Magic-Number Gold Nanoclusters with diameter 1 to 3.5 nm: Relative Stability and Catalytic Activity for CO Oxidation

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Supporting Information Placeholder

ABSTRACT: Relative stability of geometric magic-number gold nanoclusters with high point-group symmetry (Ih, D5h, O) and size up to 3.5 nm, as well as structures obtained by global optimization using an empirical potential, is investigated using density-functional theory (DFT) calculations. Among high-symmetry nanoclusters, our calculations suggest that from Au(147) to Au(923), the trend of stabilities in the order of Ih > D5h > O is still reserved. However, at the largest size of Au(923), the computed cohesive energy differences among high-symmetry Ih, D5h and O isomers are less than 4 meV/atom (at PBE level of theory), suggesting the larger-sized high-symmetry clusters are similar in stability. This conclusion supports a recent experimental demonstration of controlling morphologies of high-symmetry Au(923) clusters (J. Am. Chem. Soc. 2014, 136, 7559). Moreover, at and beyond the size of Au(549), the face-centered cubic (FCC) based structure appears to be slightly more stable than the Ih structures of similar sizes, consistent with experimental observations. Also, near the size Au(561), reconstructed icosahedral and decahedral clusters with lower symmetry are slightly more stable than the corresponding high-symmetry isomers. Catalytic activities of both high-symmetry and reconstructed Ih-Au(147) and both Ih-Au(309) clusters are examined. CO adsorption on Au(309) exhibits less sensitivity on the edge and vertex sites compared to Au(147), while the CO/O co-adsorption is still energetically favorable on both gold nanoclusters. Computed activation barriers for CO oxidation are typically around 0.2 eV, suggesting that the gold nanoclusters of ~2 nm in size are highly effective catalysts for CO oxidation.

Gold nanoclusters have attracted much attention over the past two decades largely owing to their high potential in chemical, biomedical and plasmonics applications. Although bulk gold is chemically inert, gold nanoclusters and nanoparticles can exhibit exceptional catalytic activity towards a number of important chemical reactions, such as CO oxidation, hydrogenation, dehydrogenation, and selective oxidation. A particularly interesting aspect is the effect of cluster size on chemical and physical properties. For example, gold nanoclusters with different sizes can show markedly different electronic structures and activities, thereby giving size- and site-dependent activation barriers and reaction rates. In addition, a main topic in cluster science is to understand structure evolution of clusters versus their size, and how chemical and physical properties of clusters evolve from small to large size and ultimately to the bulk limit. To date, the atomic structure of gold anion clusters AuN− in the size range of N = 3 − 20 (or 0.3 − 0.5 nm) have been well established via numerous joint experimental and theoretical studies. Notably, the anion clusters Au4− − Au11− exhibit two-dimensional (2D) planar structures, Au5− − Au7− possess shell-like flat cage structures, Au9− − Au18− possess hollow-cage structures, and Au19− − Au30− possess compact pyramidal structures (golden pyramids). The hollow cage-to-pyramidal structure transition occurs at Au18− as both the cage and pyramidal isomers co-exist in the cluster beam. In the size range of 21 ≤ N ≤ 24, hollow tubular structures become energetically more competitive than the pyramidal-like structures. Au35− appears to be the smallest gold cluster to exhibit a core-shell structure with a single atom core and 24-atom shell, while Au37, Au38, and Au30 possess a one-atom core as well. Although neutral Au32 was predicted to exhibit an icosahedral cage structure, several studies show that anion-
ic Au$_{52}^-$ possesses a core-shell structure.\textsuperscript{40-43,45} We previously reported that Au$_{13}$ \textsuperscript{2+} features a three-atom triangular core while Au$_{13}^+$ to Au$_{38}^+$ all contain a four-atom tetrahedral core. The tetrahedral Au$_4$ core is a highly robust motif for low-lying medium-sized gold structures.\textsuperscript{44,45} More recently, Jiang and Walter predicted that the electronic magic-cluster Au$_{10}$ exhibits a twisted pyramidal core-shell structure with the Au$_4$ tetrahedral core as well. If this pyramidal core-shell structure is confirmed experimentally, it would show that the tetrahedral Au$_4$ core can survive within an unusually large size range, possibly from Au$_{13}$ to Au$_{39}$. Beyond Au$_{39}$, determination of atomic structures of gold clusters becomes increasingly challenging because, similar to Au$_{11}^+$, Au$_{29}^+$, and Au$_{39}^+$, many medium-sized gold clusters have two or more coexisting isomers in the cluster beam. Wang, Gong and co-workers predicted that the electronic magic-number (i.e., shell-closing) Au$_{38}^+$ cluster exhibits a core-shell structure with an Au$_4$ core.\textsuperscript{47}

