Supporting Information for:

Probing active site chemistry with differently charged Au$_{25}^{q}$ nanoclusters (*q* = -1, 0, +1)

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Experimental and Computational Methods

General. Au_{25}^- clusters capped with phenylethylthiol ($-SCH_2CH_2Ph$) ligands were synthesized according to previously published methods.[1] All aqueous solutions were prepared with certified ACS grade KOH or $KHCO_3$ (Fisher Scientific) and deionized water purified through a Barnstead Easypure II water purification system (Thermo Scientific). Spectroscopic grade dimethylformamide (DMF; 99.8%, Acros Organics) was dried over molecular sieves prior to use. All gases were ultra-high purity (UHP) grade.

Isolation of particular Au_{25}^q charge states. Different Au_{25}^q charge states were isolated according to our previously published method.[2] $Au_{25}(PET)_{18}^-$ was dissolved in N_2 purged DMF and transferred into a sealable, septum-capped cuvette. The cuvette was wrapped with Al foil to exclude ambient light and the solution was purged with N_2 for 30 minutes. Excluding ambient light during this initial step is important because O_2 can photo-oxidize Au_{25}^- into Au_{25}^0.[2] UV-Vis absorbance spectra of Au_{25}^- were then collected on an on an Agilent 8453 photodiode array spectrophotometer. Au_{25}^0 was isolated by bubbling the solution with O_2 for 1 hour while the solution was illuminated with a 350 W Xe-arc lamp through a 650 nm long-pass optical filter (hν ≤ 1.9 eV). The light contained energy greater than the Au_{25}^q HOMO–LUMO energy gap of ~1.4 eV and it promoted excited state Au_{25}^q–O_2 charge transfer.[2] Light containing less energy than the Au_{25}^q HOMO-LUMO gap does not initiate excited-state charge transfer. UV-Vis spectroscopy confirmed the isolation of Au_{25}^0 (see ref. 2 and figure 1c in the main text). This is a one electron process that stops after Au_{25}^0 formation. Au_{25}^+ was isolated by adding ~10-20 molar excess of tetrabutylammonium perchlorate (TBAP) and bubbling O_2 through a Au_{25}^- or Au_{25}^0 solution during illumination with $\lambda \geq 650$ nm light. The perchlorate anion stabilized Au_{25}^+ while the TBA^+ cation stabilized O_2^-. This process stopped after Au_{25}^+ formation and UV-Vis spectroscopy confirmed the isolation of Au_{25}^+. The Au_{25}^0 or Au_{25}^+ absorbance spectra stabilized after ~20-30 minutes of illumination. However, a one hour illumination period was used to ensure complete charge state conversion.

Precipitation onto the Carbon Black Support. Particular Au_{25}^q charge states were isolated in DMF as described above. They were then sonicated with Vulcan XC-72R carbon black (CB) in the absence of light. The PET-capped Au_{25}^q are not soluble in methanol (MeOH), and MeOH addition precipitated the Au_{25}^q clusters onto the CB support. The Au_{25}^q/CB suspension was centrifuged and the liquid was decanted off. The CB-supported Au_{25}^q clusters were re-sonicated in in fresh MeOH, centrifuged again and the MeOH was decanted off. This was done a total of 3 times. Samples were then dried under N_2 for future use. The ratio of Au_{25}^q to CB was adjusted through the starting concentration of Au_{25}^q in DMF and the volume of dissolved Au_{25}^q added to CB.

Electron Microscopy. Transmission electron microscopy (TEM) was performed using a Tecnai F20 field emission microscope operating at 200kV. Images were collected in STEM mode using a high angle annular dark field (HAADF) detector for z-contrast imaging. Sample preparation

was performed by sonicating CB-supported Au_{25}^q in methanol and depositing ~10 uL onto a 50 nm thick Si_3N_4 membrane grid (Ted Pella). Caution was taken to use the lowest possible electron dosage that provided adequate contrast for imaging and subsequent particle size analysis. This experimental setup was used to avoid damaging the particles during imaging. We did not observe particle sintering or other morphological changes during TEM imaging.

X-ray Photoelectron Spectroscopy (XPS). XPS experiments were carried out in a commercial UHV chamber from Omicron Nanotechnology GmbH with a base pressure of ~$3x10^{-10}$ mbar. The Au 4f spectra of the CB-supported Au_{25}^q samples were collected using an MgKα X-ray source (DAR 400, 1253.6 eV, 75 W) and a hemispherical electron spectrometer (SPHERA Energy Analyzer) with pass energy of 20 eV at room temperature. The binding energy of the CB-supported Au_{25}^q samples was calibrated to the Au $4f_{7/2}$ peak of a clean single crystal Au(111) at 83.8 eV.

Electrochemistry. CB-supported Au_{25}^q clusters were sonicated in a mixture of 200 μL methanol and 20 μL of a 5% Nafion solution. 5-20 μL of the Au_{25}^q/CB suspension was then dropcast onto a glassy carbon electrode. The Nafion binder adheres the CB-supported Au_{25}^q to the electrode but still allows solvent and reactant access to the cluster surface. Electrochemical experiments were conducted with a Biologic SP-150 potentiostat and a Pine Instruments electrode rotation controller. Cyclic voltammetry (CV) was repeated until stable curves were obtained. Polarization curves were then taken from the stabilized CVs. A Hydroflex reversible hydrogen electrode (abbreviated RHE, from eDAQ) was used for CO_2 reduction studies. A Ag/AgCl (3.0 M NaCl, from BASi) reference electrode was used for CO oxidation and O_2 reduction studies. The Ag/AgCl electrode was calibrated against the RHE in N_2 purged 0.1M KOH after each experiment, and all potentials are reported in the RHE scale. A Pt wire counter electrode was used for CO_2 and O_2 reduction experiments. A Au wire counter electrode was used for CO oxidation reactions.[3]

Quantification of Au_{25}^q on the Electrode Surface. OH stripping voltammetry was conducted in N_2 purged 0.1 M KOH. Au_{25}^- was first dissolved in acetone and the absorbance spectrum was collected. The concentration of the Au_{25}^- solution was determined from the known molar absorptivity [$\varepsilon = 8.8x10^3$ a.u./M/cm @ 1.83 eV (680 nm, labeled peak a in figure 1c of the main text)].[4] A precise volume of dissolved Au_{25}^- (in acetone) was added to 200 μL of CB suspended in MeOH (1 mg/mL in MeOH). Additional MeOH was then added to bring the mixture volume to 300 μL. The mixture was briefly sonicated and 20 μL of Nafion was added to bring the total solution volume to 320 μL. The mixture was briefly sonicated once more and then the Au_{25}^-/CB mixture was added to a GC electrode in 5.5 μL increments. Total Au_{25}^-/CB loadings on the electrode ranged between 5.5-11 μL (1-2 additions). Cyclic voltammetry was conducted at ω = 2500 RPM between +0.44 and +1.94 V vs. RHE until stable OH⁻ stripping voltammograms were obtained. The OH stripping peak was then integrated and plotted against the moles of Au_{25}^- on the electrode surface (figure S5). Alternatively, the electrochemical surface area (ECSA) could

be estimated from the OH stripping peak area using the literature value for bulk Au (390 μC cm^{-2}_{Au}).[5]

Turnover Frequency Determination. Turnover frequencies (TOF: molecules/Au_{25}^{q}/s) were determined from the polarization curves using the current density (A/mol Au_{25}^{q}), Faraday's constant (96485 C/mole e⁻), and the experimentally determined number of electrons transferred in the reaction (n = 2e⁻ for CO_2 reduction and CO oxidation, and n = 3e⁻ for O_2 reduction).[6] Electron transfer numbers were determined by analysis of CO_2 reduction products or Levich analysis of the CO and O_2 RDE polarization curves (see figures S12 and S16). An example TOF calculation is provided below.

$$ TOF = \frac{\text{current density "}j\text{"} \left(\frac{A}{\text{mole } Au_{25}^{q}} \right)}{\left(96485 \frac{C}{\text{mole e}^{-}} \right) \left(\frac{A \cdot s}{C} \right) \left(\frac{2 \text{ e}^{-}}{\text{molecule}} \right)} $$

Example: Au_{25}^{-} produced a CO_2 reduction current density of $1.84\pm0.11\text{x}10^{7}$ A/mole at −1V. This provides a TOF of 95±6 molecules/Au_{25}^{-}/s.

CO_2 reduction product analysis. CO_2 electrolysis experiments were conducted in a sealed, two compartment H-cell at −1 V *vs*. RHE (figure S8). One compartment contained a stationary glassy carbon working electrode and a Ag/AgCl reference electrode; the Ag/AgCl electrode was calibrated against the RHE in CO_2 saturated 0.1M $KHCO_3$ prior to each electrolysis run. The other half of the H-cell contained a Pt wire counter electrode. A 0.1778 mm (0.007 inch) thick Nafion 117 cation exchange membrane separated the two chambers. This setup prevents CO_2 reduction products from escaping the working electrode chamber, but allows current to flow *via* proton conduction through the Nafion membrane. After one hour of electrolysis the products were analyzed with a Perkin Elmer Clarus 600 gas chromatograph. Faradaic Efficiencies (FE) were calculated from the integrated reaction charge and the detected reaction products.

Computational Methods. All calculations reported in this work were done with spin-polarized density functional theory (DFT) implemented in the VASP code.[7] This implementation includes total energy and atomic force calculations. Plane-wave basis sets with a cutoff energy of 600 eV were used to expand the Kohn-Sham one-electron valence states. The generalized gradient approximation (GGA) using the Perdew-Burke-Enzerhoff (PBE) functional was employed to calculate the exchange-correlation energy.[8] The interactions of the valence electrons with the core electrons and the nuclei were described by the projector-augmented wave (PAW) all-electron potentials within the frozen-core approximation.[9]

The fully ligand-protected $Au_{25}(SCH_3)_{18}^{q}$ clusters were based on the published $Au_{25}(SR)_{18}^{-}$ crystal structure[1] and a previously DFT-optimized model.[10] Following our previous work,[11] a Au_{25} core capped with 18 −SCH_3 ligands was used to construct a model for the $Au_{25}(SCH_3)_{18}^{-}$ cluster. It was placed in a cubic box of *a* = 24Å to ensure the decoupling of periodic images and a uniform compensating background charge was assumed. Models for

$Au_{25}(SCH_3)_{18}^0$ and $Au_{25}(SCH_3)_{18}^+$ clusters were built by removal of one and two electrons from this structure. Geometry optimization of adsorbates on the $Au_{25}(SCH_3)_{18}^q$ clusters was carried out using a quasi-Newton variable metric algorithm until the total force on the atoms was less than 0.03 eV/Å. A Γ-point sampling of the Brillouin zone was utilized in the calculations of the ground state. For Au, S, C, and O we used the standard PAW potentials acting on eleven ($5d^{10}$ and $6s^1$), six ($3s^2$ and $3p^4$), four ($2s^2$ and $2p^2$) and six ($2s^2$ and $2p^4$) outer core/valence electrons, respectively. A Gaussian smearing of σ = 0.2 eV was used and the corrected energy for σ → 0 was employed. The binding energy was computed using the expression E_{ads} = $E_{adsorbates+cluster}$ − ($E_{adsorbate}$ + $E_{cluster}$). $E_{adsorbates+cluster}$ is the total energy of the relaxed adsorbates-cluster system. $E_{cluster}$ and $E_{adsorbate}$ are the total energy of the relaxed bare cluster and free adsorbates, *i.e.* the adsorbates as stable molecules or radicals in the gas phase.

