The role of metal accessibility on carbon dioxide electroreduction in atomically precise nanoclusters†

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Atomically precise nanoclusters (NCs) can be designed with high faradaic efficiency for the electrochemical reduction of CO2 to CO (FE\textsubscript{CO}) and provide useful model systems for studying the metal-catalysed CO2 reduction reaction (CO2RR). While size-dependent trends are commonly evoked, the effect of NC size on catalytic activity is often convoluted by other factors such as changes to surface structure, ligand density, and electronic structure, which makes it challenging to establish rigorous structure–property relationships. Herein, we report a detailed investigation of a series of NCs \{Au\textsubscript{46–n}Ag\textsubscript{n}C\textsubscript{2}Cl\textsubscript{4}PPh\textsubscript{3}\textsubscript{2}, Au\textsubscript{24}Ag\textsubscript{20}C\textsubscript{2}Cl\textsubscript{2}, and Au\textsubscript{42}C\textsubscript{2}Cl\textsubscript{2}/Au\textsubscript{42}Ag\textsubscript{2}C\textsubscript{2}Cl\textsubscript{2}\} with similar sizes and core structures but different ligand packing densities to investigate how the number of accessible metal sites impacts CO2RR activity and selectivity. We develop a simple method to determine the number of CO2-accessible sites for a given NC then use this to probe relationships between surface accessibility and CO2RR performance for atomically precise NC catalysts. Specifically, the NCs with the highest number of accessible metal sites \{Au\textsubscript{46}C\textsubscript{2}Cl\textsubscript{2}/Au\textsubscript{42}Ag\textsubscript{2}C\textsubscript{2}Cl\textsubscript{2}\} feature a FE\textsubscript{CO} of >90% at −0.57 V vs. the reversible hydrogen electrode (RHE), while NCs with lower numbers of accessible metal sites have a reduced FE\textsubscript{CO}. In addition, CO2RR studies performed on other Au–alkynyl NCs that span a wider range of sizes further support the relationship between FE\textsubscript{CO} and the number of accessible metal sites, regardless of NC size. This work establishes a generalizable approach to evaluating the potential of atomically precise NCs for electrocatalysis.

Introduction

Heterogeneous catalysts composed of metal nanoparticles (NPs) dispersed on high-surface-area supports have been studied for more than a century, and these catalysts are of increasing interest for the electrochemical reduction of CO2 into chemical fuels and feedstocks. Gold- and silver-based NPs are particularly effective for the selective reduction of CO2 to CO. Though the effects of nanoparticle size, shape, and surface ligands on the CO2 reduction reaction (CO2RR) have been widely studied, the nonuniformity of metal NP catalysts is a long-standing challenge in the investigation of fundamental catalytic mechanisms. In particular, it is often difficult to identify the specific active sites that drive catalysis because of the wide distribution of local microenvironments in ligand-protected NPs that adopt varying sizes, shapes, and surface structures. For example, although functionalization with larger organic ligands has been shown to enhance the CO2RR activity of Au NPs, uncertainty over the exact arrangement of surface ligands makes it difficult to determine how bulky ligands impact selectivity and catalytic activity. Such molecular-level insight is, however, possible when atomically precise nanoclusters (NCs) are used as catalysts, since their uniformity allows the entire particle structure—including the ligand shell—to be resolved crystallographically.

Soon after the canonical Au\textsubscript{25}(SR)\textsubscript{18} (SR = aryl or alkylthiolate) NC was first reported, it was shown to be effective for CO2RR, featuring a high faradaic efficiency for CO (FE\textsubscript{CO}) at −1 V vs. the reversible hydrogen electrode (RHE). Though the CO2RR has since been studied for many other atomically precise Au NCs, there still remains much to be understood about how NC size, structure, and surface ligand identity influence catalytic activity and selectivity. For instance, relationships between NC size and CO2RR activity are challenging to identify because the ligand-to-metal ratio typically increases for smaller NCs, resulting in higher surface coverage. Changes to the arrangement of surface ligands and metal atoms—as well as the electronic structure of the NC—may also affect the outcome of catalytic reactions, further convoluted...
structure–property relationships. Indeed, differing trends have been reported for how NC size affects CO₂RR activity. For example, in the series Auₙ₂₅(SR)₁₈, Au₃₃(SR)₁₆, and Au₄₄₄(SR)₆₀ (SR = SC,H₄Ph), CO₂RR activity increases with increasing NC size, while other studies have found that the FECO of Au-SR NCs is not directly affected by NC size. Given the different size-dependent trends that have been observed for atomically precise NCs, the number of active sites is often a better predictor of catalytic behavior but is difficult to manipulate in a predictable fashion.

