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<https://doi.org/10.1038/s42004-018-0102-3>

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Catalyzed assembly of hollow silver-sulfide cluster through self-releasable anion template

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Hollow nanoclusters are intriguing for bridging the gap between small metal-organic cages and hollow nanoparticles and provide enormous opportunities for functional materials. Rational construction of hollow nanoclusters remains a challenge owing to the poor understanding of their formation pathways and difficulties in obtaining the intermediate structures. Here we report a catalyzed assembly strategy to construct hollow silver-sulfide clusters using a self-releasable carbonate template. The hollow Ag₅₆ cluster and the carbonate-templated Ag₃₃ intermediate are characterized by single-crystal X-ray analysis. Combining this data with a time-dependent UV-Vis spectroscopic investigation, we reveal the catalyst-like behavior of the self-releasable carbonate template and propose the corresponding mechanism. The assembly of hollow clusters using a self-releasable template may provide insight into understanding the formation mechanisms of other hollow nanoclusters and facilitate the design and construction of new hollow nanoclusters.

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Noble metal nanoclusters^{1–4} have experienced great advances in the past decade as an important bridge between smaller metal-organic coordination complexes^{5–7} and larger ligand capped nanoparticles^{8,9}, providing enormous opportunities on magnetism¹, catalysis^{4,10,11}, luminescent materials^{12–15}, biomedicine^{16,17}, and molecular sensing^{15,18}. As a prime example, thiolate-protected silver^{18–23}, gold^{3,12,24}, and the bimetallic nanoclusters^{25–27} have been studied extensively for understanding their size-dependent evolutions of structures and properties. Because atomically precise nanoclusters have the same monodisperse nature as small coordination molecules^{1,24}, they can be analyzed by single-crystal X-ray crystallography, revealing various sophisticated structures with many kinds of symmetries^{28–31}. Among these structures, hollow nanoclusters^{32–36} are particularly intriguing for bridging the gap between small supramolecular cages^{5–7} and hollow nanoparticles^{37,38}, which presents increased structural complexity and may bring more sophisticated functions. However, constructing hollow nanoclusters and precisely determining their structures remain great challenges^{39–42}, because of the lack of understanding of the formation pathway of nanoclusters^{28,43–45} and the inherent difficulties in getting high-quality single crystals of hollow structures⁴⁶. To understand the formation mechanism of hollow nanoclusters, it is crucial to track growth kinetics and obtain single-crystal structures of the intermediate clusters. Single crystals of intermediate clusters can be hard to obtain, and other characterization methods, such as advanced mass spectrometry, also could be used to monitor the growth mechanism of nanoclusters and to measure precise intermediate molecular formulas^{16,17}.

Here, we report a catalyzed assembly strategy to construct a hollow silver-sulfide cluster, $\text{Ag}_{56}\text{S}_{12}(\text{S}^t\text{Bu})_{20}(\text{Sal})_{12}$ (**1**, HS^tBu = *tert*-Butylthiol, $\text{H}(\text{Sal})$ = salicylic acid), using a self-releasable anion template. This hollow Ag_{56} cluster is synthesized from small precursors, whereas a carbonate-templated Ag_{33} nest-like intermediate is found during the growth of Ag_{56} cluster. Structures of Ag_{56} cluster and Ag_{33} intermediate are characterized by single-crystal X-ray analysis, and the growth kinetics are investigated by time-dependent ultraviolet (UV)–visible (Vis) spectroscopy, revealing the catalyst-like behavior of the self-releasable carbonate template.

Results

Structure of 1. Cluster **1** was synthesized by adding silver salicylate hydrate ($\text{Ag}(\text{Sal})\cdot\text{H}_2\text{O}$, 1.2 mmol) and AgS^tBu (4.5 mmol) into a mixture of acetonitrile, dichloromethane, and methanol ($v/v = 1:1:1$). The reaction proceeded at 80 °C for 5 days and was directly reflected by the color change from colorless to yellow and finally to orange. After reaction, orange crystals were obtained and analyzed by single-crystal XRD (Supplementary Table 1), revealing a neutral spherical $\text{Ag}_{56}\text{S}_{12}(\text{S}^t\text{Bu})_{20}(\text{Sal})_{12}$ structure of **1** (Fig. 1a and Supplementary Fig. 1). Cluster **1** have a core-shell structure containing a $[\text{Ag}_{14}\text{S}_{12}]$ core (Fig. 1b) and a $[\text{Ag}_{42}(\text{S}^t\text{Bu})_{20}(\text{Sal})_{12}]$ shell (Fig. 1c).

In the $[\text{Ag}_{14}\text{S}_{12}]$ core, 14 Ag^+ ions form a hollow rhombic dodecahedron, whereas 12 S^{2-} ions are located outside each face of Ag^+ rhombic dodecahedron to form an icosahedron. The rhombic dodecahedron@icosahedron geometry of the $[\text{Ag}_{14}\text{S}_{12}]$ core resembles the $[\text{Ag}_{14}(\text{C}\equiv\text{C}^t\text{Bu})_{12}\text{Cl}]$ and $[\text{Ag}_{14}\text{S}_{13}]$ cores in the reported clusters^{47–49}. However, all these previously reported clusters encapsulated a guest anion (Cl^- or S^{2-}) at the center of $[\text{Ag}_{14}]$ rhombic dodecahedron.

