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Predicted Structures of the Active Sites Responsible for the Improved Reduction of Carbon Dioxide by Gold Nanoparticles

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ABSTRACT: Gold (Au) nanoparticles (NPs) are known experimentally to reduce carbon dioxide (CO₂) to carbon monoxide (CO), with far superior performance to Au foils. To obtain guidance in designing improved CO₂ catalysts, we want to understand the nature of the active sites on Au NPs. Here, we employed multiscale atomistic simulations to computationally synthesize and characterize a 10 nm thick Au NP on a carbon nanotube (CNT) support, and then we located active sites from quantum mechanics (QM) calculations on 269 randomly-selected sites. The standard scaling relation is that the formation energy of *COOH (ΔE_{COOH}) is proportional to the binding energy of *CO (E_{binding}^{*CO}) so decreasing ΔE_{COOH} to boost the CO₂ reduction reaction (CO₂RR) causes an increase of E_{binding}^{*CO} that retards CO₂RR. We show that the NPs has superior CO₂RR because there are many sites at the twin boundaries that significantly break this scaling relation.
There is great interest in remediating the rapid increase of atmospheric carbon dioxide (CO$_2$) concentrations with its associated increase in global temperature.\textsuperscript{1} One strategy is to develop improved catalysts for the electrochemical reduction of CO$_2$ to value-added chemicals, such as carbon monoxide (CO), methane (CH$_4$), ethylene (C$_2$H$_4$) and ethanol (C$_2$H$_5$OH).\textsuperscript{2-3}

Of the metals known to reduce CO$_2$ to CO efficiently, Gold (Au) exhibits the highest activity and selectivity among polycrystalline metals. As first reported by Hori et al.,\textsuperscript{4} the Faradaic efficiency for CO formation is 91\% at -1.10 V vs. normal hydrogen electrode (NHE) [or -0.69 V vs. reversible hydrogen electrode (RHE)] with a partial current density of 3.7 mA cm$^{-2}$. Moreover, Au nanoparticles (NPs) have been shown to improve the CO$_2$RR performance further. For example, Chen et al. reported that an Au NP derived from Au oxide films results in CO$_2$RR to CO with Faraday efficiency more than 60\% at overpotentials as low as 0.14 V (-0.25V vs RHE).\textsuperscript{5} Feng et al. found a linear relationship between CO$_2$RR performance and the density of GBs in NPs,\textsuperscript{6} concluding that the presence of grain boundaries (GBs) on Au NPs is responsible for the improved CO$_2$RR performance. In addition, Zhu et al. concluded that for crystalline Au NPs, edge sites are the active sites for CO$_2$RR.\textsuperscript{7-8} They also showed that the size of the Au NPs is critical for controlling reaction rates: 8 nm Au NPs exhibit the best CO$_2$RR performance,\textsuperscript{7} while NPs below 2 nm are active only for hydrogen evolution reactions (HER).\textsuperscript{9} Of course, the applied electric field and the electrolyte can also influence CO$_2$RR. Using Au Nano-needles as catalysts, Liu et al. confirm that a field-induced 20-fold increased surface-adsorbed K$^+$ ion concentration enables CO$_2$RR to proceed with a partial current density for CO of 22 mA cm$^{-2}$ at −0.35 V (RHE), the best experimental results reported.\textsuperscript{10} Allying Au\textsuperscript{11} or suppressing HER\textsuperscript{12} are another directions to improve CO2RR.
Resolving the atomic structure of active sites responsible for the improved performance of Au NPs should provide clues helpful in designing improved CO$_2$RR catalysts. However, detection of the active sites directly from the experiment has not been possible. We report here computer simulation experiments aimed at synthesizing, characterizing, and resolving the active sites for CO$_2$RR on Au NP.

First, we computationally mimic the experimental chemical vapor deposition (CVD) of a 10 nm Au NP on 44.28 nm long, 8.39 nm diameter multiwall carbon nanotube (CNT) support. Here we carried out Reactive Molecular Dynamics (RMD) simulations of Au deposition on a 10 nm diameter CNT using the Embedded-Atom Model (EAM) to describe the Au-Au interactions.$^{13}$ The CVD experiments use an e-beam evaporated Au source, which we mimic by adding Au atoms into the simulation cell with a deposition rate of 3.0 Å ns$^{-1}$ for 35 ns (the experiment deposition rate is 2 Å s$^{-1}$ for 50 s).

