Electronic Supporting Information for
Bifunctional Electrocatalysis for CO_2 Reduction via Surface Capping-Dependent Metal-Oxide Interactions

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Materials

All chemicals were purchased and used as received without further purification unless otherwise stated. CO_2 (99.99%) and CO (99.3%) were purchased from Airgas. Multi-wall carbon nanotubes (CNTs) were purchased from C-Nano (product number: FT 9000). Deionized water used throughout all experiments was purified through a Milli-Q reference water purification system to reach a resistivity of 18.2 MΩ·cm (at 25 °C).

Synthesis

SnO_2/CNT. The as-received CNTs were purified and oxidized using a modified Hummers method.[1] 10 mg of the oxidized CNTs were dispersed in 36 mL of water via bath sonication. 0.7 mL of concentrated hydrochloric acid was added. Then 100 mg of $SnCl_2$ (Alfa Aesar) was added to the mixture, followed by 30 min sonication. The well-dispersed suspension was transferred into a Teflon-lined stainless-steel autoclave and heated at 160 °C for 6 h. The product was collected upon cooling, centrifuging and washing with water for three times, and lyophilizing. The mass content of SnO_2 in the SnO_2/CNT material was roughly 65%, as determined from the weight gain after the synthesis.

CF-Au and CF-Au/SnO_2. 1 mg of oxidized CNTs (or 3 mg of SnO_2/CNT) was mixed with 2 mL of H_2O and 0.15 mL of 50 mM aqueous $HAuCl_4$ (Alfa Aesar). The mixture was sonicated for 30 min. Then 0.75 mL of 64 mM aqueous L-ascorbic acid (Alfa Aesar) and 0.25 mL of 0.2 M aqueous NaOH were added to the mixture under magnetic stirring conditions. The mixture was stirred for another 10 min. The product was collected upon centrifuging and washing with water for three times, and lyophilizing. The mass content of Au was roughly 70% in the CF-Au/CNT and 34% in the CF-Au/SnO_2/CNT, as determined from the weight gain after the synthesis.

CTAB-Au. CTAB-Au nanoparticles were synthesized according to an established protocol.[2] For Au seeds, 80 mL of water, 16 mL of 0.1 M aqueous CTAB (Acros), 800 μL of 25.4 mM aqueous $HAuCl_4$ and 1 mL of 64 mM aqueous L-ascorbic acid were mixed together. Then 1 mL of 0.2 M aqueous NaOH was injected into the above solution. The mixture was well shaken and kept still for 10 min. The as-prepared Au seeds were then added to 120 mL of 100 mM CTAB aqueous solution, and 5 mL of 100 mM aqueous L-ascorbic acid was added in sequence. 60 mL of 2.54 mM aqueous $HAuCl_4$ was then infused into the above solution through a syringe pump at a flow rate of 0.3 mL/min. The formed CTAB-Au nanoparticles were then collected by centrifuge at 8000 rpm for 10 min and re-dispersed in water. The concentration of the nanoparticles was determined by lyophilizing a portion of the colloidal suspension.

Cit-Au. The protocol of ligand exchange (citrate for CTAB) was adapted from a reported procedure.[3] Specifically, 5 mL of CTAB-Au colloid (1 mg/mL) was mixed with 45 mL of 0.15 wt% poly(sodium 4-styrenesulfonate) (Na-PSS) aqueous solution and allowed to sit for 1 h. The solution was centrifuged at 8000 rpm for 10 min. The colorless supernatant was decanted, and the retentate was re-dispersed in another 45 mL of 0.15 wt% Na-PSS aqueous solution. This centrifugation-decantation-redispersion step was repeated for another three times. Following the last centrifugation and decantation, the retentate was re-dispersed in 30 mL of 5 mM sodium citrate aqueous solution. The mixture was then allowed to sit overnight. Lastly, two more centrifugation-decantation-redispersion steps, each using 30 mL of 5 mM sodium citrate aqueous solution, were performed to obtain Cit-Au. The concentration of the nanoparticles was determined by lyophilizing a portion of the colloidal suspension.