In an effort to decouple the role of metal active sites from NC size, structure, and ligand type, we designed a series of alkynyl-protected atomically precise Au/Ag NCs with similar sizes and core structures but different degrees of surface ligand coverage. We investigated the CO₂RR performance of these NCs and developed a convenient computational method to quantitatively evaluate the accessibility of potential catalytically active sites. Critically, the use of acetylene-based ligands—bearing one rotatable bond—simplifies the conformational landscape at the metal–ligand interface, thereby clarifying the effect of ligand modification on surface coverage and the number of accessible metal sites. In particular, we found that the number and accessibility of surface metal sites is directly correlated to experimental CO₂RR activity.

Results and discussion
Synthesis and characterization of alkynyl-protected Au/Ag NCs
We recently reported the isosstructural alkynyl-protected NCs Au₄₃(C≡C(Bu)₂₀ (Au₄₃) and Au₄₂Ag₁(C≡C(Bu)₂₀ (Au₄₂Ag₁), which are synthesized by reducing an oligomeric Au₁–C≡C(Bu) or Au₁Ag₁-C≡C(Bu) precursor with borane tert-butyllane then purifying via thin layer chromatography (Fig. S1A). With a nearly identical NC core but an increased density of alkynyl surface ligands, we also selected the previously reported Au₁₄₁Ag₁₆₂(C≡CPh)₂₄Cl₄(PPh₃)₂ NC (Au₁₄₁Ag₁₆₂) for comparison (Fig. S1B). To complete a series of NCs with similar sizes and varying surface ligand densities, we also targeted an Au/Ag-alkynyl NC with an even denser organic shell. This was achieved by introducing a bulky triphenylphosphine (PPh₃) ligand through the “hydride-mediated conversion” method. Specifically, [Au₉(PPh₃)₈]⁺ (ref. 40) was reduced with NaBH₄ to furnish a hydride-doped [H₃Au₉(PPh₃)₈]⁺ cluster, which was then reacted with CH₃COOAg, meta-substituted phenylacetylene ligands, and triethylamine to yield NCs with a composition of Au₉₄₆₋₄₆₋₇(C≡CPh–m–X)₂₄Cl₄(PPh₃)₂ (Au₉₄₆₋₄₆₋₇ n = 16–19, X = H, F, or CH₃) (Fig. 1, see ESI† for experimental details). Though attempts to grow single crystals of Au₉₄₆₋₄₆₋₇(C≡CPh–m–X)₂₄Cl₄(PPh₃)₂ suitable for structure determination were unsuccessful, crystalline structures were successfully determined for Au₉₄₆₋₄₆₋₇ with X = F and CH₃ (see Fig. 2). The successful crystallization of Au₉₄₆₋₄₆₋₇ with meta-substituted phenylacetylene ligands can be attributed to the additional interparticle C–H–π, or C–F–π interactions between the meta functional groups on one NC and the phenyl rings of ligands on another NC (Fig. S2 and S3†).

The solution-phase UV-vis absorption spectra of all three Au₉₄₆₋₄₆₋₇ NCs differ for different protecting ligands exhibit sharp absorption peaks centered near 400 and 690 nm (Fig. 1A). Moreover, electrospray ionization mass spectrometry (ESI-MS) analysis shows 2+ and 1+ ion peaks for the NCs (Fig. 1B). Combined with the X-ray crystallography data, the 2+ and 1+ charges are attributed to ionization in ESI-MS—not the native charge states of the NCs—and the peaks correspond to NCs that have lost one or two PPh₃ ligands, which has been commonly observed for similar atomically precise NCs (Fig. S4–S6†).

