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Introduction

Ultrasmall silver nanoparticles (e.g., few-atom clusters, <1 nm) represent the embryo states of larger silver nanoparticles (typically >2 nm) to some extent, which have defined molecular structures and compositions and thus can deepen the understanding on the size evolution of silver nanoparticles.¹ Given this, X-ray single crystal structures become a prerequisite to get atomic-level information including the surface ligands, inorganic-organic interfaces and silver atoms packed in silver nanoparticles.² While chasing large silver nanoclusters such as Ag14, Ag21, Ag23, Ag44, Ag₅₀, Ag₆₂, Ag₆₇, Ag₇₄, and Ag₁₄₁ and even the largest known Ag₃₇₄,³ chemists almost neglect the significance of the embryo states of silver nanoparticles that however are quite difficult to be captured due to their typical kinetics-controlled growth course.4 Therefore, controlling the reductive transformation from Ag(1) to Ag^0 and then trapping the transient Ag aggregates into the thermodynamically stable crystalline product during the self-assembly is an urgent need and thus a major challenge.

Unusual fcc-structured Ag_{10} kernels trapped in Ag_{70} nanoclusters \dagger

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Controlled trapping atom-precise ultrasmall silver nanoparticles into silver nanoclusters is challenging; thus only limited progress has been made in this area. We are therefore inspired to isolate two novel silver nanoclusters, $Ag_{10}@Ag_{70}$ (SD/Ag80a and SD/Ag80b; SD = SunDi), where a novel fcc-structured Ag_{10} kernel built from two single-edge opened Ag_6 octahedra by sharing one edge is trapped. The bioctahedral Ag_{10} kernel is locked by a pair of $Mo_7O_{26}^{10-}$ anions to form an inner $Ag_{10}@(Mo_7O_{26})_2$ core which is further encapsulated by an outer Ag_{70} shell to form three-shell $Ag_{10}@(Mo_7O_{26})_2@Ag_{70}$ nanoclusters. Notably, the bioctahedral Ag_{10} kernel has not been observed in silver nanoclusters ever before, thus representing a new embryo state of silver nanoparticles. SD/Ag80a emits in the near infrared (NIR) region ($\lambda_{em} = 730$ nm) at low temperature. This work will deepen our understanding on the atomic-level growth of silver nanoparticles and complicated three-shell self-assembly involving polyoxometalate (POM) and two different silver nanoclusters.

Learning from the solvent-controlled synthesis of multipletwin decahedral and icosahedral silver nanoparticles with special favourable [111] facets,⁵ we found that DMF (*N*,*N*-dimethylformamide), compared to widely used NaBH₄, is a much more mild reductive agent which facilitates the formation of Ag₆ octahedral kernels during the slow reduction process as seen in Ag₃₄ and Ag₆₂ nanoclusters.⁶ Such Ag₆ octahedra can be seen as the smallest fragment cut from the unit cell of face-centered cubic (fcc) bulk silver metal, whereas other silver nanoclusters smaller than the most common icosahedral Ag₁₃ are still not directly observed in any reported silver nanoclusters.⁷ Thus, the species in the early evolution from discrete Ag atoms to the metallic state are still largely vague and the exploration of a suitable synthesis strategy to trap them is scientifically desired.

With these considerations in mind, we used a DMFcontaining mixed solvent system to isolate two novel silver nanoclusters [Ag10@(MO7O26)2@Ag70(MOO4)2(CyhS)36(CF3SO3)16- $(DMF)_6$] · 2DMF · 4ⁿPrOH (**SD/Ag80a**; SD = SunDi; CyhSH = cyclohexanethiol) and [Ag₁₀@(Mo₇O₂₆)₂@Ag₇₀(MoO₄)₂(ⁱPrS)₃₆- $(CF_3SO_3)_{16}(DMF)_6$ (SD/Ag80b). Two silver nanoclusters have the same metallic core but different organic coatings. In the innermost of cluster, an unusual fcc-structured Ag10 nanocluster constructed from two single-edge opened Ag₆ octahedra by sharing one edge is locked by a pair of $Mo_7O_{26}{}^{10-}$ anions to form an inner Ag10@(MO7O26)2 core which acts as a template to support the outer Ag₇₀ nanocluster to form a final three-shell Ag₁₀@(Mo₇-O₂₆)₂@Ag₇₀ nanocluster. This unprecedented bioctahedral Ag₁₀ nanocrystal can be deemed as a new nanofragment cut from fcc silver metal and represents a possible transient species in the growth of large silver nanoparticles.



