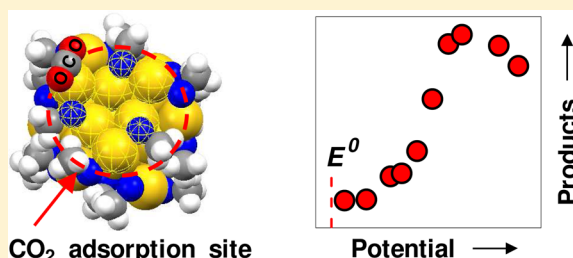


Experimental and Computational Investigation of Au₂₅ Clusters and CO₂: A Unique Interaction and Enhanced Electrocatalytic ActivityDouglas R. Kauffman,^{*,†,‡} Dominic Alfonso,[†] Christopher Matranga,[†] Huifeng Qian,[§] and Rongchao Jin[§][†]National Energy Technology Laboratory (NETL), United States Department of Energy, Pittsburgh, Pennsylvania 15236, United States[‡]URS, P.O. Box 618, South Park, Pennsylvania 15129, United States[§]Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States

Supporting Information

ABSTRACT: Atomically precise, inherently charged Au₂₅ clusters are an exciting prospect for promoting catalytically challenging reactions, and we have studied the interaction between CO₂ and Au₂₅. Experimental results indicate a reversible Au₂₅–CO₂ interaction that produced spectroscopic and electrochemical changes similar to those seen with cluster oxidation. Density functional theory (DFT) modeling indicates these changes stem from a CO₂-induced redistribution of charge within the cluster. Identification of this spontaneous coupling led to the application of Au₂₅ as a catalyst for the electrochemical reduction of CO₂ in aqueous media. Au₂₅ promoted the CO₂ → CO reaction within 90 mV of the formal potential (thermodynamic limit), representing an approximate 200–300 mV improvement over larger Au nanoparticles and bulk Au. Peak CO₂ conversion occurred at –1 V (vs RHE) with approximately 100% efficiency and a rate 7–700 times higher than that for larger Au catalysts and 10–100 times higher than those for current state-of-the-art processes.



INTRODUCTION

The chemistry of Au surfaces and Au nanoparticles has been the focus of intense study,^{1–3} but recent synthetic advances have introduced a new class of “small” ligand-protected Au clusters with unique chemical and electronic properties.^{2,4–6} Sub-2-nm clusters differ from larger nanoparticles because their energy levels become quantized and they develop molecule-like electronic structures.^{2,4} Crystallographic efforts have confirmed that such small Au clusters form into atomically precise structures and that ligand-protected Au₂₅ clusters, possess an inherent anionic (negative) charge.^{7,8} Ligand-protected Au₂₅ clusters are a unique platform to study catalytic reactions because they bridge the size gap between molecules and larger nanoparticles, they possess an anionic charge, and their surface structure is precisely known. Despite these features, the catalytic activities of Au₂₅ and similar atomically precise clusters have only been investigated experimentally for a handful of reactions, such as the oxidation of styrene and cyclohexane,^{9–12} the hydrogenation of aldehydes and ketones,^{13,14} and the electrochemical reduction of O₂.¹⁵ One particularly appealing catalytic challenge to consider for the negatively charged Au₂₅ cluster is the reduction of carbon dioxide. Not only is CO₂ an important greenhouse gas, but it also represents an abundant starting material for the generation of fine chemicals and fuels.^{16–19}

Herein we report a spontaneous and reversible electronic interaction between CO₂ and ligand-protected Au₂₅(SC₂H₄Ph)₁₈[–] clusters (abbreviated as Au₂₅). *In situ*

nonaqueous spectroelectrochemistry was used to manipulate the charge state of Au₂₅ and establish a benchmark for adsorbate-induced spectroscopic changes. These benchmarking studies were required to gain insight into the subtle electronic structure changes noted during the coupling of Au₂₅ and CO₂ in dimethylformamide (DMF). Specifically, the introduction of CO₂ reversibly induced spectroscopic and electrochemical changes that were similar to those seen during Au₂₅ oxidation. We also used density functional theory (DFT) to model the interaction between Au₂₅ and CO₂. This type of study is a valuable complement to experimental efforts because it allows direct, atomic-scale determination of favorable binding sites and adsorption structures. Previous computational efforts have considered the binding of adsorbates such as O₂ and CO on ligand-free or partially ligand-protected clusters.^{20,21} In our calculations, several physisorbed linear CO₂ states were identified on fully S–CH₃ protected Au₂₅ clusters. From a theoretical standpoint, first-principles investigations focusing on the adsorption properties of fully ligand-protected clusters are scarce, and relatively little is known about the effects of molecular physisorption on the cluster's electronic structure. Our results correlate experimental and computational data to demonstrate that molecular physisorption can *reversibly* perturb the Au₂₅ electronic structure and impact optical and electrochemical properties.