The ESI-MS spectrum of Au₉₄₆₋₄₆₋₇(C≡CPh–m–F)₂₄Cl₄(PPh₃)₂ contains peaks corresponding to n = 16, 17, and 18 (Fig. S5†), consistent with the crystallographically refined composition of Au₉₄₆₋₄₆₋₇(C≡CPh–m–F)₂₄Cl₄(PPh₃)₂ (Tables S1 and S2†). When HCC≡CPh–m–CH₃ was used instead, three peaks corresponding to n = 17, 18, and 19 were found, which is consistent with the higher refined Au:Ag ratio in Au₉₄₆₋₄₆₋₇(C≡CPh–m–CH₃)₂₄Cl₄(PPh₃)₂ (Tables S3 and S4†). The small inconsistency between MS and X-ray crystallography data has also been observed for other heterogeneous NCs, which are known to be dynamic—and prone to rearrangement—in solution. Regardless, the similar UV-vis and ESI-MS spectra for Au₉₄₆₋₄₆₋₇(C≡CPh–m–F)₂₄Cl₄(PPh₃)₂ and Au₉₄₆₋₄₆₋₇(C≡CPh–m–X)₂₄Cl₄(PPh₃)₂ (X = F, CH₃) NCs along with the fact that the same synthesis conditions were used—suggest that the three NCs are isosstructural. Note that small differences in absorption features near 400 nm and shifts in MS can be attributed to the different alkynyl ligands used.

The series of five atomically precise Au/Ag NCs exhibit similar core structures. Specifically, Au₉₄₆₋₄₆₋₇ has an icosahedral Au₉₄₆₋₄₆₋₇ kernel (n = 4–7 with Au and Ag randomly distributed), a dodecahedral Au₉₄₆₋₄₆₋₇ inner shell, and an icosahedral Au₁₄₁ outer shell with two additional Ag atoms on the surface (Fig. 2A). Each of the additional Ag atoms on the surface of Au₉₄₆₋₄₆₋₇ is bonded to two chloride ligands, one Au atom in the outer shell, and one PPh₃ ligand. Four chloride ligands are necessary for Au₉₄₆₋₄₆₋₇ to adopt a closed-shell superatomic...
The electronic configuration \((46 - 24 - 4 = 18 \text{ e}^-)\) similar to \(\text{Au}_{24}\text{Ag}_{20}\) with two chloride ligands \((24 + 20 - 24 - 2 = 18 \text{ e}^-)\). The structure of \(\text{Au}_{24}\text{Ag}_{20}\) also consists of an icosahedral \(\text{Au}_{12}\) kernel, a dodecahedral \(\text{Ag}_{20}\) inner shell, and an icosahedral \(\text{Au}_{12}\) outer shell (Fig. 2B), while \(\text{Au}_{43}\text{Ag}_{1}\) has an icosahedral \(\text{Au}_{12}\) kernel, a dodecahedral \(\text{Au}_{20}\) inner shell, and an incomplete icosahedral \(\text{Au}_{11}\) or \(\text{Au}_{10}\text{Ag}_{1}\) outer shell with a single vacant surface site (Fig. 2C).

![Fig. 2](https://example.com/fig2.png)

**Fig. 2** Structures of (A) \(\text{Au}_{46-2n}\text{Ag}_{24-2n}\text{Cl}_4\text{(PPh}_3\text{)}_2\) \((n = 16–19, X = \text{F or CH}_3\text{)}\), (B) \(\text{Au}_{24}\text{Ag}_{20}\text{Cl}_2\), and (C) \(\text{Au}_{43}\text{Cl}_2\text{Ag}_{1}\text{CtBu}_2\). Color code: magenta = \text{Au}; violet = \text{Ag}; light pink = \text{Au}/\text{Ag}; orange = \text{P}; green = \text{Cl}; light green = \text{F}; grey = \text{C}; white = \text{H}. The vacant surface sites in \(\text{Au}_{43}\text{Cl}_2\text{CtBu}_2\) and \(\text{Au}_{42}\text{Ag}_{1}\text{CtBu}_2\) are indicated with a dashed circle.

