Evidence of hollow golden cages

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The fullerenes are the first “free-standing” elemental hollow cages identified by spectroscopy experiments and synthesized in the bulk. Here, we report experimental and theoretical evidence of hollow cages consisting of pure metal atoms, Auₙ (n = 16–18), to our knowledge, free-standing metal hollow cages have not been previously detected in the laboratory. These hollow golden cages (“bucky gold”) have an average diameter >5.5 Å, which can easily accommodate one guest atom inside.

anion photoelectron spectroscopy | density functional calculation | hollow gold cages | lowest-energy clusters

The isolation and detection of carbon-free hollow cages have attracted much interest since the discovery (1) and synthesis (2) of the buckyball C₆₀ and the higher fullerenes. Although “free-standing” inorganic cages have been synthesized (3), bare elemental metal cages have not been observed in nature or detected in the laboratory. Among metals, gold has some unique properties including the strong relativistic effects and aurophilic attraction (4). Recently, a fullerene-like hollow cage with 32 Au atoms was predicted to be highly stable (5, 6). However, photoelectron spectroscopy (PES) combined with theoretical calculations shows that at the relatively large size the overwhelming population of low-lying clusters for Au₃₂ near room temperature appears to consist of only compact structures because of the entropic factor (7). Other, larger gold clusters with cage-like local minimum structures also have been suggested (8, 9), but none has been observed experimentally. Conversely, it has been established from both ion-mobility (10) and PES (11) experiments that the most stable anion gold clusters (Auₙ⁻) in the size range n = 5–13 possess planar structures and that a structural transition from planar to three-dimensional (3D) structures occurs at n = 14. Beyond n = 14, previous global-minimum searches based on empirical potential functions of gold (12, 13) or semiempirical tight-binding models of gold (14) suggest that all low-lying isomers of gold clusters assume space-filling compact structures. Among the larger gold clusters, Au₁₅₂ is the most interesting; it has been found to possess a pyramidal structure with tetrahedral symmetry just as carved out of the bulk face-centered cubic crystal (15).

Results and Discussion

To elucidate the structural transition from the planar Au at n = 13 to the pyramidal Au₂₀, we carried out a joint experimental PES and theoretical study on Auₙ⁻ for n = 15–19. The measured spectra (see Methods below) are shown in Fig. 1A with numerous well resolved features in the lower binding energy part, which are used to compare with theoretically simulated spectra (Fig. 1B and C and Methods below; see also Fig. 3, which is published as supporting information on the PNAS web site) with the candidate lowest-energy structures (see Fig. 4, which is published as supporting information on the PNAS web site). The vertical detachment energies (VDEs) (given by the location of the first major peak near the threshold) for this feature are given in Table 1, compared with the theoretical VDEs from the lowest-energy structures. Note that the threshold of the lowest-binding-energy feature in each spectrum (see Table 2, which is published as supporting information on the PNAS web site) defines the electron affinity of the neutral clusters.

The theoretically obtained top-10 lowest-energy structures (see Methods) are given in Fig. 4. Among these top-10 isomers, we selected those isomers within 0.2 eV (1 eV = 1.602 × 10⁻¹⁹ J) from the lowest-energy isomer and simulated their photoelectron spectra (Figs. 1B and C and 3). We regard these selected isomers as the candidates for the lowest-energy structure owing to the intrinsic error bar (<0.2 eV) of density-functional theory (DFT) electronic energy calculations (16–18) and the basis-set effects. The number of candidate lowest-energy isomers ranges from one for Au₁₇ (Fig. 4E) to five for Au₁₅ (Fig. 4A) and Au₁₆ (Fig. 4B), and six for Au₁₇ (Fig. 4C) and Au₁₈ (Fig. 4D).

Remarkably, we observed that all but a total of three candidate lowest-energy isomers of Au₁₆, Au₁₇, and Au₁₈ are “hollow cages” with an empty interior space (Fig. 4B–D). The interior space (typically with length scale >5.5 Å) of these hollow cages can easily host a foreign atom. Among the five candidate lowest-energy structures of Au₁₅ (Fig. 4A), Au₁₆a, Au₁₆b, and Au₁₆c are flat-cage structures, whereas Au₁₅c and Au₁₆d are pyramid-like structures. Previous studies have shown that in stable gold clusters, gold atoms tend to have maximum coordination number of six, e.g., in the 2D planar structures of Au₁₅–Au₁₇ (10, 11) and in the pyramidal structure of Au₂₀ (15). Hence, it is understandable that both the flat-cage and pyramid-like structures are energetically competitive for the gold clusters within the size range Au₁₄ to Au₂₀. Conversely, it is quite surprising that the hollow-cage structures dominate the low-lying population of Au₁₆ to Au₁₈ clusters. Specifically, at Au₁₆ only Au₁₆d (among the five candidate lowest-energy structures) has flat-cage structure whose interior length scale can be <5 Å (Fig. 4B). The isomer Au₁₆a can be viewed as a relaxed structure of the pyramidal Au₁₅d with four missing corner atoms but maintains the tetrahedral symmetry of Au₁₅ (15). At Au₁₇, only Au₁₇a among the six candidate lowest-energy structures has a flat-cage structure (Fig. 4C), whereas at Au₁₈, only Au₁₈d among the six candidate lowest-energy structures exhibits pyramid-like (non-hollow-cage) structure (Fig. 4D). Note that Au₁₇a can be viewed as placing one atom on top of Au₁₆b, whereas Au₁₈d can be viewed as placing one atom on top of Au₁₇a. Both Au₁₇a and Au₁₈d possess C₅ symmetry. At Au₁₉, there is only one single candidate for the lowest-energy structure, namely, Au₁₉a whose energy is 0.2–0.3 eV lower (depending on the basis set) than the second-lowest-energy isomer (Au₁₉b) and ~0.5 eV lower than the third-lowest-energy isomer (Au₁₉c). Au₁₉b exhibits a pyramidal structure, which is similar to the pyramidal Au₁₅ (15) with one missing corner atom. This structural similarity is expected because Au₁₉ is only one atom less than the highly stable (magic-number) pyramidal cluster Au₂₀ (15). Compared with Au₁₉b, the