We observed the rapid development of supersaturated Au vapor that in 0.3 ns began to condense. As the concentration of Au vapor reached 0.5 Au atom/nm$^3$, we observed the formation of Au nuclei containing ~18 atoms on the CNT surface that grew quickly in various directions until their boundaries met. After 35 ns, we obtained a coarse Au NP on CNT with a nominal thickness of about 10 nm, which is consistent with the size of the experimental catalyst.

Then, we employed simulated annealing to heal the defects arising from the fast deposition rate. The peak temperature in the simulated annealing is 1,164K (100K higher than the experimental melting point of Au metal). Each annealing cycle contained a ten ps heating ramp from 300 K to 1,164 K followed by five ps NVT simulation at 1164 K, and then a 10ps cooling ramp from 1,164 K to 300K. Finally, we carried out a 15 ps NVT simulation at 300 K. After 120 such annealing cycles; we found that all grains boundaries disappeared to form a single fully-
crystallized Au NP. From the annealing trajectories, we extracted an Au NP structure that most closely resembled the experiment catalyst (after 63 annealing cycles).

To further refine the Au NP structure and the interface between the Au NP and the CNT support, we carried out 20 ps of reactive dynamics at 300 K using the ReaxFF reactive force field trained to reproduce the equation of state of Au FCC metal and the geometry of graphene on the Au (111) surface. Finally, we removed under-coordinated Au atoms (with coordination number less than five) expected to be washed away under the experimental conditions. The final Au NP structure consists of 211,619 atoms (43,200 Carbon atoms + 168,419 Au atoms) with a nominal thickness of 10 nm, as shown in Figure 1A.

Figure 1. (A) The atomic structure of the Au nanoparticle (NP) “synthesized” computationally by simulating the Chemical Vapor Deposition (CVD) experiment. (B) Predicted Transmission electron microscopy (TEM) images of the predicted Au NP. The yellow marker label three of the grain boundaries (GBs).
This NP leads to an X-Ray Powder Diffraction (XRD) pattern (see Figure S1) showing the typically broadened diffraction peaks of FCC Au due to the small grains, which is consistent with experiment. Our predicted TEM images (Figure 1B) show the GBs in the Au-NP, while our dislocation analysis reveals that 1/6\textlangle112\textrangle Shockley partial dislocations are the most abundant, leading to stacking faults on the surface. The total length of this dislocation is 3,224 Å, which corresponds to a GB density of 224 µm$^{-1}$ (as defined experimentally). The XRD pattern and TEM images which confirm that the simulated Au NP structure is consistent with experiment.

In our previous work\textsuperscript{16} and research from other groups,\textsuperscript{17-19} the reaction mechanism of CO$_2$RR to CO on copper (Cu) is as following:

\begin{equation}
\ell$CO_2$ → *$b$-CO$_2$$^{\delta-}$ → *COOH → *CO → CO
\end{equation}

In this pathway, physisorbed linear CO$_2$ [$\ell$-CO$_2$] was first reduced to chemisorbed CO$_2$ ($b$-CO$_2$$^{\delta-}$) facilitated by a partial electron transfer ($\delta\cdot e^-$). In our previous work using PBE-D3 density functional theory (DFT) calculations on the Cu(100) surface with 5 layers of H$_2$O, we found that $b$-CO$_2$$^{\delta}$ is in a mixed coordination structure with one C-O bond (1.33 Å) parallel to the surface and one bond (1.29 Å) tilted by \textasciitilde60°.\textsuperscript{16} These distances are close to the C-O bond (1.26) of free CO$_2^-$. The following proton-coupled electron transfer [(1-$\delta$)-e$^-$] reaction leads to *COOH formation, which completes the first electron reduction reaction. The *COOH dehydration reaction leads to *CO formation. Finally, *CO desorbs and releases the reaction site completing the catalysis cycle. In this reaction pathway, $b$-CO$_2$$^{\delta-}$ formation is the rate-determining step (RDS), and *COOH formation is the potential-determining step (PDS). Therefore, we took the formation energy of RDS ($\Delta E_{*\text{COOH}}$) as a descriptor (as previously proposed by Peterson and Nørskov)\textsuperscript{20} to characterize the activity of surface sites toward CO$_2$RR:

