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Unusual fcc-structured Ag₁₀ kernels trapped in Ag₇₀ nanoclusters†

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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, Ag₁₀@Ag₇₀ (SD/Ag80a and SD/Ag80b; SD = SunDi), where a novel fcc-structured Ag₁₀ kernel built from two single-edge opened Ag₆ octahedra by sharing one edge is trapped. The bioctahedral Ag₁₀ kernel is locked by a pair of Mo₇O₂₆¹⁰⁻ anions to form an inner Ag₁₀@(Mo₇O₂₆)₂ core which is further encapsulated by an outer Ag₇₀ shell to form three-shell Ag₁₀@(Mo₇O₂₆)₂@Ag₇₀ nanoclusters. Notably, the bioctahedral Ag₁₀ 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 (λ_{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.

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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(I) to Ag⁰ 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.

Learning from the solvent-controlled synthesis of multiple-twin 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 DMF-containing 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·(CF₃SO₃)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 Mo₇O₂₆¹⁰⁻ 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@(Mo₇O₂₆)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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Results and discussion

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

SD/Ag80a and SD/Ag80b were synthesized through a facile one-pot solvothermal reaction of silver-thiolate polymeric precursors, $\text{CF}_3\text{SO}_3\text{Ag}$ 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 brown-yellow 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 $P\bar{1}$ 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 ($1.0 \times 1.4 \times 2.1$ nm) that sits on the crystallographic inversion center (i). The Ag_{80} nanocluster is composed of a Ag_{70} shell and a Ag_{10} kernel. The Ag_{70} shell is capped by 36 CyhS^- , 16 CF_3SO_3^- , 2 MoO_4^{2-} 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 CF_3SO_3^- anions exhibit three different coordination fashions including $\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^0$, $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1$, and $\mu_2\text{-}\eta^1\text{:}\eta^1\text{:}\eta^0$. Two MoO_4^{2-} anions (yellow tetrahedra in Fig. 1) adopt a $\mu_8\text{-}\eta^2\text{:}\eta^3\text{:}\eta^3$ mode to bind in the equatorial region of the Ag_{70} shell. Six DMF molecules as terminal ligands finished the organic ligand coverage on the surface of the Ag_{70} 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 Ag_{70} shell was further consolidated by the argentophilic interaction⁸ ranging from 2.833(2) to 3.4394(16) Å. The surface of the Ag_{70} shell consists silver trigons, tetragons, pentagons and heptagons (Fig. 1c). The silver trigons, tetragons,



Fig. 1 (a) and (b) The X-ray crystal structure of $\text{Ag}_{10} @ (\text{Mo}_7\text{O}_{26})_2 @ \text{Ag}_{70}$ nanoclusters viewed along two orthogonal directions. The inner silver atoms of the Ag_{10} kernel are highlighted in black. $\text{Mo}_7\text{O}_{26}^{10-}$ and MoO_4^{2-} are represented by green and yellow polyhedra, respectively. (c) The $\text{Ag}_{70}\text{S}_{36}$ 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 $\text{Mo}_7\text{O}_{26}^{10-}$ anions under the Ag_{70} shell (Fig. 2a). During the synthesis of SD/Ag80a and SD/Ag80b, although different Mo sources, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and $[(^n\text{Bu}_4\text{N})_2\text{Mo}_6\text{O}_{19}]$, were used, respectively, the same $\text{Mo}_7\text{O}_{26}^{10-}$ anion was trapped as the template in the final silver nanoclusters. Thus, the novel $\text{Mo}_7\text{O}_{26}^{10-}$ anions should be *in situ* transformed from $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ or $[(^n\text{Bu}_4\text{N})_2(\text{Mo}_6\text{O}_{19})]$ in different solvent environments. We used Bond-Valence Sum (BVS) calculations for seven Mo atoms of $\text{Mo}_7\text{O}_{26}^{10-}$, which confirmed that all of them are in the +6 oxidation state (Table S5[†]).⁹ The $\text{Mo}_7\text{O}_{26}^{10-}$ is constructed from seven edge-shared MoO_6 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 $\text{Mo}_7\text{O}_{26}^{10-}$ totally binds 35 silver atoms. Among them, 7 are from the inner Ag_{10} kernel and the remaining 28 are from the Ag_{70} 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 Ag_{10} kernel underlying the equatorial region of the Ag_{70} shell which is built from two single-edge opened Ag_6 octahedra by sharing one edge (Fig. 2c). The shared edge is the longest $\text{Ag}\cdots\text{Ag}$ edge ($\text{Ag}38\cdots\text{Ag}38^i = 3.457(1)$ Å, symmetry code $i: -x + 1, -y + 1, -z + 1$) within the Ag_{10} kernel, which is out of the normal $\text{Ag}\cdots\text{Ag}$ interaction range. All other eleven $\text{Ag}\cdots\text{Ag}$ edges are



