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Selective Electrocatalytic Reduction of CO₂ into CO at Small, Thiol-Capped Au/Cu Nanoparticles

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ABSTRACT. The electrochemical CO₂ reduction reaction (CO₂RR) is a promising approach for converting fossil fuel emissions into environmentally-sustainable chemicals and fuels. The ability to control the surface structure of CO₂RR nanocatalysts provides an opportunity to tune product selectivity. Bimetallic gold-copper catalysts have been identified as emerging electrocatalyst candidates, but Cu incorporation typically lowers product selectivity compared with pure Au. Here we show sustained CO selectivity and activity up to 49% Cu content in small (<2nm), thiol-capped Au/Cu nanoparticles (NPs). Bimetallic NPs containing 49% Cu selectivity converted CO₂ into CO with $100 \pm 6\%$ CO Faradaic efficiency and average mass activity of ~ 500 mA/mg during a 12-hour electrolysis experiment at $-0.8V$ vs. RHE. Au/Cu NPs synthesized without thiol ligands selectively produced H₂, whereas larger (>10 nm), thermally-dethiolated Au/Cu NPs produced a wider product distribution including H₂, CO, and C₂H₄. Density functional theory (DFT) modelling of CO₂RR and H₂ evolution at realistic, thiol-capped Au/Cu NP structures indicated copper-thiol surface structures sustained CO selectivity by stabilizing key *CO intermediates while making *H binding less favorable. Calculations also predicted that removing a significant fraction of the thiol ligands would increase *CO binding strength such that desorption of CO product molecules could become the most thermodynamically challenging step. This result, coupled with increased *H stability on dethiolated nanocluster, points to decreased CO₂RR selectivity for small, ligand-free catalysts, which is in line with experimental observations from our group and others. Our results demonstrate that thiol-ligand surface structures can sustain the CO selectivity of bimetallic Au/Cu NPs and reduce precious metal requirements for CO₂RR.

INTRODUCTION

The electrochemical CO₂ reduction reaction (CO₂RR) is an appealing strategy for addressing CO₂ emissions because it can use excess renewable energy to produce carbon-neutral chemicals and fuels.¹ The CO₂RR has a rich structure-sensitivity, and recent efforts have focused on improving reaction rates and product selectivity by tuning the size, composition, crystallographic orientation, and active site density of nanostructured electrocatalysts.²⁻⁵ Gold can selectively convert CO₂ into CO,^{5,6} which is a versatile chemical building block that can be processed into a wide range of products, such as methanol, hydrocarbons, fuel additives, and plastics.⁶⁻⁸ Copper is another popular CO₂RR catalyst because it is an earth abundant metal that can produce a variety of hydrocarbons and alcohols.⁹⁻¹¹ However, Cu often demonstrates wide product distributions that will require additional chemical separation steps and reduce overall system efficiencies.

Bimetallic Au/Cu nanocatalysts have emerged as promising candidates for selective CO₂ conversion with reduced precious metal content.¹²⁻¹⁹ Cu incorporation into Au can boost overall current density, but it can also decrease product selectivity. This presents practical challenges because costs associated with down-stream product separation may hinder large-scale deployment of CO₂RR technologies.²⁰ From a fundamental perspective, the composition, surface structure, and specific arrangement of Au and Cu atoms have been predicted to impact electrochemical overpotentials, catalytic activity, and product

selectivity.^{13,18,19} This presents opportunities for designing catalyst systems that maximize product selectivity and reduce precious metal requirements.

Organic capping ligands have been shown to stabilize specific surface structures that can influence CO₂RR product distributions.²¹⁻²⁶ We used organo-thiol ligands to synthesize a series of monodisperse, sub-2nm Au/Cu NPs with unique copper-thiol surface moieties. Electron microscopy, X-ray absorption spectroscopy, and extended X-ray absorption fine structure (EXAFS) analysis quantified the particle size, probed the NP electronic structure, and characterized the copper-thiol groups at the catalyst surface. In contrast to other reported Au/Cu catalysts,¹³⁻¹⁹ the thiol-capped Au/Cu NPs retained excellent CO selectivity and catalytic activity up to 49% Cu content.

Thiol-capped NPs containing 49% Cu demonstrated 94±5% CO Faradaic efficiency (FE) between -0.5V and -1.0V vs. RHE. A maximum CO mass activity ~1360 mA/mg and nearly quantitative CO FE (99.9%) was obtained at -1V vs. RHE. The 49% Cu NPs also showed sustained CO selectivity with 100 ± 6% CO FE at ~500 mA/mg during a 12-hour electrolysis experiment at -0.8V vs. RHE. Complementary DFT calculations with realistic, thiol-capped NP structures predicted Cu-thiol surface structures stabilized key CO₂RR intermediates and reduced H₂ evolution. In contrast, both experiment and theory indicate reduced CO₂RR selectivity and increased H₂ evolution at ligand-free NPs. Our combination of experiment and DFT modeling provides atomic-level structure-property relationships and demonstrates ligand-directed surface structuring as a design consideration for tuning the selectivity of CO₂RR nanocatalysts.

