Supporting Information

Boosting the Syngas Production of a $SrTiO_3$ Photocathode via Plasmonic Hot Electron Injection from an Ag Underlayer

Galyam Sanfo[a#], Aejaz ul Bashir[b#], Nusrat Rashid[a#], Siming Huang[a], Pravin Popinand Ingole[b*], Mojtaba Abdi-Jalebi[a*]

[a] *Institute for Materials Discovery, University College London, Malet Place, London, WC1E 7JE, United Kingdom.*

[b] *Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi, 110016, India.*

* Corresponding Authors.

ppingole@chemistry.iitd.ac.in (Pravin Popinand Ingole)

m.jalebi@ucl.ac.uk (Mojtaba Abdi Jalebi)

[#]The authors contributed equally.

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Figure S1: KPFM Histograms.

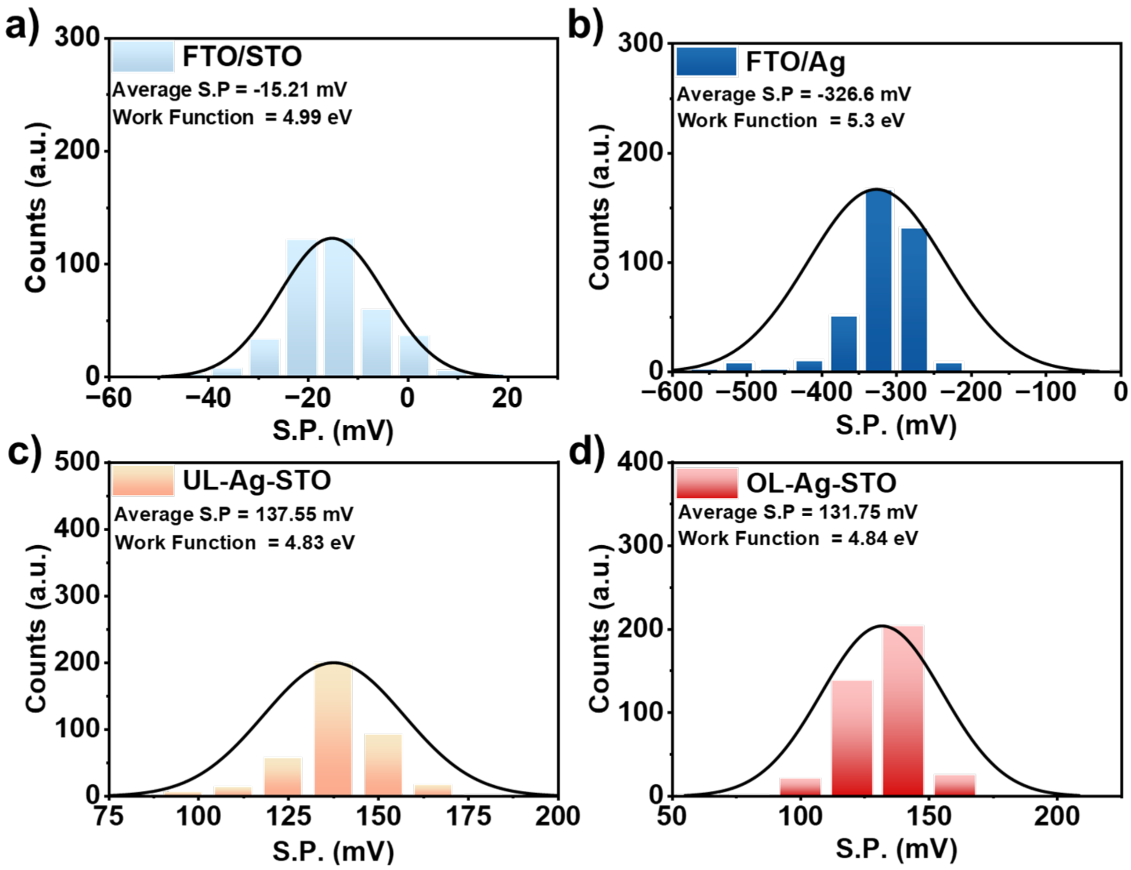

Figure S1 (a-d): KPFM histograms show the Gaussian distributions in surface potentials across FTO/STO, FTO/Ag, UL-Ag-STO and OL-Ag-STO samples. The subsequent averages were used to calculate consequent work functions for each sample.