(a)

Icosahedral Au$_{13}$ Core

(Au$_2$S$_3$)$_6$ "Ligand Shell"

Au$_{25}$(SR)$_{18}^-$ Cluster

1 nm

(b)

Au$_{25}$(SC$_2$H$_4$Ph)$^-$$_{18}$ with Tetraoctylammonium (TOA$^+$) Counter Ion

Rotate 90°

~2.4 nm

TOA$^+$ Counter Ion

(c) Au$_{25}$(SC$_2$H$_4$Ph)$^-$$_{18}$ Spacefill Model
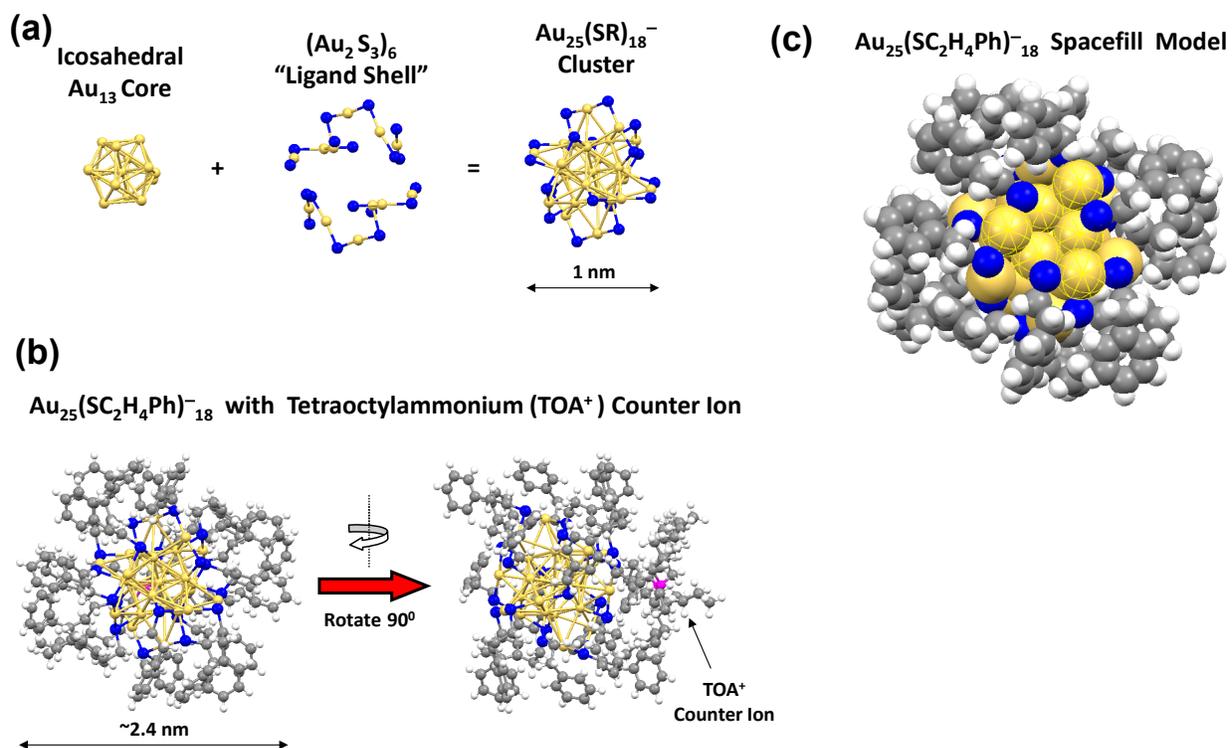
Figure S1. Components of the Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}^-$–TOA$^+$ crystal structure. Images were created from the crystallographic information files published in references 1a and 1b. The clusters are abbreviated as Au$_{25}^q$ (q = −1, 0, +1) in this manuscript. (a) The Au$_{25}^q$ cluster contains an Au$_{13}$ "core" surrounded by a "ligand shell" with six (Au$_2$S$_3$) semi-ring structures. (b) Organic phenylethylthiol (PET) ligands extend off the S atoms in the ligand shell. Au$_{25}^-$ is stabilized by a positive tetraoctylammonium (TOA$^+$) counter ion. The cluster is approximately 1 nm in diameter excluding the organic ligands and ~2.4 nm including the organic PET ligands. (c) A space fill model of the Au$_{25}^q$ cluster. The cluster's molecular adsorption "pocket" is highlighted with yellow cross-hatches.[11]
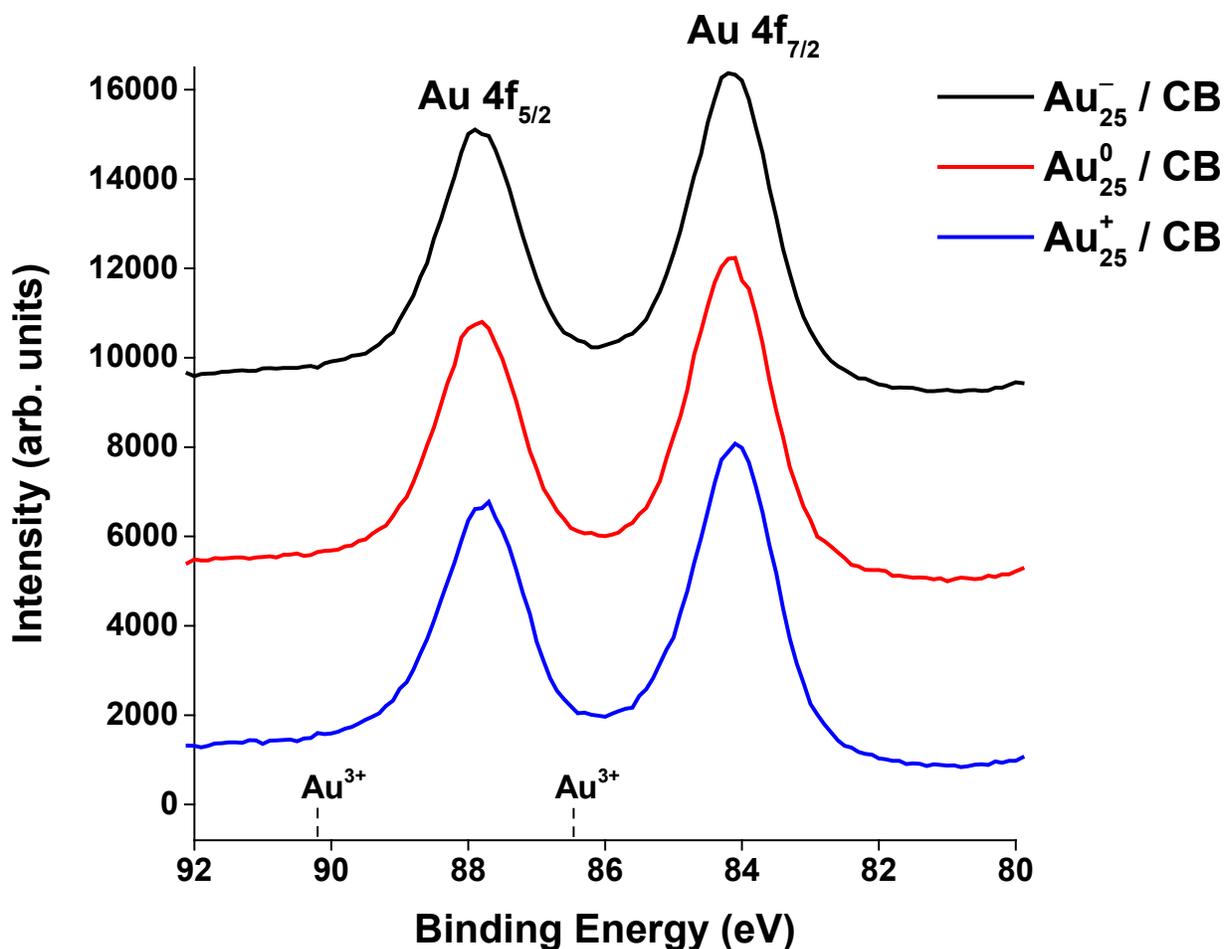
Figure S2. Au 4f region X-ray photoelectron spectroscopy (XPS) of the CB-supported Au_{25}^{q} clusters. The spectra are offset for clarity and the expected position of Au^{3+}-containing oxide peaks are indicated.