METHODS

Synthesis and Optical Spectroscopy. Au/Cu NPs were synthesized using a dendrimer-template method developed by the Crooks group.²⁷ Detailed synthetic procedures are presented in the Supporting Information. Briefly, aqueous Au^{3+} and Cu^{2+} ions were complexed inside G4-PAMAM-OH dendrimers, reduced with NaBH_4 , and then extracted into toluene using 2-phenylethanethiol (PET) ligands. NP compositions were analyzed with inductively coupled plasma mass spectrometry (ICP-MS; Figure S1). Optical absorption and near infrared photoluminescence (NIR PL) spectra were collected in N_2 purged toluene using an Agilent 8453 spectrophotometer and a Horiba Jobin-Yvon Fluorolog 3 spectrofluorometer.

Deposition onto carbon black (CB). Thiol-capped NPs were dissolved in CH_2Cl_2 and sonicated with Vulcan XC-72R CB to achieve a final catalyst loading of 9 wt %. The PET ligands are not soluble in methanol, and NPs were precipitated onto the CB support by adding methanol. The resulting CB-supported NPs were then centrifuged, decanted, and re-sonicated in fresh methanol three times before drying under N_2 . CB-supported NP samples were used for TEM, X-ray spectroscopy, and electrochemical experiments. The CB provided a conductive support for electrochemical experiments, prevented charging during X-ray spectroscopy, and reduced particle coalescence during TEM imaging. Deposition onto the CB support did not change NP composition (Figure S1).

Transmission Electron Microscopy. High-angle annular dark field scanning transmission electron microscopy (STEM) imaging was conducted on a 200kV FEI Tecnai F20 TEM. Atomic-resolution annular dark-field STEM images were acquired at the Brookhaven National Laboratory's Center for Functional Nanomaterials using a FEI Talos F200X operated at 200 keV.

X-ray photoelectron spectroscopy (XPS). XPS and Auger electron spectroscopy were performed on a PHI 5600ci spectrometer equipped with $k\alpha$ Al radiation (1486.6 eV). Cu foil, Cu₂O and CuO were sputtered with Ar⁺ prior to measurement to remove native oxides and surface contaminants. CB-supported Au/Cu NPs were *not* sputtered to preserve the thiol ligands. No charge neutralization was used during measurement and all binding energies were calibrated to the C1s of the CB support at 285 eV. Spectra were analyzed every 25-50 scans to rule out X-ray induced reduction of Cuⁿ⁺ species.

X-ray Absorption Spectroscopy (XAS). Cu and S L-edge spectra of CB-supported Au/Cu NPs were collected in total electron yield mode at beamline 8-2 of the Stanford Synchrotron Radiation Lightsource (SSRL). Spectra were collected with 0.1 eV step energy, 0.5 second per step integration time, and normalized against the incident photon flux. Photon energies were calibrated to the Cu L edge of a simultaneously-measured CuO internal standard at 931.2 eV. A linear pre-edge background was subtracted from the Cu L-edge spectra and the curves were normalized to a peak intensity of one. Each curve represents one scan. The endstation did not have sputtering capabilities so a Cu foil was sanded prior to introduction into the vacuum chamber. Brief exposure to air created a native oxide layer containing both Cu⁺ and

Cu²⁺ species.²⁸ The sulfur L-edge spectra represent three averaged scans and the background was fit with a single exponential decay function (see Supporting Information). No obvious X-ray induced spectral changes were observed between scans.

Cu K-edge absorption spectra were collected the high energy X-ray absorption spectroscopy (HEXAS) beamline at the Louisiana State University's J. Bennett Johnston, Sr., Center for Advanced Microstructures and Devices (CAMD). CB-supported Au/Cu NPs were deposited onto Kapton tape and measured in air. Spectra were collected in fluorescence mode from 200 eV below to ≥ 750 eV above the Cu K edge, and photon energies were calibrated with a simultaneously measured Cu foil reference. The reported Cu K-edge spectra represent the average of two to five scans with no obvious X-ray damage between scans. Data was analyzed using the IFEFFIT software package.

Electrochemistry. Electrochemical experiments were performed in N₂ purged (pH = 8.9) and CO₂ saturated (pH = 6.8) 0.1M KHCO₃ using a Biologic SP-150 potentiostat and a Basi Epsilon bipotentiostat. All experiments used a Pt wire counter electrode and a Ag/AgCl reference electrode that was regularly calibrated against a commercially-available Hydroflex reversible hydrogen electrode (RHE). The uncompensated resistance was determined using impedance spectroscopy and automatically corrected at 85% using the instrument software. Rotating ring-disk electrode (RRDE) experiments were conducted at 2500 rpm using a Pine Instruments electrode rotator and a RRDE electrode with a Pt ring and an interchangeable GC disk.