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





Fig. 2 (a) Two $\text{Mo}_7\text{O}_{26}^{10-}$ anions in *SD/Ag80a* shown in polyhedral (left) and ball-and-stick modes (right). (b) Binding fashion of $\text{Mo}_7\text{O}_{26}^{10-}$ toward 35 Ag atoms (black: Ag from the Ag_{10} kernel; purple: Ag from the Ag_{70} shell). (c) Animation showing the formation of a Ag_{10} bioctahedron from two single-edge opened Ag_6 octahedra by fusing one Ag–Ag edge. (d) The Ag_{10} bioctahedron locked by a pair of $\text{Mo}_7\text{O}_{26}^{10-}$ anions. (e) The Ag_{10} bioctahedron (claybank space-filling balls) residing in the Ag_{70} shell.

distributed in the range of 2.659(2)–2.980(1) Å (Fig. S2†) and the average $\text{Ag}\cdots\text{Ag}$ distance is 2.814 Å, which is 2.5% shorter than the $\text{Ag}\cdots\text{Ag}$ distance in metallic silver (2.886 Å),¹¹ indicating strong argentophilic interactions as in bulk silver metal. All exposed trigons of the Ag_{10} bioctahedral kernel are [111] facets which are capped by $\text{Mo}_7\text{O}_{26}^{10-}$ anions through Ag–O bonding (Ag–O distances: 2.284(10)–2.433(10) Å; Fig. 2d). As such, the Ag_{10} bioctahedron is doubly clamped by a pair of $\text{Mo}_7\text{O}_{26}^{10-}$ anions to form an inner $\text{Ag}_{10}@\text{(Mo}_7\text{O}_{26})_2$ core, which was enwrapped by an outer Ag_{70} shell to form a three-shell $\text{Ag}_{10}@\text{(Mo}_7\text{O}_{26})_2@\text{Ag}_{70}$ nanocluster. The two polar sites of the Ag_{10} bioctahedron are also linked with the outer Ag_{70} shell through argentophilic interactions ($\text{Ag}\cdots\text{Ag}$: 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 $\text{Me}_2\text{NCOOH}^{14}$ which can be recognized from the ^{13}C NMR (nuclear magnetic resonance) of HCl digested reaction mother solution (Fig. S4†). In the chemical shift scale corresponding to aldehydes and carboxylates ($\delta = 150\text{--}200$ ppm), two peaks appeared at $\delta = 164.64$ and 162.92 ppm, which are assigned to the carbon resonances of DMF and Me_2NCOOH , respectively.

We didn't observe any peaks in ^{13}C NMR corresponding to the oxidation product of $^n\text{PrOH}$, which clearly excluded the possible reductive effect of $^n\text{PrOH}$ in this assembly system. These results clearly evidenced the redox reaction between $\text{Ag}(\text{i})$ and DMF occurred during the self-assembly process. The emergence of a fcc-structured Ag_{10} nanocluster, on the other hand, answered an important question, which is how the common observed smaller Ag_6 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 Ag_{10} 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 Ag_{10} 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 A_u -symmetry HOMO-1 and HOMO. HOMO-1 and HOMO exhibit different components. HOMO involves in the 5s orbitals of two ends of Ag_{10} , while HOMO-1 concentrates on the 4d orbitals of two ends of Ag_{10} . Moreover, HOMO-2 features A_g symmetry with similar components to HOMO-1, and LUMO consists of 5s orbitals in the centre of Ag_{10} .

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 Ag_{10} kernel (1st shell), which exposes highly active [111] facets that are quickly passivated by the formation of Ag–O interaction with $\text{Mo}_7\text{O}_{26}^{10-}$ (2nd shell). The inner $[\text{Ag}_{10}@\text{(Mo}_7\text{O}_{26})_2]$ core acts as the authentic template to support an outer Ag_{70} shell, forming the final core–shell type silver nanoclusters. Such a formation route resembled the mechanism revealed in the $[\text{Ag}_6@\text{(MoO}_4)_7@\text{Ag}_{56}]$ family by electrospray ionization mass spectrometry.^{6b}

We also noted that the $\text{Au}_{21}(\text{S-Adm})_{15}$ 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



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