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Introduction

Atomically precise metal clusters with crystallographically solved structures are ideally composed of an exact number of metal atoms.¹⁻⁴ The knowledge gained from the study of these clusters has provided valuable information about the evolution from the metallic state to the molecular exciton state,^{5,6} the origin of the chiral structure,⁷ the fundamental understanding of heterogeneous catalysis⁸ and so on, which are currently not available from typical nanoparticles. Recently, significant advances have been made in the precise synthesis of metal clusters, thereby building the library of metal clusters with rich size and structure diversity. The icosahedron is perhaps the most popular structure in nanoclusters. Among reported clusters, many clusters are formed from single or multiple-twinned icosahedra, such as Au₂₅(SR)₁₈, Au₃₈(SR)₂₄, Au₁₃₃(SR)₅₂, Au₁₄₄(SR)₆₀, Au₂₅(PPh₃)₁₀(SR)₅Cl₂, Au₃₇(PPh₃)₁₀(SR)₁₀Cl₂, Au₅₅(- $PPh_3)_{12}Cl_6$, $Au_{60}Se_2(PPh_3)_{10}(SeR)_{15}$, $Au_{12}Ag_{60}(SR)_{31}Br_9(Dppp)_6$,

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Here we report a diachronic evolvement from tetra-icosahedral $Au_{30}Ag_{12}(C \equiv CR)_{24}$ to quasi-hcp (hexagonal close-packed) $Au_{47}Ag_{19}(C \equiv CR)_{32}$ via a one-step reduction, in which the size/structure conversion of the two clusters is not a typical Oswald growth process, but involves interface shrinking followed by core rearrangement and surface polymerization. $Au_{30}Ag_{12}(C \equiv CR)_{24}$ has an aesthetic $Au_{18}Ag_8$ kernel that is composed of four interpenetrating $Au_{10}Ag_3$ icosahedra, while $Au_{47}Ag_{19}(C \equiv CR)_{32}$ has a twisted Au_{19} core capped by a $Au_{12}Ag_{19}$ shell that are stacked in a layer-by-layer manner with a quasi-hcp pattern. The discovery of the two clusters not only provides further evidence for icosahedral clusters with longer excited-state lifetime compared to hcp-like clusters, but also discloses a double increase in catalytic reactivity for electrocatalytic oxidation of ethanol over quasi-hcp clusters in comparison with icosahedral clusters. This work provides the rationale for reversing the bottom-up growth process to remake bimetal clusters.

*etc.*⁹⁻²² Interestingly, hcp or hcp-like structures are rarely observed in the library of clusters.²³⁻²⁶ Currently, the understanding of the formation mechanism of clusters is still lacking, as it is difficult to directly observe dynamic processes of such small metal ions and ligands in the solution phase. As a result, manipulating the assembly of atoms into the target structure *via* the bottom-up process remains a challenge.

One alternative way to solve the issue is the interconversion strategy from the parent clusters to target structures such as hcp-like clusters, in which the atomically precise starting point with clusters can permit tracing the growth process via experiments coupled with theory. In fact, the size/structure transformation of metal clusters into another new ones is well precedented.27-34 For example, Xie and colleagues reported a three-stage size growth mechanism from $[Au_{25}(SR)_{18}]^{-}$ to $[Au_{44}(SR)_{26}]^{2-}$ monitored by time-course electrospray ionization mass spectrometry (ESI-MS): kinetically controlled accumulation of Au25 reaction with AuSR; Au25-mediated size growth with bottom-up Lamer and volcano-shaped growth patterns; thermodynamically driven size-focusing into Au44.35 Jin and colleagues proposed a shuttling-out mechanism for the formation of $[Au_{24}(PPh_3)_{10}(SR)_5Cl_2]^+$ from its parent $[Au_{25}(PPh_3)_{10}(SR_{5}Cl_{2}^{2+}$ based on density functional theory (DFT) simulations and ESI-MS: adsorption of a PPh3 onto a gold atom located at the waist position to initiate the reaction; Au-S bond breaking and the gold atom at the center dislocating toward the surface; the Au(PPh₃)₂ moiety formed on the surface eventually detaching from the Au₂₅ to result in hollow Au₂₄.³⁶ To enrich the metal functionality. clusters with tailored structure and



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a fundamental understanding of the critical growth event from non-hcp to hcp-like clusters is thus most needed.