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The observation of spontaneous coupling between the negatively charged Au_{25} cluster and CO_2 motivated us to investigate Au_{25} as a catalyst for the electrochemical reduction of CO_2 . Typical electrocatalysts require large overpotentials to convert CO_2 into useful products,^{16–19} ultimately creating a challenge for large-scale deployment. In this application, Au_{25} catalyzed the two-electron conversion of CO_2 into CO within 90 mV of the formal potential (thermodynamic limit) of -0.103 V vs the reversible hydrogen electrode (RHE).¹⁹ The low overpotential is significant because it represents an approximate 200–300 mV reduction in potential compared to the larger Au nanoparticles and bulk Au tested in this study and those in previously published reports.^{18,19,22} Moreover, Au_{25} showed peak $\text{CO}_2 \rightarrow \text{CO}$ conversion at -1.0 V with approximately 100% Faradaic efficiency and a rate 7–700 times higher than those for the larger Au catalysts tested in this study and 10–100 times higher than those for current state-of-the-art processes.²³ In practical terms, CO is a very useful chemical that can be converted into a variety of valuable hydrocarbon species, and a low-voltage, high-efficiency process for converting CO_2 into CO could be instrumental in developing new carbon management technologies.^{16,17}

RESULTS AND DISCUSSION

Spectroelectrochemical Properties of Au_{25} . Figure 1 presents the structure, energy level diagram, and optical spectra of Au_{25} . The structure of Au_{25} contains a Au_{13} core surrounded by a shell of six Au_2S_3 semiring structures (the organic $\text{C}_2\text{H}_4\text{Ph}$ ligands and tetraoctylammonium counterion are shown in Figure S1 of the Supporting Information).^{7,8} The origins of the Au_{25} optical absorption spectrum have been interpreted,⁸ albeit some uncertainty remains because electronic and geometric coupling between core and shell atoms contribute to the spectral features.^{4,24,25} The onset of the absorption spectrum at approximately 1.4 eV corresponds to the energy gap (E_g) between the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO).^{8,26,27} Recent computational and experimental studies have identified the a' and a absorbance features as HOMO $\rightarrow$ LUMO transitions originating from closely spaced, nondegenerate orbitals.^{24,25,28} Absorbance feature b is attributed to both HOMO $\rightarrow$ LUMO + $1/2$ and HOMO $- 2 \rightarrow$ LUMO transitions, and absorbance feature c represents a HOMO $- 5 \rightarrow$ LUMO transition. The Au_{25} photoluminescence (PL) profile remained unchanged if excited at absorbance feature b (2.78 eV) or a (1.81 eV), although excitation at absorbance feature a produced lower PL intensity (Figure S2). Equivalent emission profiles at different excitation energies indicate LUMO $\rightarrow$ HOMO emission,²⁷ and the PL shoulder at 1.38 eV corresponded to the expected E_g in a variety of solvents. PL below 1.38 eV suggests relaxed emission from midgap states,²⁷ and the apparent spectral structure below 1.1 eV results from the optical transmittance of the solvent (Figure S3).

The Au_{25} optical absorbance and PL spectra are very sensitive to charge transfer, and characteristic spectral changes have been observed after chemical oxidation with oxygen^{29,30} or dissolved cations,^{31,32} ligand exchange,^{30,33–35} and the application of electrochemical potentials.²⁷ Accordingly, electrochemical modification of the Au_{25} optical properties provides an excellent benchmark to compare adsorbate-induced changes. Nonaqueous electrochemistry was used to apply oxidizing or reduction potentials to Au_{25} clusters in DMF (Figure S4),^{27,36} and the *in situ* spectroelectrochemical oxidation of Au_{25} is

