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### Introduction

Heterogeneous catalysts composed of metal nanoparticles (NPs) dispersed on high-surface-area supports have been studied for more than a century,<sup>1-3</sup> and these catalysts are of increasing interest for the electrochemical reduction of  $CO_2$  into chemical fuels and feedstocks.<sup>4-6</sup> Gold- and silver-based NPs are particularly effective for the selective reduction of  $CO_2$  to  $CO.^7$  Though the effects of nanoparticle size,<sup>8-10</sup> shape,<sup>11,12</sup> and surface ligands<sup>13,14</sup> on the  $CO_2$  reduction reaction ( $CO_2RR$ ) have been widely studied, the nonuniformity of metal NP catalysts is a long-standing challenge in the investigation of fundamental catalytic mechanisms.<sup>1,15</sup> 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

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# 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 CO<sub>2</sub> to CO (FE<sub>CO</sub>) and provide useful model systems for studying the metal-catalysed CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR). 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 а detailed investigation of a series of NCs  $[Au_nAg_{46-n}(C \equiv CR)_{24}Cl_4(PPh_3)_2, Au_{24}Ag_{20}(C \equiv CR)_{24}Cl_2, and Au_{43}(C \equiv CR)_{20}/Au_{42}Ag_1(C \equiv CR)_{20}] with a standard sta$ similar sizes and core structures but different ligand packing densities to investigate how the number of accessible metal sites impacts CO<sub>2</sub>RR activity and selectivity. We develop a simple method to determine the number of CO<sub>2</sub>-accessible sites for a given NC then use this to probe relationships between surface accessibility and CO<sub>2</sub>RR performance for atomically precise NC catalysts. Specifically, the NCs with the highest number of accessible metal sites [Au₄3(C≡CR)20 and Au₄2Ag1(C≡CR)20] feature a FE<sub>CO</sub> 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<sub>CO</sub>. In addition, CO<sub>2</sub>RR studies performed on other Au-alkynyl NCs that span a wider range of sizes further support the relationship between FE<sub>CO</sub> 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.

structures.<sup>16,17</sup> For example, although functionalization with larger organic ligands has been shown to enhance the CO<sub>2</sub>RR activity of Au NPs,<sup>18,19</sup> 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.<sup>20–23</sup>

Soon after the canonical  $Au_{25}(SR)_{18}$  (SR = aryl or alkylthiolate) NC was first reported, it was shown to be effective for  $CO_2RR$ , featuring a high faradaic efficiency for CO (FE<sub>CO</sub>) at –1 V vs. the reversible hydrogen electrode (RHE).<sup>24</sup> Though the  $CO_2RR$  has since been studied for many other atomically precise Au NCs,<sup>25–28</sup> 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 CO<sub>2</sub>RR activity are challenging to identify because the ligand-to-metal ratio typically increases for smaller NCs,<sup>29–31</sup> 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 convoluting

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structure–property relationships.<sup>32</sup> Indeed, differing trends have been reported for how NC size affects  $CO_2RR$  activity. For example, in the series  $Au_{25}(SR)_{18}$ ,  $Au_{38}(SR)_{24}$ , and  $Au_{144}(SR)_{60}$  $(SR = SC_2H_4Ph)$ ,  $CO_2RR$  activity increases with increasing NC size,<sup>33</sup> while other studies have found that the FE<sub>CO</sub> of Au-SR NCs is not directly affected by NC size.<sup>34</sup> 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 alkynylprotected atomically precise Au/Ag NCs with similar sizes and core structures but different degrees of surface ligand coverage. We investigated the  $CO_2RR$  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  $CO_2RR$  activity.