In this study, we initially present the synthesis of an icosahedron-based Au₃₀Ag₁₂(C=CR)₂₄ cluster (where HC=CR is 1-ethynyl-2,4-dimethylbenzene) through the co-reduction of the AuC \equiv CR and AgC \equiv CR by tert-butylamine borane $(C_4H_{11}NBH_3)$. Au₃₀Ag₁₂ $(C \equiv CR)_{24}$ contains a Au₁₈Ag₈ core that is fused from four Au₁₀Ag₃ icosahedral units. Notably, the Au₃₀- $Ag_{12}(C \equiv CR)_{24}$ cluster is then reduced by $C_4H_{11}NBH_3$ and further transformed into a new Au₄₇Ag₁₉(C=CR)₃₂ cluster with quasi-hcp structure, which is composed of a layered-like Au₁₉ core encapsulated by a Au₁₂Ag₁₉ shell. The transformation from tetra-icosahedral Au30Ag12(C=CR)24 to quasi-hcp Au47Ag19(- $C \equiv CR$)₃₂ proceeds *via* a stepwise mechanism, with the surface staples shrinking sequentially with the core growing. More notably, tetra-icosahedral Au30Ag12(C=CR)24 and quasi-hcp Au₄₇Ag₁₉(C=CR)₃₂ show diversity in physicochemical properties pursued by our studies.

Results and discussion

The total structure of the Au₃₀Ag₁₂(C \equiv CR)₂₄ (hereafter Au₃₀Ag₁₂) cluster was solved by single-crystal X-ray diffraction (Table S1†). As shown in Fig. 1, Au₃₀Ag₁₂ has a *S*₄ symmetry and can be viewed as a tetra-icosahedral structure. The Au₁₈Ag₈ kernel in Au₃₀Ag₁₂ can be seen as an assembly of four icosahedral Au₁₀Ag₃ building blocks (Fig. 1a and S1†). Interestingly, the central atoms of the four icosahedra that are respectively marked with 1, 2, 3, 4 compose a Au₄ tetrahedron. The four icosahedra are assembled through interpenetration sharing a M₇ pentagonal bipyramid (Fig. S1†), and they are slightly distorted, which may be ascribed to the asymmetric introduction of Ag atoms into the icosahedra. The Au₁₈Ag₈ kernel is further stabilized by four trimeric RC=C-Au-C₂(R)-Ag-C₂(R)-Au-RC=C (motifs A and B in Fig. 1b) and four monomeric RC=C-Au-C=CR (motif C in Fig. 1b). In motif A, all four alkyne ligands interact with metal atoms *via* σ - π bonds



Fig. 1 (a) Au₁₈Ag₈ kernel formed by four interpenetrating Au₁₀Ag₃ icosahedra. (b) Three different motifs. (c) Total structure of Au₃₀-Ag₁₂(C=CR)₂₄. Color codes: orange/green, Au; blue, Ag; gray, C. The H atoms are omitted for clarity.

and the Ag atom in the middle interacts with two alkyne ligands *via* π bonds, while in motif B, one alkyne ligand adopts a bridge mode with only a σ interaction μ_2 - η^1 (Au), η^2 (Ag). The chemical formula of Au₃₀Ag₁₂(C=CR)₂₄ is further confirmed by ESI-MS (Fig. S2[†]).

Next, the Au₃₀Ag₁₂(C=CR)₂₄ cluster can be further converted to another new cluster using C₄H₁₁NBH₃. Adding thimbleful reductant into the dichloromethane solution of Au₃₀Ag₁₂ clusters, the green solution turned purple tardily. We monitored the transformation process using time-resolved UV-vis adsorption spectroscopy. From Fig. 2a and S3,† after the addition of the reducing agent, the three characteristic peaks at 444, 594 and 687 nm of $Au_{30}Ag_{12}$ became weak, accompanied by the redshift of the peak at 444 nm, indicating that the cluster structure gradually dissociated. After 6 h, a peak appeared around 550 nm, gradually intensified and redshifted. At 20 h, the peak offset to around 450 nm began to intensify and continued to redshift. After 28 h, deduced from the optical absorption from the reaction solution, no significant change was observed in the range of 300-900 nm, which suggested that a new cluster was formed in the solution and finally exhibited two distinct peaks at 460 and 554 nm (Fig. 2a and S4[†]).