![Fig. 3](https://example.com/fig3.png)

**Fig. 3** (A) LSV and (B) FE\text{CO} for \(\text{CO}_2\text{RR}\) for the series of NC-based catalysts. (C) Chronoamperometry data for the \(\text{Au}_{43}\)-based catalyst at different applied potentials. (D) \(j_{\text{CO}}\) and (E) TOF\text{CO} for the NC-based catalysts at different applied potentials during \(\text{CO}_2\text{RR}\). (F) FE\text{CO} for the NC-based catalysts at \(-0.57\text{ V vs. RHE}\) during \(\text{CO}_2\text{RR}\) over an extended time period. All experiments were conducted in a 0.5 M \(\text{KHCO}_3\) solution saturated with \(\text{CO}_2\). In panels A, B, D, E, and F, magenta represents \(\text{Au}_{43}\text{Cl}_2\text{CtBu}_2\), purple represents \(\text{Au}_{42}\text{Ag}_{1}\text{CtBu}_2\), indigo represents \(\text{Au}_{24}\text{Ag}_{20}\text{CtBu}_2\text{Cl}_2\), blue represents \(\text{Au}_{46-2n}\text{Cl}_4\text{(PPh}_3\text{)}_2\), sky blue represents \(\text{Au}-\text{SC}_2\text{H}_4\text{Ph NPs}\), and cyan represents the Au layer.

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Adding or removing a single metal atom to or from the surface of NCs has provided insight into the optical and electronic properties of thiolate-capped metal NCs. The successful synthesis of our series of NCs with the same core (M₄₆, M₄₄, and M₄₃; M = Au and/or Ag) represents—to the best of our knowledge—the first demonstration of atom-by-atom evolution for alkynyl-stabilized metal NCs structure. Moreover, the linear directionality of alkynyl ligands in alkynyl-stabilized NCs offer advantages for catalytic studies since the NC/electrolyte interface is dominated by Au–C≡C bonds with similar local arrangements. Note that for Au₄₄Ag₂₀ and Au₄₃Ag₂₀, Ag atoms are located in the inner dodecahedral Ag₁₂ shell and/or the icosahedral Au₄₄Ag₁₂ kernel which are not accessible to substrates interacting with the surface of the NC. The calculated number of accessible metal sites (Table 1) for all atomically precise NC catalysts evaluated here, CO was the major CO₂RR product, and H₂ was the sole byproduct with no liquid products detected by ¹H NMR spectroscopy. The faradaic efficiency for CO production (FE CO) was assessed for each catalyst by calculating the percentage of transferred charge that was directed toward CO production (see ESI† for details), and the highest FE CO were 92.1 ± 1.7% and 90.9 ± 1.4% for Au₄₃ and Au₄₄Ag₁, respectively, at a potential of −0.57 V vs. RHE (Fig. 3B). At the same potential, FE CO for Au₄₄Ag₂₀ and Au₄₃Ag₄₆⁻ were just 72.9 ± 1.0% and 59.5 ± 2.5%, respectively (Fig. 3B). These lower efficiencies can be attributed to more densely packed surface ligands, which likely favors the hydrogen evolution reaction (HER) over CO₂RR. The Au–S NPs have an even lower FE CO (38.7 ± 0.8%) at the same potential, which is consistent with previously reported studies. If FE CO is related to the density of surface ligands, one might assume that a ligand-free Au layer would have the...
highest efficiency. However, the FE\textsubscript{CO} for the Au layers is only 20.4 ± 1.6% at −0.57 V vs. RHE, highlighting the important role of the microenvironments created by nanostructured catalysts in driving CO\textsubscript{2}RR.\textsuperscript{3,50,51}