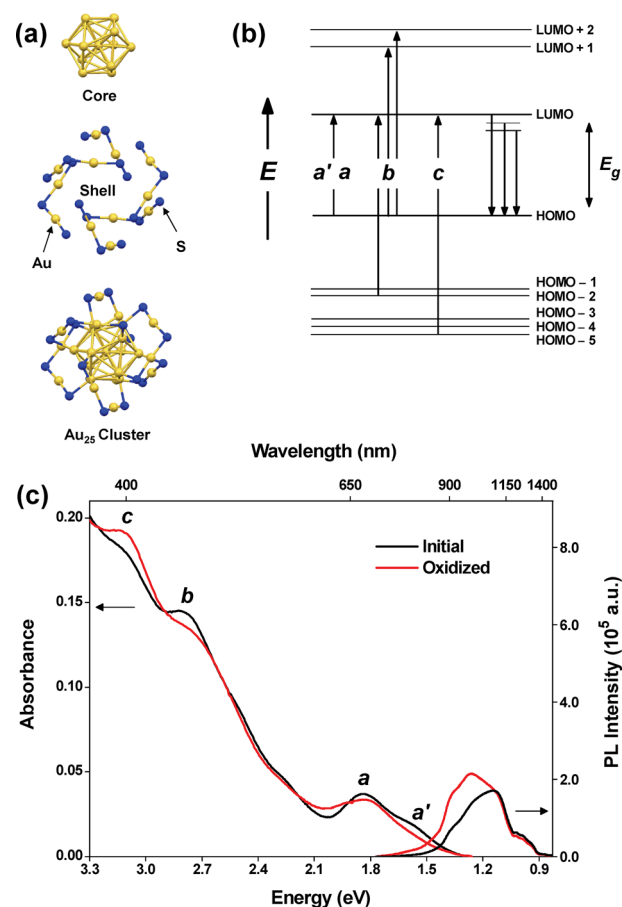


Figure 1. Structure, energy level diagram and spectroelectrochemical properties of Au_{25} . (a) Au_{25} structure: the $\text{C}_2\text{H}_4\text{Ph}$ ligands and tetraoctylammonium (TOA^+) counterion are shown in Figure S1 in the Supporting Information.^{7,8} (b) Au_{25} energy level diagram. (c) *In situ* spectroelectrochemistry demonstrating oxidation-induced changes to Au_{25} optical properties in N_2 purged DMF + 0.1 M TBAP; the labeled absorbance features correspond to the transitions identified in panel b.

presented in Figure 1c. The application of an oxidizing potential bleached the a' , a , and b absorbance features due to electronic depletion of the HOMO.²⁷ Furthermore, an oxidation-induced geometric change increased both the absorbance at 2.04 eV and the peak area of absorbance feature c .²⁹ The origins of the oxidation-induced PL increase are still debated in the literature,^{27,30,33} but the blue-shifted PL maximum suggests that oxidation may inhibit photoexcited electrons from relaxing into midgap states. Both the absorbance and PL changes were qualitatively reversible with the application of a sufficiently reducing potential, but the PL blue shift did not reverse regardless of the applied potential (Figure S5).

Interaction between Au_{25} and CO_2 . Figure 2a and b presents the optical spectra of an initially N_2 purged Au_{25} solution that was subsequently saturated with CO_2 . The introduction of CO_2 bleached the a' , a , and b absorbance features and increased the absorbance at both 2.04 eV and feature c . Additionally, the normalized PL maximum showed an increase and blue shift; non-normalized PL spectra are shown in Figure S6 for reference. The spectroscopic changes were reproducible from sample to sample (Table S1) and consistent with those noted during spectroelectrochemical oxidation