These X-ray photoelectron spectra confirm the absence of Au-oxide species on the Au_{25}^{0} and Au_{25}^{+} surface. We did not detect significant shits in Au 4f binding energy between the different Au_{25}^{q} charge states. The observed change in electron density between Au_{25}^{q} charge states would apparently be averaged across all 25 Au atoms in the cluster. This difference would be an apparent $\Delta e^{-} = -1/25\ e^{-}$ per Au atom for Au_{25}^{0} and $\Delta e^{-} = -2/25\ e^{-}$ per Au atom for Au_{25}. Any spectral shifts associated with these small, apparent Δe^{-} changes are likely below the resolution of our XPS instrument.
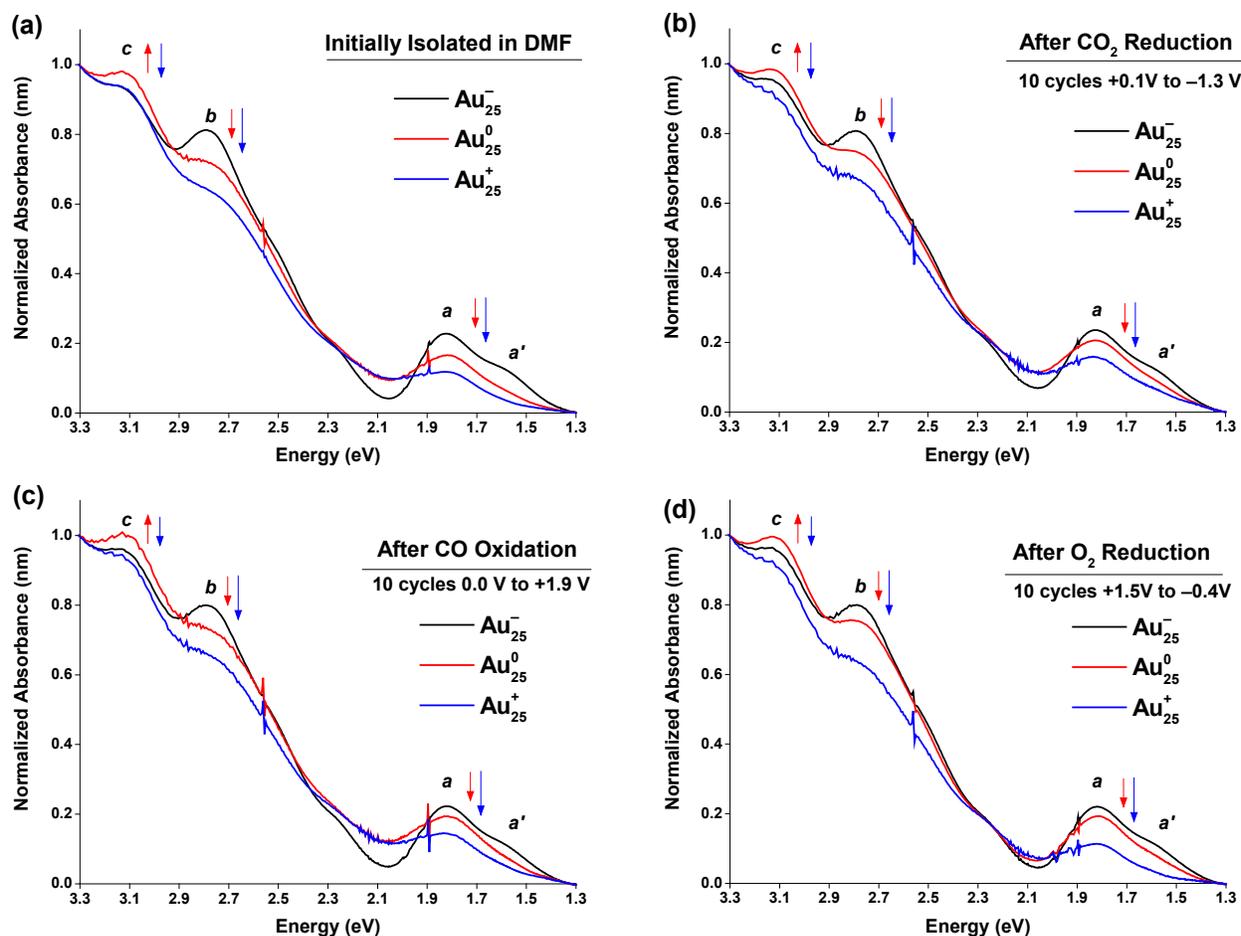
Figure S3. Optical absorbance spectra of Au_{25}^q charge states (a) initially isolated in DMF, and after electrocatalytic (b) CO_2 reduction, (c) CO oxidation, and (d) O_2 reduction. After the electrocatalytic reactions the electrode was rinsed with water, dried under N_2 and the clusters were extracted back into DMF. The red and blue arrows show the general peak trends between the different Au_{25}^q charge states. Retention of characteristic charge state-dependent optical spectra strongly suggest the Au_{25}^q clusters were stable during electrocatalytic reactions in aqueous electrolyte.

We characterized the optical absorbance spectra of Au_{25}^q clusters before electrocatalytic CO_2 reduction, CO oxidation and O_2 reduction reactions. Changes to the characteristic optical spectra would indicate if the cluster changed oxidation states or became degraded during the reaction. Specifically, changes in charge state or cluster degradation would have produced new optical signatures.

Au_{25}^q charge states were isolated in fast-drying CH_2Cl_2 or acetone and dropcast directly onto a glassy carbon electrode. We did not use DMF to isolate the clusters because it dries extremely slowly on the electrode surface. During the dropcasting procedure we shrouded the electrode in flowing N_2 and protected it from direct light to prevent cluster photo-oxidation. The

dropcast clusters were then cycled between the indicated potentials 10 times at 50 mV/sec in CO_2, CO or O_2 saturated solution. After the electrocatalytic experiments were complete the electrode was rinsed with DI water and dried under N_2. The clusters were then extracted off the electrode into DMF and their absorbance spectrum was recorded. These results show the clusters were stable during the electrocatalytic reactions, and we confidently attribute the catalytic activity differences to the particular $Au_{25}{}^q$ cluster's ground state charge.

We would like to point out that charge state stability is unique to aqueous environments, and aqueous electrochemistry cannot resolve discrete $Au_{25}{}^q$ orbitals.[12] Rather, aqueous electrochemical potentials promote the adsorption and reaction of ions and molecules at the cluster surface. Conversely, *nonaqueous* electrochemistry can resolve discrete $Au_{25}{}^q$ orbitals and directly control the cluster charge state. [2, 12-13]
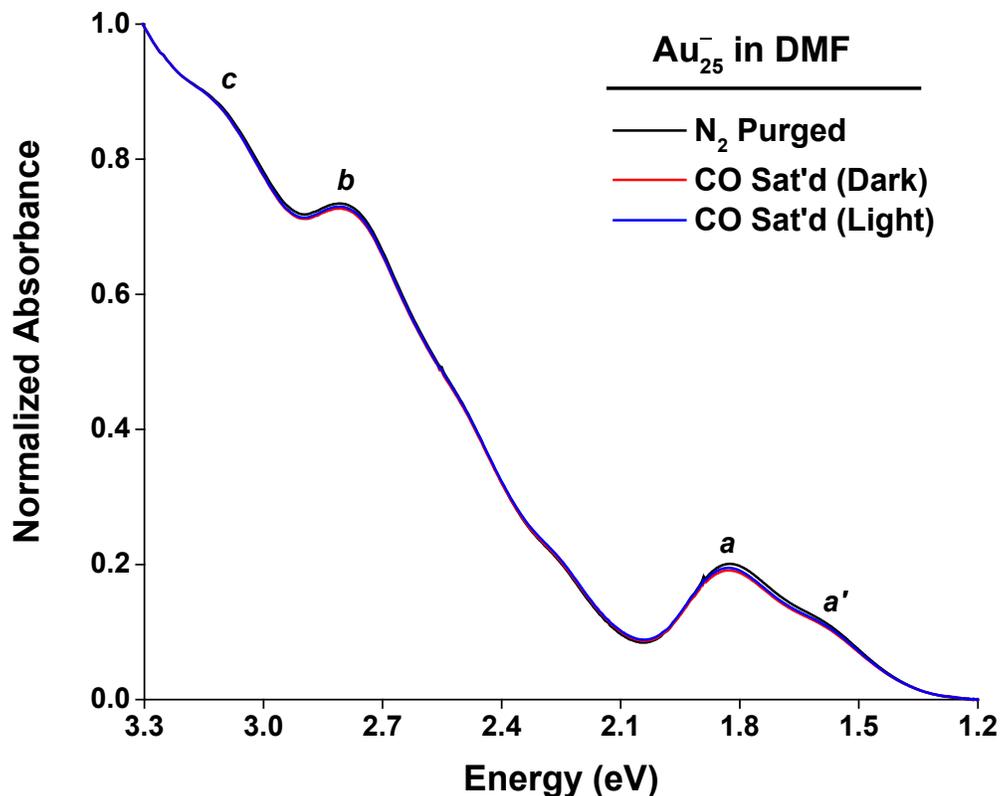
Figure S4. Optical absorbance spectrum of Au_{25}^- in N_2 purged DMF (black curve), after saturating the solution with CO gas in the dark (red curve), and after saturating the solution with CO during illumination with light containing energy greater than the Au_{25}^- HOMO-LUMO energy gap (blue curve; $h\nu < 1.9$ eV; $\lambda > 650$ nm light).

Exposing a Au_{25}^- solution to pure CO gas did not induce spectral changes in the absence or presence of light containing energy greater than the cluster HOMO-LUMO gap. This indicates CO gas does not engage in spontaneous charge transfer with the ground-state or excited-state cluster. These results are in line with previous calculations that predict Au_{25}^q–CO charge transfer requires removal of cluster ligands.[14] Please see references 2 and 11 for the optical absorbance spectra of Au_{25}^- in O_2 and CO_2 saturated DMF.
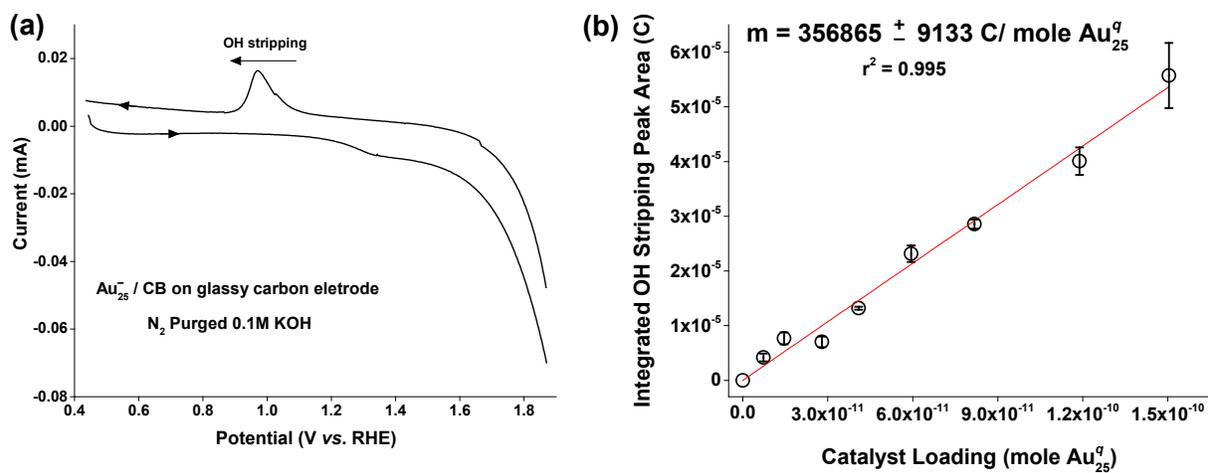
Figure S5. (a) RDE voltammogram of Au_{25}^-/CB in N_2 purged KOH showing the OH^- stripping peak at approximately +1.0 V vs. RHE (ω = 2500 rpm; 50 mV/s scan rate). (b) Integrated OH stripping peak area *vs.* catalyst loading. Error bars at each catalyst loading represent three OH stripping experiments with freshly deposited Au_{25}^q/CB.
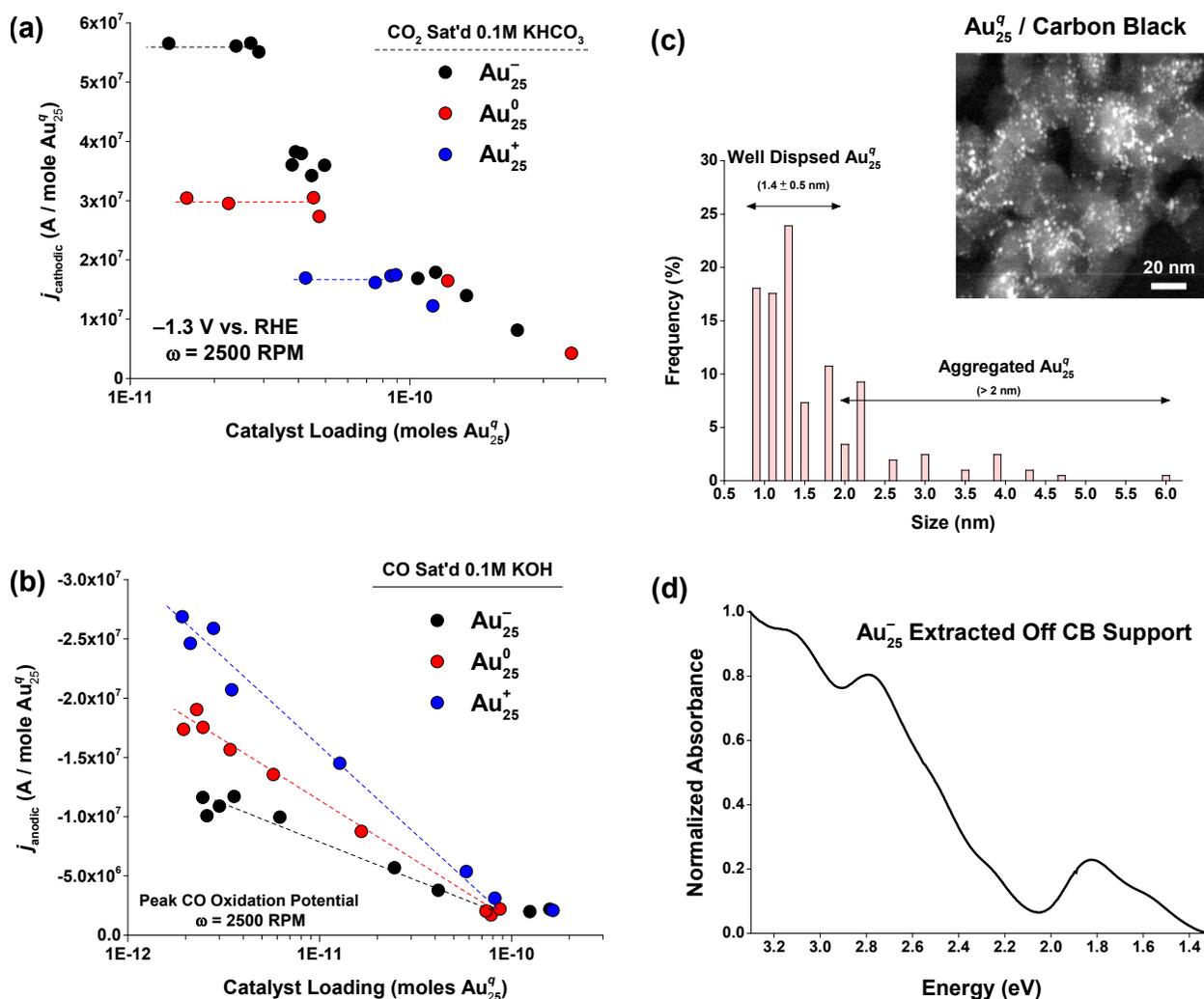
Figure S6. Variation in measured current density *j* (A / mole Au_{25}^{q}) *vs.* catalyst loading (moles Au_{25}^{q}) for (a) CO_2 reduction (measured at −1.3 V vs. RHE) and (b) CO oxidation reactions (measured at peak CO oxidation potential). Data points represent the raw data collected from polarization curves and the dashed lines serve as a guide to the eye. (c) TEM image and particle size distribution of an Au_{25}^{q}/CB sample in the high Au_{25}^{q} loading regime. (d) Optical absorbance spectra of Au_{25}^{-} extracted back off the CB support. Retention of optical absorbance spectra indicates the larger Au_{25}^{q} aggregates in figure S6c are likely closely spaced, individual Au_{25}^{q} clusters, and necessarily rules out the clusters sintering into larger particles.