Characterization

SEM and EDS measurements were performed on a Hitachi SU8230 cold field emission SEM microscope. XRD patterns were obtained using a Rigaku SmartLab X-ray diffractometer equipped with a Cu-target X-ray tube ($\lambda = 0.154$ nm) and operated at 40 mA and 44 kV. XPS analysis was conducted with a PHI Versa Probe II system using a monochromatic 1486.7 eV Al K_α X-ray source.

Electrode preparation

To prepare the CF-Au, SnO_2 and CF-Au/SnO_2 electrodes, 2 mg of CF-Au/CNT, SnO_2/CNT, or CF-Au/SnO_2/CNT was dispersed in 2 mL of ethanol. 6 µl of 5 wt% Nafion perfluorinated resin solution (Sigma Aldrich) was added to the mixture, which was then sonicated for 30 min. 300 µL (in the case of CF-Au and SnO_2) or 450 µL (in the case of CF-Au/SnO_2) of the ink was then drop-casted onto a 3 × 1 cm^2 Teflon-treated carbon fiber paper (Toray 030, Fuel Cell Store) to cover a 1 cm^2 area. The electrodes were fully dried under an IR lamp.

To prepare the CTAB(Cit)-Au and CTAB(Cit)-Au/SnO_2 electrodes, 1.5 mL of 1 mg/mL CTAB(Cit)-Au nanoparticle dispersion was centrifuged at 8000 rpm for 10 min, after which the colorless supernatant was decanted. The retentate was well mixed with 1 mL of 1 mg/mL oxidized CNTs dispersed in ethanol (or 3 mL of 1 mg/mL SnO_2/CNT dispersed in ethanol). 7.5 µl (in the case of CTAB(Cit)-Au) or 13.5 µL (in the case of CTAB(Cit)-Au/SnO_2) of 5 wt% Nafion perfluorinated resin solution (Sigma Aldrich) was added to the mixture, which was then sonicated for 30 min. 100 µL (in the case of CTAB(Cit)-Au) or 300 µL (in the case of CTAB(Cit)-Au/SnO_2) of the ink was then drop-casted onto a 3 × 1 cm^2 Teflon-treated carbon fiber paper (Toray 030, Fuel Cell Store) to cover a 1 cm^2 area. The electrodes were fully dried under an IR lamp.

Electrolyte purification

500 mL of 0.5 M $KHCO_3$ (Sigma Aldrich) aqueous solution was purified by a two-step electrolysis using two 10 × 5 cm^2 high-purity Ti foil (99.99%, Alfa Aesar) electrodes in a two-electrode setup. The first electrolytic step was conducted at 2.5 V until the current decreased to 150 µA. The second step was performed at a constant current of 150 µA for at least 20 h. During the electrolysis, the solution was magnetically stirred. The Ti electrodes were removed from the solution before the electrolysis was terminated, in order to avoid re-dissolution of electrodeposited impurities into the solution.

Electrochemical measurements

Electrochemical experiments were performed using a Bio-Logic VMP3 Multi Potentiostat and a custom-designed gas-tight two-compartment electrochemical cell. The graphite rod counter electrodes were purchased from Sigma Aldrich and the Ag/AgCl reference electrodes (-0.199 V vs SHE) were purchased from Pine Research Instrumentation. The cathode compartment and the anode compartment were separated by a Nafion 115 membrane (Fuel Cell Store). Each compartment contained 12 mL of electrolyte and ~18 mL of gas headspace. For all experiments, the pre-purified 0.5 M $KHCO_3$ was used as the electrolyte. Before each measurement, the electrolyte was pre-saturated with CO_2 or CO by bubbling the gas for at least 15 min. Gas was continuously bubbled into the electrolyte during electrolysis (or flowed into the headspace during cyclic voltammetry measurements) at a flow rate of 20 sccm. Before the start of each electrolysis, the ohmic drop between the working electrode and the reference electrode was determined using potentiostatic electrochemical impedance spectroscopy (PEIS) at -0.50 V vs Ag/AgCl between 200 kHz and 1 Hz with an amplitude of 10 mV. This ohmic drop was then compensated during the electrolysis. Current densities were calculated based on the catalyst-covered geometric area of the working electrode. All potentials were converted to the reversible hydrogen electrode (RHE) scale using the following formula: V (vs RHE) = V (vs Ag/AgCl) + 0.199 V + 0.0592 V × pH.