Catalyst inks were created by sonicating the CB-supported NPs in 200 μL MeOH and 8 μL Nafion solution. The inks were dropcast onto 3mm diameter glassy carbon electrodes at a total NP loading of $5.0 \pm 0.1 \mu\text{g}/\text{cm}^2$ for potential dependent product distribution experiments. Control experiments were also conducted with larger, $7.3 \pm 0.7 \text{ nm}$ Au NPs that were synthesized as previously reported²⁹ and dropcast onto the GC electrode at a loading of $24 \mu\text{g}/\text{cm}^2$. This higher loading was required to achieve current densities similar to the thiol-capped NPs and to ensure sufficient product formation for quantification with gas chromatography.

CO_2RR products were quantified in a two-compartment H-cell separated with a Nafion 117 membrane. Gaseous products were analyzed using a Perkin Elmer Clarus 600 gas chromatograph equipped with thermal conductivity and flame ionization detectors. Specific sampling details are provided in the Supporting Information and representative gas chromatograph traces are presented in Figure S2. Faradaic efficiency (FE) was calculated as $FE = \left(\frac{F \cdot ne^- \cdot \text{mol product}}{\text{Electrolysis Charge (C)}} \right) = \%$, where F represents Faraday's constant and ne^- is the number of electrons required to form the product molecule. Energy efficiency (EE) was calculated as $EE = FE \cdot (E^0_{\text{cell}}/E_{\text{applied}}) = \%$, where E^0_{cell} is the formal potential for CO_2RR and water oxidation, and E_{applied} is the total applied cell voltage (we assumed a 500 mV overpotential at the anode).

Computational Details. Density functional theory (DFT) models were constructed from a previously optimized $\text{Au}_{144-x}\text{Cu}_x(\text{SH})_{60}$ nanocluster structure.³⁰ The organic portion of the

ligands were substituted with H atoms to reduce computational demand. This approach has proven to be a computationally tractable way to accurately model the electronic structure and reactivity of ligand-protected nanoclusters.^{24,30-32} The Au₁₄₄(SH)₆₀ structure contains a Au₁₁₄ core protected by a shell of 30 (-SH-Au-SH-) staple units.³⁰ The Au₁₁₄Cu₃₀(SH)₆₀ structure was constructed by symmetrically substituting one Cu atom into each of the 30 ligand staple units. The Au₉₀Cu₅₄(SH)₆₀ structure was then constructed by substituting an additional 12 Cu atoms onto the core surface and 12 Cu atoms into the core interior. Finally, the Au₇₂Cu₇₂(SH)₆₀ structure was constructed by substituting 30 Cu atoms into the ligand shell and 42 Cu atoms into the core interior.

The total energy of nanocluster-adsorbate models were calculated using the Vienna Ab Initio Simulation Package (version 5.3),³³ a plane-wave self-consistent periodic DFT code. The generalized gradient approximation formulation of Perdew, Burke and Enzerhoff was used.³⁴ CO₂RR and H₂ evolution reaction (HER) reaction free energy diagrams were constructed following the computational hydrogen electrode method.³⁵ The proton-electron pair was related to hydrogen using the standard hydrogen electrode as a reference such that the free energy of the reaction $\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2} \text{H}_2(\text{g})$ is zero at standard conditions ($p = 1$ bar, $T = 298$ K, solution pH = 0 and $U = 0$ V). When the applied potential and solution pH differed from zero, the free energy was corrected *via* shift in energy by $-eU$ and $kT \ln[\text{H}^+]$, respectively. The initial state for both models was defined as $\Delta G = 0$ for a vacant active site (denoted as *) and gaseous CO₂. Additional computational details are provided in the Supporting Information.

RESULTS AND DISCUSSION

Characterization. Thiol-capped NPs containing 0%, 23%, 49% and 64% Cu were synthesized in an aqueous PAMAM dendrimer template²⁷ and then extracted into toluene with phenylethanethiol (PET) ligands. Atomic compositions were confirmed with ICP-MS (Figure S1). The thiol-capped NPs had an average diameter of 1.5 ± 0.4 nm was independent of particle composition (Figure S3 and Table S1). **Figure 1a** presents the size distribution for all NP compositions alongside an atomic resolution, annular dark-field scanning transmission electron microscope image of a single 49% Cu NP. The NPs were not “atomically-precise” with known single-crystal structures, but our synthetic strategy provided good compositional control with a narrow size distribution. The synthetic method could not produce thiol-capped 100% Cu NPs, and NP synthesis in the absence of dendrimers produced larger, irregularly-shaped particles that could not be extracted into organic phase with PET ligands (Figure S4).