We noticed an inverse relationship between catalyst loading and catalytic current density for CO_2 reduction and CO oxidation reactions. The current density *j* (A / mol Au_{25}^{q}) increased as the catalyst loading (mol Au_{25}^{q}) decreased. Catalyst loadings were adjusted by varying the ratio of Au_{25}^{q} to CB support. Loadings were quantified by integrating the OH^{-} stripping peak (see figure S5 on the previous page). The trend of increasing current density eventually stabilized for

CO_2 reduction. Catalyst loadings from the stabilized loading regime were chosen to compare the CO_2 activity of differently charged $Au_{25}{}^q$ clusters.

No current density stabilization was observed for the CO oxidation reaction within the range of accurate OH stripping peak area measurement. Equivalent $Au_{25}{}^q$ loadings between 2×10^{-12} and 4×10^{-12} moles were used for comparison of CO oxidation activity.

The data in figure S6a,b support predictions that closely spaced or aggregated nanocatalysts will have overlapping diffusion regions.[15] Such "catalyst crowding" limits the transport of reactants to the catalyst surface and effectively lowers the apparent catalytic activity of the material. Decreasing the catalyst loading increases the spacing between individual particles and lessens the diffusional overlap. Therefore, lowering the catalyst loading will increase reactant access to each $Au_{25}{}^q$ cluster and increase the observed catalytic current density. The trends in figure S6a,b highlight that care that must be taken when comparing the electrocatalytic activity of supported catalysts, as high catalyst loading can cause "catalyst crowding" and artificially lower the apparent activity.

Figure S6c presents a dark-field transmission electron microscope (TEM) image and a particle size histogram of the CB-supported $Au_{25}{}^q$ clusters. A high $Au_{25}{}^q$ loading was used to facilitate TEM imaging. The $Au_{25}{}^q$ clusters appear as small bright spots and the CB support appears dark. In this high loading regime we found a combination of well-dispersed, apparently isolated $Au_{25}{}^q$ clusters (1.4±0.5 nm; n=189) and larger $Au_{25}{}^q$ aggregates. This cluster size is consistent with the ~1nm diameter expected from the $Au_{25}{}^q$ crystal structure[1, 16] and other TEM images of supported Au_{25} clusters.[17]

Pradeep and coworkers noted that $Au_{25}{}^q$ clusters can experience electron-induced sintering during TEM imaging.[18] To avoid cluster damage we used the lowest possible electron dosage that provided adequate contrast for imaging, and we did not observe particle sintering during TEM imaging. $Au_{25}{}^q$ clusters retained their characteristic optical spectra once extracted off the CB support (Figure S6d), whereas sintered $Au_{25}{}^q$ clusters should lose their characteristic, molecule-like optical spectra and develop plasmon resonances associated with larger Au nanoparticles. The retention of the $Au_{25}{}^-$ optical spectrum indicates the $Au_{25}{}^q$ aggregates seen in figure S6c contain multiple, closely spaced ~1nm clusters. This apparent $Au_{25}{}^q$ aggregation in a high loading sample correlates well with the "catalyst crowding" concept presented in figures S6a,b.
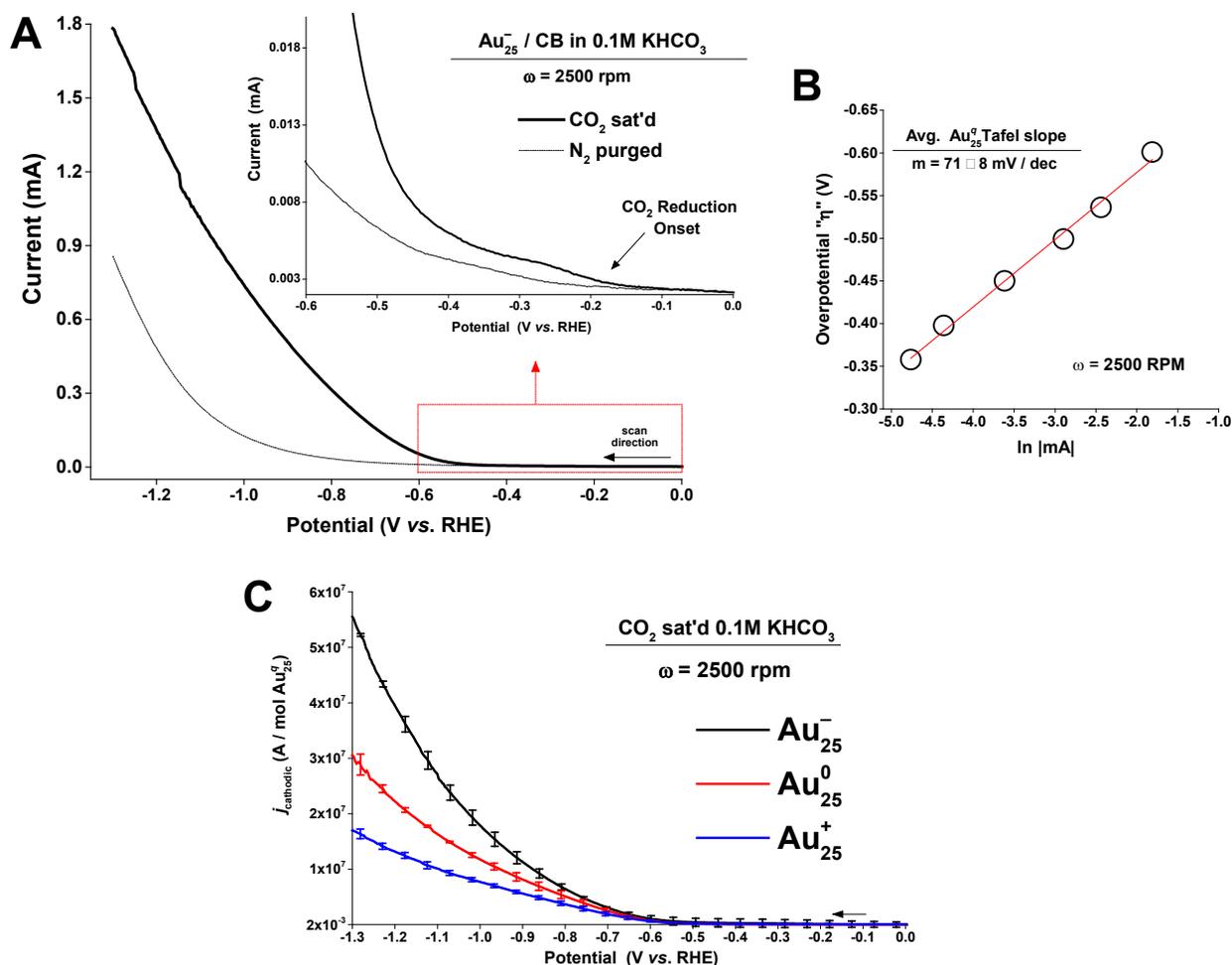
Figure S7. (a) Polarization curves of CB-supported Au_{25}^- in N_2 purged (dashed line) and CO_2 saturated (solid curve) 0.1M $KHCO_3$. The inset shows the onset of CO_2 reduction at -0.223 ± 0.049 V *vs.* RHE. A relatively high catalyst loading of 5×10^{-11} moles Au_{25}^- was used in panel A to demonstrate the CO_2 reduction onset. (b) Representative Tafel plot of CB-supported Au_{25}^- in CO_2 saturated 0.1M $KHCO_3$. (c) Average polarization curves of Au_{25}^q in CO_2 saturated 0.1M $KHCO_3$ (ω = 2500 rpm). Cluster loadings for panels c and were within the stable catalyst loading *vs.* current density regime for each Au_{25}^q cluster to ensure accurate comparison; see figures S5 and S6 for further details concerning catalyst loading *vs.* catalytic current density. Error bars are from three separate experiments with freshly deposited Au_{25}^q/CB.