It is known that clusters with certain special numbers of atoms are much more abundant than others when generated in typical cluster experiments, and these numbers are called geometric “magic numbers.”\textsuperscript{48} For nanoclusters of close-packed metals, the geometric magic numbers normally are 13, 55, 147, 309, 561, and 923 corresponding to highly symmetric structures such as icosahedral, Ino-decahedral, and cuboctahedral, with Ih, D$_{3h}$, and O$_h$ symmetry, respectively (see Figure 1). The magic numbers coincide with the closure of 1, 2, 3, 4, 5, and 6 shells, respectively. The Ih and D$_{3h}$ structures are commonly observed in nanoparticles while their five-fold symmetry is prohibited in crystals by the crystallographic translational-symmetry rules.\textsuperscript{49} Magic-number gold nanoclusters can exhibit special properties. For example, it has been suggested that the Au(55) cluster is a superior oxidation catalyst due to large oxidation resistance.\textsuperscript{50,59}

Density functional theory (DFT) methods have been widely used to study structural, chemical and physical properties of gold clusters. For gold nanoclusters in the size range of 1–1.7 nm. H"aberlen et al. performed scalar relativistic DFT calculations of several icosahedral, octahedral, and cuboctahedral clusters with size up to Au(147). They showed that the cohesive energy and other physical properties converge linearly toward those of the bulk with increasing cluster size.\textsuperscript{24} Another DFT study by Barnard et al. showed that among the geometric magic clusters with size < 1 nm, the most stable one exhibits the cuboctahedral geometry, but as the size gradually increases to 1.7 nm they exhibit truncated octahedral, octahedral and truncated cube structure, respectively.\textsuperscript{24} Pei et al. performed a DFT-based basin-hopping search of low-energy structures of neutral Au(55) clusters and found that a disordered lowest-energy structure is 0.47 eV lower in energy than the high-symmetry Ih$_7$Au(55) isomer.\textsuperscript{25} Both DFT and empirical model calculations suggest that the icosahedral structure is more stable than either Ino-decahedral or cuboctahedral structures for Au(147), with the stabilities of icosahedron > Ino-decahedral > cuboctahedron at this size.

Numerous experimental studies of the structure of gold nanoclusters with size > 1 nm have been reported. For instance, the X-ray powder diffraction analysis by Cleveland et al. suggests the truncated–decahedral motif in three classes of gold nanoclusters with sizes of 1–2 nm.\textsuperscript{53} Wang and Palmer studied dynamical behavior of size-selected Au(55) clusters using scanning transmission electron microscopy (STEM) and they found that Au(55) clusters exhibit chiral-type structure rather than high-symmetry structures.\textsuperscript{54} Koga et al. studied larger gold nanoclusters of 2–3 nm and drew similar conclusions.\textsuperscript{55} Later, the transition from the icosahedral to decahedral morphology is resolved from high-resolution electron microscopy (HREM) measurement for gold nanoparticles with size 3–14 nm.\textsuperscript{56} The STEM studies indicate that the Au(309±6) clusters have similar stabilities among Ino-decahedral, cuboctahedral, and icosahedral structures, as the three distinct structures can be detected by high–angle annular dark field (HAADF) detectors.\textsuperscript{57,58} Another HAADF-STEM study on larger Au(923±23) clusters shows that I$_7$ structures undergo structural transformations to decahedral (D$_h$) or FCC isomers after electron radiation, indicating the FCC structure is already thermostatically more stable than the I$_7$ structure.\textsuperscript{59} On the other hand, theoretical calculations based on the Gupta empirical potential also predict relative stability of gold clusters changing with the number of atoms.\textsuperscript{57,58} In the range of $N = 500$–1,000, the stability rankings are predicted to be I$_7$-decahedral < I$_{icosahedral}$ < cuboctahedral, while the rankings become cuboctahedral < I$_{icosahedral}$ for $N > 1000$.\textsuperscript{57} Barnard et al predicted that gold nanoparticles with size > 3 nm favor a modified truncated octahedral structure. Their prediction was based on a shape-dependent thermodynamics model combined with surface energies obtained from a slab model.\textsuperscript{60} However, to our best knowledge, first-principles calculations of relative stabilities of gold nanoclusters with size > 2 nm have not been reported in the literature largely due to high computing costs. With the recent development of linear scaling DFT methods and more powerful computers, first-principles calculations of core clusters up to 1000 atoms are feasible.