Sub-3nm, thiol-capped NPs occupy a size regime between molecules and bulk metals, and they often demonstrate unique optical properties compared with larger, plasmonic nanocrystals.³⁶ The thiol-capped Au/Cu NPs lacked obvious plasmon resonances and produced composition-dependent near infrared photoluminescence (NIR PL) that shifted to longer wavelengths with increasing Cu content (Figure S5). The NIR PL is hypothesized to originate from metal-sulfur states at the NP-ligand interface,³⁷ and the observed spectral shifts are consistent with the incorporation of Cu atoms into the Au/Cu NPs.³⁸ These optical

features also function as convenient markers for monitoring NP stability because changes in the particle size,³⁹ composition,³⁸ or ligand structure^{37,40,41} can impact the absorption and emission profiles. Thiol-free NPs remaining in the PAMAM dendrimer did not produce photoluminescence.

Cu L-edge X-ray absorption spectroscopy (XAS) probes the excitation of Cu 2p electrons into unoccupied 3d and 4s states, and characteristic spectral features can be used to determine oxidation state.⁴² **Figure 1b** compares the Cu L-edge XAS of Au/Cu NPs with CuO powder and an ambiently-oxidized Cu foil. The spectra reveal predominantly Cu⁺ species within the Au/Cu NPs. The NP Cu⁺ features were upshifted approximately 1.7 eV from the bulk reference, suggesting the thiol ligands influenced the electronic structure of Cu atoms within the Au/Cu NPs. Sulfur L-edge XAS provided complementary evidence for Cu-S interaction (Figure S6), and composition-dependent spectral changes suggest either Cu-induced perturbation of S-centered states and/or the introduction of new metal-sulfur states.⁴³ A small Cu²⁺ feature in the Au/Cu NP spectra also indicated minor oxidation from oxygen, water, or hydroxyl adsorption under ambient conditions.⁴⁴ Laboratory-based X-ray photoelectron and Auger spectroscopy also identified predominantly Cu⁺ species that were offset from bulk Cu₂O (Figure S7 and Table S2).

Extensive crystallographic and theoretical work has revealed many thiol-capped Au NPs contain a metal “core” protected by a “ligand-shell” of gold-thiol staple units constructed from (–SR–Au–SR–), (–SR–Au–SR–Au–SR–), and other structurally-similar motifs.³⁶ In fact, a growing body of literature suggests that metal-thiol staples are a near-ubiquitous surface

structure present on thiol-capped Au NPs.³⁶ Experimentally-solved crystal structures have only been reported for a few bimetallic Au/Cu nanoclusters,⁴⁵⁻⁴⁹ and total structure determinations for Au/Cu nanoclusters capped entirely with thiol ligands are scarce.^{46,47,49,46,47,46,47} However, crystallographic work with atomically-precise $\text{Au}_{12+n}\text{Cu}_{32}(\text{SR})_{30+n}$, $\text{Au}_{38-x}\text{Cu}_x(\text{SR})_{24}$, and $\text{Au}_{21-x}\text{Cu}_x(\text{SR})_{15}$ nanoclusters,^{46,47,49} DFT-optimized structures for $\text{Au}_{145,144-x}\text{Cu}_x(\text{SR})_{60}$ and $\text{Au}_{25-x}\text{Cu}_x(\text{SR})_{18}$ nanoclusters,^{30,50} and experimental XAS measurements of differently-sized, “non atomically-precise” systems, including $\sim 1\text{ nm}$ $\text{Au}_{25-x}\text{Cu}_x(\text{SR})_{18}$ nanoclusters and thiol-capped 2-3 nm Au/Cu NPs,^{51,52} all provide evidence that copper atoms can occupy metal-thiol staple structures at the NP surface.

We used Cu K-edge XAS and extended X-ray absorption fine structure (EXAFS) analysis to identify copper-thiol bonding in the ligand staple units. **Figure 2** shows unique EXAFS features for the thiol-capped 49% Cu NPs compared with metallic Cu and the Cu-oxide standards. The 49% Cu NP EXAFS curve was fit with Cu-S and Cu-Au scattering paths from a similarly-sized, DFT-optimized $\text{Au}_{114}\text{Cu}_{30}(\text{SH})_{60}$ nanocluster structure³⁰ and a Cu-O scattering path from CuO (Table S3). The main peak at 1.8 Å represents Cu-S bonding in the ligand-shell staple structures,^{51,52} and a small feature ~ 2.6 Å identifies some Au-Cu bonding in the NP core. The peak at 1.5 Å also identifies the presence of some Cu-O bonding under ambient conditions, which is consistent with the minor Cu^{2+} feature found in the Cu L-edge spectrum. The 23% and 64% Cu NPs showed similar EXAFS patterns with dominant Cu-S features and some Cu-O bonding, and Cu K-edge XAS and EXAFS data for all samples are presented in Figure S8. In contrast, Cu K-edge EXAFS analysis of similarly-sized, *ligand-free*

Au/Cu NPs reported by Mistry *et al.* indicated nearly exclusive Cu-O bonding.¹⁶ The combination of our Cu L-edge and Cu K-edge X-ray data confirm the thiol ligands created unique copper-thiol sites on the NP surface that prevented the complete oxidation of copper into Cu²⁺.