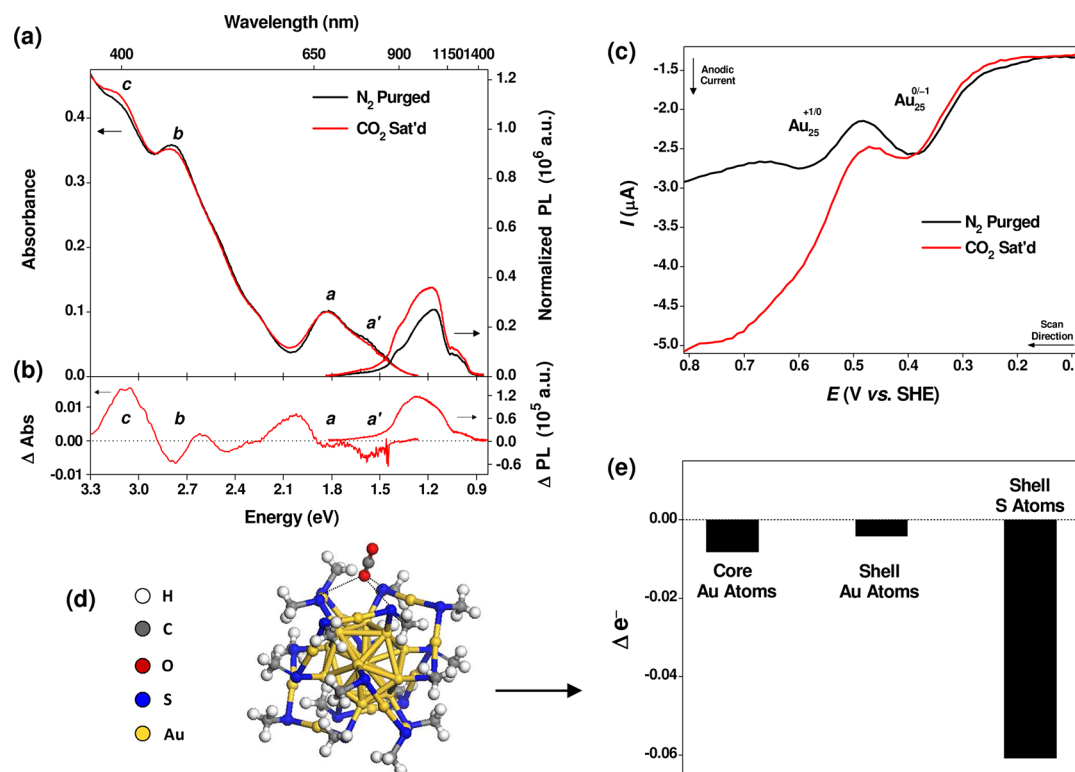


Figure 2. Experimental results and density functional theory (DFT) modeling of the Au₂₅–CO₂ couple. (a) Optical absorbance and PL spectra, and (b) difference spectra (Δ abs and Δ PL) of Au₂₅ in N₂ purged and CO₂ saturated DMF; PL spectra were normalized to the absorbance peak area at $\lambda_{\text{ex}} = 2.78$ eV (i.e., absorbance feature b). (c) Square wave voltammetry of Au₂₅ in N₂ purged and CO₂ saturated DMF + 0.1 M TBAP; anodic (oxidizing) currents are negative, and scans were collected at 0.05 V s⁻¹. (d) DFT model of stable CO₂ adsorption where an O atom of CO₂ interacts with three S atoms in the Au₂₅ shell. (e) Bader charge analysis showing the change in Au₂₅ valence electrons upon CO₂ adsorption; negative values indicate electron loss. Additional DFT results are presented in Figures S14–S17.

(Figure 1c). The apparent interaction between Au₂₅ and CO₂ was somewhat unexpected because CO₂ shows little electronic interaction with traditional gold surfaces.³⁷ Control experiments have shown that the optical changes did not result from drift in the spectrometer signal, the purge gas, solvent evaporation, solvent polarity, instability of Au₂₅ optical properties, or the inadvertent introduction of trace atmospheric moisture (Figures S7–S12). Furthermore, pH-induced spectral changes are unlikely in aprotic solvents,³⁸ and we confidently attribute the phenomenon to an interaction between Au₂₅ and CO₂. We note that the CO₂-induced spectral changes were somewhat smaller than those in previous reports of Au₂₅ oxidation.^{29–33,39} Nonetheless, the above cited examples of Au₂₅ oxidation were not easily reversed, and the restoration of Au₂₅ optical properties, when attempted, required strong reducing agents or electrochemical potentials. In the current study, the CO₂-induced optical changes were reversed by simply purging the solution with N₂ (Figure S13), suggesting a comparatively weak interaction between the Au₂₅ cluster and CO₂.

CO₂ also affected the electrochemical properties of Au₂₅. The redox waves presented in Figure 2c represent quantified charge injection into the Au₂₅ HOMO.^{27,36} We found that the introduction of CO₂ induced a small but significant 21 ± 2 mV shift in the Au₂₅^{0/-1} redox wave (>99% confidence level, CL; $n = 3$). Positive potentials are considered oxidizing,⁴⁰ and a positive shift in the Au₂₅^{0/-1} redox potential is consistent with electronic depletion of the Au₂₅ HOMO (e.g., a larger potential will be required to withdraw electrons from an oxidized

species).³⁴ The electrochemical and spectroscopic results are consistent with the energy level diagram presented in Figure 1b, since depletion of the HOMO is expected to induce concomitant spectral bleaching and positive redox shifts. We could not identify CO₂-induced shifts in the Au₂₅^{+1/0} redox wave because this feature was masked by a broad current increase. We hypothesize this phenomenon was related to potential-induced desorption of CO₂ from the Au₂₅ surface. Lastly, the electrochemical changes were reversed by purging the solution with N₂ (Figure S13). In comparison to previous studies, both Murray and co-workers^{34,35} and Devadas et al.⁴¹ have reported that electron-withdrawing ligand groups can irreversibly shift the Au₂₅^{0/-1} wave by several hundred millivolts. The observed CO₂-induced changes are smaller than those for the above cited examples, but again, the smaller and more reversible shift in redox potential indicates a comparatively weak interaction between Au₂₅ and CO₂.

Impressive strides have been made in the theoretical modeling of Au clusters.^{6,8,20,21,28,35,42,43} However, investigation of strongly bound adsorbates like O₂ and CO required activating the cluster by removing ligand groups.^{20,21} Some molecules, such as CO₂, are not expected to chemisorb to the Au₂₅ surface, and the effects of weaker physisorption-type interactions have remained unaddressed. In our work, an extensive search for stable CO₂ adsorption configurations was undertaken using DFT. Specifically, our model utilized Au₂₅ clusters capped with 18 S–CH₃ ligands to mimic the fully ligand-protected cluster used in our experiments. CO₂ adsorption was found to occur at a specific “pocket”, or site,