The strong structure-size-property relationship for the gold nanoclusters is manifested in their catalytic activity as a function of the size of clusters. In a previous review, Norskov et al. summarized from many early experiments that the gold nanoclusters with size < 3.5 nm are most active, whereas the nanoclusters with size > 10 nm are generally inert to most chemical reaction.\textsuperscript{57} The high catalytic activity of gold nanoclusters is largely attributed to the existence of low-coordinated gold sites, such as the corner and edge sites. More recent experiments confirm unequivocably the importance role played by the corner and edge sites of gold nanoclusters in CO oxidation.\textsuperscript{70} Several recent theoretical studies also elucidated the importance of the low-coordinated sites and the protrusive sites in subnanometer gold nanoclusters to the high activity for CO oxidation.\textsuperscript{73,74} For gold nanoclusters beyond 1 nm, both chemical and structural environment of gold atoms is expected to be different from that of subnanometer clusters. Hence, it is of fundamental importance to investigate catalytic activity of gold nanoclusters with size > 1 nm.\textsuperscript{75,76}
In this letter, we employ DFT methods to study relative stability of magic-number gold nanoclusters with icosahedral, Ino-decahedral, and cuboctahedral structures in the range of 1.1–3.5 nm (containing 2–7 atomic shells of 55–923 atoms). In addition, the structures of global minima for Au(147) and Au(309) clusters (Figure 2a-c) determined based on the global optimization using saddle traversals (GOUST) scheme coupled with an effective medium–theory (EMT) potential are also examined. Both clusters can be viewed as reconstructed structures from the corresponding icosahedral or decahedral motif, as shown in Figure 2a-c. In convenience, the reconstructed icosahedral and decahedral structures are denoted as Rec-Ico and Rec-Dec, respectively. Moreover, three highly ordered gold clusters near the magic number \( N = 561 \), i.e., Au(549) based on FCC motif (Figure 2d), decahedral Au(559) (Figure 2e), and a reconstructed icosahedral Au(564) (Figure 2f), are also considered. A previous DFT study showed that the truncated octahedral gold nanocluster (or bulk FCC-like gold structure) is energetically very competitive compared to the high-symmetry icosahedral and decahedral structures. Hence, we also compute cohesive energy of a truncated octahedral Au(586) (Figure 2g). Lastly, an FCC isomer of the Au(923) determined experimentally in Ref. 59 (Figure 2h) is considered for comparison.

Specifically, we use the QUICKSTEP program implemented in the CP2K software package. The generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) is selected, and the core electrons of gold atom are described by the Goedecker-Teter-Hutter (GTH) norm-conserving pseudo-potential. The basis sets are a combination of the polarized double-\( \zeta \) quality Gaussian basis and a plane-wave basis set (with an energy cutoff of 280 Ry). The structures of all gold nanoclusters are fully relaxed until the maximum force on each atom is no larger than \( 4.5 \times 10^{-4} \) Hatree/Bohr. The meta-GGA Tao-Perdew-Staroverov-Scuseria (TPSS) functional has been proven to yield more accurate energy rankings among isomers of small gold clusters. Thus, in this study, we also present computed TPSS energies of gold nanoclusters based on the geometries optimized at the PBE level of theory. Lastly, to locate the transition state of CO oxidation on gold nanoclusters, we adopt the linear and quadratic synchronous transit (LST/QST) method at the PBE level with the double polarizable (DPN) basis set, implemented in the DMol\(^3\) software package. Only the CO oxidation on the medium-sized Au(147) and Au(309) clusters is investigated, due to the high computation cost for the larger gold nanoclusters.