#### Results and discussion

#### Synthesis and characterization of alkynyl-protected Au/Ag NCs

We recently reported the isostructural alkynyl-protected NCs  $\operatorname{Au}_{43}(C \equiv C^t \operatorname{Bu})_{20}$  (Au<sub>43</sub>) and  $\operatorname{Au}_{42}\operatorname{Ag}_1(C \equiv C^t \operatorname{Bu})_{20}$  (Au<sub>42</sub>Ag<sub>1</sub>), which are synthesized by reducing an oligometric  $Au^{I}-C \equiv C^{t}Bu$ or Au<sup>I</sup>/Ag<sup>I</sup>-C $\equiv$ C<sup>t</sup>Bu precursor with borane *tert*-butylamine then purifying via thin layer chromatography (Fig. S1A<sup>+</sup>).<sup>35</sup> With a nearly identical NC core but an increased density of alkynyl surface ligands, we also selected the previously reported Au24- $Ag_{20}(C \equiv CPh^tBu)_{24}Cl_2$ NC  $(Au_{24}Ag_{20})$ for comparison (Fig. S1B<sup>†</sup>).<sup>36,37</sup> To complete a series of NCs with similar sizes and varying surface ligand densities, we also targeted an Au/Agalkynyl NC with an even denser organic shell. This was achieved by introducing a bulky triphenylphosphine (PPh<sub>3</sub>) ligand through the "hydride-mediated conversion" method.38,39 Specifically,  $[Au_9(PPh_3)_8]^{3+}$  (ref. 40) was reduced with NaBH<sub>4</sub> to furnish a hydride-doped [HAu<sub>9</sub>(PPh<sub>3</sub>)<sub>8</sub>]<sup>2+</sup> cluster, which was then reacted with CH3COOAg, meta-substituted phenylacetylene ligands, and triethylamine to yield NCs with a composition of  $Au_nAg_{46-n}(C \equiv CPh-m-X)_{24}Cl_4(PPh_3)_2$  (Au<sub>n</sub>- $Ag_{46-n}$ , n = 16-19, X = H, F,  $CH_3$ ) (Fig. 1, see ESI<sup>†</sup> for experimental details). Though attempts to grow single crystals of  $Au_nAg_{46-n}(C \equiv CPh)_{24}Cl_4(PPh_3)_2$  suitable for structure determination were unsuccessful, crystal structures were successfully determined for  $Au_nAg_{46-n}$  with X = F and  $CH_3$  (see Fig. 2). The successful crystallization of  $Au_nAg_{46-n}$  with meta-substituted phenylacetylene ligands can be attributed to the additional interparticle C-H··· $\pi$ , or C-F··· $\pi$  interactions between the *meta* functional groups on one NC and the phenyl rings of ligands on another NC (Fig. S2 and S3<sup>†</sup>).<sup>41,42</sup>



Fig. 1 (A) UV-vis-NIR absorption spectra and (B) ESI-MS of Au<sub>n</sub>-Ag<sub>46-n</sub>(C=CPh-m-X)<sub>24</sub>Cl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> (n = 16–19, X = H, F, or CH<sub>3</sub>).

The solution-phase UV-vis absorption spectra of all three  $Au_n Ag_{46-n}$  NCs with 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 PPh<sub>3</sub> ligands, which has been commonly observed for similar atomically precise NCs (Fig. S4-S6<sup>†</sup>).<sup>43,44</sup> The ESI-MS spectrum of Au<sub>n</sub>Ag<sub>46-n</sub>(C=CPh-m-F)<sub>24</sub>Cl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> contains peaks corresponding to n = 16, 17, and 18 (Fig. S5<sup>†</sup>), consistent with the crystallographically refined composition of  $Au_{17,67}Ag_{28,33}(C \equiv CPh-m-F)_{24}Cl_4(PPh_3)_2$  (Tables S1 and S2<sup>+</sup>). When  $HC \equiv CPh-m-CH_3$  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 Au<sub>19</sub>Ag<sub>27</sub>(C=CPh-m-CH<sub>3</sub>)<sub>24</sub>Cl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> (Tables S3 and S4<sup>†</sup>). The small inconsistency between MS and X-ray crystallography data has also been observed for other heterometallic NCs, which are known to be dynamic-and prone to rearrangement-in solution.45,46 Regardless, the similar UV-vis and ESI-MS spectra for Au<sub>n</sub>- $Ag_{46-n}(C \equiv CPh)_{24}Cl_4(PPh_3)_2$ and  $Au_nAg_{46-n}(C \equiv CPh-m X_{24}Cl_4(PPh_3)_2$  (X = F, CH<sub>3</sub>) NCs—along with the fact that the same synthesis conditions were used-suggest that the three NCs are isostructural. 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,  $Au_nAg_{46-n}$  has an icosahedral  $Au_nAg_{12-n}$  kernel (n = 4-7 with Au and Ag randomly distributed), a dodecahedral  $Ag_{20}$  inner shell, and an icosahedral  $Au_{12}$  outer shell with two additional Ag atoms on the surface (Fig. 2A). Each of the additional Ag atoms on the surface of  $Au_nAg_{46-n}$  is bonded to two chloride ligands, one Au atom in the outer shell, and one PPh<sub>3</sub> ligand. Four chloride ligands are necessary for  $Au_nAg_{46-n}$  to adopt a closed-shell superatomic