Figure S2: SEM surface Imaging.

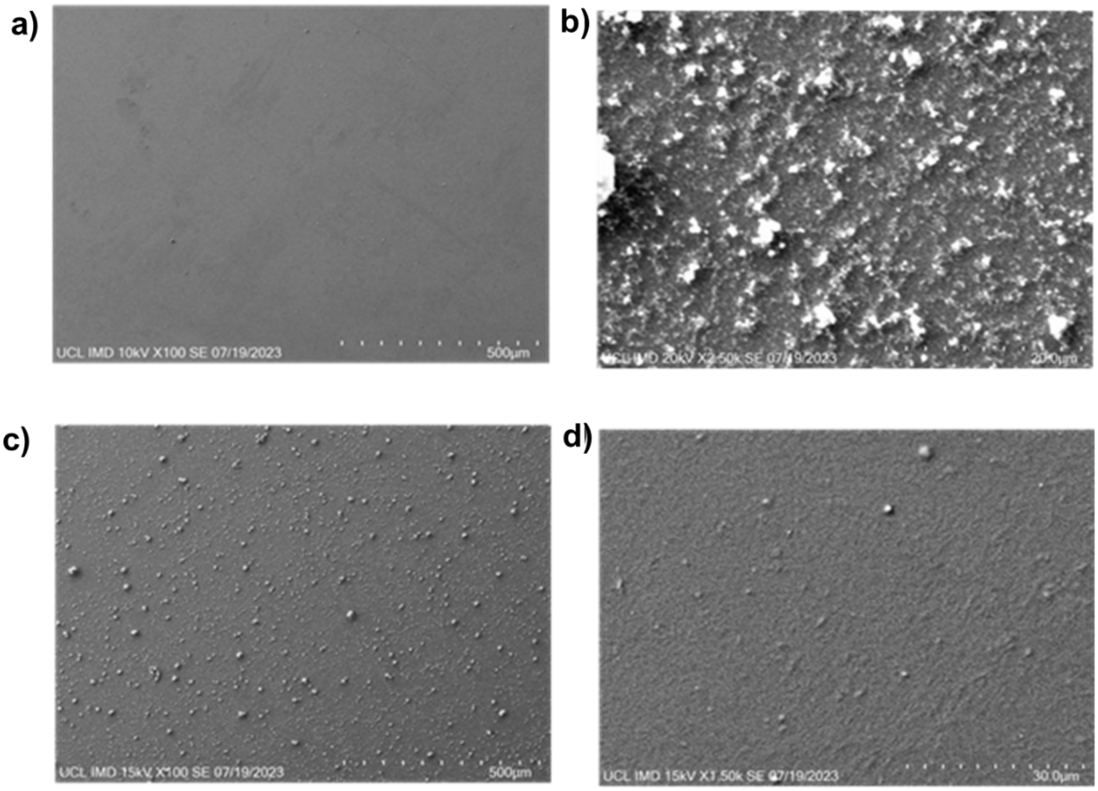

Figure S2: SEM images of different catalysts and reference films fabricated. (a) FTO/Ag, (b) FTO/STO, (c) UL-Ag-STO, and (d) OL-Ag-STO.

Calculation of Faradaic efficiency for the ECR products

$$\mathrm{F.E_g} = \frac{\mathrm{q_{output}}}{\mathrm{q_{input}}} \quad \text{......Equation 1}$$

$$\mathrm{q_{output}} = \mathrm{N_p} \times \mathrm{n_e} \times \mathrm{F} \quad \text{......Equation 2}$$

$$\mathrm{N_p} = \mathrm{C_p(ppm)} \times 10^{-6} \times \frac{\mathrm{PV}}{\mathrm{RT}} \quad \text{......Equation 3}$$

$$\mathrm{N_p} = 40.89 \times 10^{-12} \times \mathrm{C_p(ppm)} \quad \text{......Equation 4}$$

