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## Unusual fcc-structured Ag<sub>10</sub> kernels trapped in Ag<sub>70</sub> 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, Ag<sub>10</sub>@Ag<sub>70</sub> (SD/Ag80a and SD/Ag80b; SD = SunDi), where a novel fcc-structured Ag<sub>10</sub> kernel built from two single-edge opened Ag<sub>6</sub> octahedra by sharing one edge is trapped. The bioctahedral Ag<sub>10</sub> kernel is locked by a pair of Mo<sub>7</sub>O<sub>26</sub><sup>10-</sup> anions to form an inner Ag<sub>10</sub>@(Mo<sub>7</sub>O<sub>26</sub>)<sub>2</sub> core which is further encapsulated by an outer Ag<sub>70</sub> shell to form three-shell Ag<sub>10</sub>@(Mo<sub>7</sub>O<sub>26</sub>)<sub>2</sub>@Ag<sub>70</sub> nanoclusters. Notably, the bioctahedral Ag<sub>10</sub> 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<sub>em</sub> = 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.<sup>1</sup> 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.<sup>2</sup> While chasing large silver nanoclusters such as Ag<sub>14</sub>, Ag<sub>21</sub>, Ag<sub>23</sub>, Ag<sub>44</sub>, Ag<sub>50</sub>, Ag<sub>62</sub>, Ag<sub>67</sub>, Ag<sub>74</sub>, and Ag<sub>141</sub> and even the largest known Ag<sub>374</sub>,<sup>3</sup> 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.<sup>4</sup> Therefore, controlling the reductive transformation from Ag(I) to Ag<sup>0</sup> 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,<sup>5</sup> we found that DMF (*N,N*-dimethylformamide), compared to widely used NaBH<sub>4</sub>, is a much more mild reductive agent which facilitates the formation of Ag<sub>6</sub> octahedral kernels during the slow reduction process as seen in Ag<sub>34</sub> and Ag<sub>62</sub> nanoclusters.<sup>6</sup> Such Ag<sub>6</sub> 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 Ag<sub>13</sub> are still not directly observed in any reported silver nanoclusters.<sup>7</sup> 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 [Ag<sub>10</sub>@(Mo<sub>7</sub>O<sub>26</sub>)<sub>2</sub>@Ag<sub>70</sub>(MoO<sub>4</sub>)<sub>2</sub>(CyhS)<sub>36</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>16</sub>·(DMF)<sub>6</sub>]·2DMF·4<sup>n</sup>PrOH (SD/Ag80a; SD = SunDi; CyhSH = cyclohexanethiol) and [Ag<sub>10</sub>@(Mo<sub>7</sub>O<sub>26</sub>)<sub>2</sub>@Ag<sub>70</sub>(MoO<sub>4</sub>)<sub>2</sub>(<sup>i</sup>PrS)<sub>36</sub>·(CF<sub>3</sub>SO<sub>3</sub>)<sub>16</sub>(DMF)<sub>6</sub>] (SD/Ag80b). Two silver nanoclusters have the same metallic core but different organic coatings. In the innermost of cluster, an unusual fcc-structured Ag<sub>10</sub> nanocluster constructed from two single-edge opened Ag<sub>6</sub> octahedra by sharing one edge is locked by a pair of Mo<sub>7</sub>O<sub>26</sub><sup>10-</sup> anions to form an inner Ag<sub>10</sub>@(Mo<sub>7</sub>O<sub>26</sub>)<sub>2</sub> core which acts as a template to support the outer Ag<sub>70</sub> nanocluster to form a final three-shell Ag<sub>10</sub>@(Mo<sub>7</sub>O<sub>26</sub>)<sub>2</sub>@Ag<sub>70</sub> nanocluster. This unprecedented bioctahedral Ag<sub>10</sub> 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, <sup>13</sup>C 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 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)<sup>†</sup> for details. Details of the synthesis and some basic characterization are shown in the ESI.<sup>†</sup>

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.<sup>†</sup> Selected details of the data collection and structure refinements are listed in Table S3.<sup>†</sup>