Fig. 2 Structures of (A)  $Au_nAg_{46-n}(C \equiv CPh - m - X)_{24}Cl_4(PPh_3)_2$  (n = 16 - 19, X = F or  $CH_3$ ), (B)  $Au_{24}Ag_{20}(C \equiv CPh^tBu)_{24}Cl_2$ , and (C)  $Au_{43}(C \equiv C^tBu)_{20}$  and  $Au_{42}Ag_1(C \equiv C^tBu)_{20}$ , Color code: magenta = Au; violet = Ag; light pink = Au/Ag; orange = P; green = Cl; light green = F; grey = C; white = H. The vacant surface sites in  $Au_{43}(C \equiv C^tBu)_{20}$  and  $Au_{42}Ag_1(C \equiv C^tBu)_{20}$  are indicated with a dashed circle.

electronic configuration  $(46 - 24 - 4 = 18 \text{ e}^{-})$  similar to  $Au_{24}Ag_{20}$  with two chloride ligands  $(24 + 20 - 24 - 2 = 18 \text{ e}^{-})$ . The structure of  $Au_{24}Ag_{20}$  also consists of an icosahedral  $Au_{12}$  kernel, a dodecahedral  $Ag_{20}$  inner shell, and an icosahedral  $Au_{12}$  outer shell (Fig. 2B), while  $Au_{43}/Au_{42}Ag_1$  has an icosahedral  $Au_{12}$  kernel, a dodecahedral  $Au_{20}$  inner shell, and an incomplete icosahedral  $Au_{11}$  or  $Au_{10}Ag_1$  outer shell with a single vacant surface site (Fig. 2C).



Fig. 3 (A) LSV and (B)  $FE_{CO}$  for  $CO_2RR$  for the series of NC-based catalysts. (C) Chronoamperometry data for the Au<sub>43</sub>-based catalyst at different applied potentials. (D)  $j_{CO}$  and (E)  $TOF_{CO}$  for the NC-based catalysts at different applied potentials during  $CO_2RR$ . (F)  $FE_{CO}$  for the NC-based catalysts at -0.57 V vs. RHE during  $CO_2RR$  over an extended time period. All experiments were conducted in a 0.5 M KHCO<sub>3</sub> solution saturated with  $CO_2$ . In panels A, B, D, E, and F, magenta represents  $Au_{43}(C \equiv C^tBu)_{20}$ , purple represents  $Au_{42}Ag_1(C \equiv C^tBu)_{20}$ , indigo represents  $Au_{24}-Ag_{20}(C \equiv CPh^tBu)_{24}Cl_2$ , blue represents  $Au_nAg_{46-n}(C \equiv CPh)_{24}Cl_4(PPh_3)_2$ , sky blue represents  $Au-SC_2H_4Ph$  NPs, and cyan represents the Au layer.

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Fig. 4 The metal sites accessible to  $CO_2$  on the surface of different Au/Ag-alkynyl NCs.

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.47,48 The successful synthesis of our series of NCs with the same core  $(M_{46}, M_{44}, and M_{43}; M = Au and/or Ag)$  represents—to the best of our knowledge- the first demonstration of atom-by-atom evolution for alkynyl-stabilized metal NCs structure (Fig. 2). Moreover, the linear directionality of alkynyl ligands in alkynylstabilized 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  $Au_nAg_{46-n}$  and  $Au_{24}Ag_{20}$ , Ag atoms are located in the inner dodecahedral  $Ag_{12}$ shell and/or the icosahedral  $Au_nAg_{12-n}$  kernel which are not accessible to substrates interacting with the surface of the NC (Fig. 2, highlighted by the dashed red box). Importantly, the surface ligand density varies systematically across the series: 24 alkynyl, 4 chloride, and 2 phosphine ligands for  $Au_nAg_{46-n}$ , 24 alkynyl and 2 chloride ligands for Au24Ag20, and only 20 alkynyl ligands for Au<sub>43</sub> and Au<sub>42</sub>Ag<sub>1</sub>. Thus, this series of atomically precise NCs provides a powerful platform to study relationships between metal site accessibility and CO2RR activity.