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[†] Electronic supplementary information (ESI) available: IR, ¹³C NMR, CV, UV, EDS, PXRD and luminescence decay curve, and details of the data collection and structure refinements, and crystal data. CCDC 1850394 and 1850395 for **SD/Ag80a** and **SD/Ag80b**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8sc03396j

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Results and discussion

X-ray structures of SD/Ag80a and SD/Ag80b

SD/Ag80a and SD/Ag80b were synthesized through a facile onepot solvothermal reaction of silver-thiolate polymeric precursors, CF₃SO₃Ag and molybdates in different DMF-containing mixed solvent systems (Scheme 1). In spite of several attempts, we still couldn't isolate SD/Ag80a and SD/Ag80b using the same Mo sources. Their samples were collected as brownyellow and red crystals, respectively, after evaporation of solvents at room temperature for 1–2 weeks. Several synthetic parameters were optimized and are listed in Tables S1 and S2 (ESI)† for details. Details of the synthesis and some basic characterization are shown in the ESI.†

The molecular structures of **SD/Ag80a** and **SD/Ag80b** were revealed by single-crystal X-ray diffraction (SCXRD) analysis. They crystallize in monoclinic $P2_1/n$ and triclinic $P\overline{1}$ space groups, respectively. In each asymmetric unit only half of the corresponding clusters were resolved. Due to the structural similarities, only that of **SD/Ag80a** is described in detail here. The structural diagrams of **SD/Ag80b** are shown in Fig. S1.† Selected details of the data collection and structure refinements are listed in Table S3.†

SD/Ag80a is an elongated spheroid $(1.0 \times 1.4 \times 2.1 \text{ nm})$ that sits on the crystallographic inversion center (*i*). The Ag_{80} nanocluster is composed of a Ag₇₀ shell and a Ag₁₀ kernel. The Ag₇₀ shell is capped by 36 CyhS⁻, 16 CF₃SO₃⁻, 2 MoO₄²⁻ and 6 DMF (Fig. 1a and b). All cyclohexyl groups of 36 CyhS⁻ ligands show a unified chair configuration. Two different coordination modes (μ_3 and μ_4) are found in 36 CyhS⁻ ligands capped on the silver trigons or tetragons (Ag–S distances: 2.389(5)–2.722(5) Å). The 16 CF₃SO₃⁻ anions exhibit three different coordination fashions including $\mu_3 - \eta^1 : \eta^2 : \eta^0$, $\mu_3 - \eta^1 : \eta^1 : \eta^1$, and $\mu_2 - \eta^1 : \eta^1 : \eta^0$. Two MoO₄²⁻ anions (yellow tetrahedra in Fig. 1) adopt a μ_8 - η^2 : η^3 : η^3 mode to bind in the equatorial region of the Ag₇₀ shell. Six DMF molecules as terminal ligands finished the organic ligand coverage on the surface of the Ag₇₀ shell. Three different O donor ligands ($CF_3SO_3^-$, MOO_4^{2-} , and DMF) interact with Ag atoms with the bonding distances in the ranges of 2.406(15)-2.789(17), 2.251(11)-2.568(11) and 2.390(13)-2.458(14) Å, respectively. The Ag₇₀ shell was further consolidated by the argentophilic interaction⁸ ranging from 2.833(2) to 3.4394(16) Å. The surface of the Ag₇₀ shell consists silver trigons, tetragons, pentagons and heptagons (Fig. 1c). The silver trigons, tetragons,

Na₂MoO₄·2H₂O

R=Cyh

 $[(^{n}Bu_{4}N)_{2}Mo_{6}O_{19}]$

R=ⁱPr

SD/Ag80a

SD/Ag80b

Scheme 1 Synthetic routes for SD/Ag80a and SD/Ag80b.

