A reasonable approach for the generation of hollow icosahedral kernels in metal nanoclusters

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Although the hollow icosahedral M12 kernel has been extensively observed in metal nanoclusters, its origin remains a mystery. Here we report a reasonable avenue for the generation of the hollow icosahedron: the kernel collapse from several small nano-building blocks to an integrated hollow icosahedron. On the basis of the Au alloying processes from Ag28Cu12(SR)24 to the template-maintained AuAg28−xCu12(SR)24 and then to the template-transformed Au12CuAg32−y(SR)30, the kernel evolution/collapse from “tetrahedral Ag4 + 4*Ag5” to “tetrahedral Au4 + 4*M3 (M = Au/Ag)” and then to “hollow icosahedral Au12” is mapped out. Significantly, the “kernel collapse” from small-sized nano-building blocks to large-sized nanostructures not only unveils the formation of hollow icosahedral M12 in this work, but also might be a very common approach in constructing metallic kernels of nanoclusters and nanoparticles (not limited to the M12 structure).
Metal nanoclusters are an emerging class of modular nanomaterials, and have been sparking great research interests owing to their atomically precise structures and intriguing properties. The physicochemical properties of these nanomaterials, such as chirality, luminescence, catalysis, magnetism, and electrochemistry, can be rationalized in terms of their quantum size effect as well as discrete electronic states. Besides, the atomically precise nature of these modular nanomaterials is of the most interest — indeed, compared with large-sized nanoparticles, nanoclusters (typically <2 nm of the metallic kernel) present more precise compositions/ constructions, and thus allow for the atomic-level elucidation of structural evolutions and structure-property correlations.

Of all reported nanoclusters with precise structures, the icosahedral configuration is the most typical, which is frequently observed in both metal kernels and ligand shells of Au-alloying-induced transformation from M40(SR)24 to M44(SR)30. This work, based on the Au-alloying-induced nanocluster transformation from M40(SR)24 to M44(SR)30 (M = Ag/Cu/Au), a reasonable avenue for the generation of hollow icosahedral M12 kernel has also served as a basic nano-building block of nanoclusters (e.g., Ag28Cu12(SR)24, Au12Cu32(SR)30, Ag28PPh4)30(SR)20, etc.). Structurally, it is accepted that the non-hollow icosahedron might be more energetically favorable than the corresponding hollow one due to the extra 12 metal—metal interactions in M41@M12; accordingly, the hollow icosahedral kernel is unlikely to arise in the initial stage of the nanocluster growth. Besides, the hollow M12 kernel is also less likely to originate from its non-hollow counterpart because the 12 metal—metal interactions make it difficult to extract the innermost metal atom. In this context, the origin of such hollow icosahedral kernels remains a mystery.

In this work, based on the Au-alloying-induced nanocluster transformation from M40(SR)24 to M44(SR)30, a possible avenue for constructing metallic kernels of nanoclusters and nanoparticles (not limited to the M12 structure).

**Results**

**Structural anatomy of M40(SR)24 and M44(SR)30 nanoclusters.** For the clarity of the structural transformation and the corresponding kernel collapse, the nanocluster structures involved in this work are first discussed (Fig. 1) —

(i) M40(SR)24 (M = Au/Ag/Cu; SR = SPhCl2): the M40(SR)24 nanoclusters start from the bi-metallic Ag28Cu12(SR)24. Figure 1a–d depict the structure anatomy of Ag28Cu12(SR)24. Ag28Cu12(SR)24 adopts a three-shell configuration, in a form of Ag12(M40-S1)@Ag28(M40-S2)@4*Cu12(SR)30(M40-S3). The innermost Ag12 is in tetrahedral (Fig. 1a). The 24 Ag atoms on M40-S2 can be divided into two categories, and each of 12 Ag atoms constitute four Ag3 triangles (Fig. 1b). The Ag atoms highlighted in dark blue connect with inward SR ligands on M40-S3 (Fig. 1c, highlighted in yellow); in contrast, the Ag atoms in light blue links outward SR ligands (highlighted in red) on M40-S3.

(ii) M44(SR)30 (M = Au/Ag/Cu; SR = SPhCl2): the Au12Ag32(SR)30 nanocluster is adopted to analyze the structure of M44(SR)30. Au12Ag32(SR)30 also has a three-shell configuration: Au12(Ag4-S1)@Ag28(M44-S2)@6*Ag32(SR)30(M44-S3). Of note, the Au12 kernel is a hollow icosahedron (Fig. 1e).