\begin{equation}
\Delta E_{*\text{COOH}} = E_{*\text{COOH}} - (E_{*} + E_{\text{CO}_2} + 0.5\times E_{\text{H}_2})
\end{equation}
A lower $\Delta E^\ast_{\text{COOH}}$ indicates increased CO$_2$RR. We also calculated the energy of CO desorption ($\Delta E^\ast_{\text{CO}}$):

$$\Delta E_{\text{CO}} = (E^\ast + E_{\text{CO}}) - E^\ast_{\text{CO}}$$  \hspace{1cm} (3)

This non-electrochemical reaction step determines the rate of CO is leaving the surface sites: the lower $\Delta E^\ast_{\text{CO}}$ indicates, the higher CO$_2$RR.

Thus the binding energy of CO can be written as:

$$E^\ast_{\text{binding,CO}} = E^\ast_{\text{CO}} - (E^\ast + E_{\text{CO}}) = -\Delta E^\ast_{\text{CO}}$$  \hspace{1cm} (4)

To extract the active sites on Au NP, we randomly selected 269 sites out of 11,360 sites (2.4%) from the catalysis surface. This random sampling introduces no presumptions, ensuring that the statistical distribution represents the overall distribution of the reactive sites. We calculated $\Delta E^\ast_{\text{COOH}}$ and $\Delta E_{\text{CO}}$ using cluster models. These cluster models were cut from the simulated nanoparticle by taking the selected sites as the center with a cut-off of 8 Å. Such 8 Å provides a computational accuracy 0.02 eV, which we considered as the best balance of accuracy and efficiency.
Figure 2. The distribution of CO binding energies ($E_{\text{binding CO}}$, in eV) from PBE-D2 DFT on 269 Au NP surface sites selected randomly. The solid black line refers to the right axis as the cumulative percent (%). Two Gaussian functions were employed to fit the binding energies. One takes -0.65 eV ($\Delta E_{\text{CO}}$ of edge site) as the center with a width of 0.077 eV (in blue), and the other takes -0.42 eV ($\Delta E_{\text{CO}}$ of facet site) as the center with a width of 0.105 eV (in purple).

Figure 2 shows the statistical distribution of $E_{\text{binding CO}}$ of 269 surface sites ranging from -0.1 eV to -0.9 eV. To compare with the fully crystalline Au NP, we built an Au octahedron (shown in Figure S2) with a length of 6.93 nm (10,425 Au atoms), which consists of 2,024 facet sites (87.77%), 276 edge sites (11.97%) and six corner sites (0.26%). The DFT CO energy changes (negative is bound), $E_{\text{binding CO}}$, are -0.42 eV facet site and -0.65 eV edge site. Taking these two energies as a reference, we fitted the $\Delta E_{\text{CO}}$ distribution using Gaussian functions centering at -0.42 eV and -0.65 eV as shown in Figure 2. This fitting indicates that the most abundant binding site are rhombus sites [(111)-like sites] and step sites [(110)-like sites]. These predictions are consistent with experimental electrochemical surface characterizations showing that (111) and (110) facet are dominant. However, the distribution on our CVD derived Au NP is much broader than for the polyhedron crystalline Au NP due to the additional defects created by CVD deposition (primarily GBs and twin boundaries). This broad variation in binding site provides a site library, among which active sites exist responsible for CO$_2$RR.