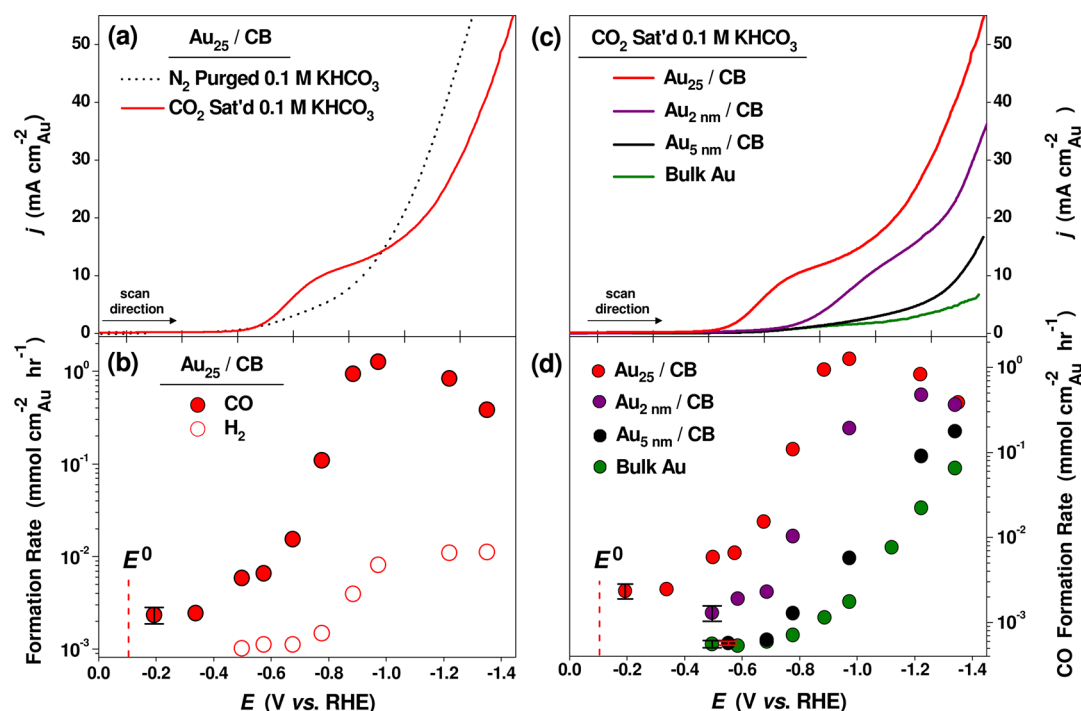


Figure 3. Electrochemical reduction of CO₂ in aqueous 0.1 M KHCO₃; cathodic (reducing) currents are positive, all scans were collected at a rate of 0.01 V s⁻¹, and error bars are from three separate runs with freshly prepared samples. (a) Linear sweep voltammograms (LSVs) of carbon black (CB) supported Au₂₅ in quiescent (unstirred) N₂ purged (pH = 9) and CO₂ saturated (pH = 7) 0.1 M KHCO₃. (b) Potential-dependent H₂ and CO formation rates for Au₂₅/CB; solutions were stirred at a constant rate during electrolysis runs to prevent product (bubble) buildup on the electrode surface. (c) LSVs of various Au catalysts in quiescent CO₂ saturated 0.1 M KHCO₃ (pH = 7). (d) Potential-dependent CO formation rates for the various Au catalysts; solutions were stirred at a constant rate during electrolysis runs to prevent product (bubble) buildup on the electrode surface. Product values are listed in Tables S2 and S3 in the Supporting Information section.

on the Au₂₅ surface with binding energies that ranged between -0.07 and -0.14 eV (Figure S14). Our calculations predict similar CO₂ binding at finite temperatures, and comparable binding energies were also found at 300 K. Figure 2d presents one stable configuration where an oxygen atom of CO₂ interacts with three sulfur atoms in the Au₂₅ shell. This specific adsorption configuration had a calculated binding energy of 0.13 eV and a O-S separation between 3.31 and 3.45 Å. We found the bound CO₂ to be essentially linear, and the calculated O-C-O angle differs by only 1–2° with respect to the free CO₂. The small perturbation in the internal structure of the molecule is consistent with CO₂ physisorption.

Analysis of the electronic properties indicated that CO₂ adsorption only induced minor perturbations to the Au₂₅ density of states (Figure S15) and withdrew less than 0.1 electrons from the Au₂₅ cluster. However, complementary Bader charge analysis^{44,45} revealed the major consequence of CO₂ adsorption was charge redistribution *within* the Au₂₅ cluster. Figure 2e presents the change in Au₂₅ valence electrons after the adsorption of a CO₂ molecule, clearly showing the depletion of S atom electrons. The three predicted CO₂ adsorption configurations consistently depleted electron density from the S atoms, although charge redistribution between the core and shell Au atoms varied between the different Au₂₅-CO₂ configurations (Figure S16).