Product quantification

Gas products of electrocatalysis were analyzed by a GC (SRI 8610C, Multiple Gas Analyzer #5) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). High-purity N_2 was used as the carrier gas. The peak areas of the products (H_2 and CO) were converted to gas volumes using calibration curves that were obtained using a standard gas diluted to different concentrations with CO_2. Liquid products were quantified after electrocatalysis by ^{1}H NMR on an Agilent 400 MHz NMR instrument with solvent (H_2O) suppression. 400 μL of electrolyte was mixed with 100 μL of 10 mM dimethyl sulfoxide (DMSO) and 50 mM phenol in D_2O as internal standards for ^{1}H NMR analysis. Faradaic efficiencies (FEs) for the gas-phase products were average values from three measurements in a single electrolysis experiment. The FE_{HCOO^-} value at each potential was measured and calculated after a 30 min electrolysis.

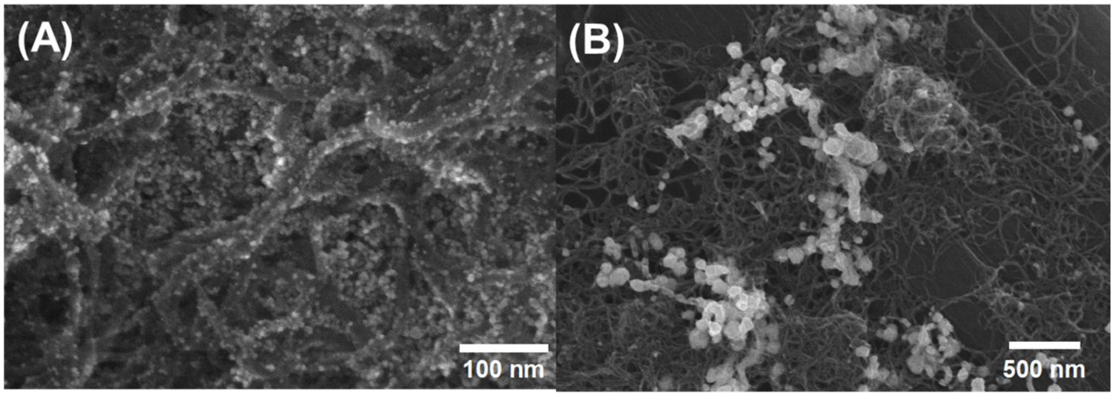


Figure S1. SEM images of (A) SnO_2 and (B) CF-Au nanoparticles supported on CNTs.

