0$$

$$\text{then, } \frac{S_1}{S_2} < 1 \text{ and vice versa.}$$

III: Solution phase thiol infrared spectra

2-Mercaptopropionic acid

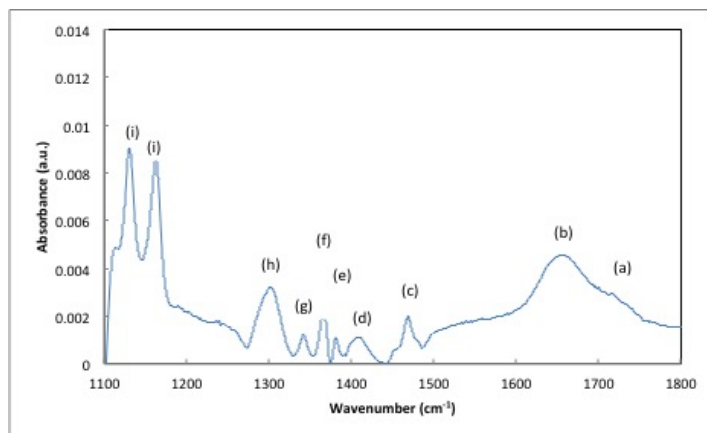


Figure S3: Infrared Spectrum of *2-Mercaptopropionic acid* in ethanolic solution.

Table S1: Peak assignment⁵ for Figure S3;

Peak	Wavenumber (cm ⁻¹)	Assignment
a	1723	C=O stretching in -COOH
b	1642	-COO ⁻ asymmetric stretching
c	1463	-CH ₃ asymmetric stretching
d	1398	-COO ⁻ symmetric stretching
e	1378	-CH ₃ symmetric stretching
f	1362	-COO ⁻ symmetric stretching
g	1337	-OH deformation
h	1294	C-C stretching
i	1128 & 1159	C-O stretching

4-pyridylethylmercaptan

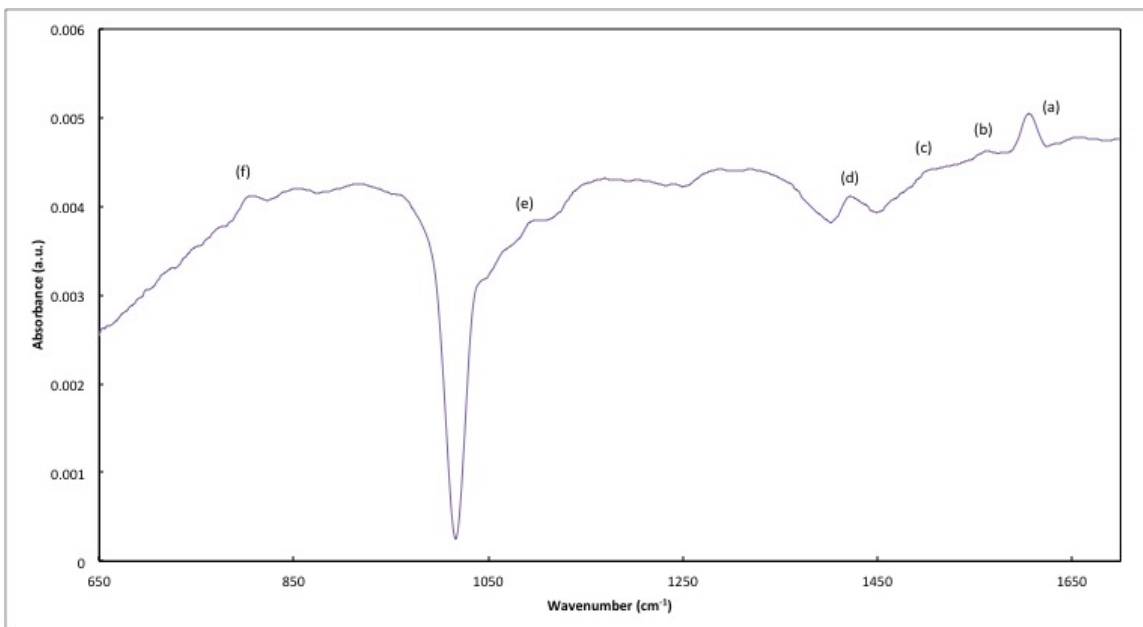


Figure S4: Infrared Spectrum of *4-pyridylethylmercaptan* in methanolic solution.