#### Evaluation of CO<sub>2</sub>RR activity and selectivity

To investigate their efficacy for  $CO_2RR$  catalysis, synthesized atomically precise NCs were mixed with carbon black (20 wt% NC loading) and deposited on a carbon paper electrode. For comparison, a carbon electrode was also prepared with spherical Au-SC<sub>2</sub>H<sub>4</sub>Ph NPs (Au-S NPs) with an average diameter of  $3.1 \pm 0.4$  nm (Fig. S1C<sup>+</sup>) that were mixed with carbon black at the same mass loading. To provide an additional comparison, an 85 nm thick bulk gold layer was also deposited on one carbon paper electrode (referenced as Au layer) by electron beam deposition. Linear sweep voltammetry (LSV) was then performed for each electrode in CO2-saturated 0.5 M KHCO3 solution. For the atomically precise NCs, the current density  $(j_{\text{total}})$  was found to increase in the order of  $Au_n Ag_{46-n} < Au_{24} Ag_{20}$ < Au<sub>42</sub>Ag<sub>1</sub> < Au<sub>43</sub> (Fig. 3A). Larger sized Au-S NPs exhibited a lower  $j_{\text{total}}$  than all atomically precise NCs, and  $j_{\text{total}}$  for the Au layer was the lowest of all catalysts investigated here (Fig. 3A). We note that the NC catalysts were not activated before electrocatalysis to minimize possible ligand stripping, and the LSV curves taken before and after chronoamperometric CO<sub>2</sub>RR catalysis (potential range of -0.47 V to -0.77 V vs. RHE) were in close agreement (Fig. S7<sup>†</sup>). Moreover, the NC-based catalysts display a steady current density over at least 40 min at each applied voltage (-0.47 V, -0.57 V, -0.67 V and -0.77 V vs. RHE; Fig. 3C), and the absorption spectra of NCs recovered from the electrode after catalysis matched those of as-synthesized NCs (Fig.  $S8^{\dagger}$ ), confirming the stability of the NCs during  $CO_2RR$ catalysis.

For all atomically precise NC catalysts evaluated here, CO was the major CO<sub>2</sub>RR product, and H<sub>2</sub> was the sole byproduct with no liquid products detected by <sup>1</sup>H NMR spectroscopy. The faradaic efficiency for CO production (FE<sub>CO</sub>) was assessed for each catalyst by calculating the percentage of transferred charge that was directed toward CO production (see ESI<sup>†</sup> for details), and the highest FE  $_{\rm CO}$  were 92.1  $\pm$  1.7% and 90.9  $\pm$  1.4% for  $Au_{43}$ and  $Au_{42}Ag_1$ , respectively, at a potential of -0.57 vs. RHE (Fig. 3B). At the same potential, FE<sub>CO</sub> for Au<sub>24</sub>Ag<sub>20</sub> and Au<sub>n</sub>- $Ag_{46-n}$  were just 72.9  $\pm$  1.0% and 59.5  $\pm$  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.25,26,49 The Au-S NPs have an even lower FE<sub>CO</sub> (38.7  $\pm$  0.8%) at the same potential, which is consistent with previously reported studies.<sup>27,33</sup> If FE<sub>CO</sub> is related to the density of surface ligands, one might assume that a ligand-free Au layer would have the

Table 1 The calculated number of accessible metal sites (*N*) for a series of alkynyl-protected NCs, along with their experimentally determined  $FE_{CO}$ ,  $j_{CO}$ ,  $TOF_{CO}$ , and  $TOF_{CO}/N$  values for  $CO_2RR$  electrocatalysis at -0.57 V vs. RHE. All experiments were conducted in a 0.5 M KHCO<sub>3</sub> solution saturated with  $CO_2$ 