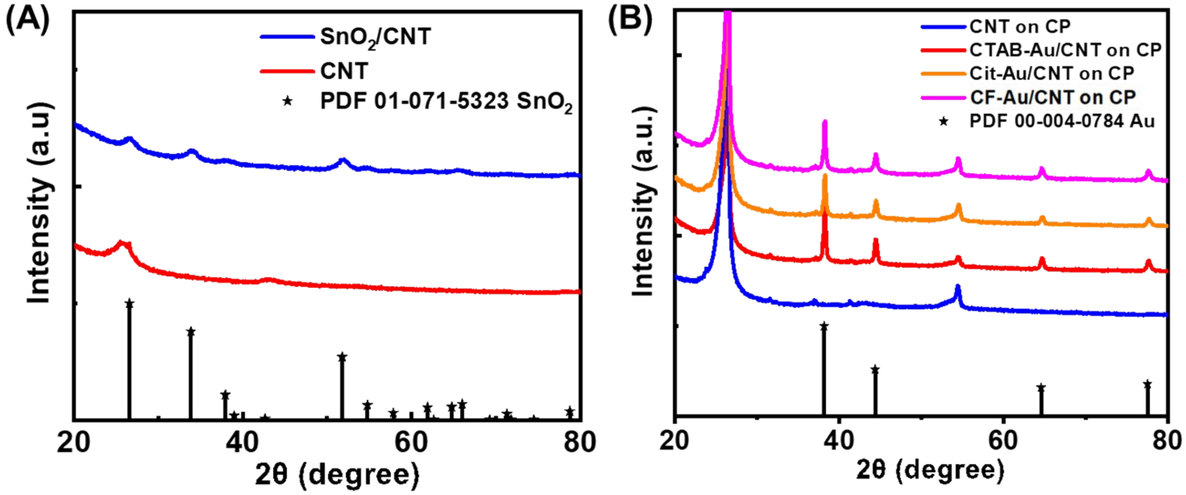


Figure S2. Powder XRD pattern for (A) SnO_2 and (B) CF-Au, CTAB-Au and Cit-Au nanoparticles supported on CNTs. In some of the measurements, carbon paper (CP) was used as the substrate.

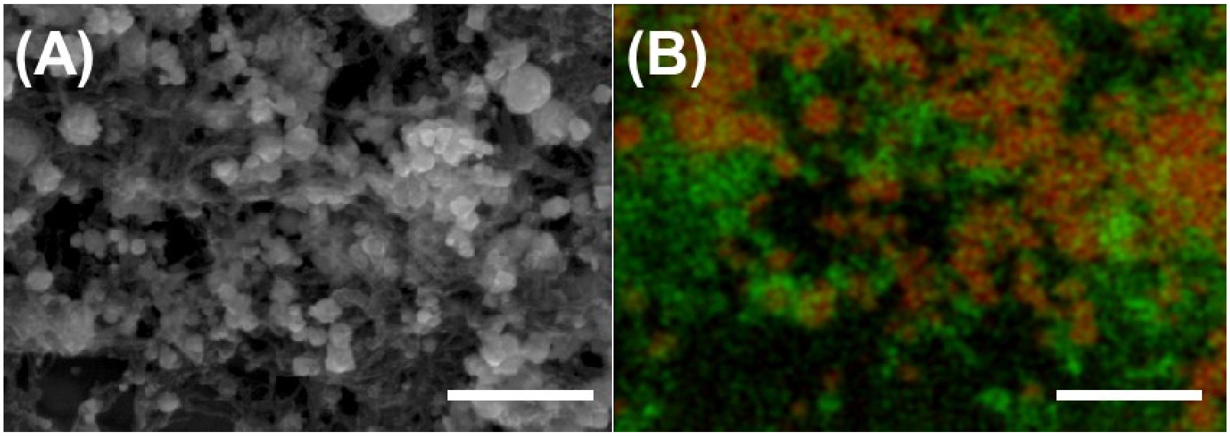


Figure S3. (A) SEM image and (B) EDS map for CF-Au/SnO_2 supported on CNTs. (Red: Au; Green: Sn; Scale bars: 500 nm)