Electrocatalytic CO₂RR. Rotating ring-disk electrode voltammetry was used to determine product formation onset potentials (E_{onset}) and we observed a ~120 mV cathodic shift in the E_{onset} between 100% Au NPs and 64% Cu NPs (Figure S9). Product distributions, Faradaic efficiencies (FE), and electrochemical activity were then quantified between E_{onset} and -1.1V vs. RHE in a two-chamber H-Cell. Gas chromatography determined CO and H₂ as the major products, and **Figure 3a** compares the potential-dependent CO FE for each catalyst. An overall FE of 91±7% was determined for the thiol-capped NPs beyond -0.6V vs. RHE considering both CO and H₂. This confirmed the detection of majority CO₂RR products in this potential range and liquid products were not analyzed. Duplicate runs at E_{onset} and -1.1V vs. RHE indicate reproducibility with error bars. The catalyst-free CB support exclusively produced H₂,⁵³ and control experiments with larger ~7 nm, thiol-free Au NPs (Figure S10) found selective CO production with FEs that were consistent with other, similarly sized Au NPs.^{17,54,55} Full H₂ and CO FE plots are presented in Figure S11.

The 49% Cu NPs were the most selective ligand-protected NPs with an average 94 ± 5% CO FE between E_{onset} and -1.0V vs. RHE. However, increased H₂ evolution at very negative potentials reduced CO FE to 77±2% at -1.1V vs. RHE. Excellent CO selectivity at moderate

overpotentials is consistent with the expected behavior of gold electrocatalysts,^{5,6,54-56} but the retention of high CO selectivity with large Cu content is a unique characteristic of thiol-capped Au/Cu NPs.¹²⁻¹⁹ Post CO₂RR analysis revealed consistent particle diameter (1.5 ± 0.3 nm), nearly identical composition (47%), and the retention of thiol ligands, Cu⁺ oxidation state, and characteristic optical properties (Figure S12). Optical spectroscopy is especially sensitive tool for monitoring NP stability due to its structural and compositional sensitivity. Specifically, particle growth should induce an obvious surface plasmon resonance in the absorption spectrum,³⁹ whereas Cu leaching or substantial changes in the thiol ligand structure should significantly alter the NIR PL spectrum.^{37,38,41} The absence of significant optical and physicochemical changes indicates NP stability during CO₂RR.

In contrast, 49% Cu NPs synthesized *without* thiol ligands, *i.e.* still encapsulated within the PAMAM dendrimer, evolved H₂ with 95% selectivity at -1.0V vs. RHE and only produced minor amounts of CO (4% FE). Predominant H₂ evolution is consistent with the recently reported behavior of similarly sized, dendrimer-encapsulated 100% Au NPs,⁵⁷ as well as other small, ligand-free Au,⁵⁸ Au/Cu,¹⁶ and Cu⁵⁹ nanocatalysts. The selective H₂ production of small, ligand-free NPs is hypothesized to stem from a large fraction of undercoordinated surface sites that stabilize adsorbed *H intermediates and favor H₂ evolution over CO₂ reduction.^{54,60,61} On the other hand, larger (>5 nm), ligand-free Au/Cu nanocatalysts have demonstrated a wider product distribution that includes H₂ and a variety of C₁ and C₂₊ products.^{14,15,17} To highlight this size difference we thermally annealed the thiol-capped 49% Cu NPs at 300 C to desorb the thiol ligands⁶² and increase the particle

diameter to approximately 10 nm (Figure S13). These larger, dethiolated 49% Cu NPs produced less CO (77% FE), more H₂ (13% FE), and began to evolve C₂H₄ (6% FE) at -1.0V vs. RHE. The comparison between small thiol-capped Au/Cu NPs, small ligand-free NPs, and larger (>5 nm) ligand-free Au/Cu NPs highlights the unique CO selectivity of small, thiol-capped Au/Cu NPs.

Figures 3b and 3c compare the CO partial geometric current density (mA_{CO}/cm²) and mass activity (mA_{CO}/mg) of 1.5nm, thiol-capped Au/Cu NPs with larger, thiol-free 7 nm Au NPs. The Au/Cu NPs demonstrated comparable CO partial current density and mass activity up to a Cu content of 49%. The 64% Cu NPs showed reduced activity at lower overpotentials due to increased H₂ evolution and reduced CO FE in that potential range. Tafel analysis of steady-state CO partial current density provided an average slope of 180±10 mV dec⁻¹ for all thiol-capped NP compositions (Figure S14). This value is close to the ~120 mV dec⁻¹ expected for a rate determining step (RDS) involving the initial electron transfer to CO₂,⁵⁶ and the data indicates a common RDS for all NP compositions.