$$\mathrm{q_{input}} = \mathrm{i} \times \mathrm{t} \quad \text{......Equation 5}$$

$$\mathrm{t} = \frac{\mathrm{V\ (cm^3)}}{\mathrm{r_F\ (cm^3\ min^{-1})}} \quad \text{......Equation 6a}$$

$$\mathrm{t} = \frac{1\ \mathrm{cm^3} \times 60\ \mathrm{s}}{20\ \mathrm{cm^3}} = 3\ \mathrm{s} \quad \text{......Equation 6b}$$

$$\mathrm{F.E_g} = \frac{1.32 * 10^{-6} \times \mathrm{n_e} \times \mathrm{C_p(ppm)}}{i} \quad \text{......Equation 7}$$

where, $\mathrm{q_{output}}$ is the total charge consumed to generate products, $\mathrm{q_{input}}$ is the total charge supplied to the system, $\mathrm{N_p}$ is the number of moles of the product, $\mathrm{n_e}$ the number of electrons required for generating one molecule of the product, F (96485 C) is the Faraday constant, $\mathrm{x_p(ppm)}$ is the concentration of product in ppm (obtained from GC), P is the pressure (101325 N m^{-2}), V (cm^3) the loop volume, R (8.314 J K^{-1} mol^{-1}) universal gas constant, T (298 K) is the absolute temperature, t is the time required to fill a 1 cm^3 sample loop, and $\mathrm{r_F}$ (sccm= cm^3min^{-1}) is the flow rate.

Figure S3: Fitted EIS spectra and light-dark charge transfer comparison.