**Au-alloying-induced transformation from M40(SR)24 to M44(SR)30.** The Au-alloying structural transformation started from the bi-metallic Ag28Cu12(SR)24 (Fig. 2). The slight Au alloying on Ag28Cu12(SR)24 resulted in a tri-metallic AuAg28-Cu12(SR)24 (x = 1.32) nanocluster, wherein the tetrahedral Ag5 kernel of Ag28Cu12(SR)24 was partially alloyed by the incorporated Au (Fig. 2 and Supplementary Fig. 1). When more Au heteroatoms were doped into M40(SR)24 (AuAg28-Cu12(SR)24, x = 7.56; Fig. 2), all sites of the tetrahedron were entirely occupied by Au; besides, the redundant Au heteroatoms were further arranged onto M40-S2, invading the Ag sites that related to outward SR thiols (light blue triangles in Fig. 1b and Supplementary Figs. 2–3). Of note, throughout the above-mentioned Au-alloying processes the M40(SR)24 framework retained. Furthermore, the overdose of Au heteroatom induced the structural transformation from M40(SR)24 to M44(SR)30. Structurally, from the crystal structure of Au12Cu32(SR)30, (M44-S30) y = 0–6; Avg. 3.74; Fig. 2 and Supplementary Fig. 4), the M44(SR)30 nanocluster reached its stable state when Cu atoms only occupied the M44-S3. The corresponding bond lengths in M40(SR)24 (including Ag28Cu12(SR)24, AuAg28-Cu12(SR)24, (x = 1.32), AuAg28-Cu12(SR)24, (x = 7.56), and Au4Ag24Cu12(SR)24 or M44(SR)30 (including Au12Cu32(SR)30 and Au12CuAg23(SR)30, y = 3.74) nanoclusters were compared in detail (Supplementary Figs. 5–6 and Supplementary Tables 1–2).

Despite our repeated best efforts to obtain the crystal structure of AuAg24Cu12(SR)30, its perfect crystal data remains unavailable. Herein, for acquiring an excellent crystal data of Au12Cu32Ag23(SR)30, we promoted the co-crystallization between the M44(SR)30 and a small-sized M40(SR)24 nanoclusters (Supplementary Figs. 7–9). Fortunately, the structures of both two nanoclusters were excellently determined (AuAg24Cu12(SR)24 and Au12CuAg23(SR)30 (y = 3.74)) although both displayed strongly negative valence state (i.e., “−4”). In this context, the presence of (PPh4)4+ cations neutralized the electrostatic repulsion between these clusters (Supplementary Fig. 8) and thus promoted the nanocluster co-crystallization, which was different from previously reported co-crystallized nanocluster cases with both “0” or opposite valence states.

In the crystal lattice of the co-crystallized nanoclusters, three types of nanoclusters were observed (Supplementary Fig. 7) — L-AuAg28-Cu12(SR)24 (Au, Aβ), R-AuAg28-Cu12(SR)24 (Ba, Bβ), and Au12CuAg23(SR)30 (y = 3.74; Ca, Cβ), among which the α- and β-nanoclusters were identical, but arranged in different rotation angles (Supplementary Fig. 7a–c). In contrast to the crystallization of homogeneous nanoclusters, which are typically packed into superlattices with simple translational symmetry, such as ABAB or ABCABC packing pattern, the (AuAgCu)40 and (AuAgCu)44 nanoclusters were packed with a more complex pattern (Supplementary Fig. 7d–f). From the x-axis view, the clusters were packed with an Aα-Ba-Ca-Af-Bβ-Cβ-Pattern. α- and β-nanoclusters were arranged separately along the z-direction, giving rise to α- and β-cluster lines (Supplementary Fig. 7f). In either cluster line, the adjacent three nanoclusters constituted a repetitive unit, Aα-Ba-Ca or Aβ-Bβ-Cβ, which was labeled by red or black frames, respectively. Such repetitive units were also observed from y-axis and z-axis views (Supplementary Fig. 7).