We observed the standard scaling relation, a negative correlation between $\Delta E_{\text{COOH}}$ and $\Delta E_{\text{CO}}$ (as shown in Figure 3), with a slope of -0.98. These results are consistent with previous DFT calculations. Both small $\Delta E_{\text{COOH}}$ (corresponding to a low overpotential) and $\Delta E_{\text{CO}}$ (promote CO desorption) are favorable to promote CO$_2$RR. The negative correlation indicates that reduction in overpotential (decrease of $\Delta E_{\text{COOH}}$) occurs at the expense of increasing the CO
adsorption (an increase of $\Delta E_{\text{CO}}$). The sites with strong CO binding (large $\Delta E_{\text{CO}}$) are also responsible for promoting the hydrogen evolution reaction (HER), therefore suppressing CO$_2$RR.$^9$ The optimal sites for CO$_2$RR is a balance between $\Delta E^{*}_{\text{COOH}}$ and $\Delta E_{\text{CO}}$. Experimental results suggest that edge sites provide the best balance, increasing activity for CO$_2$RR. Facet sites have a $\Delta E^{*}_{\text{COOH}}$ that is too large, leading to high overpotential, while corner sites have exhibited strong binding for $^*$CO and $^*$H, which favors HER. Therefore, the surface sites responsible for promoting CO$_2$RR on the Au NP are expected to be those highlighted in the upper left part of Figure 3, which exhibit smaller $\Delta E^{*}_{\text{COOH}}$ without increasing $\Delta E_{\text{CO}}$ (site $\alpha$) or reducing $\Delta E_{\text{CO}}$ without increasing $\Delta E^{*}_{\text{COOH}}$ (site $\beta$) as highlighted in Figure 3.

Figure 3. The reaction energy of $^*$COOH formation ($\Delta E^{*}_{\text{COOH}}$) versus the binding energy of $^*$CO ($\Delta E_{\text{CO}}$). The blue circles are the results of 269 surface sites from random sampling. The yellow stars are the results of the facet, edge and corner sites on Au octahedron (as shown in...
Figure S2). The yellow filled region highlight the sites breaking linear scaling relationship (promote CO$_2$RR). The red arrows highlight two sites (α site and β site) with CO$_2$RR performance better than edge site as predicted.

Figure 4. *CO binding on edge site (A), α site (C) and β site (E). *COOH binding on edge site (B), a site (D) and b site (F). The colors are Au in yellow, C in silver, H in white and O in red. We highlighted the binding sites in blue for viewing convenience. Black arrows show the directions of the twin boundaries.
Therefore, these two sites should be superior in increasing CO$_2$RR. Figure 4C and Figure 4D show *COOH and *CO on α site. Figure 4E and Figure 4F show *COOH and *CO on β site. The common feature of these two sites is that they are on the twin boundaries. To compare, Figure 4A and Figure 4B show *COOH and *CO on edge site. The α site lies on the twin boundary leading to a 0.17 eV decrease in $\Delta E^*_{COOH}$ (0.14 eV) compared to 0.31 eV for an edge site, while he $\Delta E_{CO}$ does not change (0.64 eV vs. 0.65 eV). For the β site, the rhombus site lies on the twin boundary leading to 0.26 eV decrease in $\Delta E^*_{COOH}$ (0.33 eV) compared with that (0.59 eV) of a facet site, which is very close to the $\Delta E^*_{COOH}$ (0.31 eV) of an edge site, while $\Delta E_{CO}$ decreases by 0.14 eV (0.50 vs. 0.36 eV), which is less than the increase in $\Delta E^*_{COOH}$. Therefore, these surface sites on twin boundaries are superior in CO$_2$RR, because they significantly decrease $\Delta E^*_{COOH}$.

To summarize, we employed multiscale simulations to computationally “synthesize” an Au NP with a thickness of 10 nm on a CNT support. The XRD of this Au NP (Figure S1) shows the FCC crystal structure, consistent with the experimental results. The simulated TEM image (Figure 1B) show clear GB structures. A dislocation analysis shows that 1/6<112> Shockley partial dislocations are most abundant, which induces stacking defects on the surface.

To locate the active sites for CO$_2$RR, we randomly selected 269 response sites out of 11,360 total sites (2.4%) for QM calculations. The QM results show a linear relationship between the $\Delta E^*_{COOH}$ and $\Delta E_{CO}$, showing that most sites exhibit the normal scaling relationship between *COOH stabilization, *CO desorption, and HER. However, we find a substantial fraction (10%) of NP sites on grain boundaries or twin boundaries that significantly decrease $\Delta E^*_{COOH}$ without increasing $\Delta E_{CO}$, leading to superior CO$_2$RR performance.

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Notes

The authors declare no competing financial interests.

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Supporting Information Available: Simulation details, Simulated XRD patterns, Equation of state of FCC Au, an Au octahedral model and ReaxFF parameters of Au and C.
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