Direct comparison to literature values is not straightforward because previous DFT efforts utilized models that were based on bare or partially ligand-protected clusters. For example, intermediately bound states with energies of approximately -1.0 eV were found for CO adsorption on bare Au_{*n*} (*n* = 16–35) clusters.²⁰ A similar bound state was also predicted for O₂

adsorption on partially ligand-protected Au₂₅ clusters, and O₂ binding energies of -0.62 and -0.72 eV were found after Au₂₅ was activated by removing one or two ligand groups.²¹ In the present case, the Au₂₅ cluster was not artificially activated by ligand removal. Under these conditions, our work provides theoretical evidence of weakly bound CO₂, and this result is in line with the observation of reversible CO₂-induced spectroscopic and electrochemical changes. Finally, the computational results indicate the major consequence of CO₂ adsorption was the redistribution of charge within the Au₂₅ cluster. This finding is interesting because Murray and co-workers have suggested that polar ligand groups can induce oxidation-like effects through charge redistribution and Au-S bond polarization.^{33–35} This hypothesis is reasonable because most Au₂₅ orbitals contain a significant S atom contribution (Figure S17),⁸ meaning charge redistribution and/or Au-S bond polarization could disrupt geometric and electronic coupling within the cluster and produce the experimentally observed optical and electrochemical changes noted above.^{4,24}

CO₂ is not a polar molecule, but it does have a rather strong quadrupole moment and it can couple with anionic species.⁴⁶ We suspect that CO₂ adsorption was promoted, in part, by an electrostatic attraction to the negatively charged Au₂₅ cluster. The electrostatic potential that developed between the adsorbed CO₂ quadrupole and Au₂₅ redistributed charge within the cluster to produce reversible oxidation-like optical and electrochemical phenomena. Finally, the Au₂₅ electronic structure was restored by simply purging the solution with N₂ to desorb the weakly bound CO₂.

Electrochemical Reduction of CO₂. The unique interaction between Au₂₅ and CO₂ provided an exciting opportunity

to test CO₂ reduction with a negatively charged nanocatalyst. From a practical standpoint, the electrochemical reduction of aqueous CO₂ is attractive because the mechanisms are well understood and water represents an inexpensive and environmentally benign solvent for scaled-up processes.^{18,19} Figure 3 compares the electrocatalytic activity of Au₂₅ (~1 nm)^{7,8} and larger Au catalysts for the electrochemical reduction of CO₂ in aqueous 0.1 M KHCO₃. Potential-dependent product analysis (Figure 3b) identified significant and reproducible CO formation at an onset potential of -0.193 V vs RHE (>95% CL, *n* = 3). Electrolysis in N₂ purged KHCO₃ ruled out spurious CO evolution from Au₂₅'s organic ligands or the carbon black support. Remarkably, the onset of CO formation was within 90 mV of the CO₂ → CO formal potential (-0.103 V vs RHE).¹⁹ This low overpotential constitutes an approximate 200–300 mV reduction compared to the case of the larger Au catalysts in this study (Figure 3d) and those in previous literature reports.^{18,19,22}

Peak CO production from the Au₂₅ catalyst was found at -1.0 V vs RHE with approximately 100% Faradaic efficiency (FE) and a rate 7–700 times higher than 2–5 nm Au nanoparticles and bulk Au (Figure 3d and Table S2). Our previous experiments with CB-supported catalysts showed CO production from the CB support was negligible compared to the case of Au₂₅ (at -0.9 V CB: 5×10^{-9} mol CO h⁻¹ vs Au₂₅: 6.2×10^{-6} mol CO h⁻¹);⁴⁷ please note these rates are *not* normalized to the electrochemical surface area of Au. FE relates the amount of reaction product to the total number of electrons passed through the electrode (Figure S18). For Au₂₅, CO formation at -1.0 V occurred with approximately 100% FE, meaning almost every electron injected into the catalyst layer was utilized for CO₂ reduction. Au is known to selectively reduce CO₂ into CO,^{18,19} and CO selectivities ranged between 80.8 and 99.6% for Au₂₅, 71.0–96.9% for the larger Au nanoparticles and 26.9–92.9% for bulk Au, depending on the applied voltage (Table S3). However, the higher FE of the Au₂₅ cluster enhanced its CO production rate compared to the those for the other Au catalysts (Figure 3d and Table S2).

Potential-dependent CO₂ reduction rates have also been noted by Chen and Kanan for Sn-oxide catalysts,⁴⁸ but the decreased rates beyond -1.0 V likely stem from gaseous products blocking the Au₂₅ surface (Figure 3b,d). On the basis of the peak CO production rate of 1.26 mmol cm⁻² h⁻¹, we can estimate a maximum turnover frequency (TOF) of 87 CO molecules site⁻¹ s⁻¹ for the Au₂₅ catalyst; sites are defined as accessible Au atoms and determined from electrochemical surface area measurements.⁴⁹ This TOF value is approximately 10–100 times higher than those of current state-of-the-art electrochemical processes²³ and is comparable to previous reports of CO oxidation on ligand-free Au_{*n*} clusters (*n* = 4–19).⁵⁰