Figure S7a shows the onset for CO_2 reduction. Equivalent onset potentials of E_{onset} = -0.223 ± 0.049 V *vs.* RHE were determined for the differently charged Au_{25}^q clusters. Adsorbed CO_2 is reversible reduced into CO_2^- between E = -0.2 V and -0.4 V (Equation S1). H^+ coadsorption / H_{ads} formation begins at approximately E = -0.5 V vs. RHE (Equation S2) as evidenced by the onset of minor H_2 evolution.[11] Dramatically increased CO production rates coincide with H^+ coadsorption / H_{ads} formation and CO_2 reduction proceeds through Equations

S3 and S4. This mechanism was determined from the potential product distribution described in reference 11.

Figure S7b shows a representative Tafel plot for CO_2 reduction at Au_{25}^-. Equivalent Tafel slopes indicate a common mechanism for CO_2 reduction at the Au_{25}^q clusters. Tafel slopes of 71 ± 8 mV dec^{-1} are close to the reversible limit of 59 mV dec^{-1}. Such Tafel slope values indicate a mechanism involving an initial reversible electron transfer to CO_2 (Equation S1) followed by a rate-determining chemical step.[19]

CO_2 reduction: $\mathbf{CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O}$ -- $E^0 = -0.103$ V *vs*. RHE**.**

Equation S1: $CO_2 + e^- \rightarrow CO_2{}^-{}_{ads}$

Equation S2: $H^+ + e^- \rightarrow H_{ads}$

Equation S3: $CO_2{}^-{}_{ads} + H_{ads} \rightarrow COOH_{ads}$

Equation S4: $COOH_{ads} + H^+ \rightarrow CO + H_2O$
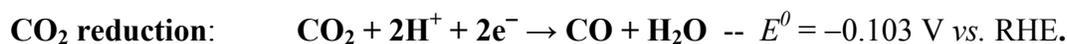
Alternative CO_2 Reduction mechanism (no H_{ads}; low potential regime, very slow)

Equation S5: $CO_2{}^-{}_{ads} + e^- + 2H^+ \rightarrow CO + H_2O$
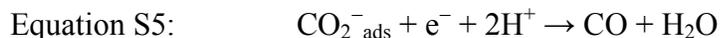
We note that an alternative, low-overpotential CO_2 reduction mechanism can occur in the absence of H_{ads} (Equation S5). In the low overpotential regime (before H_{ads} formation) the initial electron transfer to CO_2 is reversible (Equation S1). However, $CO_2{}^-{}_{ads}$ can be reduced into CO through sequential proton capture and electron transfer steps. This low-potential process is kinetically sluggish as seen from potential-dependent product analysis[11] and small CO_2 reduction current (figure S7a).
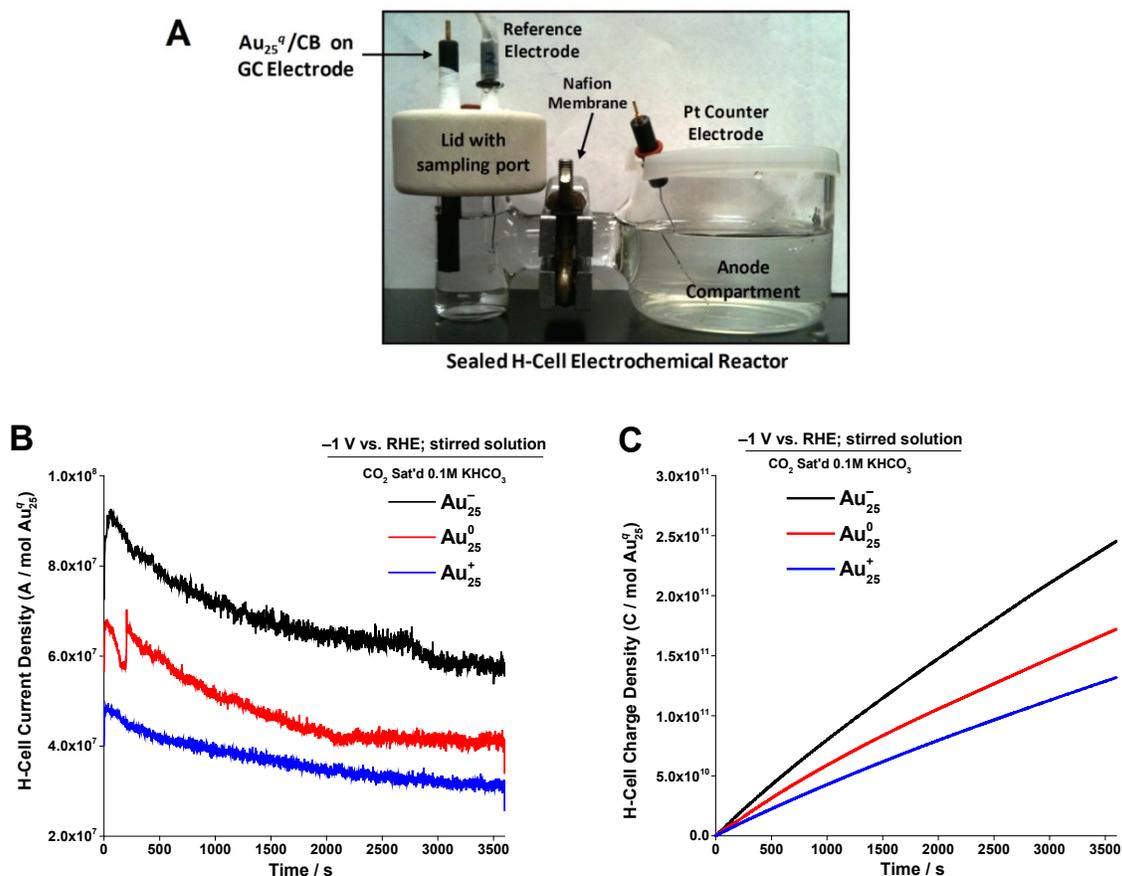
Figure S8. (a) Photograph of the H-Cell electrochemical reactor for analysis of CO_2 reduction products. Representative (b) current density (A / mole Au_{25}^q) and (c) charge density (C / mole Au_{25}^q) *vs.* time plots of the Au_{25}^q clusters at −1 V in stirred, CO_2 saturated 0.1M $KHCO_3$. Catalyst loadings between 2×10^{-12} and 4×10^{-12} mole Au_{25}^q were used for H-Cell experiments.

An electrochemical H-cell reactor was used to quantify reaction products. The cell consisted of two chambers separated by a Nafion cation exchange membrane. One chamber was gas-tight and contained a stationary GC electrode and an Ag/AgCl reference electrode. The other compartment contained a Pt-wire counter electrode. This configuration keeps the reaction products in the working-electrode chamber, but the Nafion membrane still allows current flow *via* proton conduction. The solution was vigorously stirred at a constant rate and −1V *vs.* RHE was applied to the working electrode for 1 hour; this potential was previously identified as the optimal H-cell potential for selective $CO_2 \rightarrow CO$ conversion.[11] Products in the headspace and electrolyte were analyzed with gas chromatography after one hour of electrolysis (values shown below).

The H-Cell reactor produced current densities and TOFs that were approximately 3-4 times higher than RDE polarization experiments. These higher current densities resulted from the experimental setup. For example, the H-Cell used a stationary GC working electrode placed ~5

mm above a stir bar to prevent bubble build-up during electrolysis. The rapidly stirred solution produced the higher current density and TOFs compared with the RDE experiments. The retention of charge state-dependent CO_2 activity indicates the Au_{25}^q clusters were stable during CO_2 reduction.

CO Production Rates from H-Cell Reactor

	mol Au_{25}^q	CO TOF (molec./Au_{25}^q/s)	CO selectivity (%)	CO FE (%)	ECSA (cm^{-2}_{Au})	CO Production Rate ($mmol/cm_{Au}^2/hr$)
Au_{25}^-	$(1.93\pm0.06)\times10^{-12}$	328 ± 10	97.7 ± 0.8	99 ± 4	0.00177 ± 0.00005	1.29 ± 0.04
Au_{25}^0	$(2.8\pm0.2)\times10^{-12}$	213 ± 5	96 ± 1	82 ± 7	0.0026 ± 0.0002	0.84 ± 0.2
Au_{25}^+	$(3.6\pm0.2)\times10^{-12}$	156 ± 9	97.9 ± 0.5	81 ± 1	0.0033 ± 0.0002	0.62 ± 0.04

Au_{25}^- converted CO_2 into CO with $99 \pm 4\%$ Faradaic efficiency (FE) at $-1V$. Minor amounts of H_2 were also evolved. Lower FEs were observed for Au_{25}^0 ($82 \pm 7\%$ FE) and Au_{25}^+ ($81 \pm 1\%$ FE), although their CO selectivities were still high. Control experiments showed the CB support contributed less than 2% of the observed CO, and electrolysis in N_2 purged solutions produced H_2 and trace amounts of CO ($< 0.1\%$ of that formed during electrolysis in CO_2 saturated solutions). Faradaic Efficiencies (FE) were calculated from the detected reaction products, the integrated reaction charge, Faraday's constant (96485 C/mol e$^-$) and the number of electrons required for product formation (CO = 2e$^-$). For example:

$$FE = 100\% * \left\{ \frac{\text{detected mol CO}}{[\text{electrolysis charge (C)}] \left(\frac{1 \text{ mol } e-}{96485 \text{ C}} \right) \left(\frac{\text{CO molecule}}{2e-} \right)} \right\}$$

We previously normalized our reaction rates to the electrochemical surface area of the Au_{25}^q cluster using the value for bulk Au (390 $\mu C/cm^2_{Au}$).[5] The ECSA and ECSA-normalized values are summarized in the table above. The ECSA-normalized CO production rate for Au_{25}^- is statistically identical to our previously determined value of 1.26 $mmol/cm^2_{Au}/hr$.[11] However, it is difficult to estimate the TOF from these values because one must assume bulk areal density of gold. Our current method of precisely measuring the moles of Au_{25}^q on the electrode surface (figure S5) provides more accurate TOF estimates.
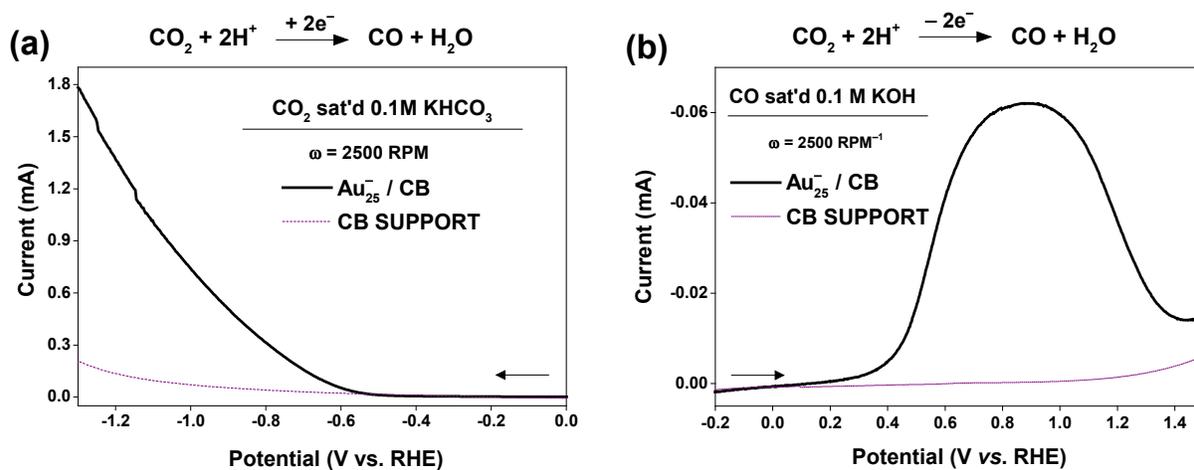
Figure S9. Comparison of (a) CO_2 reduction and (b) CO oxidation at CB-supported Au_{25}^- and the catalyst-free CB support. The CB support shows negligible activity for CO_2 reduction and CO oxidation compared with Au_{25}^q.