Catalyst	Number of accessible metals ( <i>N</i> )				
		$FE_{CO}$ (%)	$j_{ m CO}~({ m mA~cm}^{-2})$	$ ext{TOF}_{ ext{CO}}\left(h^{-1} ight)$	$\mathrm{TOF_{CO}}/N\left(\mathrm{h}^{-1} ight)$
Au <sub>43</sub>	16	$92.1\pm1.7$	2.5	4718	295
$Au_{42}Ag_1$	16	$90.9 \pm 1.4$	2.4	4458	279
$Au_{24}Ag_{20}$	12	$72.9 \pm 1.0$	1.3	2597	216
$Au_n Ag_{46-n}$	5	$59.5\pm2.5$	0.8	1427	285
Au <sub>44</sub>	12	$74.5\pm1.3$	1.0	2045	170
Au <sub>36</sub>	9	$69.7 \pm 1.6$	0.7	1325	147
Au <sub>23</sub>	6	$66.7\pm2.5$	0.7	794	132



Fig. 5 (A/D) LSV, (B/E) FE<sub>CO</sub> at different applied potentials (left), or at -0.57 V vs. RHE for prolonged time (right), and (C/F)  $j_{CO}$  at different applied potentials during CO<sub>2</sub>RR for NC-based catalysts conducted in CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub> solution. Magenta represents Au<sub>43</sub>(C $\equiv$ C<sup>t</sup>Bu)<sub>20</sub>, pink represents Au<sub>23</sub>(C $\equiv$ C<sup>t</sup>Bu)<sub>20</sub>, orange represents Au<sub>44</sub>(C $\equiv$ CPh)<sub>28</sub>, and yellow represents Au<sub>36</sub>(C $\equiv$ CPh)<sub>24</sub>.

highest efficiency. However, the  $FE_{CO}$  for the Au layers is only 20.4  $\pm$  1.6% at –0.57 V vs. RHE, highlighting the important role of the microenvironments created by nanostructured catalysts in driving CO<sub>2</sub>RR.<sup>3,50,51</sup>

To further evaluate catalytic performance, CO partial current densities  $(i_{CO})$  were determined and compared across the NC series. Generally,  $j_{CO}$  decreases with increasing ligand density on the surface (Fig. 3D): Au<sub>43</sub>/Ag<sub>42</sub>Ag<sub>1</sub> (20 surface ligands) >  $Au_{24}Ag_{20}$  (26 surface ligands) >  $Au_nAg_{46-n}$  (30 surface ligands). For  $Au_{43}$ ,  $j_{CO}$  is slightly higher than for  $Au_{42}Ag_1$ , suggesting that substitution of a single surface Au atom for Ag leads to a small decrease in CO<sub>2</sub>RR performance, particularly at more negative potentials. Furthermore, Au43 shows a high CO turnover frequency (TOF\_{CO}) of 4718  $h^{-1}$  at -0.57 V and 15193  $h^{-1}$  at -0.77 V vs. RHE (Fig. 3E), which exceeds the values for Au<sub>24</sub>Ag<sub>20</sub>  $(2597 \text{ h}^{-1} \text{ at} -0.57 \text{ V} \text{ and } 10658 \text{ h}^{-1} \text{ at} -0.77 \text{ V}) \text{ and } Au_nAg_{46-n}$  $(1427 h^{-1} at -0.57 V and 6400 h^{-1} at -0.77 V)$ . 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<sup>†</sup>). In addition, differences in catalytic activity cannot be attributed to differences in NC stability as the  $FE_{CO}$  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,<sup>52</sup> it is often challenging to experimentally determine the number of catalytically active sites in a nanostructured material, and theoretical models are required.<sup>53,54</sup> 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  $CO_2RR$  since  $CO_2RR$  and HER frequently occur simultaneously. For example, previous studies have shown that  $Au_{25}(SR)_{18}$  and  $Au_{38}(SR)_{24}$  exhibit different  $CO_2RR$  behavior even though the NCs have almost the same ECSA.<sup>33,49</sup> The ligand-to-metal ratio can serve as a proxy for active site density when the sizes of NCs are similar,<sup>55</sup> 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  $Au_{38}(SR)_{24}$  NCs with the same ligand-to-metal ratio have shown significant differences in  $CO_2RR$  catalysis.<sup>34</sup>