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Abbreviations: DFT, density-functional theory; PES, photoelectron spectroscopy; VDE, vertical detachment energy.

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Fig. 1. Experimental photoelectron spectra of Au$_n$ ($n = 15–19$) compared with those simulated theoretically. (A) Experimental spectra measured at 193 nm (6.424 eV). (B) The simulated spectra for one (or two) lowest-lying isomer that matches the first and second major peaks of the measured spectra. (C) The simulated spectra for the non-hollow-cage candidate isomer, which appears not to match the observed spectra.
hollow-cage structures such as $\text{Au}^{16}_{10}$ and $\text{Au}^{16}_{10}$ are no longer energetically competitive (Fig. 4D). In other words, the structural transition from hollow-cage to pyramid-like structure appears to occur at $\text{Au}^{19}_{19}$. To illustrate the structural evolution of gold clusters from 2D planar to 3D flat-cage, hollow-cage, and pyramid-like structures, we highlight in Fig. 2 those candidate lowest-energy clusters that can provide reasonable match to the first two to four major peaks of the experimental photoelectron spectra (Fig. 1A and B).

Our first-principles global search provides the electronic energy-based evidence that the overwhelming majority of the low-lying clusters of $\text{Au}^{15}_{15}$ to $\text{Au}^{18}_{18}$ exhibit hollow-cage structures. Moreover, our measured/simulated PES provides additional spectroscopic evidence to the existence of free-standing hollow golden cages. Here, we used the time-independent DFT (see Methods) to obtain approximated theoretical PES for all of the candidate lowest-energy structures of $\text{Au}^{15}_{15}$ to $\text{Au}^{19}_{19}$ (Figs. 1 and 3). Note also that the combined experimental and theoretical PES study has been used by many researchers to explore structures of small- to medium-sized clusters. This approach is particularly effective to identify structures of highly stable (magic-number) clusters such as the buckyball $C_{60}$ or golden pyramid $\text{Au}^{20}_{20}$ (15) because magic-number clusters are notably lower in energy than other isomers (i.e., they are the undisputed lowest-energy cluster). In this sense, $\text{Au}^{19}_{19}$ is the sole candidate for the lowest-energy cluster of $\text{Au}^{19}_{19}$, can be viewed as a magic-number cluster because of the overwhelming stability of the pyramidal $\text{Au}^{20}_{20}$ (15). As such, the simulated PES of $\text{Au}^{19}_{19}$ should match well with the measured one. Indeed, the location of the first two peaks near the threshold, which are directly related to the frontier orbitals and the VDE of the cluster, are in very good agreement with the measured one (including the weak doublet feature of the second major peak). Because the simulated PES based on DFT was obtained from the negatives of the Kohn–Sham (KS) eigenenergies (ground-state energy values), the simulated PES is not expected to match peak-for-peak with the measured PES beyond the threshold (energies of excited states). In summary, the location of the first two major peaks offers a critical structural “fingerprint” of the $\text{Au}^{19}_{19}$. Conversely, the simulated PES for the second lowest-energy isomer ($\text{Au}^{19}_{18}$), which is also pyramid-like, corresponding to the removal of an atom from the edge of the tetrahedral $\text{Au}^{20}_{20}$ (15), does not agree with the experiment. The VDE of the first simulated peak is too high compared with the experiment (Fig. 1).

For other $\text{Au}^{n}_{n}$ clusters ($n = 15–18$), each has five or six candidate lowest-energy structures (Fig. 4). Moreover, previous PES studies of the endohedral gold-cage cluster $\text{W}^{0}_{12}$ (19, 20) have shown that the gold cage is fluxional. In other words, the energy barriers separating structurally similar isomers (e.g., hollow cages) can be quite small. As a result, it is conceivable that multiple isomers may contribute to the experimental spectra. Hence, our first priority was to use the measured PES as a “filter” to identify those candidate isomers that cannot match the measured PES well (see Fig. 1C). Again, our main focus has been placed on the location of the first two major peaks and, to a lesser extent, the number of peaks in the 4– to 5-eV binding energy range. For example, at $\text{Au}^{15}_{15}$, the two pyramid-like low-lying isomers $\text{Au}^{15}_{16}$ and $\text{Au}^{15}_{16}$ can be ruled out (Fig. 3A). In fact, the simulated PES of the two flat-cage isomers $\text{Au}^{15}_{16}$ and $\text{Au}^{15}_{16}$ seem to match the measured PES (Fig. 1A and B), particularly on the location of the two major peaks near the threshold.