The optical absorptions of the obtained nanocluster crystals (dissolved in CH2Cl2) were compared (Supplementary Fig. 10). Along with the Au-alloying process from Ag28Cu12(SR)24 to AuAg28-Cu12(SR)24 (x = 1.32) and AuAg28-Cu12(SR)24 (x = 7.56), there was no significant alteration of the optical absorptions (405, 465, and 555 nm). By contrast, when the nanocluster template transformed from M40(SR)24 to M44(SR)30, these absorptions shifted to 390, 490, and 595 nm immediately (Supplementary Fig. 10), demonstrating the remarkable change over electronic structures with the template transformation. Time-dependent UV-vis of the transformation from Ag28Cu12(SR)24 to AuAg28-Cu12(SR)24 and then to Au12CuAg23(SR)30 were performed to track the cluster
transformation (Supplementary Fig. 11a). The changes of UV-vis contained two stages: (stage 1, from Ag$_{28}$Cu$_{12}$(SR)$_{24}$ to Au$_x$Ag$_{28-}$$x$Cu$_{12}$(SR)$_{24}$) eight isoabsorption points at 360, 385, 420, 445, 485, 550, 570, and 640 nm were observed (Supplementary Fig. 11b); (stage 2, from Au$_x$Ag$_{28-}$$x$Cu$_{12}$(SR)$_{24}$ to Au$_{12}$Cu$_y$Ag$_{32-}$$y$(SR)$_{30}$) three isoabsorption points at 400, 485, and 510 nm were detected (Supplementary Fig. 11c). The observation of these isoabsorption points suggested that the overall cluster transformation was a proportional conversion. Accordingly, both transformations from Ag$_{28}$Cu$_{12}$(SR)$_{24}$ to Au$_x$Ag$_{28-}$$x$Cu$_{12}$(SR)$_{24}$ and from Au$_x$Ag$_{28-}$$x$Cu$_{12}$(SR)$_{24}$ to Au$_{12}$Cu$_y$Ag$_{32-}$$y$(SR)$_{30}$ followed an "intramolecular rearrangement" approach, but not an "intermolecular decomposition-recombination" approach.

Besides, along with the Au-alloying process, the thermal stability of nanoclusters was enhanced. As shown in Supplementary Fig. 12, UV-vis characteristic absorptions of the Ag$_{28}$Cu$_{12}$(SR)$_{24}$ nanocluster (dissolved in CH$_2$Cl$_2$) gradually decreased in intensity after 1 h and completely disappeared in ~4 h, indicating degradation. In contrast, the UV-vis absorptions of Au$_{28}$Cu$_{12}$(SR)$_{24}$ ($x = 1.32$) were essentially identical in the first 2 h, and gradually decreased as time went on. Of note, the optical absorptions of Au$_{28}$Cu$_{12}$(SR)$_{24}$ ($x = 7.56$) was almost retained within 24 h, suggesting the enhanced thermal stability of Au$_{28}$Cu$_{12}$(SR)$_{24}$ over other two M$_{40}$(SR)$_{24}$ nanoclusters. In this context, the sequence of the thermal stability of these three M$_{40}$(SR)$_{24}$ nanoclusters was determined as Au$_{28}$Cu$_{12}$(SR)$_{24}$ ($x = 7.56$) > Au$_{28}$_Cu$_{12}$(SR)$_{24}$ ($x = 1.32$) > Ag$_{28}$Cu$_{12}$(SR)$_{24}$ ($x = 3.74$) > Ag$_{28}$Cu$_{12}$(SR)$_{24}$ ($x = 1.32$). Color labels: light blue, Ag; orange, Au; green, Cu; red, S. All C and H atoms are omitted for clarity.