As shown in Table 1, our DFT calculations suggest that the cohesive energy of the high-symmetry icosahedral, Ino-decahedral, and cuboctahedral structures are very close to each other. Nevertheless, the cohesive energy order of \( I_h > D_{9h} > O_h \) is still kept from Au(55) to Au(923) for the high-symmetry magic-number nanoclusters. However, for Au(561) and Au(923), the computed cohesive energy difference between \( I_h, D_{9h} \) and \( O_h \) isomers is less than 4 meV/atom (at PBE level of theory; see Table 1), suggesting the larger high-symmetry clusters are practically equally stable. This conclusion supports a recent experimental demonstration of the control of cluster morphology of high-symmetry Au(923) clusters by small changes in growth conditions. Moreover, our DFT calculations show that the reconstructed icosahedral Au(147) (Rec-Ico-Au(147)) is notably more stable than the three high-symmetry isomers. For Au(309), the recon-
structured decahedral structure (Rec-Dec-Au(309)) has greater cohesive energy than that of the reconstructed icosahedral counterpart. Starting from Au(549), the FCC structure becomes energetically most favorable, suggesting that gold nanoclusters already favor the FCC structure at a size of 2.2 nm. Indeed, the experimentally proposed FCC Au(923) cluster has slightly larger cohesive energy than the icosahedral isomer.

Table 1. Computed cohesive energy (eV) of icosahedra ($I_h$), Ino-decahedra ($D_{inh}$), cuboctahedra ($O_h$) Au($N$) ($N = 55, 147, 309, 561$, and 923), truncated octahedra ($O_t$) Au(586), as well as reconstructed icosahedra, decahedra, and cuboctahedra, FCC, and experimentally proposed Au(923) nanoclusters. Values given outside and inside parenthesis are computed based on PBE and TPSS functional, respectively.

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<th>Icosahedra</th>
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<tr>
<td>Au(923)</td>
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a. Disordered Au(55) or chiral-type Au(55) is more stable than Ico-Au(55).

b. The cohesive energy of Rec-Ico-Au(147).

c. The cohesive energy of Rec-Ico-Au(309) (c1) and Rec-Dec-Au(309) (c2).

d. Cohesive energy of Rec-Ico-Au(564) (d1), decahedral Au(559) (d2), and FCC Au(549) (d3).

e. Cohesive energy of the truncated octahedral Au(586).

f. Experimentally proposed FCC Au(923) in Ref 59.

The cohesive energy per atom exhibits a linear relationship with the size of gold nanoclusters, as shown in Figure 1. The cohesive energy of $I_h$ structures (based on the PBE and TPSS calculations) as a function of size $N$ can be fitted to the following two relations:

$$E_{c}^{\text{PBE}}(I_{h}) = 2.913 - 2.029 \times N^{-1/3}$$ (1)

and

$$E_{c}^{\text{TPSS}}(I_{h}) = 3.285 - 2.478 \times N^{-1/3}$$ (2) .

The extrapolated cohesive energy of bulk gold from Eq. (1) is 2.91 eV, consistent with previous PBE calculation of bulk gold.\(^{50}\) The extrapolated cohesive energy of bulk gold from Eq. (2) (3.28 eV) is closer to the experimentally measured value (3.84 eV). As mentioned above, both PBE and TPSS calculations give rise to cohesive energy in the order of icosahedra > ino-decahedra > cuboctahedra. This ordering is contrary to the one obtained from the Gupta empirical potential, i.e., $D_{inh} > I_{h} > O_{h}$ for Au(N) ($N > 500$).

At $N = 147$, the reconstructed icosahedron appears to be the most stable structure. At $N = 509$, the cohesive energy (2.622 eV via PBE, and 2.923 eV via TPSS) of reconstructed decahedral structure is already greater than the reconstructed icosahedral structure (2.619 eV via PBE, and 2.920 eV via TPSS), indicating a structure transition from reconstructed icosahedra to decahedra at $N < 309$. This conclusion is consistent with the STEM investigation of Au(309±6) clusters on carbon film.\(^{57}\) For the clusters with close to $N = 509$, the FCC structure Au(549) (2.678 eV via PBE, and 2.992 eV via TPSS) has a slightly greater cohesive energy than both reconstructed icosahedral Au(564) (2.675 eV via PBE, and 2.989 eV via TPSS) and decahedral Au(559) (2.676 eV via PBE, and 2.991 eV via TPSS), indicating a structure transition from reconstructed decahedra to FCC at a size $N ~ 549$. Computed cohesive energy of the truncated octahedral Au(586) (2.685 eV via PBE, and 3.000 eV via TPSS) is also greater than interpolated energy (2.671 eV via Eq. (1), and 2.989 eV via Eq. (2)) at $N = 586$, confirming that the FCC structure is more stable beyond $N = 549$.