The thiol-free, 7 nm Au NPs produced current density and mass activity that was comparable to other, similarly sized Au NPs.¹⁷ However the 1.5nm, thiol-capped Au/Cu NPs produced much larger mass activity due to their small size and higher surface-to-volume ratio. We previously reported a CO mass activity of ~1650 mA/mg for ~1nm, CB-supported Au₂₅(SR)₁₈ nanoclusters operating at -1V vs. RHE on carbon paper electrodes.⁶³ Jin and coworkers also recently reported CO mass activities approaching 2000 mA/mg for CB-supported Au₂₅(SR)₂₅ nanoclusters at -1V vs. RHE on a glassy carbon electrode.²⁶ In the

present case, the thiol-capped 49% Cu NPs produced a comparably high mass activity of 1363 mA/mg at -1.0 V *vs.* RHE with approximately one-half the precious metal concentration. In comparison, larger, ~10nm thiol-free Au/Cu NPs containing 25% Cu were reported to produce a CO mass activity of ~240 mA/mg and a ~56% CO FE at -0.73 V *vs.* RHE,¹⁷ while ~7 nm 50% Cu NPs with specific atomic ordering achieved ~800 mA/mg_{Au} (Au loading basis) and ~80% CO FE at -0.77V *vs.* RHE.¹³ These mass activities comparable well with our thiol-capped 49% Cu NPs on both total metal and Au-loading bases, and they confirm that ligand-protected, bi-metallic Au/Cu NPs can sustain excellent CO selectivity and impressive activity with reducing precious metal requirements.

The 49% Cu NPs also showed consistent CO Faradaic efficiency and during a 12-hour CO₂RR electrolysis at -0.8V *vs.* RHE (**Figure 3d**). Bubble formation at the electrode surface produced spikes in the measured current despite vigorous stirring. The experiment contained three start/stop cycles to mimic the intermittent availability of excess renewable energy. The electrode was removed from the H-Cell after the first cycle and dried overnight in air. The second and third cycles were separated by a 10 minute “off” period with the electrode held at open circuit in the catholyte. The 49% Cu NPs demonstrated 100±6% CO FE and an average CO mass activity of 514 ± 71 mA/mg, although the catalyst did experience an approximate 18% decrease in activity during the 12-hour electrolysis.

We also estimate an average energy efficiency of approximately 53% (assuming a 500 mV overpotential at the anode). Commercially-available water electrolyzers produce H₂ with 65-75% energy efficiency at 500-700 mV total overpotential,⁶⁴ and improved anode catalysts and

reactor designs could realize energy efficiencies rivaling state-of-the-art water electrolyzers. Ongoing efforts in our laboratory will incorporate promising catalysts into realistic gas-diffusion electrode (GDE) style electrolyzers to produce CO₂RR systems with both high CO selectivity and improved geometric current density.

Computational Modelling. We used density functional theory (DFT) to model CO₂RR and the competitive H₂ evolution reaction (HER) at thiol-capped Au/Cu NPs. The precise crystal structures of the experimentally-tested Au/Cu NPs are unknown. However, the experimentally-determined particle size, composition, and copper-sulfur bonding in the ligand-shell staple motifs are closely approximated by a previously DFT-optimized Au₁₄₄-xCu_x(SR)₆₀ nanocluster system.³⁰ Therefore, this model system should capture trends that identify the influence of composition, copper location, and the presence of metal-thiol staple structures.

Figure 4 presents the DFT-optimized Au₁₄₄(SH)₆₀, Au₁₁₄Cu₃₀(SH)₆₀, Au₉₀Cu₅₄(SH)₆₀ and Au₇₂Cu₇₂(SH)₆₀ nanocluster structures. The specific compositions were chosen to represent 100% Au NPs, Au/Cu NPs with Cu atoms located exclusively in the ligand-shell, and Au/Cu NPs with Cu atoms located in the core and the ligand-shell. The full phenylethyl thiol ligands were substituted with -SH units.³¹ In the absence of infinite computational resources, this choice is dictated by the balance between accuracy and computational tractability. This is reasonable as it approximately mimics the single bond between S and C in the more computationally expensive -SCH₃ moiety.^{24,30-32} Moreover, similar to SCH₃, the use of SH

fragment maintains the role of electron-withdrawing ligands represented by the metal-thiolate units.

Copper containing $\text{Au}_{144-x}\text{Cu}_x(\text{SH})_{60}$ nanoclusters were predicted to have smaller formation energies than $\text{Au}_{144}(\text{SH})_{60}$ (Table S4 and ref. 30), and Bader charge analysis indicated electron donation into ligand S atoms from both Cu atoms in the metal-thiol staples as well as Au atoms at the NP surface.³⁰ The predicted thiol-metal charge transfer is consistent with the X-ray spectroscopic identification of Cu-S electronic interaction, and the shared electron donation from both Au and Cu atoms into S head groups likely prevented thiol ligands from completely oxidizing Cu atoms into Cu^{2+} .

We used the computational hydrogen electrode method³⁵ to model the CO_2RR at $\text{Au}_{144-x}\text{Cu}_x(\text{SH})_{60}$ nanoclusters based on the following, commonly accepted steps:⁵⁴

where * represents a vacant active site. The reaction step with the largest free energy change (ΔG_{max}) identifies a thermodynamic bottleneck that can be used to predict E_{onset}

($E_{\text{onset}} = \Delta G_{\text{max}}/e^-$) and Tafel slope⁶⁵ differences between the NP structures. We did not consider other CO_2RR products because the experimentally-tested NPs selectively produced CO.