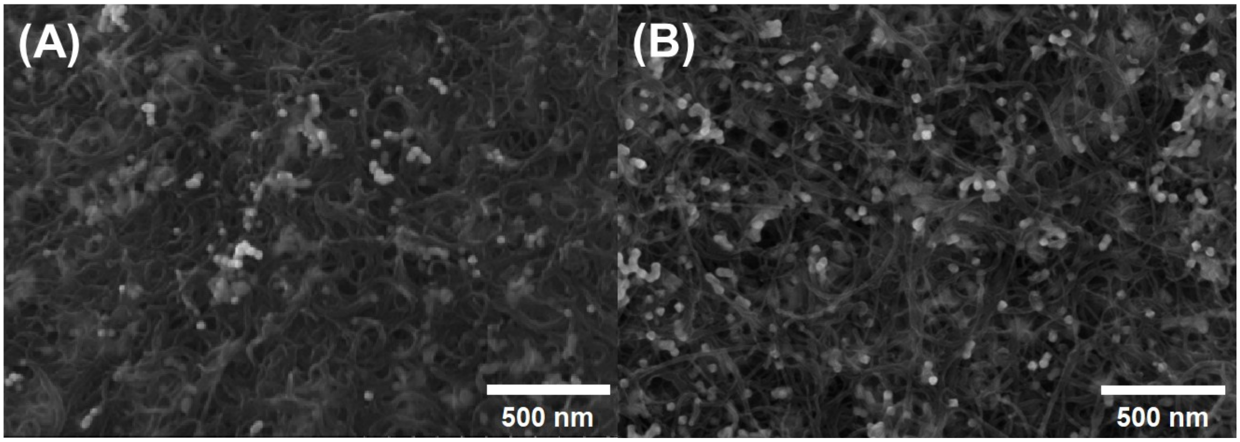


Figure S4. SEM images of (A) CTAB-Au and (B) Cit-Au nanoparticles supported on CNTs.

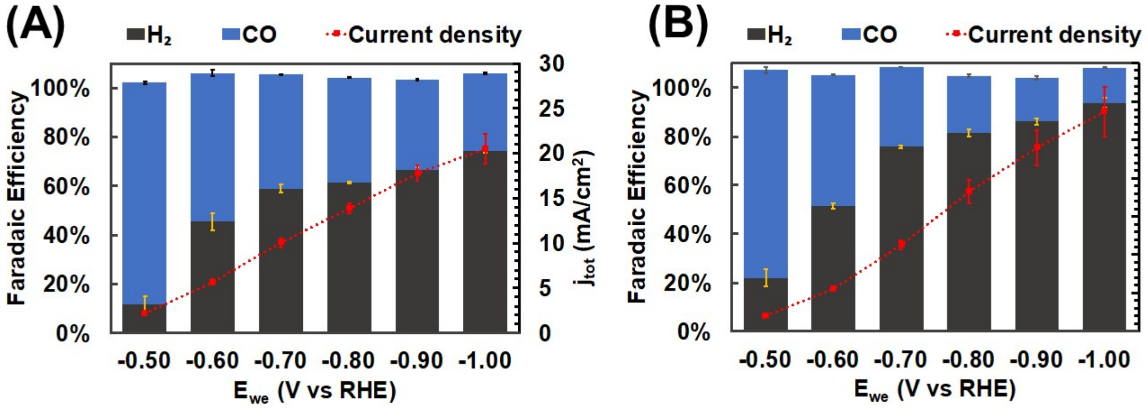


Figure S5. Potential-dependent catalytic performance of (A) CTAB-Au and (B) Cit-Au. Error bars represent standard deviations from multiple measurements.

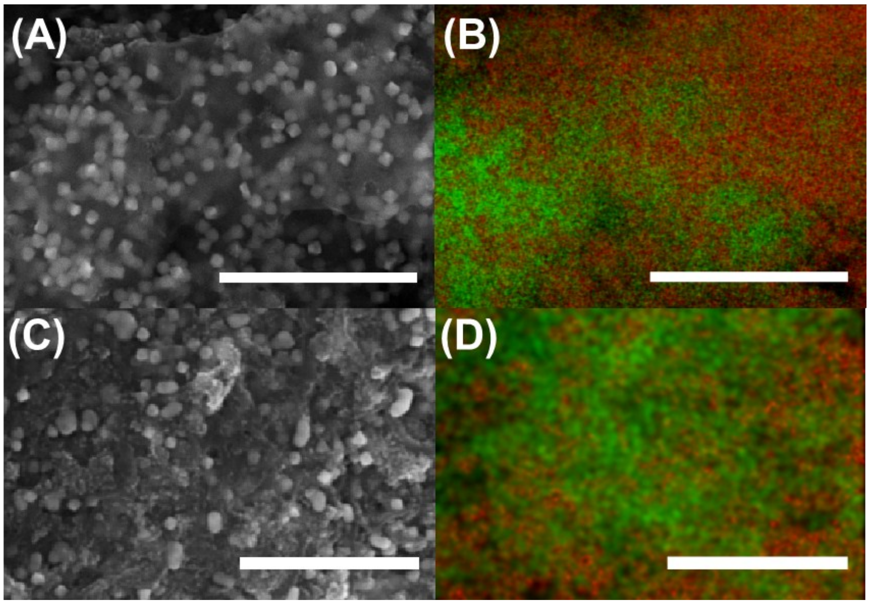


Figure S6. SEM images and EDS maps for (A, B) CTAB-Au/SnO_2 and (C, D) Cit-Au/SnO_2 supported on CNTs. (Red: Au; Green: Sn; Scale bars: 500 nm)