Electrospray ionization mass spectrometry (ESI-MS) was then performed on nanocluster crystals (dissolved in CH$_2$Cl$_2$), and the mass results confirmed the compositions of these ~4"-charged M$_{40}$(SR)$_{24}$ and M$_{44}$(SR)$_{30}$ nanoclusters (Supplementary Fig. 13). Besides, the in-situ Au-alloying process and the nanocluster template transformation were tracked by exploiting the ESI-MS (Supplementary Figs. 14–18). At the very beginning process (1–2 min in
Kernel transformation from tetrahedron to hollow icosahedron. Figure 3 depicts the kernel collapse from the “tetrahedral Au4 + 4*M3” to “hollow icosahedral Au12,” induced by the Au alloying. Specifically, the initial Au-doping process transported the Au heteroatoms to the tetrahedral kernel, converting the Ag4 kernel to the alloyed Au4, and the final Au (Fig. 3a). The further Au-alloying sites on M40 predominantly located at the four M3 triangles that adhered to a vertex-to-face relationship to the tetrahedral Au4 kernel (Fig. 3b and Supplementary Fig. 3c); in contrast, the other four triangles on M40, following a face-to-face relationship to the Au4 tetrahedral kernel, maintained unalloyed as Ag3 (Supplementary Fig. 3d). For easily distinguishing these M3 positions, we define these Au4 positions as “stable location” (Supplementary Fig. 3e) and “unstable location” (Supplementary Fig. 3d). However, the Au doping on stable locations is simply concluded from the crystallography, and the Au positions may change throughout the crystallization process. From ESI–MS results (Supplementary Fig. 14), a maximum of 18–19 Au heteroatoms could be doped into the M40 cluster framework, >16 positions from the M4 kernel and 4*M3 stable locations; accordingly, there are other Ag positions in M40 that could be occupied by the introduced Au. X-ray absorption fine structure spectroscopy (XAFS) measurements were then performed for grasping the in-situ Au-doping process (Supplementary Figs. 29 and 30 and Supplementary Tables 3–4). The XAFS results demonstrated that the introduced Au occupied the innermost M4 tetrahedron first, and then substituted the Ag atoms in unstable locations, different from the crystal results wherein the unstable locations were maintained as undoped Ag throughout. We further crystallized this cluster sample and the crystal data suggested the Au heteroatoms on stable locations (i.e., Au4Ag8–xCu12(SR)24, x = 7.76), demonstrating the intracluster Au–Ag metal exchange throughout the crystallization. In this context, we made some speculations on mass signals (Supplementary Fig. 14): the introduced Au heteroatoms occupied the innermost tetrahedron first, and then substituted Ag atoms on M40, 52 randomly; the mass signals i represented the dominant Au-occupation in stable locations, whereas the signals ii represented the unstable locations, resulting in two groups of signals in the 3-min mass spectrum (Supplementary Fig. 14). In the 3-min sample, the M40 with Au-occupation in unstable locations might be the main product by referring XAFS results. Then, the M40 clusters of signals ii would transform to M44 clusters of signals iii, and then decomposed due to their instability. By comparison, the M40 clusters of signals i were continually doped by Au and transformed to M44 clusters of signals iv finally. In this context, the driving force for the transformation from M40 to M44 was determined as the Au-occupying at unstable locations, which rendered the M40 nanoclusters unstable molecules and triggered the kernel collapse from several small nano-building blocks to an integrated hollow icosahedron. Significantly, the further Au-alloying induced the transformation from M40(SR)24 to M44(SR)30, among which process the hollow icosahedral Au12 was generated (Fig. 3b, c). Structurally, the pre-transformed Au4Ag8–xCu12(SR)24 possesses a “tetrahedral Au4 + 4*M3” kernel (M = Au/Ag with a high Au proportion). Upon the nanocluster conversion, the M4 triangles collapsed inward to the Au4 tetrahedron, and finally rearranged into the hollow icosahedral Au12 kernel in Au4Cu12Ag8–x(SR)30 (Fig. 3c). Of note, there are 16 metal atoms in the “tetrahedral M4 + 4*M3” kernel while the icosahedral kernel only contains 12 metal atoms; in this context, a structural rearrangement occurred in this structural and kernel transformation (indeed, the “kernel +surface” configurations between M40(SR)24 and M44(SR)30 nanoclusters are different). However, due to the existence of several isosorption points in the UV-vis spectra, the structure transformation from M40(SR)24 to M44(SR)30 should follow an “inmolecular rearrangement” approach, but not an “intermolecular decomposition-recombination” approach. Accordingly, it is reasonable to conjecture the formation of icosahedral M12 in M44(SR)30 as the kernel collapse from “tetrahedral Au4 + 4*M3”. Besides, all sites in the hollow icosahedron are fully occupied by Au (i.e., Au12); in vivid contrast, the non-hollow M0@M12 kernels of previously alloy clusters are always partially occupied by two or more types of metals. We proposed that the complete Au occupation of the hollow icosahedron resulted from the kernel collapse in which process only the collapse of Au atom to Au12 was the most energetically favorable.