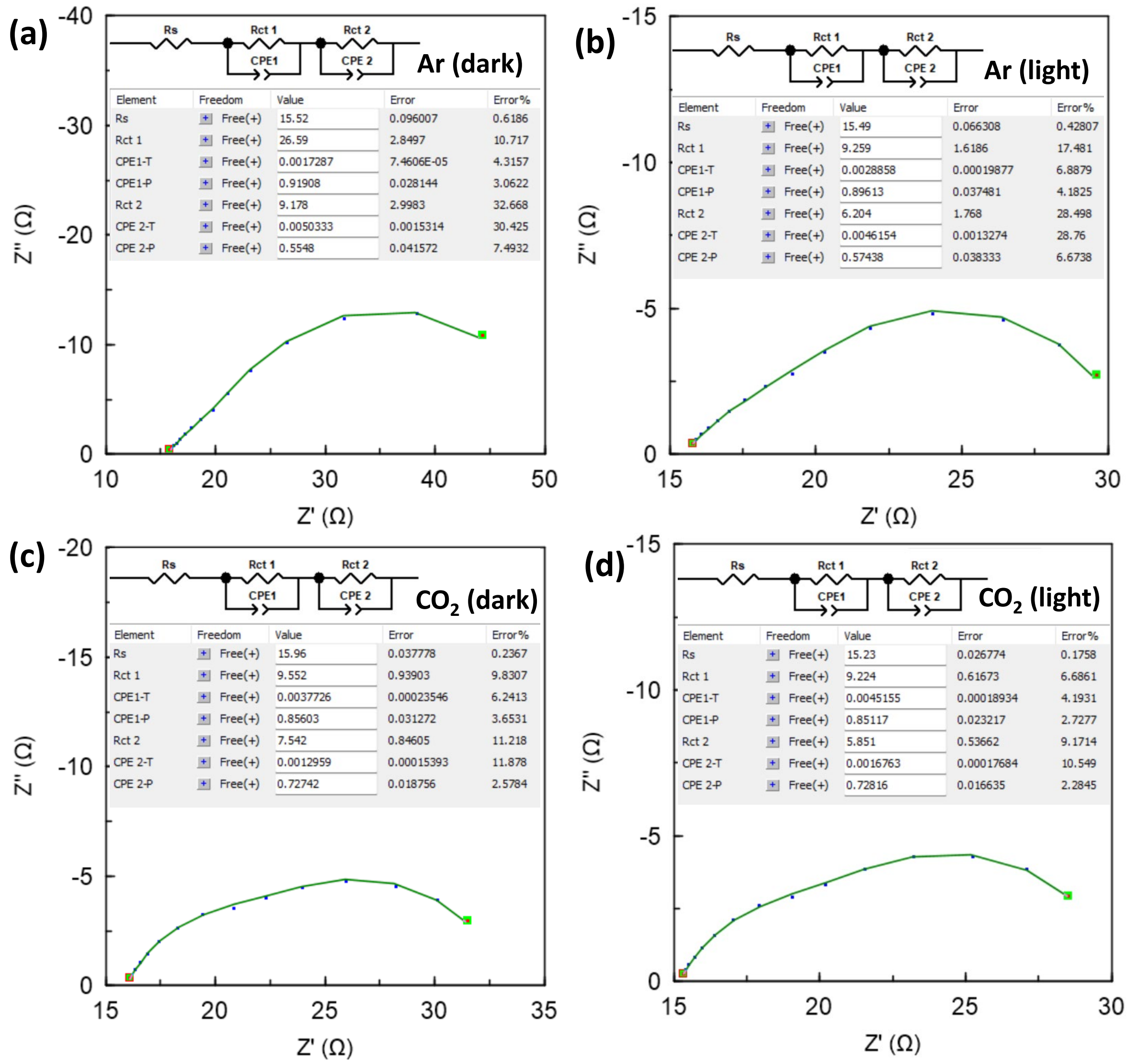

Figure S3: Fitted EIS spectra demonstrating fitted two-time constant equivalent circuit (R_s-(R_{ct1}/CPE_1)-(R_{ct2}/CPE_2)) under light and dark conditions for UL-Ag-STO.

Table S1: EIS Fitted Parameters - comparison of EIS parameters for UL-Ag-STO under different conditions obtained after fitting.

Conditions	R_s (Ω)	R_{ct1}(Ω)	R_{ct2} (Ω)	CPE_1 (F)	CPE_2 (F)
Ar (dark)	15.50	9.20	26.60	0.55	0.92
Ar (light)	15.50	6.20	9.30	0.57	0.89
CO_2 (dark)	16.00	7.50	9.60	0.72	0.86
CO_2 (light)	15.20	5.90	9.10	0.85	0.72

Where R_s is the contact resistance, R_{ct1} is the charge transfer resistance at the Ag/STO interface, and R_{ct2} is the charge transfer resistance at the STO/PBS for CO_2 reduction, while CPE_1 and CPE_2 are the corresponding capacitance values.