Figure S10. Ball-and-stick representations of CO_2 + H^+ coadsorption geometries and their binding energies. The O−3S coadsorption geometry is presented as a space-filled model in main text Figure 2c. *Atom colors: Au: gold, S: blue, C: grey, H: white, O: red.*

We compared CO_2 + H^+ coadsorption on realistic, fully ligand-protected $Au_{25}(SCH_3)_{18}^q$ cluster models (q = -1, 0, +1). Our calculations identified several common coadsorbed states at the differently charged Au_{25}^q clusters. One such state includes H bound to one ligand-shell Au atom of the negatively charged Au_{25}^- cluster with calculated H-Au distance of 1.61 Å. CO_2 coordinates with three ligand-shell S atoms in the previously identified adsorption pocket[11] with O-S distances ranging between 3.55-3.71 Å. This coadsorption geometry is labeled as O−3S in figure S10. Two additional stable configurations were identified and H and CO_2 were both bound to ligand-shell Au atoms. CO_2 attached to the ligand-shell Au atom with its C atom (C−Au configuration) or O atom (O−Au configuration). In both cases the O-C-O bond axis of the molecule is roughly parallel with the S-Au-S moiety in the ligand. The structure of the cluster remained intact in all CO_2 + H^+ coadsorption geometries.

The binding energies are summarized in figure S10, and the stability of different coadsorbed states were equivalent at any one Au_{25}^q charge state. An important finding here is that binding energies of coadsorbed states at Au_{25}^- are consistently larger. This finding represents more stable reactant adsorption at the negatively charged cluster. The relationship between TOF and CO_2 + H^+ binding energy (Figure 2b in the main text) highlight that reactant adsorption is a key parameter affecting the CO_2 reduction rate.

CO_2 + H^+ Coadsorption Energies (eV)			
	O–3S	**C–Au**	**O–Au**	**Average**
Au_{25}^-	-12.23	-12.24	-12.27	-12.25 ± 0.02
Au_{25}^0	-9.96	-10.05	-10.09	-10.03 ± 0.07
Au_{25}^+	-8.32	-7.91	-8.06	-8.06 ± 0.23

Au$_{25}$(SCH$_3$)$_{18}$^{q} + CO$_2$

r (O-S)=3.33 – 3.48 Å

O–3S

r (O-Au)=3.72 Å

O–Au

r (C-Au)=3.55-3.62 Å

C–Au

r (O-S)=3.65 – 3.71 Å

r (C-S)=3.79 Å

O–2S and C–S

Au$_{25}$^{q}–CO$_2$ Binding Energies (eV)

	O–3S	O–Au	C–Au	O–2S and C–S	Average
Au$_{25}$$^{-}$	-0.14	-0.14	-0.097	x	-0.13 ± 0.02
Au$_{25}$^{0}	-0.14	-0.15	-0.088	x	-0.13 ± 0.04
Au$_{25}$$^{+}$	x	-0.14	-0.11	-0.61	-0.29 ± 0.28

Average Au$_{25}$^{q}–CO$_2$ binding: −0.18 ± 0.16 eV

Figure S11. Ball-and-stick representations and binding energies of the singly-bound Au$_{25}$^{q}–CO$_2$ system. *Atom colors: Au: gold, S: blue, C: grey, H: white, O: red.*
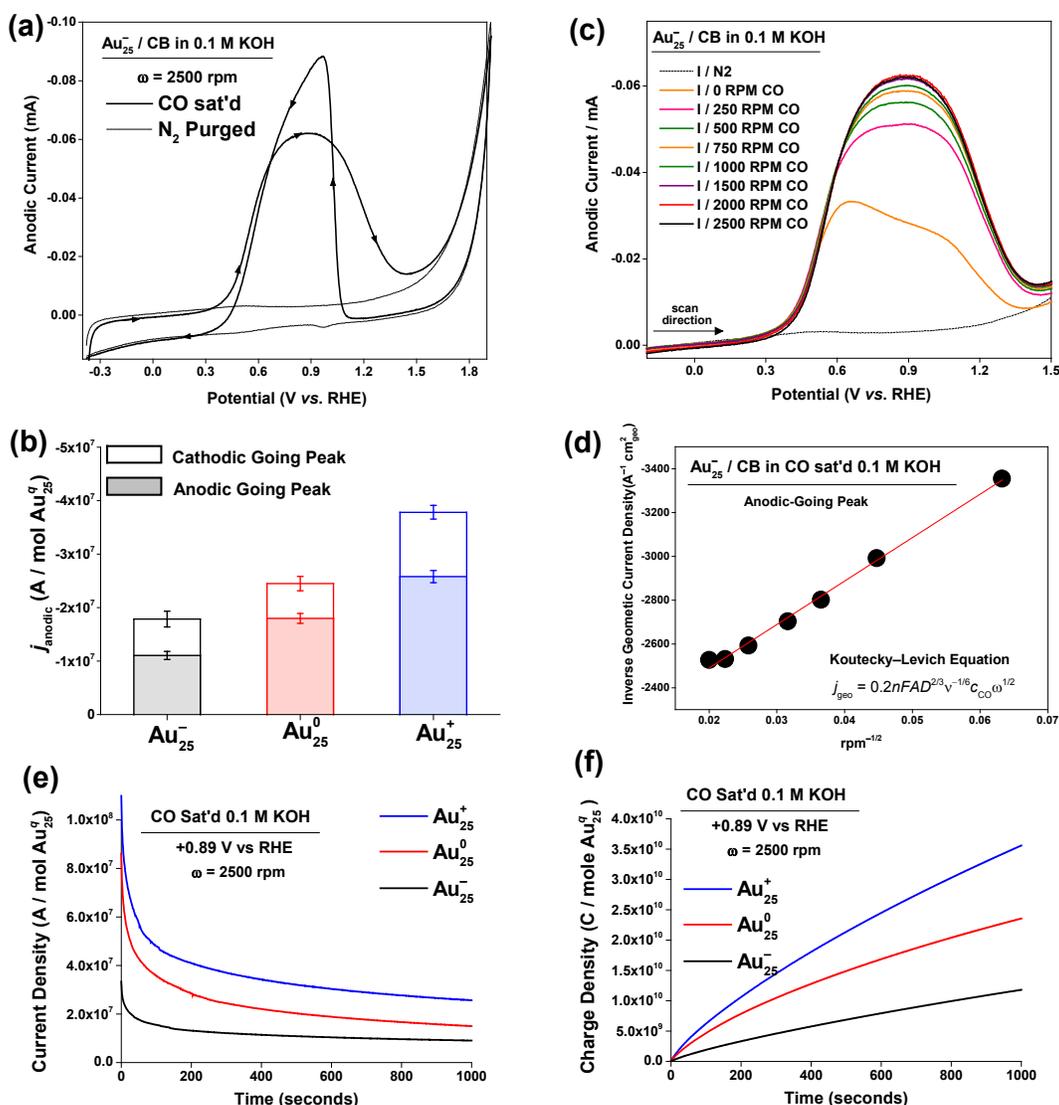
Figure S12. (a) Cyclic voltammograms of CB-supported Au_{25}^- in CO saturated and N_2 purged 0.1M KOH (ω = 2500 rpm; ν = 50 mV/s). (b) Comparison of CO oxidation current density from the anodic- and cathodic-going scan directions; error bars are from three separate measurements with freshly deposited Au_{25}^q/CB. (c) Representative RDE curves at different rotation rates. (d) Levich analysis of RDE polarization curves.[20] (e,f) Constant potential electrolysis of CO at +0.89 V *vs.* RHE, electrode rotation rate ω = 2500 rpm. Equivalent catalyst loadings of $2-4\times10^{-12}$ mole Au_{25}^q were used for CO activity comparison and TOF determinations (see figs. S5 and S6).

CO oxidation: $CO + 2OH^- - 2e^- \rightarrow CO_2 + H_2O$ -- $E^0 = -0.103$ V *vs.* RHE

Equation S6: $2OH^- - 2e^- \rightarrow 2OH_{ads}$

Equation S7: $CO_{ads} + OH_{ads} \rightarrow COOH_{ads}$

Equation S8: $COOH_{ads} + OH_{ads} \rightarrow CO_2 + H_2O$
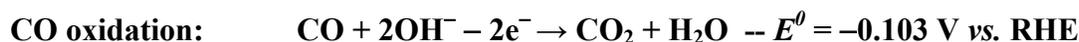
It is generally agreed that CO oxidation proceeds through a Langmuir-Hinshelwood mechanism with adsorbed OH⁻ acting as the oxidant (Equations S6-S8). [3, 21] This means the CO oxidation rate depends on the availability of adsorbed OH. In fact, the large overpotentials required for CO oxidation stem from OH adsorption at the catalyst surface.[22] The cyclic voltammograms in Figure S12a show CB-supported Au_{25}^- in N_2 purged and CO saturated 0.1 M KOH (ω = 2500 rpm; v = 50 mV/s). Equivalent anodic-going Tafel slopes of 95 ± 17 mV/dec were found for the differently charged Au_{25}^q clusters, which are consistent with other Au catalysts.[19, 21]

The CO oxidation current decreased beyond +1V. This phenomenon has previously been attributed to preferential OH⁻ adsorption blocking CO sites.[22] This interpretation is reasonable because the electrochemical OH⁻ stripping peak occurs at approximately +1V with CB-supported Au_{25}^q clusters (figure S5 and Table S1). Water splitting above ~1.6 V produced a large current increase. In the reverse, cathodic (negative)-going potential sweep a peak represents the oxidation of CO by preadsorbed OH. Figure S12b shows reproducible CO oxidation peak current densities in both scan directions.