With these challenges in mind, we sought to establish a simple method for determining the number of metal sites accessible to  $CO_2$  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  $CO_2$ , Fig. S9†).<sup>36</sup> Metal atoms with a positive contact area with  $CO_2$  (Fig. S10†) were counted as accessible since these atoms have sufficient space to accommodate a covalent bond with  $CO_2$ . 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  $\sim$ 1 hour. Notably, the number of accessible metal atoms, N, for  $Au_{43}/Au_{42}Ag_1$ ,  $Au_{24}Ag_{20}$ , and  $Au_nAg_{46-n}$  are 16, 12, and 5, respectively, which is consistent with a greater density of CO2-accessible surface metal sites driving increased CO<sub>2</sub>RR activity. The role of CO<sub>2</sub>-accessible metal sites is further supported by the fact that we observe little variation in  $TOF_{CO}$ when it is normalized to the number of accessible metal sites on each NC (TOF<sub>CO</sub>/N). Specifically, TOF<sub>CO</sub>/N for Au<sub>43</sub>, Au<sub>42</sub>Ag<sub>1</sub>,  $Au_{24}Ag_{20}$ , and  $Au_nAg_{46-n}$  is 294 h<sup>-1</sup>, 279 h<sup>-1</sup>, 216 h<sup>-1</sup> and 285  $h^{-1}$ , respectively, at -0.57 V vs. RHE (Table 1 and Fig. S11<sup>+</sup>). This suggests that the number of CO<sub>2</sub>-accessible metal sites—rather than the degree of Ag doping,57 surface ligand functional groups,<sup>58</sup> or the electronic structure<sup>59</sup> 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:  $Au_{23}(C \equiv C^{t}Bu)_{15}$  (Au<sub>23</sub>),<sup>60</sup> Au<sub>36</sub>(C \equiv CPh)<sub>24</sub> (Au<sub>36</sub>), and Au<sub>44</sub>(- $C \equiv CPh)_{28}$  (Au<sub>44</sub>)<sup>61</sup> (Fig. S12<sup>†</sup>). Within this series, Au<sub>44</sub> has the highest number of  $CO_2$ -accessible metal sites (N = 12) and the highest CO<sub>2</sub>RR activity, while Au<sub>23</sub> has the lowest number of CO<sub>2</sub>-accessible sites and the lowest CO<sub>2</sub>RR activity (Fig. 5). The activity of Au44, however, is much lower than that of Au43, which is consistent with the greater number of CO<sub>2</sub>-accessible metal sites (N = 16) for the latter NC (Table 1 and Fig. S13<sup>†</sup>). The relationship between the number of accessible metal sites and  $FE_{CO}$ ,  $j_{CO}$  is plotted in Fig. S14.<sup>†</sup> This highlights that even though larger sized Au-alkynyl NCs often have increased CO2RR activities, just like their Au-thiolate counterparts,<sup>33</sup> the number of accessible surface metals 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 Au<sub>42</sub>Ag<sub>1</sub> NCs are isostructural, their slight difference in CO<sub>2</sub>RR activity could be due to replacing a surface Au atom with a more electropositive Ag atom.35 Though Au24Ag20 and Au44 NCs have the same number of metal atoms (44) as well as the number of accessible metals (12),  $Au_{44}$  exhibits a slightly higher  $FE_{CO}$  and lower  $j_{CO}$  than Au<sub>24</sub>Ag<sub>20</sub>. 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 CO<sub>2</sub>RR activity.<sup>59</sup> The performance of Au<sub>43</sub> and Au<sub>42</sub>Ag<sub>1</sub> 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  $CO_2RR$  activity. A simple computational method was developed to calculate the number of metal sites on the NCs that are accessible to  $CO_2$ . The highest faradaic efficiencies for  $CO_2RR$  were observed for  $Au_{43}$  and  $Au_{42}Ag_1$ , which feature the largest number of accessible metal sites. When the  $TOF_{CO}$  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  $CO_2RR$ .

### 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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