Figure S4: Faradic efficiency of photocathodes**.**

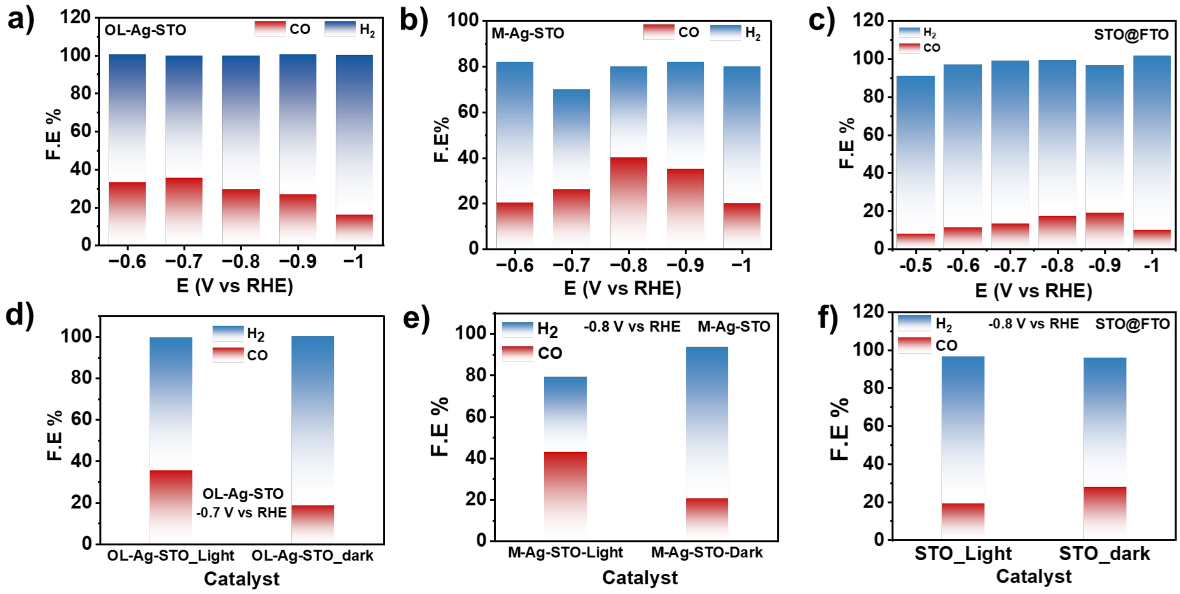

Figure S4: %F.E. plots for various photocathodes at various potentials: (a) OL-Ag-STO, (b) $AgTiO_2$-STO, (c) STO, and F.E. % comparison plots under dark and light conditions. (d) OL-Ag-STO, (e) M-Ag-STO, and (f) STO in CO_2 saturated PBS.

Figure S5: Time-dependent cyclic stability.

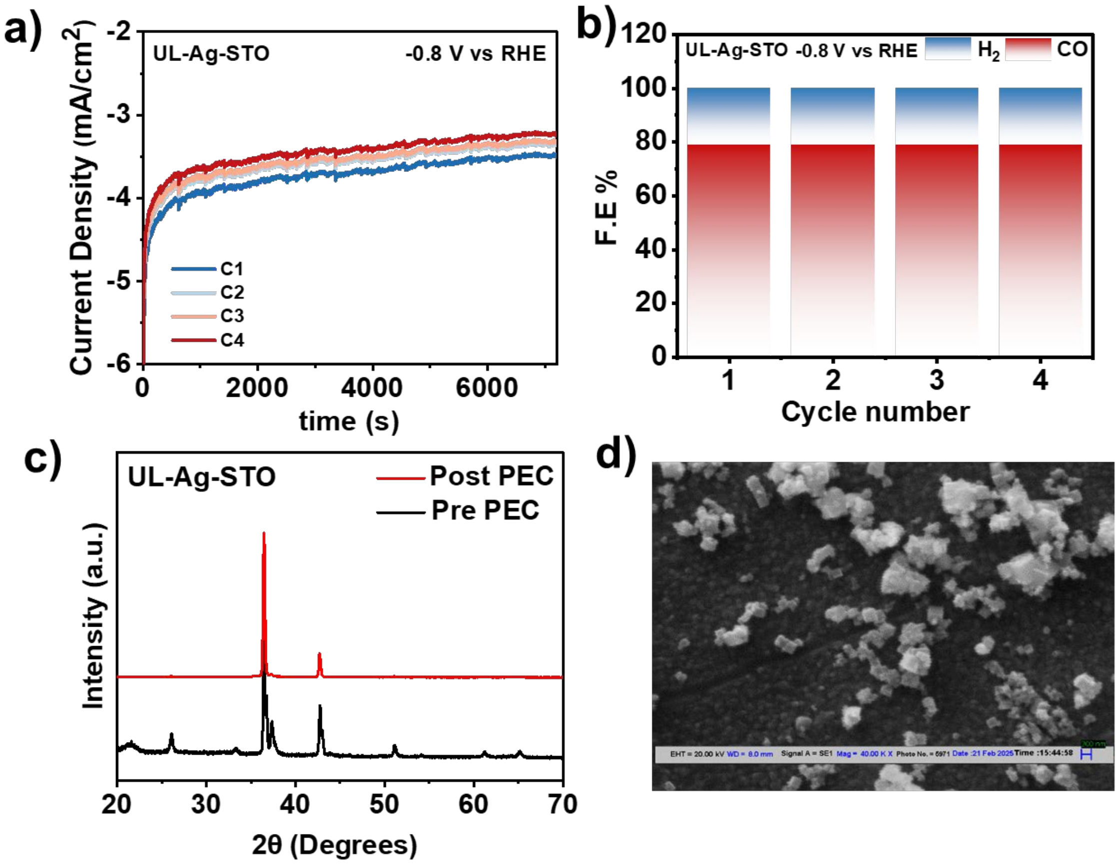

Figure S5: (a-b) Cyclic stability of UL-Ag-STO at -0.8 V vs RHE in CO_2 saturated PBS, (c) post-XRD analysis, and (d) post SEM analysis after 10 hours of continuous operation.