This avenue (i.e., kernel collapse) is of great importance since it maps out a reasonable avenue for the generation of the hollow...
icsahedral M$_{12}$ kernel in metal nanoclusters. Besides, the kernel collapse might be a very common approach in constructing metallic kernels of nanoclusters and nanoparticles (not limited to the hollow icosahedron, but also compliant to other configurations such as non-hollow icosahedron, FCC/BCC kernels, etc.), because the routine growth of several large-sized nanoclusters shell-by-shell should be not that energetically favorable. We also note that the kernel collapse should not be the unique approach for the generation of hollow icosahedra (or other structures) in metal nanoclusters and nanoparticles; other approaches may exist and are still worth mapping out.

**Discussion**

In summary, on the basis of the Au-alloying-induced transformation from M$_{40}$(SR)$_{24}$ to M$_{44}$(SR)$_{30}$ (M=Ag/Cu/Au), a reasonable avenue—kernel collapse—for the generation of the hollow icosahedral M$_{12}$ kernel in metal nanoclusters has been mapped out. The Au alloying on Ag$_{28}$Cu$_{12}$(SR)$_{24}$ produced template-maintained Au$_4$Ag$_{28}$Cu$_{12}$(SR)$_{24}$ (x = 1.32), Au$_{12}$Ag$_{32}$Cu$_{12}$(SR)$_{24}$ (y = 7.56), and template-transformed Au$_3$Cu$_2$Ag$_{32}$(SR)$_{30}$ (y = 3.74) step by step, accompanying with which processes the cluster kernel stepwisely evolved from "tetrahedral Ag$_4$ + 4 Cu$_{8}$S$_{6}$" to "tetrahedral Au$_4$ + 4 Ag$_{8}$S$_{6}$", then to "tetrahedral Au$_4$ + 4 Au$_{8}$S$_{6}$", and finally to "hollow icosahedral Au$_{12}$". The entire process was tracked by ESI-MS, and the crystal structures of the key nodes (altogether five crystal structures) have been determined. Overall, this work presents a reasonable avenue for comprehending the generation of hollow icosahedra in metal nanoclusters, and the "structure collapse" might be a very common approach for constructing kernel structures (not limited to the hollow icosahedron) in the size growth of nanoclusters and nanoparticles.

**Methods**

**Materials** All reagents were purchased from Sigma-Aldrich and used without further purification: silver nitrate (AgNO$_3$, 99% metal basis), tetraethylammonium (TMA) acid (H$_2$AUC$_3$H$_9$O, 99.99% metal basis), copper(I) acetylacetonate (Cu$_2$(O$_2$C$_5$H$_7$)$_2$, 99%, metal basis), sodium borohydride (NaBH$_4$, 97%), tetraphenyldisiloxane bromide ((PPh$_4$)Br, 95%), dichloromethane (CH$_2$Cl$_2$, HPLC, Sigma-Aldrich), methanol (CH$_3$OH, HPLC, Sigma-Aldrich), N,N-dimethyformamide (DMF, HPLC, Sigma-Aldrich), hexane (C$_6$H$_{12}$, HPLC, Sigma-Aldrich), and ethyl ether (C$_2$H$_5$O, HPLC, Sigma-Aldrich).

**Synthesis of Au(I)-SPhCl$_2$**

For the Au(I)-SPhCl$_2$ complexes synthesis, HAuCl$_4$·3H$_2$O (1 mmol) was dissolved in 5 mL CH$_3$OH, and 2,4-dichlorobenzenethiol (HSPhCl$_2$, 99%), copper(II) acetylacetonate (Cu$_2$(O$_2$C$_5$H$_7$)$_2$, 99%, metal basis), 2,4-dichlorobenzenethiol (HSPhCl$_2$, 99%), sodium borohydride (NaBH$_4$, 97%), tetraphenyldisiloxane bromide ((PPh$_4$)Br, 95%), dichloromethane (CH$_2$Cl$_2$, HPLC, Sigma-Aldrich), methanol (CH$_3$OH, HPLC, Sigma-Aldrich), N,N-dimethyformamide (DMF, HPLC, Sigma-Aldrich), hexane (C$_6$H$_{12}$, HPLC, Sigma-Aldrich), and ethyl ether (C$_2$H$_5$O, HPLC, Sigma-Aldrich). For the crystal date of Ag$_{28}$Cu$_{12}$(SPhCl$_2$)$_{24}$, Ag$_{4}$Cu$_{28}$Ag$_{32}$(SPhCl$_2$)$_{24}$ (x = 1.32), Au$_{4}$Ag$_{32}$Cu$_{12}$(SPhCl$_2$)$_{24}$ (y = 7.56), and Au$_{12}$Ag$_{32}$Cu$_{12}$(SPhCl$_2$)$_{24}$ (y = 3.76). Expanding the reaction time from 2 min to 8 min would make the Au$_{4}$Ag$_{32}$Cu$_{12}$(SPhCl$_2$)$_{24}$ (Sample 1).