Table S2: Peak assignment⁵ for Figure S4;

Peak	Wavenumber (cm ⁻¹)	Assignment
a	1602	C=C Ring stretching
b	1556	C=C Ring stretching
c	1496	C=N Ring stretching
d	1417	C=C Ring stretching
e	1089	Pyridine C-H deformation
f	798	Pyridine C-H deformation

Cysteamine

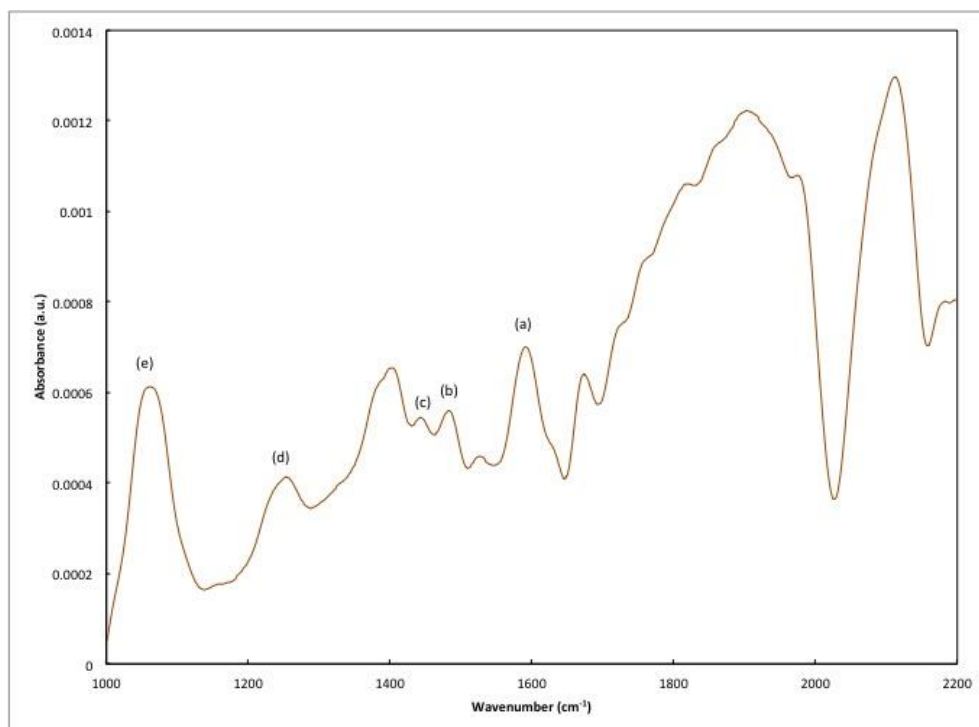


Figure S5: Infrared Spectrum of *Cysteamine* in aqueous solution.

Table S3: Peak assignment⁵ for Figure S5;

Peak	Wavenumber (cm ⁻¹)	Assignment
a	1587	N-H deformation
b	1475	C-H deformation –CH ₂ –
c	1437	C-H deformation in –CH ₂ -S-
d	1243	C-H wagging in –CH ₂ -S-
e	1055	C-N stretching

IV: Atomic Force Microscope (AFM)

The roughnesses of the surfaces were characterized with AFM. The reduced surface roughness on functionalized Au suggests a uniformly packed structure.⁶

Table S4: Surface roughness of samples.

Surface	RMS (nm)
Au	7.38
MPA-Au	2.60
4-PEM-Au	2.08
CYS-Au	2.27

Reference:

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2. Bard, A. J.; Faulkner, L. R.; Leddy, J.; Zoski, C. G., *Electrochemical methods: fundamentals and applications*. Wiley New York: 1980; Vol. 2.
3. Kim, S. K.; Zhang, Y.-J.; Bergstrom, H.; Michalsky, R.; Peterson, A., Understanding the Low-Overpotential Production of CH₄ from CO₂ on Mo₂C Catalysts. *ACS Catalysis* **2016**, 6 (3), 2003-2013.
4. Davis, M. E.; Davis, R. J., *Fundamentals of chemical reaction engineering*. Courier Corporation: 2012.
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