Shuttling single metal atom into and out of a metal nanoparticle

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It has long been a challenge to dope metal nanoparticles with a specific number of heterometal atoms at specific positions. This becomes even more challenging if the heterometal belongs to the same group as the host metal because of the high tendency of forming a distribution of alloy nanoparticles with different numbers of dopants due to the similarities of metals in outermost electron configuration. Herein we report a new strategy for shuttling a single Ag or Cu atom into a centrally hollow, rod-shaped Au24 nanoparticle, forming AgAu24 and CuAu24 nanoparticles in a highly controllable manner. Through a combined approach of experiment and theory, we explain the shuttling pathways of single dopants into and out of the nanoparticles. This study shows that the single dopant is shuttled into the hollow Au24 nanoparticle either through the apex or side entry, while shuttling a metal atom out of the Au25 to form the Au24 nanoparticle occurs mainly through the side entry.
Nanoparticles play a central role in the rapidly growing nanoscience and nanotechnology fields, with a wide range of applications being developed including nanocatalysis, sensing, optical, and biology.

Atomic level understanding of nanoparticle structure is of great importance in order to establish definitive structure–property relationships, thereby facilitating systematic tailoring of material properties and developing of various applications of nanoparticles. Recent success in the synthesis of atomically well-defined nanoparticles has attracted great interest in recent years for both fundamental research and technological applications. Recent success in the synthesis of atomically well-defined nanoparticles has offered exciting opportunities to pursue fundamental understanding of the stability, isomerism, optical, chiroptical, catalytic, and magnetic properties of Au nanoparticles.

Single-atom doping has gained significant interest for its potential to design novel bi-functional heterogeneous catalysts with superior or new properties compared to the homo-gold counterparts. For example, it has been demonstrated that a single atom of Pd, Pt, Cd, and Hg can be successfully doped into gold nanoparticles not only to enhance the stability of the nanoparticle but also to tune the catalytic and optical properties of the nanoparticle. It is worth noting that the reported single-atom doped/ alloyed gold nanoparticles are mainly limited to heterometals from a different group of elements rather than in the same group as gold (i.e., Cu, Ag). For example, a work done by Copley et al. shows that reaction between [Au11(PMePh2)10]+ and [MCl(PMePh3)] (M = Ag or Cu) results in the formation of a nanocluster with multiple heterometals, i.e., [Au9M4Cl4(PMePh2)8]+. This reaction is believed to occur through intermediate cations containing different numbers of metal dopants, e.g., [Au10M3Cl3(PMePh2)9]+. Another interesting finding by Bakr and co-workers is that the single Pd atom in the Pd1Ag24 nanocluster could be replaced by a gold atom, resulting in single gold atom-doped Au1Ag24. Despite many efforts, preparation of gold nanoparticles doped with a single Cu or Ag atom still remains challenging due to the similar electron configuration of outmost electrons of Cu and Ag as that of Au. This similarity leads to easy formation of a distribution of Cu or Ag dopants in the alloy nanoparticles.

Although the similarity in electronic structure of Ag and Cu with Au poses a major challenge for single-atom doping of gold nanoparticles, we rationalize that a single atom of Ag or Cu should easily fill into a vacancy if the latter is pre-formed within the gold nanoparticle. This method may be able to circumvent the limitation from the similar electron configuration of the same group metals. In terms of hollow gold nanoparticles, Das et al. reported a centrally hollow [Au24(PPh3)10(SC2H4Ph)Cl2]+ nanoparticle formed by reaction of non-hollow [Au25(PPh3)10(SC2H4Ph)5Cl2] with excess triphenylphosphine (PPh3). Single crystal X-ray diffraction analysis shows that the nanoparticle consists of two incomplete icosahedral Au12 units linked by five thiolate linkages. In comparison to the vertex-sharing bicicosahedral [Au125(PPh3)10(SC2H4Ph)6Cl2]2+, the Au24 nanoparticle lacks the central Au atom (i.e., the shared vertex atom in the bicicosahedral Au25), which exerts a major influence on the optical properties of the nanoparticle. This hollow structure opens up the possibility of re-filling the central vacancy of the Au24 nanoparticle by another atom from the same group as gold. Since there is only one vacancy in the Au24 nanoparticle, we expect that single-atom doping can be realized by using hollow Au24 as a template. Furthermore, by subsequently hollowing the resultant single-atom alloyed nanoparticles and then re-filling with a heterometal atom, one may achieve atom-by-atom doping in a highly controlled fashion.