We separated and purified the transformation product to obtain the novel cluster, whose chemical formula was analyzed by matrix-assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS). The two dominant broad peaks at 15.184 and 10.377 kDa were assigned to Au47Ag19(C=CR)30 (expected $m/z = 15\,184$) and Au₃₉Ag₁₉(C \equiv CR)₅ (expected m/z =10378), respectively (Fig. S5[†]). Therefore, we speculated that the new cluster might contain 47 Au atoms and 19 Ag atoms (short for Au₄₇Ag₁₉). Moreover, MALDI-TOF-MS was performed to identify stable intermediate species during the cluster transformation. For pure Au₃₀Ag₁₂, MALDI-TOF-MS gave a main peak at 10.302 kDa, which matched the formula weight of Au₃₀Ag₁₂(-C≡CR)₂₄. And two slight peaks at 9.177 and 6.230 kDa were assigned to Au₂₈Ag₁₀(C=CR)₂₀ and Au₂₂Ag₈(C=CR)₈, respectively (Fig. 2b and S6[†]). At 6 h after the addition of the reducing agent, the main peaks still existed, but a series of new peaks appeared around 9.3 kDa, corresponding to $Au_{28}Ag_{10}(C \equiv CR)_{20}$, $Au_{29}Ag_{11}(C \equiv CR)_{20}$, $Au_{28}Ag_{12}(C \equiv CR)_{21}$ and so on, indicating that the surface structural units of Au₃₀Ag₁₂ began to dissociate (Fig. 2b and S7^{\dagger}). At 20 h, the characteristic peak of Au₃₀Ag₁₂ disappeared, and peaks with smaller molecular weight appeared around 9.0 kDa and larger substances were generated: the peak at 11.059 kDa is assigned to Au₃₂Ag₁₃(C=CR)₂₆, and the peak around 15.2 kDa is assigned to Au₄₇Ag₁₉(C=CR)₃₀ (Fig. 2b and S8[†]). At 28 h, peaks around 9.0 kDa decreased and were replaced by a series of peaks around 5.5 kDa (Fig. 2b, S9–S12†). At 34 h, the characteristic peaks of the cluster and a bunch of peaks below 2.5 kDa were left, indicating that the cluster and Au-alkyne complexes were finally present in the solution.

Furthermore, the total structure of $Au_{47}Ag_{19}(C \equiv CR)_{32}$ was determined by single-crystal X-ray diffraction (Table S2†). As shown in Fig. 2c, the cluster is protected by 32 alkyne ligands and hence its chemical formula can be unambiguously identified as $Au_{47}Ag_{19}(C \equiv CR)_{32}$. Different from the parent $Au_{30}Ag_{12}$ cluster, $Au_{47}Ag_{19}$ can be viewed as a core-shell structure arranged along

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Fig. 2 (a) Time-resolved UV-vis spectra and (b) MALDI-TOF-MS spectra obtained from the transformation from Au₃₀Ag₁₂(C \equiv CR)₂₄ to Au₄₇-Ag₁₉(C \equiv CR)₃₂. Formulae of intermediates captured in MALDI-TOF-MS: α, Au₂₈Ag₁₀(C \equiv CR)₂₀; β, Au₂₉Ag₁₁(C \equiv CR)₂₀; γ, Au₂₆Ag₁₂(C \equiv CR)₂₀; δ, Au₁₈Ag₈; ε, Au₂₂Ag₈(C \equiv CR)₄. (c) Total structure of Au₄₇Ag₁₉(C \equiv CR)₃₂. (d) Au₁₉ core, Au₁₂Ag₁₉ shell and Au₁₉@Au₁₂Ag₁₉. (e) Two different motifs. Color codes: orange/green, Au; blue, Ag; gray, C. The H atoms are omitted for clarity.