Figures S12c,d present typical positive-going RDE polarization curves and their analysis with Levich plots.[20] The RDE polarization curves were analyzed using the equation j_{geo} = $0.2nFAD^{2/3}v^{-1/6}C\omega^{1/2}$. Here, j_{geo} is the limiting geometric current density (normalized to the geometric area of the electrode), n is the number of electrons transferred in the electrocatalytic reaction, F is the Faraday constant (96485 C/mol e⁻), A is the geometric area of the electrode (0.1963 cm²), $D^{2/3}$ is the diffusion coefficient of CO in water (2×10^{-5} cm²/s), v is the kinetic viscosity of water (0.01 cm²/s), C is the concentration of dissolved CO in the bulk solution (1×10^{-6} mol/cm³), and ω is the rotation rate in rpm (250–2500 rpm).[3a] A constant of 0.2 is used when the rotation rate is described in rpm.[23] A plot of the inverse geometric current density vs. the inverse rotation rate produces a slope proportional to the electron transfer number n.[20] Analysis of anodic (positive)-going RDE polarization curves confirmed the complete oxidation of CO at the differently charged Au_{25}^q clusters with equivalent electron transfer numbers of n = 2.08±0.06 e⁻. This value is consistent with Equations S6-S8.

The CO oxidation peak in the reverse, cathodic-going sweep produced an electron transfer number of n = 1.49±0.11 e⁻. This smaller value represents the oxidation of CO by OH groups that were already adsorbed during the forward-going sweep. The oxidation peak in the reverse, negative-going sweep is very sharp because CO is rapidly oxidized by preadsorbed OH. The cathodic-going peak is a special consequence of preferential OH⁻ adsorption at large positive potentials, and it is not typically used for determining electron transfer numbers, Tafel slopes, or reaction rates.[3, 21]

Figures S12e,f show that charge state dependent CO oxidation activity was sustained during constant potential electrolysis. The retention of charge state-dependent CO activity indicates the Au_{25}^q charge state influences reactivity over extended periods of time.
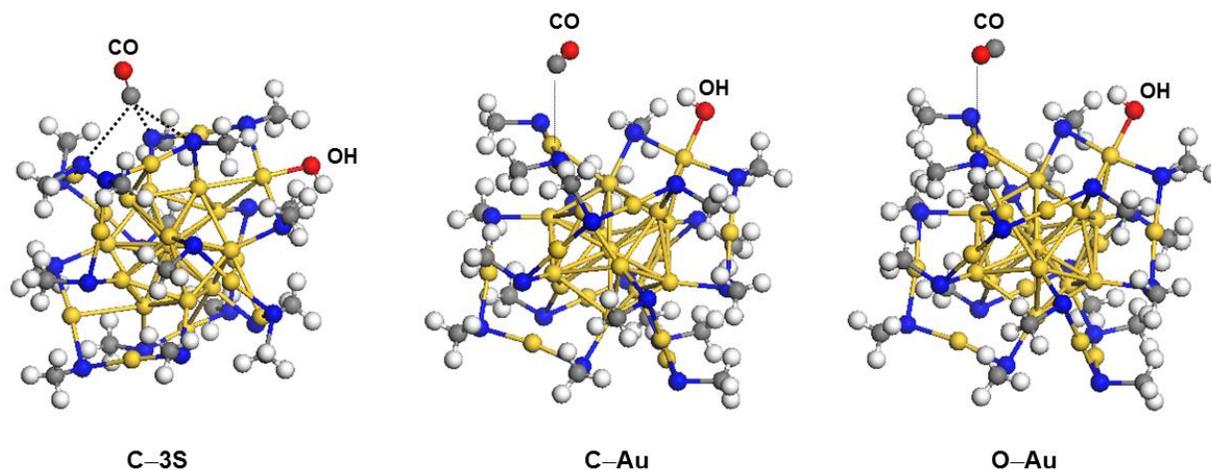
CO + OH⁻ Coadsorption Energies (eV)

	C–3S	C–Au	O–Au	Average
Au_{25}^{-}	-0.01	x	x	-0.01
Au_{25}^{0}	-2.44	-2.35	-2.35	-2.38 ± 0.05
Au_{25}^{+}	-4.91	-4.66	-4.71	-4.76 ± 0.13

Figure S13. Ball-and-stick representations of CO + OH⁻ coadsorption geometries at Au_{25}^{q} and their binding energies. The C–3S coadsorption geometry is presented as a space-filled model in main text Figure 2F. *Atom colors: Au: gold, S: blue, C: grey, H: white, O: red.*

Our DFT calculations predict several CO + OH⁻ coadsorbed states. The "C–3S" coadsorbed state was common among all three Au_{25}^{q} charges states. Here, OH⁻ adsorbs at a ligand-shell Au atom with a O-Au distance of 2.13 Å. CO coordinates with three S atoms in the ligand shell with C-S distance ranging from 3.56 to 3.78 Å. This was the only coadsorbed state identified for Au_{25}^{-}. Two additional coadsorbed states were identified for Au_{25}^{0} and Au_{25}^{+}. In both cases CO adsorbed to one Au atom in the ligand shell through its C atom ("C–Au" configuration) or O atom ("O–Au" configuration). The biding energies are summarized in figure S13, and the different coadsorbed states have equivalent energies at any one particular Au_{25}^{q}. A direct relationship between CO + OH⁻ adsorption strength and reaction TOF was observed (Figure 2e of the main text). This indicates cationic Au_{25}^{+} clusters enhance CO oxidation rates by stabilizing CO + OH⁻ coadsorption.

Au$_{25}$(SCH$_3$)$_{18}^q$ + CO

r (O-S)=3.52 – 3.73 Å

O–3S

r (C-S)=3.43 – 3.70 Å

C–3S

r (C-Au)=3.43-3.48 Å

C–Au

r (O-Au)=3.71-3.79 Å

O–Au

CO Binding Energies

	O–3S	C–3S	C–Au	O–Au	average
Au$_{25}^-$	-0.15	-0.16	-0.10	-0.086	-0.12 ± 0.03
Au$_{25}^0$	-0.17	-0.17	-0.11	-0.087	-0.13 ± 0.04
Au$_{25}^+$	-0.18	-0.60	-0.16	-0.14	-0.27 ± 0.22

Average Au$_{25}^q$–CO binding: −0.17 ± 0.14 eV
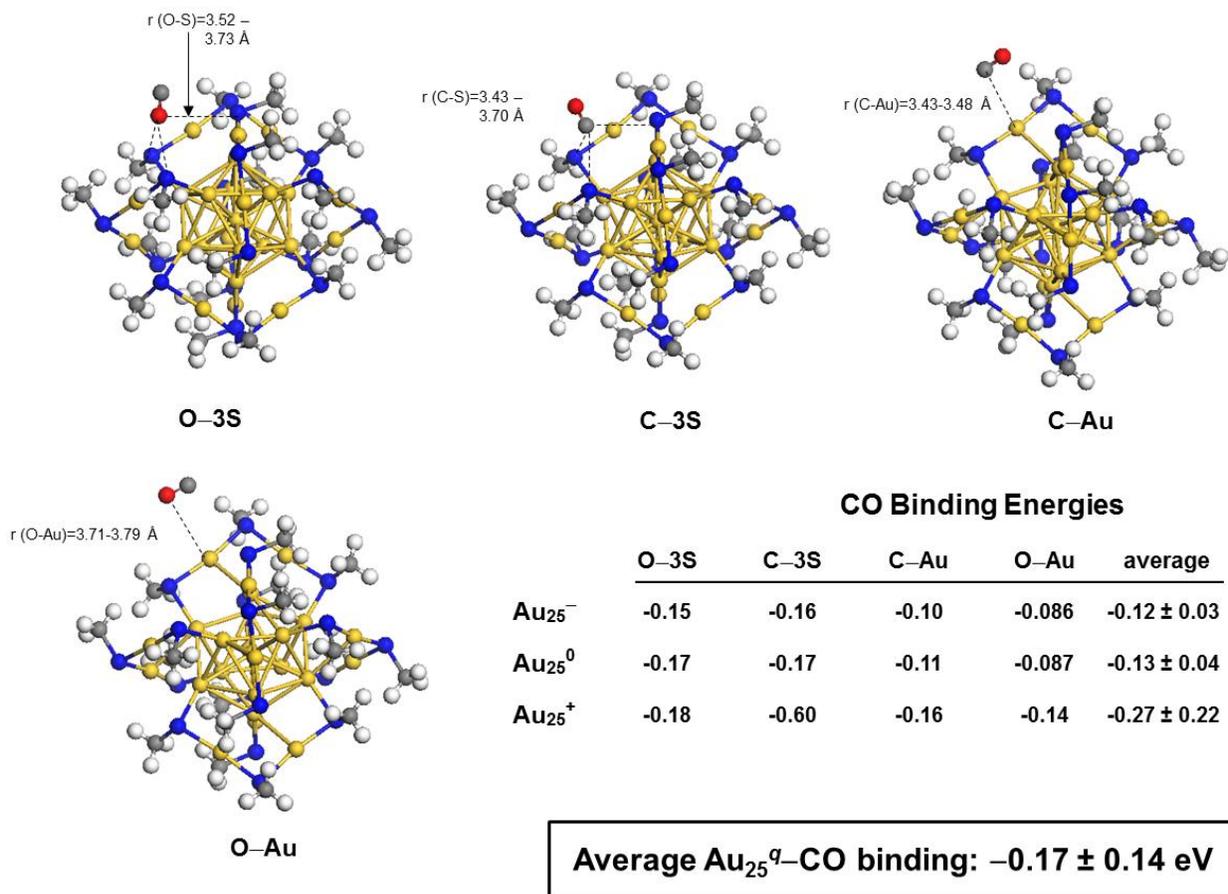
Figure S14. Ball-and-stick representations and binding energies of the singly-bound Au$_{25}^q$–CO system. *Atom colors: Au: gold, S: blue, C: grey, H: white, O: red.*
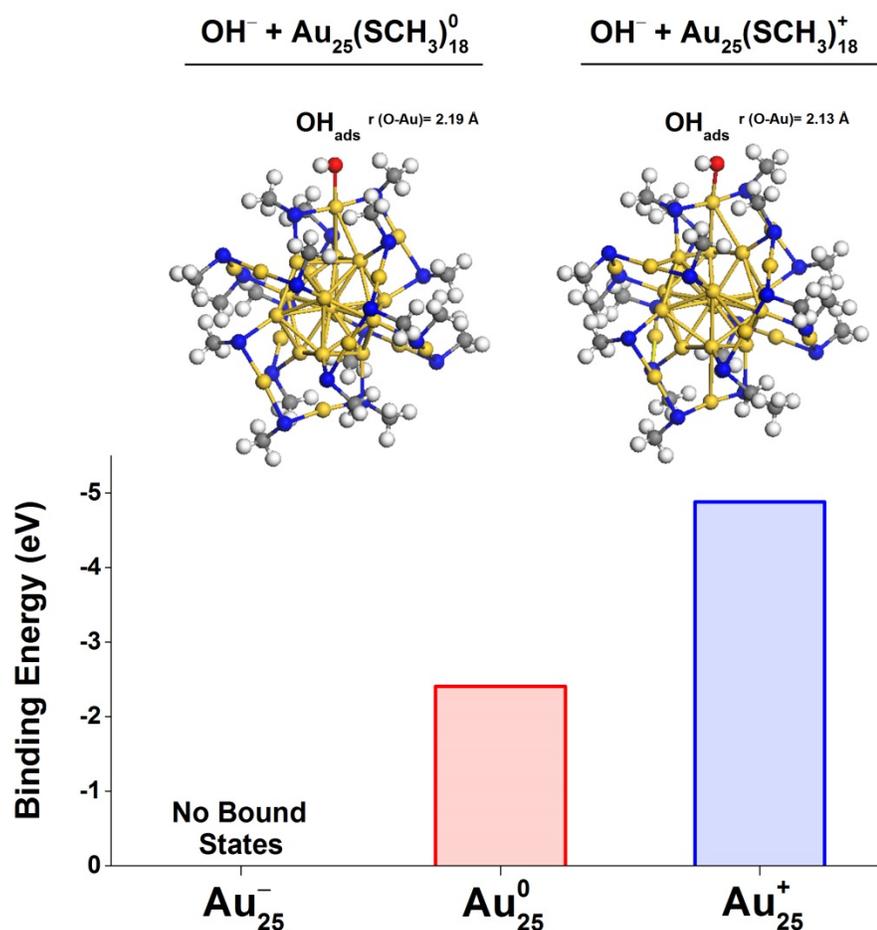
Figure S15. Calculated binding energies and DFT models of OH^- adsorption at $Au_{25}(CH_3)_{18}{}^q$ clusters ($q = -1, 0, +1$).