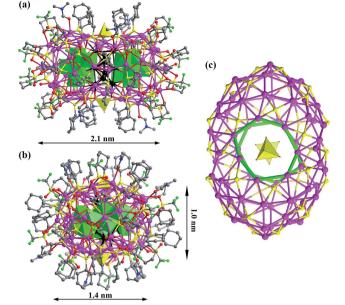


Fig. 1 (a) and (b) The X-ray crystal structure of $Ag_{10}@(Mo_7O_{26})_2@Ag_{70}$ nanoclusters viewed along two orthogonal directions. The inner silver atoms of the Ag_{10} kernel are highlighted in black. $Mo_7O_{26}^{10-}$ and MoO_4^{2-} are represented by green and yellow polyhedra, respectively. (c) The $Ag_{70}S_{36}$ shell with silver heptagons highlighted in green.

and pentagons are capped by $CyhS^-$ or $CF_3SO_3^-$, whereas MoO_4^{2-} shapes the large silver heptagons (green rings in Fig. 1c).

There are two crescent-like Mo₇O₂₆^{10–} anions under the Ag₇₀ shell (Fig. 2a). During the synthesis of SD/Ag80a and SD/Ag80b, although different Mo sources, Na₂MoO₄·2H₂O and [(ⁿBu₄N)₂- Mo_6O_{19} , were used, respectively, the same $Mo_7O_{26}^{10-}$ anion was trapped as the template in the final silver nanoclusters. Thus, the novel $Mo_7O_{26}^{10-}$ anions should be *in situ* transformed from $Na_2MoO_4 \cdot 2H_2O$ or $[(^nBu_4N)_2(MO_6O_{19})]$ in different solvent environments. We used Bond-Valence Sum (BVS) calculations for seven Mo atoms of Mo₇O₂₆¹⁰⁻, which confirmed that all of them are in the +6 oxidation state (Table S5⁺).⁹ The $Mo_7O_{26}^{10-}$ is constructed from seven edge-shared MoO₆ octahedra. The total 26 O atoms are divided into four kinds based on their binding fashion to Ag atoms, 2 μ_0 , 4 μ_1 , 16 μ_2 , and 4 μ_3 . Such highly negative-charged $Mo_7O_{26}^{10-}$ totally binds 35 silver atoms. Among them, 7 are from the inner Ag_{10} kernel and the remaining 28 are from the Ag₇₀ shell (Fig. 2b). Notably, this novel molybdate has neither been observed in classic POM chemistry nor in silver nanoclusters. More importantly, this molybdate carries the second highest negative charges¹⁰ which effectively enhanced its template effect by binding more Ag atoms (Table S6†).

The most interesting feature in **SD**/**Ag80a** is the unusual Ag₁₀ kernel underlying the equatorial region of the Ag₇₀ shell which is built from two single-edge opened Ag₆ octahedra by sharing one edge (Fig. 2c). The shared edge is the longest Ag…Ag edge (Ag38…Ag38^{*i*} = 3.457(1) Å, symmetry code *i*: -x + 1, -y + 1, -z + 1) within the Ag₁₀ kernel, which is out of the normal Ag… Ag interaction range. All other eleven Ag…Ag edges are

65 °C

[RSAg]_n

CF₃SO₃Ag

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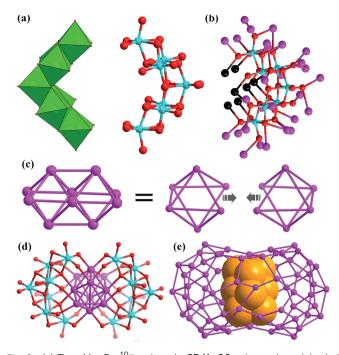


Fig. 2 (a) Two $Mo_7O_{26}^{10-}$ anions in **SD/Ag80a** shown in polyhedral (left) and ball-and-stick modes (right). (b) Binding fashion of $Mo_7O_{26}^{10-}$ toward 35 Ag atoms (black: Ag from the Ag₁₀ kernel; purple: Ag from the Ag₇₀ shell). (c) Animation showing the formation of a Ag₁₀ bioctahedron from two single-edge opened Ag₆ octahedra by fusing one Ag–Ag edge. (d) The Ag₁₀ bioctahedron locked by a pair of $Mo_7O_{26}^{10-}$ anions. (e) The Ag₁₀ bioctahedron (claybank space-filling balls) residing in the Ag₇₀ shell.