To gain additional insight into the relative stability among the magic-number nanoclusters, we compute the coordination numbers and Au-Au bond lengths of all the gold nanoclusters. As shown in Figure 3a, gold atoms in either high-symmetry or reconstructed icosahedral clusters have average coordination numbers higher than those of the decahedral and cuboctahedral clusters of similar size, and their coordination numbers increase linearly with the cluster size. For the high-symmetry structures, higher coordination number likely renders the icosahedral clusters more stable than the decahedral and cuboctahedral counterparts. However, for the reconstructed structures, higher coordination number seems less important from Au(147) to Au(564). For example, the predicted global minimum of Au(147) (based on the EMT potential) almost has the same coordination number as the high-symmetry decahedral Au(147). The reconstructed icosahedral clusters of both Au(309) and Au(564) also have much lower coordination number than the $I_h$ isomers, and the reconstructed decahedral Au(309) and Au(559) have similar coordination numbers as the $D_{inh}$ isomers. Interestingly, the FCC Au(549) which shows the highest stability, has sig-
significantly lower coordination number than all other clusters with similar size, indicating that higher coordination number is not the only factor determining the stability of large gold clusters with size beyond 2 nm.

Unlike the trend in coordination number, the Au-Au bond lengths exhibit a non-monotonous trend with cluster size, as shown in Figure 3b. The average bond length increases linearly with the cluster size from Au(55) to Au(561), and such a linear relation was also found in previous DFT study of Au(55) and Au(47). However, this linear relation no longer holds for large clusters beyond 2 nm, and the Au-Au bond lengths decreases slightly from Au(561) to Au(923) for the Ih and Ob clusters. Such a bond contraction can also be seen from the low-lying reconstructed icosahedral Au(309) to Au(564). The Au-Au bonds in the icosahedral clusters are notably longer than those in the decahedral and cuboctahedral clusters. The reconstructed icosahedral isomers also exhibit longer Au-Au bonds than the decahedral and FCC clusters Au(309) and Au(549); the Au-Au bonds of FCC Au(549) are between the shorter bond-lengths of Dh and Oh structures and longer bond-lengths of Ih structures, suggesting that highly stable, large gold clusters may favor Au-Au bond-lengths between those of the Dh and Ih geometries.

![Figure 4. CO molecules adsorbed on three different sites of (A) Ih-Au(147) and (B) Ih-Au(309) nanoclusters. The adsorption energies of CO on the vertex, edge and face sites of Ih-Au(147) (Ih-Au(309)) are -0.814 (-0.754), -0.557 (-0.578) and -0.404 (-0.463) eV, respectively.](image)

In addition to relative stabilities among gold nanoclusters with different structures, we have also investigated size and shape dependence of catalytic activity by using the CO oxidation as a benchmark. First, the adsorption energy of CO and O2 molecules on three typical (vertex, edge, and surface) sites of high-symmetry Ih-Au(147) and Ih-Au(309) clusters (see Figure 4), and atomic sites with small cone-angle on Rec-Ico Au(147) and Rec-Dec Au(309) clusters are computed. As shown in Figure 4, the CO molecule can be chemisorbed on the vertex, edge and surface sites of Ih-Au(147) and Ih-Au(309) clusters, with a C-Au bond length of ~2.0 Å. The CO ads molecule is energetically more favorable on the vertex site (adsorption energy, $E_a = 0.814$ eV) than on the edge site ($E_a = 0.557$ eV) of Ih-Au(147). Similarly, the vertex sites of Ih-Au(309) can bind the CO molecule stronger than the edge sites, but the adsorption energy difference between vertex and edge sites is less for the larger Ih-Au(309) cluster. Also, CO adsorption is weaker on the Rec-Ico-Au(147) and Rec-Dec-Au(309) ($E_a = -0.723$ and -0.627 eV, respectively) compared with the corresponding Au clusters with higher symmetry, indicating structural dependence of the CO adsorption.