Figure S6: Mott-Schottky Plots and Flat band calculations.

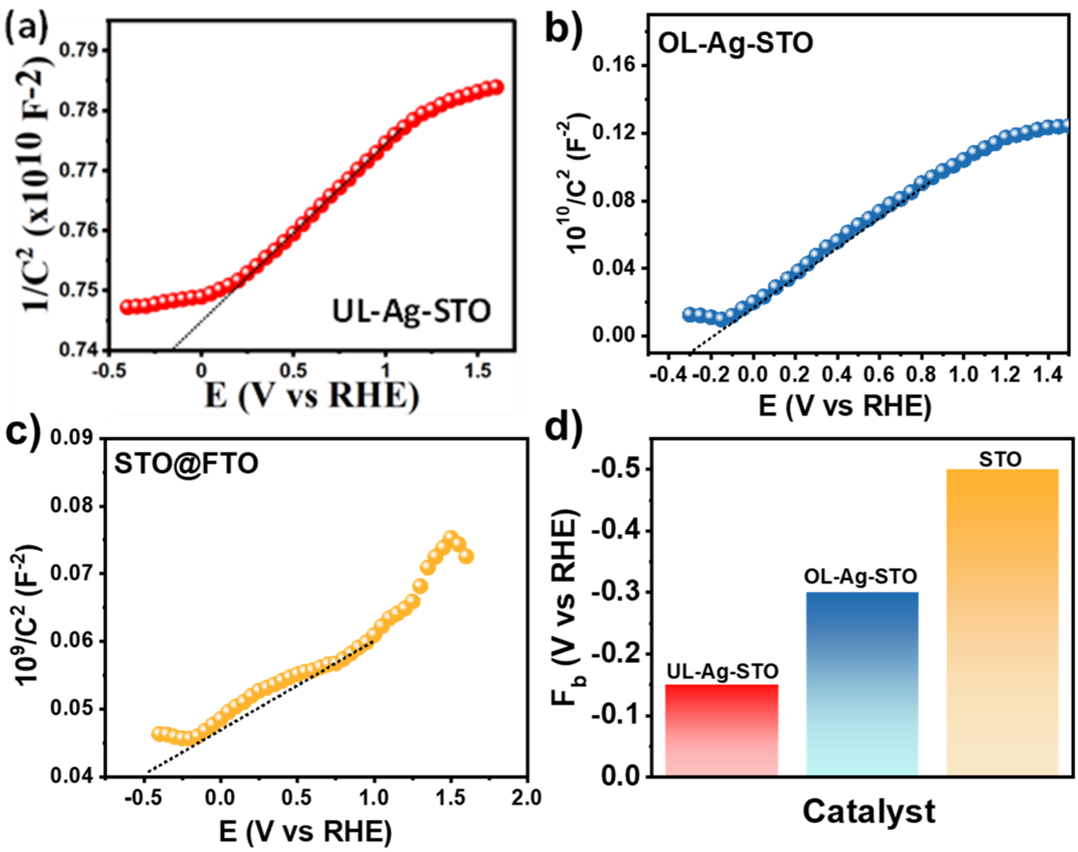

Figure S6: Mott-Schottky plots for (a) UL-Ag-STO, (b) OL-Ag-STO, (c) STO, and comparison of flat band potentials (F_b).

Table S2: Photoelectrocatalyst Benchmarking based on Ag and TiO_2.