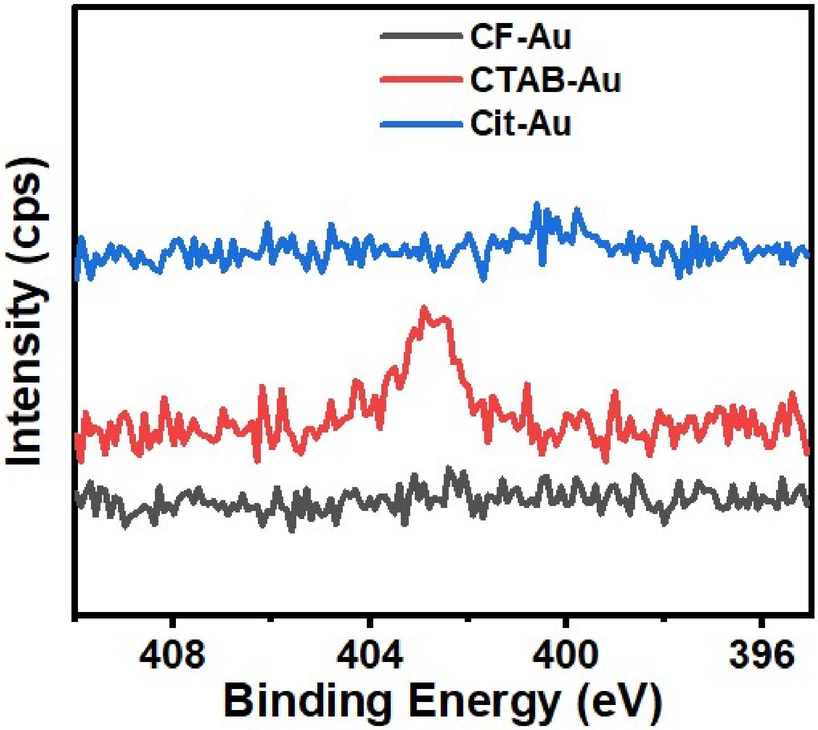


Figure S7. N 1s XPS spectra of CF-Au, CTAB-Au and Cit-Au supported on CNTs.