Herein, we report the shuttling of single metal atom(s) of Au, Ag, and Cu using the hollow Au25 nanoparticle as a model system. Surprisingly, we discover intriguing pathways of shuttling for different metals. Instead of simple filling of the central vacancy, we find that the incoming atom squeezes the pre-existent gold atom of the nanoparticle into the hollow site to produce M1Au24 nanoparticles (M = Au/Ag/Cu). The obtained non-hollow M1Au24 nanoparticles can be further converted to M2Au13 nanoparticles by the hollowing-refilling strategy. The determination of the atomic structures of Cu1Au24 and Ag1Au24 nanoparticles by X-ray crystallography, together with density functional theory (DFT) simulations, provides a clear map on how the single-atom shuttling occurs in the atomically precise nanoparticles.

![X-ray structures and UV-Vis spectra of Au24 and Au25 nanoclusters](image)

**Fig. 1** X-ray structures and UV-Vis spectra of Au24 and Au25 nanoclusters. X-ray structures of the hollow Au24 rod with the central atom dislodged (a), and the Au25 rod (b), the central gold atom in the Au25 rod is shown using space-filling model for clarity. Color code: Au, yellow; P, orange; S, red; Cl, green. C and H atoms are not shown for clarity; UV-Vis spectra of the hollow Au24 rod and the Au25 rod are shown in c and d, respectively.
Results

Shuttling a metal atom into a hollow nanoparticle. The hollow \([\text{Au}_{24}(\text{PPh}_3)_{10}(\text{SC}_2\text{H}_4\text{Ph})_5\text{Cl}_2]^+\) nanoparticle (Fig. 1a, abbreviated as \(\text{Au}_{24}\) hereafter) is chosen as a model to demonstrate the filling of the central vacancy and dislodging of an atom out of the resultant 25-atom nanoparticle (Fig. 1b, abbreviated as \(\text{Au}_{25}\) hereafter). The hollow \(\text{Au}_{24}\) nanoparticle was made by the reaction of \([\text{Au}_{25}(\text{PPh}_3)_{10}(\text{SR})_5\text{Cl}_2]^+\) with excess \(\text{PPh}_3\)36.

In the present work, we have discovered that reaction of the \(\text{Au}_{24}\) (dissolved in \(\text{CH}_2\text{Cl}_2\), Fig.1c) with \(\text{Au}(\text{I})\text{Cl}\) readily restores \(\text{Au}_{25}\) within a few seconds, evidenced by ESI-MS analysis of the final product (Fig. 2b, black line) with a major peak of 2+ charge at \(m/z = 4151.6\) Da (expected \(m/z = 4151.6\) Da), also evidenced by the UV–Vis spectrum (Fig. 2a) being identical to that of \(\text{Au}_{25}\) (Fig. 1d)37. In order to obtain single-atom doping with \(\text{Ag}\) and \(\text{Cu}\), we further tested the \(\text{Au}_{24}\) with \(\text{Cu}(\text{I})\text{Cl}\) and \(\text{Ag}(\text{I})\text{Cl}\) salts. Results show that addition of \(\text{CuCl}\) or \(\text{AgCl}\) to a dichloromethane solution of the \(\text{Au}_{24}\) leads to a rapid (~4 s) change of the solution color from red to green, indicating the possible formation of new products doped with \(\text{Cu}\) or \(\text{Ag}\). The UV–Vis spectrum of the \(\text{Cu}\)-doped nanoparticle is found to be similar to that of the \(\text{Au}_{25}\) nanoparticle (Fig. 2a, blue line), while the \(\text{Ag}\)-doped nanoparticle exhibits a slight red shift by ~11 nm (Fig. 2a, red line). ESI-MS analysis of the doped clusters (Fig. 2b) shows that the major mass peak for \(\text{Cu}\) doping is located at \(m/z = 4085.1\) Da (Fig. 2b, blue line), assigned to \([\text{Cu}_1\text{Au}_{24}(\text{PPh}_3)_{10}(\text{PET})_5\text{Cl}_2]^+\) (theoretical \(m/z = 4085.1\) Da), and for \(\text{Ag}\) doping, the peak at \(m/z = 4107.0\) Da (Fig. 2b, red line) corresponds to \([\text{Ag}_1\text{Au}_{24}(\text{PPh}_3)_{10}(\text{PET})_5\text{Cl}_2]^+\) (theoretical \(m/z = 4107.1\) Da).