The retention of characteristic optical spectra after CO₂ reduction at -1.0 V ruled out Au₂₅ decomposition under electrocatalytic conditions (Figure S19 of the Supporting Information).^{14,51–53} Specifically, the optical spectra contain contributions from states derived from both core and shell atoms,^{4,24,25} and structural deterioration, i.e. ligand desorption or destruction of the -S-Au-S-Au-S- bonding motif in the cluster's shell, should severely alter the absorbance and/or PL spectra.^{14,51–53} In contrast to Au₂₅'s ligands, alkanethiol monolayers can desorb from traditional Au surfaces during the application of even modest electrochemical potentials (c.a. -0.4 V vs RHE).⁵⁴ However, Au₂₅ is not a traditional Au

surface, and the stability of its -SR ligands has been noted before.^{51,52} Au₂₅'s stability stems from the unique -S-Au-S-Au-S- bonding motif in the cluster shell (Figure 1a). This shell stabilizes the organic ligands and protects the cluster from deterioration during chemical oxidation or reduction,^{51,52} catalytic reactions,^{9–14} and the application of electrochemical potentials (Figure S19).¹⁵

CO and H₂ were the only reaction products detected, and the potential-dependent product distribution in Figure 3b provides insight into the electrocatalytic mechanism. CO is the major CO₂ reduction product for Au electrodes, and the reaction proceeds along a two-electron, two-proton pathway through an adsorbed *CO₂⁻ intermediate;^{18,19} please see equations S1–S6 in the Supporting Information for further details. In the low potential regime (below -0.5 V), sequential proton capture and electron transfer converts adsorbed *CO₂⁻ into *COOH_(ads) before forming CO and water. A sharp increase in CO production occurred with the onset of H₂ evolution at approximately -0.5 V. In this potential range, the formation of H_{ads} occurs simultaneously with H₂ evolution, and a CO₂ → CO pathway based on the direct reduction of *CO₂⁻ with H_{ads} is likely. CO evolution onset potentials for the larger Au catalysts were comparable to previous results,^{18,19,22} and their equivalent values suggest the presence of similar active sites. Alternatively, the smaller CO evolution potential of Au₂₅ points to a unique catalytic site capable of promoting the CO₂ → CO reaction closer to the thermodynamic limit. Jin and co-workers have suggested that Au₂₅ contains a reactive site capable of promoting both C=O bond activation and H_{ads} formation.^{13,14} Our computationally identified CO₂ adsorption site is consistent with the site proposed by Jin and co-workers (Figure S20 of the Supporting Information). Accordingly, we hypothesize that enhanced electrocatalytic activity stems from Au₂₅'s anionic charge promoting CO₂ adsorption and its unique reactive site facilitating C=O bond activation and H_{ads} formation.

CONCLUSIONS

We have shown spectroscopic, electrochemical, and computational evidence to support a reversible electronic interaction between CO₂ and atomically precise Au₂₅ clusters. Specifically, CO₂ adsorption redistributed charge *within* the Au₂₅ cluster to produce optical and electrochemical changes similar to those observed during cluster oxidation. The successful correlation of experimental and computational data is exciting because it provides insight into the electronic interactions between Au₂₅ clusters and weakly bound adsorbates. Lastly, we have shown that the Au₂₅ clusters can perform as superior catalysts for the electrochemical conversion of CO₂ into CO. Specifically, Au₂₅ promoted the CO₂ → CO reaction within 90 mV of the formal potential (thermodynamic limit) and showed peak CO production at -1.0 V vs RHE that was 7–700 times higher than that for larger Au catalysts and 10–100 times higher than those for current state-of-the-art processes.

EXPERIMENTAL SECTION

Au₂₅ was synthesized as previously reported,⁵⁵ and all organic solvents were dried over 3 Å molecular sieves. Absorption spectroscopy was performed with Perkin-Elmer Lambda 1050 and Agilent 8453 spectrometers. PL spectroscopy was performed with a Jobin Yvon Horiba Fluorolog 332 spectrometer equipped with a liquid N₂ cooled InGaAs detector. All presented PL spectra are the average of 10 scans with an excitation energy of 2.78 eV (447 nm) unless otherwise noted,

and a 2.26 eV (550 nm) long-pass optical filter was placed between the sample and the detector to prevent the appearance of higher order excitation peaks in the PL spectrum. Au₂₅ solutions in DMF were placed in sealable cuvettes and initially purged overnight with N₂, bubbled with ultrahigh purity CO₂ for 1.5 h, and finally purged with N₂ again for 1.5 h; experiments with *p*-xylene as a solvent used an initial 1.5 h N₂ purge to reduce solvent evaporation. During gas exposure experiments, the PL spectra were normalized to the absorbance peak area at $\lambda_{\text{ex}} = 2.78$ eV (i.e., absorbance feature *b*); please see Figure S6 in the Supporting Information for further details.