SD/Ag80a is an elongated spheroid ( $1.0 \times 1.4 \times 2.1$  nm) that sits on the crystallographic inversion center ( $i$ ). The  $\text{Ag}_{80}$  nanocluster is composed of a  $\text{Ag}_{70}$  shell and a  $\text{Ag}_{10}$  kernel. The  $\text{Ag}_{70}$  shell is capped by 36  $\text{CyhS}^-$ , 16  $\text{CF}_3\text{SO}_3^-$ , 2  $\text{MoO}_4^{2-}$  and 6 DMF (Fig. 1a and b). All cyclohexyl groups of 36  $\text{CyhS}^-$  ligands show a unified chair configuration. Two different coordination modes ( $\mu_3$  and  $\mu_4$ ) are found in 36  $\text{CyhS}^-$  ligands capped on the silver trigons or tetragons ( $\text{Ag-S}$  distances: 2.389(5)–2.722(5) Å). The 16  $\text{CF}_3\text{SO}_3^-$  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  $\text{MoO}_4^{2-}$  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  $\text{Ag}_{70}$  shell. Six DMF molecules as terminal ligands finished the organic ligand coverage on the surface of the  $\text{Ag}_{70}$  shell. Three different O donor ligands ( $\text{CF}_3\text{SO}_3^-$ ,  $\text{MoO}_4^{2-}$ , 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  $\text{Ag}_{70}$  shell was further consolidated by the argentophilic interaction<sup>8</sup> ranging from 2.833(2) to 3.4394(16) Å. The surface of the  $\text{Ag}_{70}$  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  $\text{Ag}_{10}$  kernel are highlighted in black.  $\text{Mo}_7\text{O}_{26}^{10-}$  and  $\text{MoO}_4^{2-}$  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  $\text{CyhS}^-$  or  $\text{CF}_3\text{SO}_3^-$ , whereas  $\text{MoO}_4^{2-}$  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  $\text{Ag}_{70}$  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<sup>†</sup>).<sup>9</sup> The  $\text{Mo}_7\text{O}_{26}^{10-}$  is constructed from seven edge-shared  $\text{MoO}_6$  octahedra. The total 26 O atoms are divided into four kinds based on their binding fashion to Ag atoms, 2  $\mu_0$ , 4  $\mu_1$ , 16  $\mu_2$ , and 4  $\mu_3$ . Such highly negative-charged  $\text{Mo}_7\text{O}_{26}^{10-}$  totally binds 35 silver atoms. Among them, 7 are from the inner  $\text{Ag}_{10}$  kernel and the remaining 28 are from the  $\text{Ag}_{70}$  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 charges<sup>10</sup> which effectively enhanced its template effect by binding more Ag atoms (Table S6<sup>†</sup>).

The most interesting feature in SD/Ag80a is the unusual  $\text{Ag}_{10}$  kernel underlying the equatorial region of the  $\text{Ag}_{70}$  shell which is built from two single-edge opened  $\text{Ag}_6$  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  $\text{Ag}_{10}$  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  $\text{Ag}_{10}$  kernel; purple: Ag from the  $\text{Ag}_{70}$  shell). (c) Animation showing the formation of a  $\text{Ag}_{10}$  bioctahedron from two single-edge opened  $\text{Ag}_6$  octahedra by fusing one Ag–Ag edge. (d) The  $\text{Ag}_{10}$  bioctahedron locked by a pair of  $\text{Mo}_7\text{O}_{26}^{10-}$  anions. (e) The  $\text{Ag}_{10}$  bioctahedron (claybank space-filling balls) residing in the  $\text{Ag}_{70}$  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),<sup>11</sup> indicating strong argentophilic interactions as in bulk silver metal. All exposed trigons of the  $\text{Ag}_{10}$  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  $\text{Ag}_{10}$  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  $\text{Ag}_{70}$  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  $\text{Ag}_{10}$  bioctahedron are also linked with the outer  $\text{Ag}_{70}$  shell through argentophilic interactions ( $\text{Ag}\cdots\text{Ag}$ : 2.8523(19)–3.3621(18) Å; Fig. S3†).