We further crystallized the products and performed X-ray crystallography to determine the sites occupied by the incoming \(\text{Cu}\) and \(\text{Ag}\) atoms in the structure of the doped nanoparticles (for details see Supplementary Figs. 1–3 and Supplementary Tables 1 and 2). Since the atomic numbers of \(\text{Cu}\) (\(Z = 29\)) and \(\text{Ag}\) (\(Z = 47\)) are considerably less than that of \(\text{Au}\) (\(Z = 79\)), they can be readily differentiated in the X-ray crystallographic analysis. Partial occupancy analysis was employed to find the location of \(\text{Cu}\) and \(\text{Ag}\) atoms (details are given in the Supplementary Note 2). Results show that \(\text{Cu}\) can occupy either the apex or waist positions of the rod-shaped nanoparticle (Fig. 3, right), while \(\text{Ag}\) was only found at the apex of the nanoparticle (Fig. 3, left). Interestingly, the central position of the nanoparticle is 100% occupied by gold atom in both products, rather than a \(\text{Cu}\) or \(\text{Ag}\) atom, as one would expect since the central vacancy is ready for filling.

The results of \(\text{Au}_{24}\) reaction with \(\text{AuCl}\), \(\text{AgCl}\), and \(\text{CuCl}\) clearly demonstrate the success in single-atom doping into the gold nanoparticle. In the case of reaction with \(\text{AuCl}\), the pathway of how the central vacancy is filled cannot be revealed, but the reactions of \(\text{Au}_{24}\) with \(\text{AgCl}\) and \(\text{CuCl}\) clearly show that the copper or silver atom does not directly take the central empty position as one would initially expect, instead the \(\text{Cu}\) or \(\text{Ag}\) dopant should squeeze one surface gold atom into the central
vacancy. To map out the mechanistic details, we further carried out DFT simulations on the formation of hollow Au$_{24}$ from the Au$_{25}$ nanoparticle and the back filling of Au$_{24}$ to form MAu$_{24}$ (M = Cu or Ag).

**On the shuttling-out mechanism for the formation of hollow Au$_{24}$** Experimentally we found that excess phosphine ligands play a key role in the formation of hollow Au$_{24}$ nanoparticle from its parent Au$_{25}$ nanoparticle, in agreement with the previous study$^{36}$. DFT calculations were performed using [Au$_{25}$(PH$_3$)$_{10}$(SH)$_5$Cl$_2$]$^{2+}$ as a model of the experimental nanoparticle by simplifying PPh$_3$ to PH$_3$ and SC$_2$H$_4$Ph to SH. Results show that adsorption of a PH$_3$ onto a gold atom located at the waist position (Au1, Fig. 4, green ball) of the nanoparticle is the most likely mechanism to initiate the reaction. A PH$_3$ of the rod via a migration process (Reac $\rightarrow$ Int1, Supplementary Movie 1) may form a bond with the Au1. Of note, the Au–PPH$_3$ bond is flexible, which allows rapid exchange between the free and bound PPh$_3$.$^{38}$

Upon the formation of Au–PH$_3$ bond and subsequent Au–S bond breaking (Int1 $\rightarrow$ Int2, Fig. 4), the gold atom at the center of the nanoparticle (Au2, Fig. 4, gray ball) dislocates toward the surface of the nanoparticle, evidenced by changes in the Au–Au atomic distances (Fig. 4). The Au1–Au2 bond distance becomes 2.90 Å ($a'$ in Fig. 4) which is considerably less than the bond distance between Au2 and gold atoms located at the lower side of the waist position ($a' = 3.23$ Å, Fig. 4). Next, the Au2 is completely pulled up to the surface of the nanoparticle (Int2 $\rightarrow$ Int3). The Au(PH$_3$)$_2^+$ moiety eventually detaches from the nanoparticle to result in the [Au$_{24}$(PPh$_3$)$_9$(SR)$_5$Cl$_2$]$^+$ nanoparticle (Int3 $\rightarrow$ Int4). The generation of Au(PH$_3$)$_2^+$ ion is indeed experimentally confirmed by ESI-MS (Supplementary Fig. 4). Finally, the as-formed
AgCl

and form the hollow Ag1Au23 nanocluster; step 4, using AgCl to re-solid Au25 nanocluster; step 2, using AgCl to re-solid Au25 nanocluster; step 4, using AgCl to refill the hole and produce Ag1Au24; step 3, continue using PPh3 to make a hole in the Ag1Au24 nanocluster and form the hollow Ag1Au23 nanocluster; step 4, using AgCl to refill the hole and yield the Ag2Au23 nanocluster. Color code: Au, yellow; Ag, magenta.