a C_2 axis. The kernel of Au₄₇Ag₁₉ is a twisted Au₁₉ that is dissected in a layer-by-layer manner (Fig. 2d), in which the middle layer is a regular hexagon Au7, the two layers adjacent to the Au7 hexagon are pentagons, and two vertex atoms at both ends. The Au₁₉ kernel is surrounded by the Au₁₂Ag₁₉ shell. Au₄₇Ag₁₉ includes only monomeric RC=C-Au-C=C(R) staples that adopt two coordination modes: $\mu_2 - \eta^1(Au)$, $\eta^2(Au)$ and $\mu_2 - \eta^1(Au)$, $\eta^2(Ag)$ (Fig. 2e). Generally, nanoclusters as large as Au₄₇Ag₁₉ contain basic polyhedral structural units which can be tetrahedron, icosahedron or based on fcc, hcp or bcc (body-centered cubic) arrangements. And the basic units grow into larger structures through fusion, interpenetration, shell-by-shell and layer-bylayer modes. Strictly speaking, the basic units mentioned above are not found in Au₄₇Ag₁₉. The Au₁₉ nucleus is somewhat similar to the hcp structure, even though there is a torsion Angle between the two Au₅ layers. Therefore, the Au₁₉ core can be viewed as a quasi-hcp structure whose layers are stacking in the ABABA pattern with distortion (Fig. S13[†]). This indicates that the tetra-icosahedral Au₃₀Ag₁₂ grows towards hcp during the transformation process. The two clusters are quite robust (Fig. S14[†]) and the in-lattice connection modes of the two clusters are shown in Fig. S15 and S16[†] in detail.

To elucidate the growth from $Au_{30}Ag_{12}$ to $Au_{47}Ag_{19}$, we conducted density functional theory (DFT) calculations to model

the structural transformation based on the MALDI-TOF-MS experiment results. Fig. 2b illustrates that, except for the bunch of signals relating to the Au₃₀Ag₁₂(C=CR)₂₄ cluster persisting throughout the entire transformation process, the intermediate size decreased gradually from 0-28 h, evident in the shift of the peaks. The transition from 0-28 h might signal the size decreasing period. During this period, several intermediates, including the Au₂₈Ag₁₀(C=CR)₂₀ and Au₂₉Ag₁₁(- $C \equiv CR$)₂₀ formed at 6 h, Au₂₆Ag₁₂($C \equiv CR$)₂₀ formed at 20 h, and $Au_{22}Ag_8(C \equiv CR)_4$ and $Au_{18}Ag_8$ formed at 28 h, were notably observed with apparent intensity signals, indicating their key role in the size-decreasing process. As shown in Fig. 3a, starting from the full $Au_{30}Ag_{12}(C \equiv CR)_{24}$ cluster (isomer 1), four $HC \equiv CAuC \equiv C(H)Ag$ fragments were removed one by one with the energy preference sequence, producing the isomers from 2-5, as depicted in Fig. 3a. Among them, isomer 2 (Au₂₉Ag₁₁(- $C \equiv CR_{22}$ can transform into $Au_{29}Ag_{11}(C \equiv CR)_{20}$ via abscission of two C=CR fragments and isomer 3 was consistent with the intermediate Au₂₈Ag₁₀(C=CR)₂₀ characterized at 6 h. After that, the HC=CAuC=CH motifs were further removed stepwise, finally leaving the metal Au₁₈Ag₈ kernel. Among the isomers of 6-13, $Au_{24}Ag_8(C \equiv CR)_{12}$ (isomer 7), $Au_{22}Ag_8(C \equiv CR)_8$ (isomer 9), and $Au_{20}Ag_8(C \equiv CR)_4$ (isomer 11) can transform into $Au_{24}Ag_8(C \equiv CR_{0}$, $Au_{22}Ag_{8}(C \equiv CR)_{4}$, and $Au_{20}Ag_{8}(C \equiv CR)_{1}$ by $C \equiv CR$

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Fig. 3 (a) The proposed transformation pathway from $Au_{30}Ag_{12}(C \equiv CR)_{24}$ to the seed of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (b) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the $Au_{47}Ag_{19}(C \equiv CR)_{32}$ cluster. (c) Au - Au length of the A

abscission. These isomers confirmed the rationality of the proposed pathway.