At $\text{Au}^{16}_{16}$, the only non-hollow-cage isomer $\text{Au}^{16}_{16}$ and the isomer $\text{Au}^{16}_{16}$ can be ruled out because their first VDE seems to be lower than the experimental data (Fig. 3B). The remaining three isomers, $\text{Au}^{16}_{16}$, $\text{Au}^{16}_{16}$, and $\text{Au}^{16}_{16}$, all give reasonable VDE, but $\text{Au}^{16}_{16}$ seems to provide the best agreement with the experiment in term of the

### Table 1. Experimental first VDEs for $\text{Au}^{n}_{n}$ ($n = 15–19$) compared with computed values for the candidate lowest-energy clusters that give the best fit to the first two major peaks of the measured spectra

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Experimental</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Au}^{15}_{15}$</td>
<td>3.65 ± 0.03</td>
<td>3.777</td>
</tr>
<tr>
<td>$\text{Au}^{16}_{16}$</td>
<td>4.03 ± 0.03</td>
<td>4.179</td>
</tr>
<tr>
<td>$\text{Au}^{17}_{17}$</td>
<td>4.08 ± 0.03</td>
<td>4.053</td>
</tr>
<tr>
<td>$\text{Au}^{18}_{18}$</td>
<td>3.32 ± 0.03</td>
<td>3.320</td>
</tr>
<tr>
<td>$\text{Au}^{19}_{19}$</td>
<td>3.74 ± 0.03</td>
<td>3.720</td>
</tr>
</tbody>
</table>

All energies are in eV.

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<fig>Fig. 2. Structural evolution of mid-sized gold anion clusters from $\text{Au}^{13}_{13}$ to $\text{Au}^{20}_{20}$. (A) The 2D planar to 3D flat-cage structural transitions (11). (B) The hollow gold cages with diameters >5.5 Å. (C) The pyramid-like clusters, which resemble bulk gold (15).</fig>
first two major peaks observed between 4 and 5 eV (Fig. 1B). Hence, Au16a is likely to be the most popular isomer in the mass-selected cluster beam. However, there are some weaker features in this binding energy range, suggesting the presence of other low-lying isomers (possibly Au16b and Au16c) that may account for the observed weak features experimentally.

At Au17, the measured PES spectrum displayed five relatively sharp and quite evenly separated peaks in between 4 and 5 eV (Fig. 1). On this ground, we can rule out the only non-hollow-cage isomer Au17c (Fig. 1C) and isomer Au17e among the six candidate lowest-energy structures. The simulated spectrum of Au17d seems to agree somewhat better than others with the observed spectral pattern. However, the simulated spectra of Au17a, Au17b, and Au17g (Fig. 3C) all have transitions in the same energy range so that they may coexist with the Au17g in the cluster beam. Note that all four hollow-cage isomers can be viewed as relaxed structures by placing an atom to the surface of the Au16a cage.

Lastly, at Au18, it appears at first glance that none of the six candidate lowest-energy isomers can give good match with the measured PES (particularly the first two peaks). However, after a closer look we found that the simulated spectra of Au18a and Au18b match the first and fourth experimental peaks well (Fig. 1A and B), suggesting that the two relatively weak second and third experimental peaks were due to other isomers. Indeed, the simulated spectra of Au16a, Au16b, and Au16c (Fig. 3C) all have transitions in the appropriate spectral range and may be candidates for these transitions. It is interesting to note that except Au18a all other low-lying isomers are hollow-cage structures, which can be viewed as placing an atom to the cages of Au17. The only non-hollow-cage isomer, Au18b, is pyramid-like, which can be viewed as removing two corner atoms from Au18 (15).

Overall, the fairly good agreement between the experimental and theoretical PES lends credence to the identified lowest-energy structures for the Aun clusters (n = 16–18), which are predominately hollow cages. To date, all medium-sized metal clusters detected experimentally exhibit compact structures, a manifestation of the metallic effects due to delocalized electrons. The fact that anion gold clusters can form stable hollow cages in the mid-size range n = 16–18 is quite unusual. A natural question is why gold clusters favor hollow-cage structures in this special size range. Clearly, the strong relativistic effects and the aurophilic attraction in gold must play a key role for the special size range. Clearly, the strong relativistic effects and the aurophilic attraction in gold must play a key role for the special size range. Clearly, the strong relativistic effects and the aurophilic attraction in gold must play a key role for the special size range. Clearly, the strong relativistic effects and the aurophilic attraction in gold must play a key role for the special size range.