Electrochemical measurements were performed with a Biologic SP-150 potentiostat equipped with a low-current option. Nonaqueous electrochemistry was conducted in DMF + 0.1 M tetrabutylammonium perchlorate (TBAP) with Pt wire working and counter electrodes and a nonaqueous Ag/Ag⁺ reference electrode (0.01 M AgNO₃ + 0.1 M TBAP in CH₃CN); potentials were calibrated into the standard hydrogen electrode (SHE) scale using ferrocene (Fc/Fc⁺ = 0.7112 V vs SHE in DMF + 0.1 M TBAP).⁵⁶ *In situ* spectroelectrochemical measurements were conducted with a commercially available quartz cell from BASi.

Aqueous electrochemical experiments were conducted in 0.1 M KHCO₃ solutions prepared with ultrapure water (≥ 18.0 M Ω -cm). Catalyst inks were prepared by sonicating acetone-solvated Au₂₅ into a mixture of methanol, Vulcan XC-72R carbon black, and Nafion; catalyst inks were also prepared in an identical manner using commercially available 2 and 5 nm Au nanoparticles from BBInternational. The catalyst ink was deposited onto a glassy carbon (GC) working electrode and allowed to dry in air. Electrochemical experiments with bulk Au were conducted with a 99.99% Au wire that was cleaned in 1.0 M H₂SO₄, rinsed with ultrapure water, and used as a working electrode. A Pt wire counter electrode and a conventional Ag/AgCl reference electrode (3.0 M NaCl) were used to complete the aqueous electrochemical setup. The Ag/AgCl reference electrode was regularly calibrated against a commercially available Hydroflex reversible hydrogen electrode; $E^\circ = 0.000$ V – 0.059pH (ref 40). The solution pH was measured after each experiment to convert the Ag/AgCl reference electrode potentials into the RHE scale; typical pH values for N₂ and CO₂ saturated 0.1 M KHCO₃ were 7.0 and 9.0. The linear sweep voltammograms presented in Figure 3a and c were conducted in quiescent (unstirred) solutions.

Electrochemical CO₂ reduction reactions were performed in a gastight, two-compartment H-cell. The working and counter electrodes were housed in different compartments that were separated by a 0.1778 mm (0.007 in.) thick Nafion 117 cation exchange membrane; this experimental configuration prevented CO₂ reduction products from being oxidized at the counter electrode. During CO₂ electrolysis runs, a particular voltage was applied for 1 h and the solution was stirred at a constant rate to prevent product (bubble) buildup on the electrode surface. After 1 h of electrolysis, products were analyzed with a Perkin-Elmer Clarus 600 gas chromatograph equipped with TCD and FID detectors. Multiple blank injections accompanied each electrolysis run to establish an instrumental baseline for the CO peak area, and we have defined the CO formation onset potential as the potential where CO formation was significant above the baseline at a 95% confidence level. Electrochemical currents and product formation rates were normalized to the catalyst electrochemical surface area (ECSA), as measured by integrating the so-called Au oxide stripping peak in N₂ purged 0.1 M KHCO₃ (ref 49); this approach has previously been used to measure the ECSA of Au_{*n*} cluster electrocatalysts (*n* = 11–140) in aqueous media.¹⁵ We found the Au₂₅ clusters retained characteristic optical absorbance and PL spectral features after oxide formation/stripping (Figure S19 of the Supporting Information).

Computational Methodology. The adsorption of CO₂ on the model Au₂₅(SCH₃)₁₈^{–1} cluster was examined using the Vienna ab initio simulation package (VASP) which employs density functional theory with a basis set constructed from plane waves.^{57,58} The Perdew–Burke–Erzerhoff (PBE) generalized gradient approximation (GGA) functional was employed to calculate the exchange–correlation

energy.⁵⁹ The electron–ion interaction was described by the projector-augmented wave (PAW) method.⁶⁰

The model for the Au₂₅(SCH₃)₁₈^{–1} cluster was constructed using the DFT relaxed Au₂₅(SH)₁₈^{–1} structure determined by Aikens as a starting point.⁴² The terminating H atoms were then replaced by CH₃ to give rise to a Au₂₅(SCH₃)₁₈^{–1} structure. The cluster was placed in a cubic box with dimensions of 24 Å sides, and a uniform compensating background charge was assumed. Various binding configurations of CO₂ adsorbate on the cluster were explored, and Γ -point calculations were carried out with an energy cutoff of 600 eV. Geometries were relaxed using a quasi-Newton variable metric algorithm until the atomic forces were less than 0.03 eV/Å. The CO₂ binding energy was calculated using the expression $E_{\text{bind}} = E_{\text{CO}_2+\text{cluster}} - (E_{\text{cluster}} + E_{\text{CO}_2})$. Here $E_{\text{CO}_2+\text{cluster}}$ is the total energy of the relaxed CO₂–Au₂₅ cluster system, while E_{cluster} and E_{CO_2} are the total energies of the relaxed bare cluster and the gas phase CO₂, respectively. On the basis of this convention, a negative E_{bind} corresponds to an exothermic reaction (stable adsorption configuration).

■ ASSOCIATED CONTENT

§ Supporting Information

Additional experimental and computational data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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