From 28 h to 34 h, the peaks relating to the intermediates of $Au_{18}Ag_8$, $Au_{22}Ag_8(C \equiv CR)_4$ disappeared, and the peak signaling the production of the Au₄₇Ag₁₉ cluster emerged, implying that the generation of the Au₄₇Ag₁₉ cluster at 34 h originated from the intermediates of Au₁₈Ag₈ and Au₂₂Ag₈(C=CR)₄ at 28 h. As mentioned above, the kernel of Au₃₀Ag₁₂ can be regarded as the fusion of four M13 fragments. The four Au atoms from each of the four M₁₃ fragments constituted a central Au₄ pyramid core. Fig. 3b shows the distances of the six Au–Au bonds of the Au₄ core. For isomers 1-11, the Au-Au length did not change significantly upon the removal of the outer motifs. However, the transformation from isomer 11 to isomer 12 showed significant structural distortions. The Au₁-Au₂ and Au₁-Au₃ lengths of isomer 12 in Fig. 3b increased to 3.96 and 4.79 Å, indicating the dissociation of the central Au₄ core of the cluster and the consequent destruction of the tetra-icosahedral pattern. The transformation from isomer 12 to isomer 13, *i.e.*, naked Au₁₈Ag₈ isomer, involved the continued lengthening of the Au₁-Au₂ (4.18 Å) and Au₁-Au₃ lengths (4.95 Å). The naked Au₁₈Ag₈ intermediate (isomer 13) can easily isomerize to an isomer intermediate with similar stability, which possessed the same packing mode as the inner kernel of the Au₄₇Ag₁₉ cluster. Next, the Au₁₃Ag₆ part of the isomer intermediate can undergo

segregation^{37,38} or Au–Ag exchange with the species in the solvation environment, generating the Au_{19} species or bigger intermediates containing the Au_{19} species. This can be seen as a seed for the birth of the $Au_{47}Ag_{19}$ cluster.

The Kohn-Sham (KS) orbital energy levels and atomic orbital components in each orbital of the two clusters are shown in Fig. S17.[†] The main absorption peak of Au₃₀Ag₁₂ lies at 1.70 eV (Fig. S18[†]), which corresponds to the orbital transitions including HOMO-3 \rightarrow LUMO+2, HOMO-1 \rightarrow LUMO+3, HOMO-2 \rightarrow LUMO+4 (HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital). For Au₄₇Ag₁₉, the main absorption peaks are located at 1.41 and 2.31 eV, which include the orbital transitions of HOMO-6 \rightarrow LUMO+2, HOMO-2 \rightarrow LUMO+5 for 1.41 eV, and HOMO-48 \rightarrow HOMO, HOMO-35 \rightarrow LUMO+3 for 2.31 eV (Fig. S17a⁺), respectively. It can also be seen that the metal atoms contribute considerably to the population of the frontier orbital. Furthermore, for the Au₃₀Ag₁₂ cluster, the energies of the HOMO and LUMO orbitals are -5.38 and -4.41 eV, which lead to the HOMO-LUMO gap of 0.97 eV; for the Au₄₇Ag₁₉ cluster, the energy of the LUMO orbital slightly increases by 0.09 eV and the energy of the HOMO orbital elevates a little bit more by 0.20 eV, which eventually lowers the gap to 0.86 eV (Fig. S17b[†]). The transitions of molecular orbital topologies from the HOMO to the LUMO of the two clusters show different trends for their populations. For the Au₃₀Ag₁₂

cluster, the population of the orbital seems to narrow on the metal core from the HOMO orbital to the LUMO orbital. However, for the Au₄₇Ag₁₉ cluster, the LUMO orbital slightly extends to the outer ligands. From the UV-vis-NIR absorption spectra in the photon energy scale, the optical energy gaps of the Au₃₀Ag₁₂ and Au₄₇Ag₁₉ are determined as 0.89 and 0.82 eV, respectively (Fig. S19†). For the Square wave voltammetry (SWV) curves, there is an oxidation peak at 0.70 V (O1) and two reduction peaks at -0.05 V (R1) and -0.75 V (R2) for Au₃₀Ag₁₂, and there is an oxidation peak at 0.77 V (O1) and two reduction peaks at 0.07 V (R1) and -0.79 V (R2) for Au₄₇Ag₁₉. Therefore, the electrochemical energy gaps are calculated to be 0.75 eV for Au₃₀Ag₁₂ and 0.70 eV for Au₄₇Ag₁₉ (Fig. S19†).