**Preparation of XAFS samples.** In total, 10 mg of Ag$_{28}$Cu$_{12}$(SPhCl$_2$)$_{24}$ was dissolved in 10 mL of CH$_3$Cl$_2$ and then 3 mg of Au(I)-SPhCl$_2$ complexes was added in. After 1 min, 200 mL of hexane was poured in to pause the reaction; the precipitate was then dissolved in 5 mL of CH$_3$Cl$_2$ to yield the Au$_4$Ag$_{32}$Cu$_{12}$(SPhCl$_2$)$_{24}$ (Sample 1). In total, 10 mg of Ag$_{28}$Cu$_{12}$(SPhCl$_2$)$_{24}$ was first dissolved in 10 mL of CH$_3$Cl$_2$ and then 3 mg of Au(I)-SPhCl$_2$ complexes was added in. After 2 min, 200 mL of hexane was poured in to pause the reaction; the precipitate was then dissolved in 5 mL of CH$_3$Cl$_2$ to yield the Au$_{4}$Ag$_{32}$Cu$_{12}$(SPhCl$_2$)$_{24}$ (Sample 2). Single crystals of XAFS Sample 2 (i.e., Au$_{4}$Ag$_{32}$Cu$_{12}$(SPhCl$_2$)$_{24}$, x = 7.76) were cultivated at room temperature by vapor diffusing the ethyl ether into the DMF solution of nanoclusters.

**Crystallography**

**Preparation of XAFS samples.** XAFS measurements were performed at the beamline BL4W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. The storage ring of the SSRF was working at an energy of 3.5 GeV with an average current electron current of 300 mA. The hard X-ray was monochromatized with a Si(111) monochromator. XAFS data were collected in the transmission mode in the energy range from 200 below to 1000 eV above the Au L3-edge. The acquired XAFS data were processed according to the standard procedures using the ARTEMIS module implemented in the IFEFFIT software packages.

**X-ray crystallography**

For the crystal data of Ag$_{28}$Cu$_{12}$(SPhCl$_2$)$_{24}$, Au$_{4}$Ag$_{32}$Cu$_{12}$(SPhCl$_2$)$_{24}$ (x = 1.32), Au$_{4}$Cu$_{28}$Ag$_{32}$(SPhCl$_2$)$_{24}$, Au$_{12}$Ag$_{32}$Cu$_{12}$(SPhCl$_2$)$_{24}$ (y = 7.76), and the co-crystallized [Au$_4$Ag$_{32}$Cu$_{12}$(SPhCl$_2$)$_{24}$][Au$_4$Ag$_{32}$Cu$_{12}$(SPhCl$_2$)$_{30}$]$_4$ (y = 3.74) for the crystal structure of Ag$_{28}$Cu$_{12}$(SPhCl$_2$)$_{24}$, Au$_{4}$Ag$_{32}$Cu$_{12}$(SPhCl$_2$)$_{24}$ (x = 1.32), Au$_{4}$Cu$_{28}$Ag$_{32}$(SPhCl$_2$)$_{24}$, Au$_{12}$Ag$_{32}$Cu$_{12}$(SPhCl$_2$)$_{24}$ (y = 7.76), and the co-crystallized [Au$_4$Ag$_{32}$Cu$_{12}$(SPhCl$_2$)$_{24}$][Au$_4$Ag$_{32}$Cu$_{12}$(SPhCl$_2$)$_{30}$]$_4$ (y = 3.74) for the crystal structure of Ag$_{28}$Cu$_{12}$(SPhCl$_2$)$_{24}$.