Our previous work predicted that fully ligand-protected $\text{Au}_{25}(\text{SR})_{18}$ nanoclusters were relatively inert towards the CO_2RR , and a single thiol group was removed to create an accessible active site.²⁴ Mpourmpakis, Jin and coworkers have since validated this approach

and provided additional computational evidence that thiol desorption at catalytically-relevant potentials can form singly-dethiolated $\text{Au}_{25}(\text{SR})_{17}$ nanoclusters.²⁶ In the present case, the fully ligand-protected $\text{Au}_{144-x}\text{Cu}_x(\text{SH})_{60}$ nanocluster models were also unreactive towards CO_2RR and HER (Figure S15) so one -SH ligand was removed to create an accessible adsorption site. These sites consisted of a singly-dethiolated Au or Cu atom in the ligand “shell” that functioned as the CO_2 reduction and H_2 evolution reaction centers. The newly formed active sites contracted towards the NP “core” by 0.7 ± 0.1 Å, and the “activated” nanocluster models demonstrated a small, 5-6 meV/atom increase in overall nanocluster formation energy compared with the fully ligand-protected model (Figure S16, Tables S4 and S5). Similarly small structural changes were also observed when one -SCH₃ ligand was removed from a model $\text{Au}_{25}(\text{SCH}_3)_{18}$ nanocluster structure.²⁴

Figures 5a and 5b present atomic level reaction pathways and free energy diagrams for CO_2RR at the singly-dethiolated nanocluster structures; the active sites are marked with asterisks. All Cu-containing nanoclusters showed identical intermediate binding configurations, and full reaction pathways for all thiol-capped NPs are presented in Figure S17. The first proton/electron transfer step (*COOH formation) produced ΔG_{max} for all nanoclusters. This result predicts a Tafel slope around 120 mV dec⁻¹ that is consistent with the experimentally-determined value of ~180 mV dec⁻¹. The *COOH intermediate was stabilized in a one-fold coordination at $\text{Au}_{144}(\text{SH})_{59}$. Less favorable, two-fold *COOH binding between a ligand Cu atom and a surface Au atom increased ΔG_{max} by 130-225 meV for Cu-containing $\text{Au}_{144-x}\text{Cu}_x(\text{SH})_{59}$ nanoclusters. These values agree extremely well with the

experimentally-observed ~ 120 mV E_{onset} increase for Cu-containing NPs and reveal how NP surface structure and molecular binding can influence electrocatalytic onset potentials. The second proton/electron transfer formed a one-fold coordinated $^*\text{CO}$ intermediate at all nanocluster structures. Stronger $^*\text{CO}$ binding at Cu sites improved intermediate stability compared with $\text{Au}_{144}(\text{SH})_{59}$ (Table S6), and the final thermochemical step was endergonic at all nanocluster structures.

We also considered the competitive H_2 evolution reaction (HER; **Figure 5c**). The adsorbed $^*\text{H}$ intermediate formed in a two-fold configuration with the exposed active site and a surface Au atom at all nanocluster structures (Figure S18). $^*\text{H}$ formation was slightly exergonic at $\text{Au}_{114}(\text{SH})_{59}$, whereas weaker $^*\text{H}$ binding at Cu sites made this process less favorable at Cu-containing structures (Table S6). Much stronger $^*\text{CO}$ vs. $^*\text{H}$ binding was found at all nanocluster structures. At negative potentials where both CO_2RR and HER can proceed, stronger $^*\text{CO}$ binding should inhibit competitive $^*\text{H}$ formation at nanocluster active sites. This result suggests more favorable CO_2RR at cathodic potentials, which is consistent with the experimentally-observed high CO selectivity and minor H_2 evolution. Our DFT results suggest that thiol-capped Au/Cu NPs retain CO selectivity through a combination of $^*\text{CO}$ intermediate stabilization and less favorable $^*\text{H}$ formation.

Influence of ligand coverage. Finally, we compared CO_2RR and HER at $\text{Au}_{72}\text{Cu}_{72}(\text{SH})_{60-x}$ nanocluster models with varying numbers of ligands removed ($x=0, 1, 2, 60$). The CO_2RR and HER free energy diagrams for $\text{Au}_{72}\text{Cu}_{72}(\text{SH})_{60-x}$ are shown in **Figure 6** and the corresponding atomic structures are shown in Figure S19. Fully ligand protected nanoclusters were

relatively unreactive and demonstrated large ΔG values and weak intermediate binding for both CO₂RR and HER (Table S6). Removing one ligand decreased ΔG for *COOH formation and better stabilized the *CO intermediate. Removal of two or more ligands further increased *CO binding such that desorption of gaseous CO product molecules became the most thermodynamically challenging reaction step. This prediction suggests that desorbing gaseous CO may become a kinetically limiting step in the CO₂RR process for ligand-free nanoclusters. Sequential ligand removal also reduced the ΔG associated with *H formation at Au₇₂Cu₇₂(SH)_{60-x} (**Figure 6b**), and this process becomes thermodynamically favorable for completely dethiolated Au₇₂Cu₇₂(SH)₀.