Although the single  $\text{Ag}_6$  octahedron has been observed in several inorganic compounds<sup>12</sup> and a few silver nanoclusters,<sup>13</sup> its dimer,  $\text{Ag}_{10}$  bioctahedron, has never been observed before in silver nanoclusters. Such a  $\text{Ag}_{10}$  bioctahedron can be seen as a bigger nanofragment than a  $\text{Ag}_6$  octahedron. An important driven force for its formation should be the suitable reducibility of DMF.<sup>6</sup> The oxidation product of DMF in the assembly process is  $\text{Me}_2\text{NCOOH}^{14}$  which can be recognized from the  $^{13}\text{C}$  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  $\text{Me}_2\text{NCOOH}$ , respectively.

We didn't observe any peaks in  $^{13}\text{C}$  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  $\text{Ag}_{10}$  nanocluster, on the other hand, answered an important question, which is how the common observed smaller  $\text{Ag}_6$  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.<sup>2</sup> Based on the formulae and charge neutrality considerations, we can determine that the valence of the  $\text{Ag}_{10}$  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  $\text{Ag}_{10}$  kernel (see details in the ESI†). According to the results identified experimentally, the inner  $\text{Ag}_{10}$  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  $\text{Ag}_{10}$ , while HOMO-1 concentrates on the 4d orbitals of two ends of  $\text{Ag}_{10}$ . Moreover, HOMO-2 features  $A_g$  symmetry with similar components to HOMO-1, and LUMO consists of 5s orbitals in the centre of  $\text{Ag}_{10}$ .

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  $\text{Ag}_{10}$  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  $\text{Ag}_{70}$  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.<sup>6b</sup>

We also noted that the  $\text{Au}_{21}(\text{S-Adm})_{15}$  nanocluster has been reported by the Zhu group,<sup>15</sup> who firstly found the bioctahedral  $\text{Au}_{10}$  kernel formed by edge-sharing of two single-edge opened  $\text{Au}_6$  octahedra. However, the shared edge is not the longest one (opened edge) and the overall  $\text{Au}_6$  octahedral framework is severely disordered. Anyhow, as a counterpart of this  $\text{Au}_{10}$  kernel, the bioctahedral  $\text{Ag}_{10}$  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 ( $\sim 490$  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)<sub>n</sub> (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<sub>62</sub>S<sub>13</sub>(SBU<sup>†</sup>)<sub>32</sub>]<sup>4+</sup> cluster.<sup>16</sup> Based on the Kubelka–Munk function (Fig. S6<sup>†</sup>), 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)<sub>n</sub> 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<sub>ex</sub> = 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<sub>ex</sub> = 469 nm) in the temperature range of 173–83 K (Fig. 4), which may be related to the enhanced molecular rigidity at lower temperature.<sup>17</sup> This near-infrared (NIR) emission should be assigned to ligand-to-metal-charge-transfer (LMCT) transition from S 3p to Ag 5s orbitals.<sup>18</sup> The emission lifetime of SD/Ag80a, falling on the microsecond scale at 83 K (Fig. S7<sup>†</sup>), suggests the triplet phosphorescence origin.

## Conclusions

In conclusion, we developed a DMF-controlled strategy to successfully capture an atom-precise ultrasmall Ag<sub>10</sub> kernel into a gigantic silver nanocluster. The DMF with mild reductive ability plays a key role in the formation of such a novel cluster-in-cluster silver nanocluster. The fcc-structured Ag<sub>10</sub> kernel is built from two single-edge opened Ag<sub>6</sub> octahedra by sharing one edge and further locked by a pair of Mo<sub>7</sub>O<sub>26</sub><sup>10-</sup> anions to form an inner Ag<sub>10</sub>@(Mo<sub>7</sub>O<sub>26</sub>)<sub>2</sub> core which is finally encapsulated by an outer Ag<sub>70</sub> shell to form three-shell Ag<sub>10</sub>@(Mo<sub>7</sub>O<sub>26</sub>)<sub>2</sub>@Ag<sub>70</sub> nanoclusters. Notably, both the bioctahedral Ag<sub>10</sub> kernel and crescent-like Mo<sub>7</sub>O<sub>26</sub><sup>10-</sup> have not been observed in silver nanocluster and POM chemistry ever before, respectively. The bioctahedral Ag<sub>10</sub> 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 Ag<sub>6</sub> 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.

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