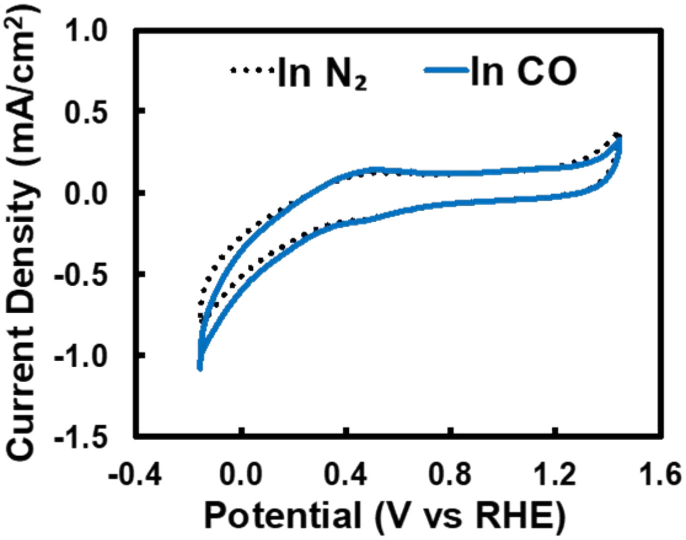
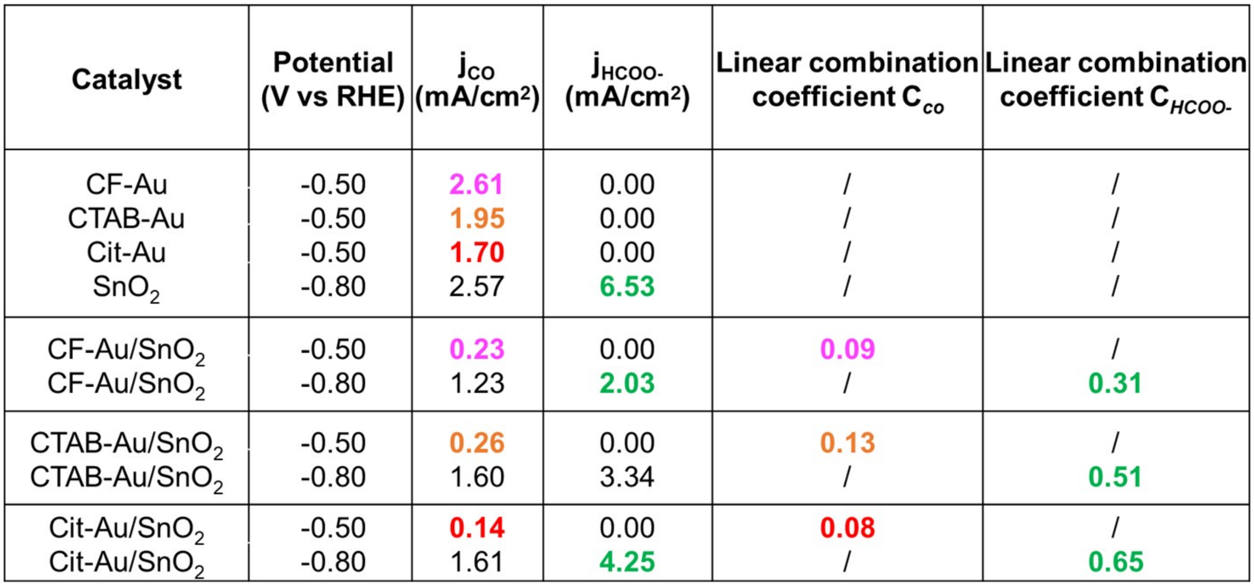


Figure S8. Cyclic voltammograms of SnO_2, in N_2 and CO in 0.5M $KHCO_3$.



Catalyst	**Potential (V vs RHE)**	**j_{CO} (mA/cm^2)**	**j_{HCOO-} (mA/cm^2)**	**Linear combination coefficient C_{co}**	**Linear combination coefficient C_{HCOO-}**
CF-Au	-0.50	**2.61**	0.00	/	/
CTAB-Au	-0.50	**1.95**	0.00	/	/
Cit-Au	-0.50	**1.70**	0.00	/	/
SnO_2	-0.80	2.57	**6.53**	/	/
CF-Au/SnO_2	-0.50	**0.23**	0.00	**0.09**	/
CF-Au/SnO_2	-0.80	1.23	**2.03**	/	**0.31**
CTAB-Au/SnO_2	-0.50	**0.26**	0.00	**0.13**	/
CTAB-Au/SnO_2	-0.80	1.60	3.34	/	**0.51**
Cit-Au/SnO_2	-0.50	**0.14**	0.00	**0.08**	/
Cit-Au/SnO_2	-0.80	1.61	**4.25**	/	**0.65**

Table S1. Calculation of the coefficients (C_{CO} and C_{HCOO-}) used in the linear combination analysis.

References

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2. H. Hu, F. Ji, Y. Xu, J. Yu, Q. Liu, L. Chen, Q. Chen, P. Wen, Y. Lifshitz, Y. Wang, Q. Zhang and S.-T. Lee, *ACS Nano*, 2016, **10**, 7323-7330.
3. J. G. Mehtala, D. Y. Zemlyanov, J. P. Max, N. Kadasala, S. Zhao and A. Wei, *Langmuir*, 2014, **30**, 13727-13730.