The Au₃₀(SR)₁₈ with a hcp pattern was previously reported to give rise to a very short excited-state lifetime due to the close packing structure.³⁹ With the two clusters in hand, a question was whether quasi-hcp Au₄₇Ag₁₉ was used to further justify the shorter TA lifetime of hcp-like clusters than non-hcp clusters. We investigated the excited-state dynamics of the two clusters by performing time-resolved transient absorption spectroscopy (TAS). Fig. 4a and b show the femtosecond (fs) TA data map of Au₃₀Ag₁₂ and Au₄₇Ag₁₉ with excitation at 380 nm (3.26 eV). Between 0.1 and 1 ps, one can observe ultrafast relaxation of excited state absorption (ESA) in both the NCs, which was rapid relaxation from higher to lower excited states. Between 1 ps and 2 ns, the TA signals (both ESA and GSB) of Au₃₀Ag₁₂ decayed to half of its maximum while the TA signals of Au₄₇Ag₁₉ decayed to zero. Fig. 4c shows the fs-TA kinetic traces and fittings of the two clusters probed at 630 nm, and the fitting parameters are shown in Table S3.† Since the TA signal of Au₃₀Ag₁₂ did not decay to zero at 2 ns, we performed nanosecond TA under the same experimental conditions (Fig. S20†). In contrast to Au₃₀Ag₁₂ that showed single exponential decay after 5 ps, Au₄₇Ag₁₉ exhibited two-exponential nanosecond decay in both GSB and ESA kinetics. The average excited state lifetime was fitted to be 2.5 ns for Au₃₀Ag₁₂ and 0.86 ns for Au₄₇Ag₁₉ (Fig. 4c and d), which was in full agreement with reported results. The shorter exciton lifetime in Au₄₇Ag₁₉ should also be ascribed to the stronger overlap of the HOMO and LUMO because of the close packed mode of the metal core.^{40,41}

We next sought to explore the catalytic properties of $Au_{30}Ag_{12}$ and $Au_{47}Ag_{19}$. As presented in Fig. 5a, using electrocatalytic oxidation of ethanol (EOR) toward CH₃COOH as a probe reaction (Fig. S21†), the $Au_{47}Ag_{19}$ catalyst exhibited over 2-fold increase in the EOR current in 1 M KOH + 1 M CH₃CH₂OH solution, compared to the $Au_{30}Ag_{12}$ catalyst. The mass activities of $Au_{30}Ag_{12}$ and $Au_{47}Ag_{19}$ were 111.2 and 242.5 mA/mg_{AuAg} at a cell voltage of 0.08 V *vs.* Ag/AgCl, respectively. As for the onset potential, $Au_{47}Ag_{19}$ also showed a significant negative shift (Fig. 5a). The electrochemically active surface areas (ECSAs) of $Au_{30}Ag_{12}$ and $Au_{47}Ag_{19}$ were measured to be 8.57 and 17.39 cm²/ mg_{AuAg}, respectively, based on the cyclic voltammogram curves



Fig. 4 Fs-TA data map of (a) $Au_{30}Ag_{12}$ and (b) $Au_{47}Ag_{19}$ with excitation at 380 nm. (c) Comparison of TA kinetic traces and fittings probed at 630 nm of two NCs. (d) Ns-TA kinetics traces of $Au_{30}Ag_{12}$ probed at 630 nm and corresponding fit.



Fig. 5 (a) CVs of the $Au_{30}Ag_{12}$ and $Au_{47}Ag_{19}$ catalysts in 1 M KOH and 1 M CH₃CH₂OH solution. (b) CVs of the two catalysts in 1 M KOH solution and the shaded areas are used to calculate the ECSAs. (c) Electrochemical impedance spectra and (d) Tafel plots for EOR obtained on the two catalysts.

(CVs) in Fig. 5b. Thus, the specific activities of EOR at 0.08 V vs. Ag/AgCl by normalizing ECSAs were 13.94 mA cm⁻² for Au₄₇Ag₁₉ and 12.97 mA cm⁻² for Au₃₀Ag₁₂ (Fig. S22†). Electrochemical impedance spectroscopy (EIS) was carried out at 0.08 V vs. Ag/ AgCl. In Fig. 5c, Au₄₇Ag₁₉ possessed a much smaller semicircle diameter than Au₃₀Ag₁₂, suggesting that the former had better conductivity and smaller electron transfer resistance, which was consistent with better EOR performance of the Au₄₇Ag₁₉ catalyst. Fig. 5d shows that the Tafel slope of Au₄₇Ag₁₉ was obviously lower than that of Au₃₀Ag₁₂, indicating that the current density of Au₄₇Ag₁₉ increased faster, thereby showing better efficiency in EOR.