**Time-dependent ESI-MS of the Au alloying process on Ag$_{28}$Cu$_{12}$(SPhCl$_2$)$_{24}$**

In total, 20 mg of Ag$_{28}$Cu$_{12}$(SPhCl$_2$)$_{24}$ was firstly dissolved in 20 mL of CH$_3$Cl$_2$ and then 5 mg of Au(I)-SPhCl$_2$ complexes (powder) was added in. The ESI-MS measurement of the reaction was performed every minute.
anisotropically, and all the hydrogen atoms were set in geometrically calculated positions and refined isotropically using a riding model. All crystal structures were treated with PLATON SQUEEZE, and the diffuse electron densities from these residual solvent molecules were removed.

Characterization. The UV-vis absorption spectra of nanoclusters were recorded using an Agilent 8453 diode array spectrometer. Electrospay ionization mass spectrometry (ESI-MS) measurements were performed by MicrOTOF-QL high-resolution mass spectrometer. The sample was directly infused into the chamber at 5 μL/min. For preparing the ESI samples, nanoclusters were dissolved in CH2Cl2 (1 mg/mL) and diluted (v/v = 1:2) by CH3OH. Energy-dispersive X-ray spectroscopy (EDS) mapping of nanoclusters were characterized by SEM (Quanta 400 F). X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250 equipped with a monochromated Al Kα (1486.6 eV) 150 W X-ray source, 0.5 mm circular spot size, flood gun to counter charging effects, and analysis chamber base pressure lower than 1 × 10⁻⁹ mbar.

Data availability. The X-ray crystallographic coordinates for structures reported in this work have been deposited at the Cambridge Crystallographic Data Center (CCDC), under deposition numbers CCDC-2009375, 2009456, 2009457, 2009397, 2009378, and 2083130. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, which has been mentioned in the article.

Received: 7 June 2021; Accepted: 29 September 2021; Published online: 26 October 2021

References

1. Chakraborty, I. & Pradeep, T. Atomically precise clusters of noble metals: emerging link between atoms and nanoparticles. Chem. Rev. 117, 8208–8271 (2017).
2. Hossain, S. et al. Alloy clusters: precise synthesis and mixing effects. Acc. Chem. Res. 51, 3114–3124 (2018).
3. Sharma, S. et al. Structurally precise dichalcogenide-protected copper and silver superatomic nanoclusters and their alloys. Acc. Chem. Res. 51, 2475–2483 (2018).
4. Konishi, K., Iwashita, M. & Shichibu, Y. Phosphine-ligated gold clusters with core-exo geometries: unique properties and interactions at the ligand-cluster interface. Acc. Chem. Res. 51, 3125–3133 (2018).
5. Bhattarai, B. et al. Chemistry and structure of silver molecular nanoparticles. Acc. Chem. Res. 51, 3104–3113 (2018).
6. Chen, T. et al. Electrospay ionization mass spectrometry: a powerful platform for noble-metal nanocluster analysis. Angew. Chem. Int. Ed. 58, 11967–11977 (2019).
7. Yang, D. et al. Controllable conversion of CO2 on non-metallic gold clusters. Angew. Chem. Int. Ed. 59, 1919–1924 (2020).
8. Giri, G. et al. Structural characterization of alkynyl-protected gold nanoclusters. J. Am. Chem. Soc. 142, 2995–3001 (2020).
9. Kenzler, S., Schrenk, C. & Schnepf, A. Au40(S2C2N2)2−: a highly symmetric nanoscale gold cluster confirms the general concept of metalloid clusters. Angew. Chem. Int. Ed. 56, 393–396 (2017).
10. Yuan, S.-F. et al. A ligand-protected golden fullerene: the dipryridylmido Au32+ cluster. Angew. Chem. Int. Ed. 58, 5906–5909 (2019).
11. Kenzler, S. et al. Synthesis and characterization of three multi-shell metalloid gold clusters Au160, 220, 330, 440. Angew. Chem. Int. Ed. 58, 5902–5905 (2019).
12. Narouz, M. R. et al. N-heterocyclic carbene-functionalized series of gold nanoclusters. Nat. Chem. 11, 419–425 (2019).
13. Tassaka, Y. et al. Electron binding in a superradical with a repulsive coulomb barrier: the case of [Ag54(S2C2N2)22]2− in the gas phase. J. Phys. Chem. Lett. 11, 3069–3074 (2020).
14. Huard, D. J. E. et al. Atomic structure of a fluorescent Ag2 cluster templated by a multistranded DNA scaffold. J. Am. Chem. Soc. 141, 11465–11470 (2018).
15. Wang, Z. et al. A hierarchically assembled Cu50 nanocluster with a faradaic efficiency of up to 96% for electrocatalytic CO2 reduction to CO. Angew. Chem. Int. Ed. 59, 3073–3077 (2020).
16. Qu, M. et al. Observation of non-FCC copper in alkynyl-protected Cu53 nanoclusters. Angew. Chem. Int. Ed. 59, 6507–6512 (2020).
17. Sun, C. et al. Atomically precise, thiolated copper-hydride nanoclusters as single-site hydrodechlorination catalysts for ketone reduction in mild conditions. ACS Nano 13, 5975–5986 (2019).
18. Baghdasaryan, A. et al. Thiolated protected copper sulfide cluster with the tentative composition Cu53S15(2-PET)45. Inorg. Chem. 59, 2200–2208 (2020).
51. Sun, Q. et al. Synthesis, structures, and photoluminescence of elongated face-centered-cubic Ag84 clusters containing lipoic acid and its amide analogue. *Inorg. Chem.* **59**, 8836–8845 (2020).