Our DFT calculations also show that the O2 molecule is weakly adsorbed on Au(147) and Au(549) clusters ($E_a = -0.080$ and -0.135 eV, respectively). However, the O2 adsorption can be enhanced to -0.155 and 0.210 eV when the O2 is co-adsorbed next to a CO molecule, a common feature reported previously for the small- and medium-sized gold clusters. It is known that the co-adsorption of CO and O2 molecules on gold clusters can be an important factor to the efficiency of CO oxidation.

The computed reaction pathways for the CO oxidation on Ih-Au(147), and Ih-Au(309) clusters are shown in Figure 5. Here, we only consider CO adsorbed initially on a vertex site.
(the most active site due to low-coordination\textsuperscript{39,40}) and O\textsubscript{2} on a neighboring edge site. As shown in Figure 5, CO oxidation on all three high-symmetry clusters exhibit double-transition-state (DTS) pathways as commonly seen with small- and medium-sized gold clusters.\textsuperscript{39,40} In the first step of CO oxidation, the C atom of CO attracts O\textsubscript{2} molecule, followed by crossing a low energy barrier of 0.00 and 0.077 eV on the high-symmetry $I_5$-Au(147) and $I_5$-Au(309), respectively, to form the OCOO bridge-like intermediate (Figure 5). In the second step, CO fully grasps an O atom of O\textsubscript{2} to form a CO\textsubscript{2} molecule. This step is the rate-determining step. The energy barriers for releasing a CO\textsubscript{2} are 0.207 and 0.185 eV on $I_5$-Au(147) and $I_5$-Au(309), respectively. So, the barrier slightly decreases with increasing the size of Au nanoclusters.

As shown in Figure 5a and 5b, CO oxidation on Rec-Ico-Au(147) and Rec-Ico-Au(309) entails very similar DTS pathways as the high-symmetry icosahedral counterparts. The computed reaction barriers for the first and the second step are 0.035 (0.045) and 0.211 (0.176) eV for Rec-Ico-Au(147) (Rec-Ico-Au(309)), respectively, comparable with those on the high-symmetry icosahedral clusters. Hence, reconstructed structures exhibit similar catalytic activity as the high-symmetry $I_5$-Au(147) and $I_5$-Au(309) nanoclusters. In other words, for relatively larger Au nanoclusters, the symmetry plays little role in the activity for the CO oxidation.

In conclusion, we have performed DFT calculations to examine relative stabilities of geometric magic-number gold nanoclusters with size up to 3.5 nm for the first time. Our calculations show that for high-symmetry clusters from Au(147) to Au(923), the cohesive energy rankings of $I_5 > D_{3h} > O_h$ are kept. However, at the size Au(309), the reconstructed decahedral seems energetically slightly more favorable than the icosahedral counterpart, while at the size Au(549), the FCC-based structure is more stable than other geometric magic-number clusters, consistent with experimental results. At the largest size of Au(923), the computed cohesive energy differences among high-symmetry $I_5$, $D_{3h}$ and $O_h$ isomers are less than 4 meV/atom (at PBE level of theory), suggesting the three high-symmetry clusters are very close in stability, although the FCC-based structure appears to be the most stable. It is known that in the bulk limit, gold crystal exhibits FCC structure. On CO adsorption, the $I_5$-Au(309) exhibits less sensitivity to the vertex and edge sites compared to $I_5$-Au(147), suggesting that as the size of nanoclusters is beyond 2 nm, gold nanoclusters exhibit weaker site-dependent properties and catalytic activities. The mutual promotion effect of CO/O\textsubscript{2} co-adsorption is also seen on large gold nanoclusters. Our DFT calculations show that the gold clusters from 1 nm to 2 nm are still highly active for the CO oxidation due to the low reaction barriers (\textasciitilde 0.2 eV). In fact, the 2 nm gold cluster entails lower reaction barrier than the 1 nm gold cluster, albeit with weaker CO and O\textsubscript{2} adsorption. It will be interesting to study size-dependent catalytic activities for the gold nanoclusters from 3 nm to 5 nm in future.

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**REFERENCES**


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**Author Contributions**

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TOC Graphic