DFT calculations were performed to further shed light on the mechanism of the electrocatalytic oxidation of ethanol on the two catalysts. Previous studies have suggested that the oxidation reaction from CH₃CH₂OH to CH₃COOH can proceed via the adsorption of the α-C atom or O atom of CH₃CH₂OH.^{42,43} The adsorption of the O atom was adopted in this work because the adsorption of the a-C atom, which was similar to quasihorizontal placement of the CH₃CH₂OH, needs to overcome a larger steric effect with respect to the adsorption of the O atom, *i.e.*, vertical placement of CH₃CH₂OH, due to the presence of the surface ligands. Due to the symmetry of $Au_{30}Ag_{12}$, five possible reactive sites can be found as in Fig. S23a.[†] The O-H scission was considered, which had the largest Gibbs free energy change (ΔG ; Fig. S24[†]). Considering the computational cost, the electronic energy change of this step was used for screening the reactive sites (Fig. S23a⁺). Upon the adsorption of the CH_3CH_2OH on the surface of the $Au_{30}Ag_{12}$ cluster, the reaction initiated via the removal of the H atom from the -OH

group of the adsorbed CH3CH2OH molecule, which had 0.79 eV increment of ΔG (Fig. S24[†]). Then, the H atom from the α -C atom was removed with the decrease of ΔG to 0.36 eV, which led to the formation of the CH₃HC=O@cluster. Then, the H₂O molecule was added producing the CH3HC(OH)2@cluster, which further lowered ΔG to -0.01 eV. Next, H atom removal from one of the two –OH groups produced the CH₃HCO(OH) @cluster. Similar to the aforementioned step, the H of the α-C atom was removed finally leading to the CH₃COOH@cluster with the release of ΔG of 1.06 eV. After the desorption of CH₃-COOH from the Au₃₀Ag₁₂ cluster, the CH₃CH₂OH was oxidized to CH₃COOH. Considering the symmetry of the Au₄₇Ag₁₉ cluster, 17 possible reactive sites existed. As shown in Fig. S23b,[†] through calculating the electronic energy change of the removal of the H atom from the O-H group of the adsorptive CH₃CH₂OH, the reactive site with lower energy alternation was applied. Following the identical reaction steps of the Au₃₀Ag₁₂ cluster, the whole reaction path leading to CH₃COOH on Au₄₇Ag₁₉ can be obtained as depicted *via* the red line of Fig. S24.[†] The largest ΔG increment of the CH₃CH₂OH oxidation reaction was 0.52 eV, which was lower than that on $Au_{30}Ag_{12}$. This meant that the catalytic performance on Au₄₇Ag₁₉ was better, which agreed with the experimental results.

Conclusions

In summary, we report the synthesis mechanism and crystal structures of two intermetallic clusters protected by alkyne ligands: $Au_{30}Ag_{12}(C \equiv CR)_{24}$ exhibits a fantastic $Au_{18}Ag_8$ kernel that is fused by four interpenetrating $Au_{10}Ag_3$ icosahedra, while

Au₄₇Ag₁₉(C=CR)₃₂ exhibits a layered Au₁₉ core capped by a Au₁₂Ag₁₉ shell. Our investigation demonstrates that one stable icosahedron-based cluster transforming into another hcp-like cluster by simple reduction is feasible, which can enrich the library of metal clusters. We also demonstrate that the atompacking matching and cooperative effect of intermetallic compounds within the two different clusters play a pivotal role in tailoring the molecular exciton state and catalytic properties. We foresee that this work provides new design rules for atomically precise intermetallic nanomaterials.

Data availability

The data are provided in the ESI.†

Author contributions

Y. Z. conceived the work. S. T. prepared the clusters and solved their single-crystals. E. W. and Y. G. performed the calculations. Y. W. and M. Z. performed the TA measurement. T. S., X. C. and W. D. gave helpful suggestions. All authors interpreted the data and co-wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

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