To further evaluate catalytic performance, CO partial current densities (j\textsubscript{CO}) were determined and compared across the NC series. Generally, j\textsubscript{CO} decreases with increasing ligand density on the surface (Fig. 3D): Au\textsubscript{43}Ag\textsubscript{20} (20 surface ligands) > Au\textsubscript{42}Ag\textsubscript{26} (26 surface ligands) > Au\textsubscript{42}Ag\textsubscript{30} (30 surface ligands). For Au\textsubscript{43}, j\textsubscript{CO} is slightly higher than for Au\textsubscript{42}Ag\textsubscript{1}, suggesting that substitution of a single surface Au atom for Ag leads to a small decrease in CO\textsubscript{2}RR performance, particularly at more negative potentials. Furthermore, Au\textsubscript{43} shows a high CO turnover frequency (TOF\textsubscript{CO}) of 4718 h\textsuperscript{-1} at −0.57 V and 15193 h\textsuperscript{-1} at −0.77 V vs. RHE (Fig. 3E), which exceeds the values for Au\textsubscript{42}Ag\textsubscript{20} (2597 h\textsuperscript{-1} at −0.57 V and 10658 h\textsuperscript{-1} at −0.77 V) and Au\textsubscript{42}Ag\textsubscript{46} (1427 h\textsuperscript{-1} at −0.57 V and 6400 h\textsuperscript{-1} at −0.77 V). Note that the same mass loading of NCs was used for all experiments. This makes it reasonable to directly compare TOF values since the NCs in this series have similar molecular weights (Table S5\textsuperscript{†}). In addition, differences in catalytic activity cannot be attributed to differences in NC stability as the FE\textsubscript{CO} of all catalysts remained constant for at least 2.5 hours at −0.57 V (Fig. 3F).

While the nature of active sites is regarded as one of the best predictors of catalytic activity,\textsuperscript{52} it is often challenging to experimentally determine the number of catalytically active sites in a nanostructured material, and theoretical models are required.\textsuperscript{53,54} Though double-layer capacitance measurements can be used to determine the electrochemically active surface area (ECSA) of catalysts, the ECSA might not reflect the surface area active specifically for CO\textsubscript{2}RR since CO\textsubscript{2}RR and HER frequently occur simultaneously. For example, previous studies have shown that Au\textsubscript{32}(SR)\textsubscript{18} and Au\textsubscript{36}(SR)\textsubscript{24} exhibit different CO\textsubscript{2}RR behavior even though the NCs have almost the same ECSA.\textsuperscript{33,49} The ligand-to-metal ratio can serve as a proxy for active site density when the sizes of NCs are similar,\textsuperscript{55} but this ratio is not directly related to the number of active sites owing to the different shapes and surface structures that similarly sized NCs can adopt. Indeed, two isomeric Au\textsubscript{38}(SR)\textsubscript{24} NCs with the same ligand-to-metal ratio have shown significant differences in CO\textsubscript{2}RR catalysis.\textsuperscript{34}

With these challenges in mind, we sought to establish a simple method for determining the number of metal sites accessible to CO\textsubscript{2} in atomically precise NCs that does not rely on computationally intensive density functional theory (DFT) calculations. Briefly, the NC structure determined by crystallography is used to generate a series of several thousand conformers accounting for the different ligand conformations that may arise due to ligand rotation in the absence of crystal packing effects (see ESI† for details). The accessible surface area of each conformation within the conformer series was then calculated for every surface atom using a 1.65 Å spherical probe (the kinetic radius of CO\textsubscript{2}, Fig. S9f).\textsuperscript{56} Metal atoms with a positive contact area with CO\textsubscript{2} (Fig. S10f) were counted as accessible since these atoms have sufficient space to accommodate a covalent bond with CO\textsubscript{2}. Accessible metal atoms for the
different alkynyl-protected NCs under investigation are highlighted in Fig. 4. Note that the NC conformation with the greatest number of accessible metal atoms (N) was used to represent the surface accessibility of each NC. Using this approach, the number of accessible metal atoms for each NC can be calculated in ~1 hour. Notably, the number of accessible metal atoms, N, for Au44/Au42Ag1, Au43Ag1, and Au43Ag20, and Au46Ag6–n are 16, 12, and 5, respectively, which is consistent with a greater density of CO2-accessible surface metal sites driving increased CO2RR activity. The role of CO2-accessible metal sites is further supported by the fact that we observe little variation in TOFCO when it is normalized to the number of accessible metal sites on each NC (TOFCO/N). Specifically, TOFCO/N for Au43, Au42Ag1, Au43Ag20, and Au46Ag6–n is 294 h–1, 279 h–1, 216 h–1 and 285 h–1, respectively, at ~0.57 V vs. RHE (Table 1 and Fig. S11†). This suggests that the number of CO2-accessible metal sites—rather than the degree of Ag doping,77 surface ligand functional groups,78 or the electronic structure79 of the cluster—is the primary driver of catalytic activity, at least for NCs with relatively similar structures and compositions.