Catalyst	E (V vs RHE)	Selectivity	F.E %	References
Cu-ZnO/GaN/n^+-p Si	+0.18	CO	70	*Angew. Chem. Int. Ed*. 2016, 55, 14262 – 14266
p-Si/SiO_2-Cu–Ag	-1.0	CO	79.8	*ACS Appl. Mater. Interfaces* 2021, 13, 16, 18905–18913
	-1.4	CH_4	59.3	
Ag/TiO_2/p-Si	-0.6	CO	47	*Appl. Sci.* 2020, *10*(10), 3487
SD-Ag/Si	+0.26	CO	95.2	*ACS Appl. Mater. Interfaces* 2024, 16, 17, 21868–21876
Ag/Cu_2O/ZS/FTO	−1.2 (Fc^+/Fc)	C_2H_4	60	Nature Energy, 6, (2021), 1124–1132
SC-TiO_2/CP	-1.8 (Ag/AgCl)	C_2H_4	46.6	*J. Env. Chem. Eng.* 10 (2022) 107441
Ag/Cu-TS-1	−0.6	C_2H_5OH	47	*Catal. Sci. Technol.,* 2022, 12, 2490
Au_3Cu / Si NW	-0.2	CO	80	*Nano Lett.* 2016, 16, 9, 5675–5680
$Ag_{50}Cu_{50}$/p-Si	−0.72	CO	26	*ACS Appl. Energy Mater.* 2023, 6, 16, 8397–8409
	−0.87	CH_4	18.2	
Si/Ag	-0.5	CO	90	*J. Mater. Chem. A*, 2018, **6**, 21906-21912
Au–TiO_2	−0.11	CO	84.2	*ACS Catal.* 2021, 11, 18, 11416–11428
Sn/TiO_2/Si	−1.0	HCOOH	68.82	*A European Journal*, 10.1002/chem.202303552, 30, 14, (2024)
UL-Ag-STO@FTO	**-0.8**	**CO**	**60 (front illumination)**	**This work**
			80 (back illumination)	

Table S3: State-of-the-art photoelectrocatalyst for CO_2 reduction.

Photocathode	**j (mA cm^{-2})**	**E (V vs RHE)**	**References**
p-Si/SiO_2-Cu-Ag	-3.0	-0.8	*ACS Appl. Mater. Interfaces* 2021, 13, 16, 18905-18913
Si/Ag_{120}-EM_{60}	-2.0	-1.0 vs. Ag/AgCl	*ACS Appl. Nano Mater.* 2023, 6, 2, 821-826
CPB-F-N-Au	-0.4	-0.8 vs. Ag/AgCl	*Energy Fuels* 2023, 37, 23, 18163-18172
Au/TiO_2/n^+p-Si	-5.5	-0.8	*Small* 2022, 18, 20, 2201882
Ni-In/SiNWs	-1.8	-0.8	*J. of Energy Chem.* 2021, 54, 422-428
Bi@ZFO NTs	-1.5	-0.8	*J. Phys. Chem. Lett.* 2022, 13, 29, 6867-6874
CuS/GaN/Si	-4.5	-0.8	*J. Am. Chem. Soc.* 2021, 143, 27, 10099-1010
CZTS/CdS (HA)	-1.8	-0.8	*Small* 2021, 17, 31, 210049
$In_{0.4}Bi_{0.6}$ + PV + light on	-5.0	-0.6	*ACS Energy Lett.* 2019, 4, 6, 1279-1286
Sn/TiO_2/Si	-4.7	-1.0	*ChemSusChem* 2022, 15, 8, e202200188
Si|TiO_2|CNT|Co^{II}(BrqPy)	-1.5	-0.11	*Angew. Chem. Int. Ed.* 2022, 61, 24, e202201086
RA-Au	-2.94	-0.11	*Adv. Energy Mater. 2017, 7, 3, 1601103*
meso-TiO_2|CoPcP	-1.53	-1.09 vs SHE	*ACS Catal. 2021, 11, 3, 1868-1876*
Ag-8.2/SiNWs	-4.1	-1.0	*Nanoscale, 2019,11, 26, 12530-12536*
STA-GO/CoPc	-2.6	-0.7	*Angew. Chem. Int. Ed. 2023, 62, 4, e202215213*
UL-Ag-STO	**-1.4**	**-0.2**	***This work***
	-1.8	**-0.6**	
	-2.6	**-0.7**	
	-4.0	**-0.8**	