Cluster models were based on the published $Au_{25}{}^-$ crystal structure[1] and a previously DFT-optimized model.[10] OH^- binding energies are listed in table S1. These DFT results support the experimentally observed trend of stronger OH binding at $Au_{25}{}^+$ (table S2).
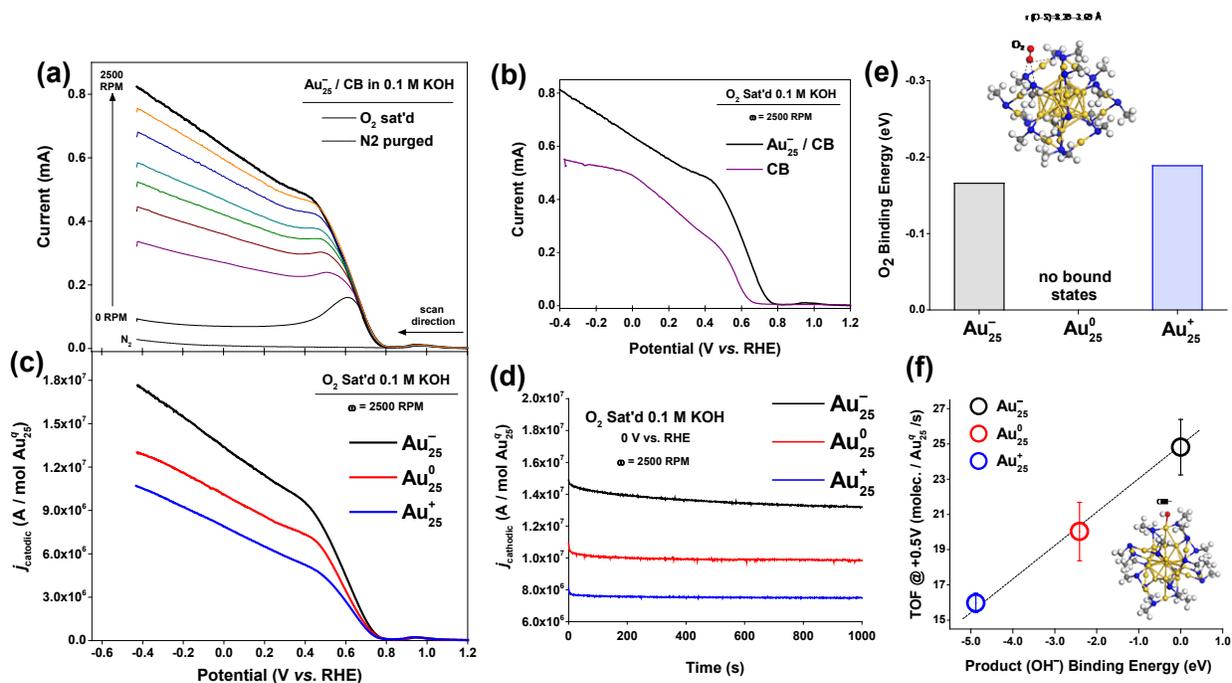
Figure S16. (a) RDE voltammograms of Au_{25}^- in N_2 purged and O_2 saturated 0.1M KOH at various rotation rates. (b) Comparison of O_2 reduction at the catalyst-free CB support and CB-supported Au_{25}^-. (c) Polarization curves of the Au_{25}^q charge states in O_2 saturated 0.1M KOH; ω = 2500 RPM. (d) RDE electrolysis at 0.0 V in O_2 saturated 0.1M KOH (ω = 2500 RPM). (e) DFT-predicted O_2–Au_{25}^q binding energies and representative model. (f) Correlation between experimentally determined ORR TOF at +0.5 V and the binding energy of the ORR reaction product (OH^-). A representative Au_{25}^+–OH model is also presented.

O_2 Reduction Reaction (in alkaline electrolyte)

Equation S9: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Equation S10: $O_2 + H_2O + 2e^- \rightarrow OH^- + OOH^-$
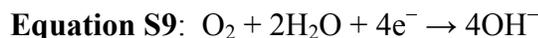
Figure S16a shows RDE polarization curves at different rotation rates in O_2 saturated 0.1M KOH. The differently charged Au_{25}^q clusters demonstrated equivalent ORR electron transfer numbers of n= 3.0±0.3 e^- between +0.5V and −0.35V *vs.* RHE (triplicate runs for each Au_{25}^q charge state). This indicates Au_{25}^q reduced O_2 through a combination of 2e^- and 4 e^- processes (Equations S9 and S10). In comparison, the CB support demonstrated an electron transfer number of n = 2.46 e^- and commercially available Pt-decorated CB (10% weight Pt; *Sigma Aldrich*) demonstrated an electron transfer number of n = 3.75 e^-. Electron transfer numbers were calculated using the Levich equation as described in figure S12 using the values C_{O2} = 1.2x10^{-6} mol/cm^3 and D_{O2} = 1.9x10^{-5} cm^2/s.

Figure S16b compares O_2 reduction at CB-supported Au_{25}^- and the catalyst-free CB support. The CB support also showed O_2 reduction activity, but the ORR onset at the catalyst free CB support was shifted by approximately -100 mV compared with the Au_{25}^q clusters. Catalyst loadings were kept between $3.3–7.7 \times 10^{-11}$ mol Au_{25}^q. No significant current density vs. catalyst loading trends were observed in this loading regime.

Polarization and electrolysis data show an ORR activity trend of $Au_{25}^- > Au_{25}^0 > Au_{25}^+$ (Figures S16c-d and Table 1 in the main text). The retention of charge state-dependent O_2 activity indicates during constant potential electrolysis indicates the Au_{25}^q charge state influence reactivity over extended periods of time. O_2 is reduced into OH^- and OOH^- in alkaline electrolytes. DFT identified weak spontaneous binding between Au_{25}^q and O_2 (Figure S16e), which confirms the need for electrochemical potentials during the ORR and previous analysis of O_2 adsorption at ground-state Au_{25}^q clusters.[2, 14] On the other hand, experimental and computational results show stronger OH binding at the positively charged Au_{25}^+ cluster (Tables S1, S2 and figure S15). Figure S16f correlates the ORR TOF at +0.5V and the reaction product (OH^-) binding energy. We chose to present TOF at +0.5V because the contribution from the CB support is small at this potential, although Au_{25}^- showed significantly higher ORR TOFs (>95% CL) at all potentials between +0.5 V and -0.4V. In this case, the positively charged Au_{25}^+ binds the ORR products more strongly compared with the other clusters. This blocks the Au_{25}^+ surface and reduces its ORR activity. Strong OH^- adsorption is also known to block the active sites of other ORR catalysts.[24] While we only specifically analyzed OH^- binding, we also expect an equivalent binding energy trend for the negatively charged OOH^- reaction product.

We can compare our ORR results to previously published studies. For example, Chen and Chen investigated the ORR activity of unsupported Au_{25}^- clusters deposited directly onto GC electrodes.[25] They reported an electron transfer number of n = 4.06 e^- and a current density of 10 mA cm^{-2}_{Au} at 0.4 V *vs.* RHE. Based on our calibration of Au_{25}^q loading in figure S5: 10 mA/cm^2_{Au} converts into $[(10\ mA/cm^2_{Au})(1A/1000\ mA)(1\ cm^2_{Au}/390 \times 10^{-6}\ C)(356865\ C/mol\ Au_{25}^q) = 9.2 \times 10^6$ A/mol Au_{25}^q. Their value is in excellent agreement with our measured ORR current density of 9.5×10^6 A/mol Au_{25}^- at 0.4 V vs. RHE (Figure S16c). The value for bulk Au electrochemical surface area (390×10^{-6} C/cm^2_{Au}) was taken from reference [5].

Table S1. Comparison of singly adsorbed and coadsorbed reactant binding at Au_{25}^{q}; all values are eV.

	Singly Adsorbed Reactants			Coadsorbed	Singly Adsorbed Reactants			Coadsorbed
	H^+	CO_2	sum	$CO_2 + H^+$	OH^-	CO	sum	$CO + OH^-$
Au_{25}^-	-12.20	-0.13 ± 0.02	-12.33 ± 0.02	-12.25 ± 0.02	0.0	-0.12 ± 0.03	-0.12 ± 0.03	-0.01
Au_{25}^0	-9.44	-0.13 ± 0.04	-9.57 ± 0.04	-10.03 ± 0.07	-2.41	-0.13 ± 0.04	-2.54 ± 0.04	-2.38 ± 0.05
Au_{25}^+	-8.21	-0.29 ± 0.28	-8.50 ± 0.28	-8.06 ± 0.23	-4.88	-0.27 ± 0.22	-5.15 ± 0.22	-4.76 ± 0.13

Table S2. OH stripping potentials from Au_{25}^q in 0.1M KOH. Potentials are referenced versus the reversible hydrogen electrode (RHE).

	0.1 M KOH (50 mV/s)	0.1M KHCO₃ (10 mV/s)
Au₂₅⁻	0.978 ± 0.010 (n = 22)	1.052 ± 0.021 (n = 15)
Au₂₅⁰	0.969 ± 0.008 (n = 19)	1.015 ± 0.034 (n = 9)
Au₂₅⁺	0.968 ± 0.009 (n = 21)	0.996 ± 0.042 (n = 12)

OH stripping from Au_{25}^+ occurred at more negative potentials compared with Au_{25}^-. While the potential differences are somewhat small, the differences between Au_{25}^+ and Au_{25}^- are significant at a confidence level greater than 99%. These experimental results are qualitatively consistent with our DFT prediction of stronger OH^- binding at the positively charged Au_{25}^+ cluster (Table S1 and figure S15).

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