52. Desereddy, A. et al. Ultrastable silver nanoparticles. *Nature* **501**, 399–402 (2013).

53. Yang, H. et al. Structural evolution of atomically precise thiolated bimetallic [Au12n-Cu12(SR)n]+ (n = 0, 2, 4, 6) nanoclusters. *J. Am. Chem. Soc.* **136**, 7197–7200 (2014).

54. Du, W. et al. Ag50(Dppm)6(SR)30 and its homologue Au56(Dppm)6(SR)30 alloy nanocluster: seeded growth, structure determination, and differences in properties. *J. Am. Chem. Soc.* **139**, 1618–1624 (2017).

55. Yan, N. et al. Unraveling the long-pursued Au144 structure by x-ray crystallography. *Sci. Adv.* **4**, eaat7239 (2018).

56. Barik, S. K. et al. Polyhydrido copper nanoclusters with a hollow icosahedral core: [Cu38H36(E2P(OR)2)12] (E=S or Se; R=IPr, iPr or iBu). *Chem. Eur. J.* **26**, 10471–10479 (2020).

57. Yan, J. et al. Asymmetric synthesis of chiral bimetallic [Ag82Cu12(SR)24]+ nanoclusters via ion pairing. *J. Am. Chem. Soc.* **138**, 12751–12754 (2016).

58. Yang, H. et al. All-thiol-stabilized Ag44 and Au12Ag32 nanoparticles with single-crystal structures. *Nat. Commun.* **4**, 2422 (2013).

59. He, L. et al. Alternative array stacking of Ag26Au and Ag24Au nanoclusters. *Angew. Chem. Int. Ed.* **58**, 9897–9901 (2019).

60. Bodiuzzaman, M. et al. Camouflaging structural diversity: co-crystallization of two different nanoparticles having different cores but the same shell. *Angew. Chem. Int. Ed.* **58**, 189–194 (2019).

61. Liu, J.-Y. et al. Different silver nanoparticles in one crystal: Ag210(iPrPhS)67(Ph3P)5Cl and Ag211(iPrPhS)67(Ph3P)6Cl. *Angew. Chem. Int. Ed.* **58**, 195–199 (2019).

62. Yan, J. et al. Co-crystallization of atomically precise metal nanoparticles driven by magic atomic and electronic shells. *Nat. Commun.* **9**, 3357 (2018).

63. APEX2 Ver.2014.11-0, SAINT Ver.8.34A, SADABS Ver.2014/15, Bruker AXS, Inc., Madison, Wisconsin, USA, 2014.

64. Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr. Sect. C Struct. Chem.** 71, 3–8 (2015).

Acknowledgements

We acknowledge the financial support by NSFC (U1532141, 21631001, and 21871001), the Ministry of Education, the Education Department of Anhui University.

Author contributions

X.K. and X.W. carried out experiments, analyzed the data and wrote the manuscript. X.L., Sih.W. and T.Y. assisted the X-ray absorption fine structure spectroscopy analysis and completed the manuscript. Sh.W. and M.Z. designed the project, analyzed the data, and revised the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-021-26528-w.

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Peer review information *Nature Communications* thanks the anonymous reviewer(s) for their contribution to the peer review of this work.

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