Fig. 6 UV-Vis and ESI-TOF-MS spectra of the secondary shuttling products. a UV-Vis spectra of \( [\text{Cu}_{25}(\text{PPh}_3)_5(\text{SR})_5\text{Cl}_2]^+ \) (x = 1,2; red line) and \( [\text{Ag}_{22}(\text{PPh}_3)_5(\text{PET})_5\text{Cl}_2]^2+ \) (red line), and; b Positive mode ESI-MS spectra of \( [\text{Cu}_{25}(\text{PPh}_3)_5(\text{PET})_5\text{Cl}_2]^+ \) (x = 1,2; blue line) and \( [\text{Ag}_{22}(\text{PPh}_3)_5(\text{PET})_5\text{Cl}_2]^2+ \) (red line).

Fig. 7 Proposed mechanism of injecting two Ag atoms into the nanoparticle via the hollowing-refilling sequence: step 1, using PPh3 to make a hole in the solid Au25 nanocluster; step 2, using AgCl to refill this hole and produce Ag1Au24; step 3, continue using PPh3 to make a hole in the Ag1Au24 nanocluster and form the hollow Ag1Au23 nanocluster; step 4, using AgCl to refill the hole and yield the Ag2Au23 nanocluster. Color code: Au, yellow; Ag, magenta.
(Fig. 5c, Path 2, shown by red arrows, Supplementary Movie 4). Our calculations using the nudged elastic band (NEB) approach show barrier energy of pathway 2 is 19.8 kcal mol\(^{-1}\) lower than that for pathway 1. This result indicates metal mobility is most likely to happen through the surface of the nanoparticle rather than the core of the icosahedron, in agreement with the mechanism for the Au\(_{34}\) formation.

**Shuttling a second heteroatom into the nanoparticle.** To shuttle a second heteroatom into the nanoparticle, the Cu\(_1\)Au\(_{24}\) and Ag\(_1\)Au\(_{24}\) nanoparticles were, respectively, used as the starting material. Reaction of the starting material with PPh\(_3\) at 40 °C produced hollow nanoparticles. As shown in Supplementary Fig. 7, the complete disappearance of the 700 nm peak indicates that all the M\(_{25}\) nanoparticles have been converted to hollow M\(_{24}\). The second step is to fill the hollow structure with heterometal atom by adding CuCl or AgCl salts to the solution. The color of the solution changed immediately from red to green. As shown in Fig. 6a, compared with Au\(_{25}\), the copper-doped product has a similar UV–Vis spectrum as that of Au\(_{24}\), however, the silver-doped nanoparticle shifted from ~685 nm (Ag\(_1\)Au\(_{24}\)) to ~712 nm. In the ESI-MS spectra (Fig. 6b), the Ag\(_2\)Au\(_{23}\) nanoparticle with +2 charge was found (m/z = 4062.8 Da, theoretical m/z = 4062.6 Da), which implies a step-by-step doping of silver to the two apex sites to the exclusive Ag atom doping at the apex of the nanoparticle, in agreement with the charge was found (Fig. 3 above) to produce the hollow Au\(_{24}\) nanoparticle, and then reaction of Au\(_{24}\) surface -Cl and -SR ligands for the shuttling-in process. The how single metal atom transfer occurs between two atomically precise metal nanoparticles, and the barrier energy of pathway 2 is 19.8 kcal mol\(^{-1}\) (Fig. 5c, Path 2, shown by red arrows, Supplementary Movie4).

**Data availability.** The X-ray crystallographic coordinates for structures reported in this work (see Supplementary Tables 1, 2, and Supplementary Note 2) have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers CCDC 1562010 and CCDC 1561987. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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S.W. and H.A. contributed equally to this work. S.W. synthesized the samples and carried
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