To further investigate the generalizability of accessible metal site number as a predictor of CO2RR activity, we also evaluated a wider range of previously reported alkynyl-protected Au NCs: Au23(C≡C•Bu)3 (Au43), Au36(C≡CPh)24 (Au46), and Au44(C≡CPh)24 (Au44). Within this series, Au44 has the highest number of CO2-accessible metal sites (N = 12) and the highest CO2RR activity, while Au36 has the lowest number of CO2-accessible sites and the lowest CO2RR activity (Fig. 5). The activity of Au44, however, is much lower than that of Au43, which is consistent with the greater number of CO2-accessible metal sites (N = 16) for the latter NC (Table 1 and Fig. S13†). The relationship between the number of accessible metal sites and FE CO J CO is plotted in Fig. S14.† This highlights that even though larger sized Au–alkynyl NCs often have increased CO2RR activities, just like their Au–thiolate counterparts,33 the number of accessible surface metal tends to be more closely related to catalyst performance. Therefore, we conclude that the number of accessible metal sites provides a useful metric for evaluating the likelihood of CO2 binding to a particular atomically precise NC and for predicting trends in catalytic activity. Since Au43 and Au42Ag1 NCs are isostructural, their slight difference in CO2RR activity could be due to replacing a surface Au atom with a more electropositive Ag atom.35 Though Au42Ag20 and Au44 NCs have the same number of metal atoms (44) as well as the number of accessible metals (12), Au44 exhibits a slightly higher FE CO and lower J CO than Au43;34 Differences in the geometric and electronic structures of the NCs may influence their CO2RR performance, but this is likely a less significant effect than the number of accessible metals. For NCs of the same core structure, more valence electrons in the frontier molecular orbitals elevate the energy of the highest occupied molecular orbital (HOMO), thereby favoring electron transfer from the NC catalyst to the substrate and thus improving the CO2RR activity.39 The performance of Au43 and Au42Ag1 NCs could also be partially attributed to more facile electron transfer during electrocatalysis. However, since the electronic structure of the NCs is determined by the number of metals and ligands, the surface coverage is still of importance. Moreover, since calculating the number of accessible metal sites is straightforward, it can serve as a quick screening tool for identifying the most promising NCs for electrochemical catalysis that is complementary to advanced DFT calculations.

Conclusions
A series of alkynyl-stabilized NCs with similar sizes and core structures but different degrees of surface ligand coverage was used to provide insight into the effect of the number of accessible metal sites on electrochemical CO2RR activity. A simple computational method was developed to calculate the number of metal sites on the NCs that are accessible to CO2. The highest faradaic efficiencies for CO2RR were observed for Au43 and Au42Ag1, which feature the largest number of accessible metal sites. When the TOFCO of the NC-based catalysts was normalized by the number of accessible sites, the differences between NCs were reduced. Collectively, these trends suggest that the number of substrate-accessible metal sites serves as a useful and generalizable predictor for evaluating the potential of atomically precise NCs for CO2RR.

Data availability
All the data are shown in the manuscript or the associated ESI.†

Author contributions
J. A. M and Y. L. conceived the project. Y. L. synthesized the NCs and grew the single crystals. Y. L. and A. E. T. performed the electrochemical studies and analysed the data. G. J. S performed the computational studies. R. D. M. and S.-L. Z. solved the crystal structures. Y. L and G. J. S wrote the manuscript with contribution from other authors.

Conflicts of interest
There are no conflicts to declare.

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