distributed in the range of 2.659(2)–2.980(1) Å (Fig. S2†) and the average Ag…Ag distance is 2.814 Å, which is 2.5% shorter than the Ag…Ag distance in metallic silver (2.886 Å),¹¹ indicating strong argentophilic interactions as in bulk silver metal. All exposed trigons of the Ag₁₀ bioctahedral kernel are [111] facets which are capped by Mo₇O₂₆^{10–} anions through Ag–O bonding (Ag–O distances: 2.284(10)–2.433(10) Å; Fig. 2d). As such, the Ag₁₀ bioctahedron is doubly clamped by a pair of Mo₇O₂₆^{10–} anions to form an inner Ag₁₀@(Mo₇O₂₆)₂ core, which was enwrapped by an outer Ag₇₀ shell to form a three-shell Ag₁₀@(Mo₇O₂₆)₂@Ag₇₀ nanocluster. The two polar sites of the Ag₁₀ bioctahedron are also linked with the outer Ag₇₀ shell through argentophilic interactions (Ag…Ag: 2.8523(19)–3.3621(18) Å; Fig. S3†).

Although the single Ag_6 octahedron has been observed in several inorganic compounds¹² and a few silver nanoclusters,¹³ its dimer, Ag_{10} bioctahedron, has never been observed before in silver nanoclusters. Such a Ag_{10} bioctahedron can be seen as a bigger nanofragment than a Ag_6 octahedron. An important driven force for its formation should be the suitable reducibility of DMF.⁶ The oxidation product of DMF in the assembly process is Me_2NCOOH^{14} which can be recognized from the ¹³C NMR (nuclear magnetic resonance) of HCl digested reaction mother solution (Fig. S4†). In the chemical shift scale corresponding to aldehydes and carboxylates ($\delta = 150$ –200 ppm), two peaks appeared at $\delta = 164.64$ and 162.92 ppm, which are assigned to the carbon resonances of DMF and Me₂NCOOH, respectively. We didn't observe any peaks in ¹³C NMR corresponding to the oxidation product of ⁿPrOH, which clearly excluded the possible reductive effect of "PrOH in this assembly system. These results clearly evidenced the redox reaction between Ag(1) and DMF occurred during the self-assembly process. The emergence of a fcc-structured Ag₁₀ nanocluster, on the other hand, answered an important question, which is how the common observed smaller Ag₆ kernel grew up to larger structures. Based on the above structural information, we can tentatively assign a new edge-fusion mode to its growth mechanism, although several other growth modes for noble metal nanoparticles have been proposed such as face-fusion, interpenetration, shell-by-shell, layer-by-layer, and tetrahedron-based vertex-sharing growth modes.2 Based on the formulae and charge neutrality considerations, we can determine that the valence of the Ag₁₀ kernel is +6, which means such a kernel carries four free electrons, belonging to a 4e superatom network. We also performed DFT calculations at the B3LYP/SDD theoretical level to study the free electron distributions on the frontier orbitals of the Ag₁₀ kernel (see details in the ESI[†]). According to the results identified experimentally, the inner Ag_{10} kernel features C_i symmetry with +6 valence and four free electrons. Thus, frontier molecular orbital analysis (Fig. S5[†]) reveals that four free electrons occupy two Au-symmetry HOMO-1 and HOMO. HOMO-1 and HOMO exhibit different components. HOMO involves in the 5s orbitals of two ends of Ag₁₀, while HOMO-1 concentrates on the 4d orbitals of two ends of Ag₁₀. Moreover, HOMO-2 features Ag symmetry with similar components to HOMO-1, and LUMO consists of 5s orbitals in the centre of Ag₁₀.

Combining the structural analysis and DMF-involved reductive process, we tentatively proposed a total shell-by-shell formation mechanism for such new silver nanoclusters. Weakly reductive DMF firstly induced the formation of an inner Ag₁₀ kernel (1st shell), which exposes highly active [111] facets that are quickly passivated by the formation of Ag–O interaction with $Mo_7O_{26}^{10-}$ (2nd shell). The inner $[Ag_{10}@(Mo_7O_{26})_2]$ core acts as the authentic template to support an outer Ag₇₀ shell, forming the final core–shell type silver nanoclusters. Such a formation route resembled the mechanism revealed in the $[Ag_6@(MoO_4)_7@Ag_{56}]$ family by electrospray ionization mass spectrometry.^{6b}

We also noted that the Au_{21} (S-Adm)₁₅ nanocluster has been reported by the Zhu group,¹⁵ who firstly found the bioctahedral Au_{10} kernel formed by edge-sharing of two single-edge opened Au_6 octahedra. However, the shared edge is not the longest one (opened edge) and the overall Au_6 octahedral framework is severely disordered. Anyhow, as a counterpart of this Au_{10} kernel, the bioctahedral Ag_{10} kernel has not been reported before in silver nanoclusters.