It is possible that a small fraction of ligands desorb during the application of electrochemical potentials. However, our experimental and computational results preclude *extensive* thiol desorption during CO₂RR due to sustained CO selectivity over H₂ evolution, indicating the majority of the catalyst surface remained ligand-protected during CO₂RR. On the other hand, removing a substantial fraction of thiol ligands should reduce CO₂RR selectivity through a combination of less favorable CO desorption and more favorable *H formation. This prediction is consistent with the larger H₂ evolution observed from *ligand-free* 49% Cu NPs. It also agrees with previous experimental observations^{16,58,59} and theoretical predictions^{54,60,61} that ligand-free NPs will preferentially evolve H₂ due to enhanced stabilization of *H intermediates and potential poisoning of undercoordinated surface sites by strongly bound *CO.

CONCLUSIONS

We have studied the CO₂RR and HER at thiol-capped Au/Cu NPs and observed selective CO₂ conversion with reduced precious metal loadings. A combination of experimental work and computational modeling helped establish atomic-level structure-property relationships. For example, the presence of Cu atoms in the ligand-shell increased CO₂RR E_{onset} due to less favorable *COOH formation at Cu-S ligand units. However, satisfactory stabilization of bound *CO intermediates coupled with unfavorable *H formation sustained CO₂RR selectivity at reduced precious metal content. Experimental data showed somewhat reduced CO₂RR selectivity and mass activity for Au/Cu NPs with high Cu content, and H₂ evolution may become more significant as the precious metal content decreases towards zero. Finally, both experiment and theory indicate the absence of surface thiol units will increase H₂ evolution due unfavorable desorption of strongly bound *CO intermediates and more favorable *H formation. These results demonstrate how ligand surface units can sustain selective CO₂ reduction with reduced precious metal requirements.

FIGURES

Figure 1. (a) Particle size histogram including all NP compositions and an atomic resolution, annular dark-field scanning transmission electron microscopy image of a single 49% Cu NP. Additional TEM images and particle size histograms of each NP composition are provided in Figure S3. (b) Normalized Cu L-edge X-ray absorption spectra of Au/Cu NPs, CuO powder, and an ambiently-oxidized Cu foil.

Figure 2. Fourier transformed, k^2 weighted Cu K-edge extended X-ray absorption fine structure (EXAFS) patterns of 49% Cu NPs compared with Cu foil, Cu₂O and CuO references.

Figure 3. Potential-dependent (a) Faradaic efficiency (FE), (b) partial geometric current density, and (c) mass activity for CO formation at 1.5nm, thiol-capped Au/Cu NPs *vs.* larger (~7nm) thiol-free Au NPs. (d) Twelve-hour CO₂RR electrolysis using 1.5 nm, thiol-capped 49% Cu NPs at -0.8V *vs.* RHE. The electrolysis contained three start/stop cycles to mimic intermittent availability of renewable energy input

Figure 4. Fully ligand-protected Au₁₄₄(SH)₆₀, Au₁₁₄Cu₃₀(SH)₆₀, Au₉₀Cu₅₄(SH)₆₀, and Au₇₂Cu₇₂(SH)₆₀ nanocluster structures based on the DFT-optimized Au_{144-x}Cu_x(SH)₆₀ system.³⁰

Figure 5. (a) Atomic-level reaction pathways and (b) free energy diagrams for CO₂RR at singly-dethiolated Au₁₄₄(SH)₅₉, Au₁₁₄Cu₃₀(SH)₅₉, Au₉₀Cu₅₄(SH)₅₉, and Au₇₂Cu₇₂(SH)₅₉ nanoclusters. One -SH unit was removed from each structure to create an accessible active site (marked with pink asterisk). All Cu-containing nanoclusters showed equivalent CO₂RR intermediate binding configurations as shown in Figure S17. (c) H₂ evolution reaction (HER) free energy diagram at singly-dethiolated nanocluster models. The HER proceeded at the same active sites marked in panels a, and atomic level HER reaction pathways are provided in Supporting Information Figure S18. CO₂RR and HER intermediate binding energies are summarized in Table S6.

Figure 6. (a) CO₂RR and (b) HER free energy diagrams as a function of thiol coverage for $\text{Au}_{72}\text{Cu}_{72}(\text{SH})_{60-x}$ nanocluster models ($x=0, 1, 2, 60$). Atomic structures and reaction intermediate binding configurations are presented in Figure S19, and intermediate binding energies are summarized in Table S6.

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Supporting Information Available: Additional experimental and computational methods; additional optical absorbance and photoluminescence, XPS, XAS, TEM, electrochemical and

computational data. This material is available free of charge via the Internet at

<http://pubs.acs.org>.

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