The optical properties of SD/Ag80a

The UV/Vis spectrum of **SD/Ag80a** was measured in the solid state using diffuse reflectance mode. As shown in Fig. 3, **SD/Ag80a** showed an absorption maximum at 344 nm and a shoulder peak in the visible region (~490 nm), which should be ascribed to ligand-based absorption and the charge transfer

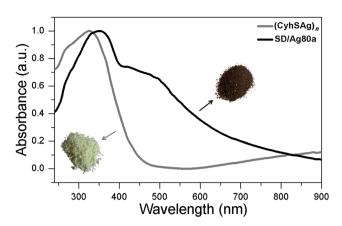


Fig. 3 Optical absorption spectra of SD/Ag80a and the silver-thiolate precursor. Insets are photographs of solid samples of SD/Ag80a (brown microcrystals) and the polymeric precursor $(CyhSAg)_n$ (pale yellow powder).

transition from the S 3p to Ag 5s orbitals, respectively. Similar assignments were also made in a hypothetical silver sulfide monomer and molecular $[Ag_{62}S_{13}(SBu^t)_{32}]^{4+}$ cluster.¹⁶ Based on the Kubelka–Munk function (Fig. S6†), the band gap of **SD**/**Ag80a** was estimated to be ~1.06 eV, which indicates that **SD**/**Ag80a** is a potential narrow-band-gap semiconductor. In comparison, the optical energy gap of the precursor (CyhSAg)_n is ~2.09 eV.

The luminescence properties of **SD/Ag80a** were studied in the solid state. As shown in the insets of Fig. 4, we can observe that **SD/Ag80a** isn't emissive under the UV light irradiation (λ_{ex} = 365 nm) at room temperature; however, it emits red luminescence at 77 K. The varied-temperature emission spectra of **SD/Ag80a** in the solid state were recorded from 293 to 83 K with 30 K as an interval, showing luminescence thermochromic behavior. When gradually cooled to 83 K, the intensity of emission shows an 18-fold enhancement, which should be assigned to the low-temperature induced increase of radiative decay. The emission maximum was blue-shifted from 754 to

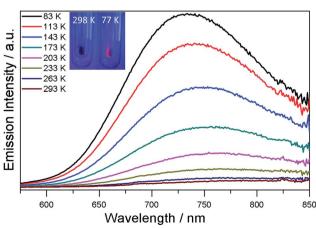


Fig. 4 Varied-temperature luminescence spectra of SD/Ag80a from 293–83 K in the solid state. Insets show the photographs of the sample SD/Ag80a under a hand-held UV lamp (365 nm) at 298 and 77 K.

730 nm (λ_{ex} = 469 nm) in the temperature range of 173–83 K (Fig. 4), which may be related to the enhanced molecular rigidity at lower temperature.¹⁷ This near-infrared (NIR) emission should be assigned to ligand-to-metal-charge-transfer (LMCT) transition from S 3p to Ag 5s orbitals.¹⁸ The emission lifetime of **SD/Ag80a**, falling on the microsecond scale at 83 K (Fig. S7†), suggests the triplet phosphorescence origin.

Conclusions

In conclusion, we developed a DMF-controlled strategy to successfully capture an atom-precise ultrasmall Ag10 kernel into a gigantic silver nanocluster. The DMF with mild reductive ability plays a key role in the formation of such a novel clusterin-cluster silver nanocluster. The fcc-structured Ag₁₀ kernel is built from two single-edge opened Ag₆ octahedra by sharing one edge and further locked by a pair of Mo₇O₂₆¹⁰⁻ anions to form an inner Ag_{10} (Mo₇O₂₆)₂ core which is finally encapsulated by an outer Ag₇₀ shell to form three-shell Ag₁₀@(Mo₇O₂₆)₂@Ag₇₀ nanoclusters. Notably, both the bioctahedral Ag₁₀ kernel and crescent-like Mo7O26¹⁰⁻ have not been observed in silver nanocluster and POM chemistry ever before, respectively. The bioctahedral Ag10 core can be deemed as a brand-new embryo state of silver nanoparticles; moreover, it also provides a new edge-fusion growth route for silver nanoparticles from the smallest Ag₆ nanofragment of metallic silver. We hope that this work can popularize the new controllable synthetic method to expand the scope of silver nanoclusters with higher complexity.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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