In the $[\text{Ag}_{42}(\text{S}^t\text{Bu})_{20}(\text{Sal})_{12}]$ shell, Ag^+ ions can be classified into two types: 18 Ag^+ ions that are only protected by thiolates, and the other 24 Ag^+ ions that are protected by both thiolate and salicylate ligands. The 20 S^tBu ligands form a dodecahedron and coordinate with Ag^+ in μ_3 and μ_4 bridge binding modes, with the $\text{Ag}-\text{S}$ bond lengths ranging from 2.419 to 2.944 Å. The 12 Sal ligands form an icosahedron and coordinate with Ag^+ in $\mu_2-\text{O}, \text{O}'$ binding mode, with $\text{Ag}-\text{O}$ bond lengths ranging from 2.257 to 2.357 Å. Therefore, cluster **1** can be resolved as five layers of polyhedral from inner to outer surface: the Ag_{14} rhombic dodecahedron, the S_{12} icosahedron, the spherical Ag_{42} polyhedron, the $(\text{S}^t\text{Bu})_{20}$ dodecahedron and the Sal_{12} icosahedron. All these polyhedra share a common S_6 symmetry axis, making the cluster achiral. In crystal, spherical clusters are packed in the $R\text{-}3c$ space group with the S_6 axis of the cluster in parallel to the c axis of the unit cell. The diameter of the spherical **1** approximately equals the lattice parameter a (27.1 Å), and the volume of one cluster is 10,436 Å³.

Structure of 2. During the synthesis of **1**, we observed an obvious color change from colorless to yellow and finally to orange (Supplementary Fig. 2). Therefore, we speculated that the synthetic pathway of **1** could go through an intermediate stage with the formation of a smaller yellow cluster. By carefully crystallizing the reaction solution at intermediate stage, we obtained a small amount of yellow hexagonal crystals of $\text{CO}_3\text{Ag}_{33}\text{S}_3(\text{S}^t\text{Bu})_{16}(\text{Sal})_9$ (**2**) concomitantly with orange rhombic crystals of **1**. Cluster **2** has a nest-like structure having a C_{3v} -symmetry (Fig. 2 and Supplementary Fig. 3), crystallized in a $P\text{-}3m1$ unit cell. The nest-like structure of **2** is similar to the reported NO_3^- -templated Ag_{33} cluster¹³. However due to the charge difference between CO_3^{2-} and NO_3^- , cluster **2** is neutral without any counter-anion outside the cluster. The 33 Ag^+ ions in **2** can be identified as two layers: the inner layer contains 9 Ag^+ ions (green in Fig. 2), holding the center CO_3^{2-} anion; and the

Fig. 1 Structure of **1**. **a** Molecular structure of **1**, $\text{Ag}_{56}\text{S}_{12}(\text{S}^t\text{Bu})_{20}(\text{Sal})_{12}$. **b** Hollow $[\text{Ag}_{14}\text{S}_{12}]$ core of **1**. **c** Quasi-fivefold symmetric $[\text{Ag}_{42}(\text{S}^t\text{Bu})_{20}(\text{Sal})_{12}]$ shell of **1**. The $[\text{Ag}_{14}\text{S}_{12}]$ core and hydrogen atoms have been omitted for clarity in **c** and the artificial large green sphere shows the inner space occupied by hollow $[\text{Ag}_{14}\text{S}_{12}]$ core. Color legend: green, Ag (core); magenta, Ag (shell); orange, S^{2-} ; yellow, S (thiolate); gray, C; red, O

Fig. 2 Structure of **2**. **a** Threefold symmetric structure of **2**, $\text{CO}_3\text{Ag}_{33}\text{S}_3(\text{S}^t\text{Bu})_{16}(\text{Sal})_9$. **b** Main structure of **2**, the *tert*-butyl groups and salicylate groups have been omitted for clarity. **c** Side view of carbonate chemical environment in the nest-like intermediate **2**. Color legend: green, Ag (inner); magenta, Ag (outer); orange, S^{2-} ; yellow, S (thiolate); gray, C; red, O

outer layer contains 24 Ag^+ ions (magenta in Fig. 2), which are connected to the inner layer by three S^{2-} ions (orange in Fig. 2) and six S^tBu ligands (yellow in Fig. 2). The Ag–O bond-length between the center CO_3^{2-} anion and the Ag^+ inner layer was measured as 2.7 Å, which is longer than the 2.3 Å Ag–O bond in Ag_2CO_3 ⁵⁰, suggesting the relatively weaker interaction between the central CO_3^{2-} anion and the Ag^+ inner layer. It was surprising that this intermediate **2** contains a CO_3^{2-} anion template, as no CO_3^{2-} species was intentionally added into the reaction. We speculated that the CO_3^{2-} was introduced from the atmospheric carbon dioxide fixation^{51,52}. To confirm the reaction pathway and understand the reaction kinetics, we added a small amount of Ag_2CO_3 (4% molar ratio to AgS^tBu) into the previously described reaction for synthesizing **1**. Two parallel reactions with and without Ag_2CO_3 were investigated by time-dependent UV–Vis spectroscopy.

Kinetics study. The UV–Vis spectra of the clusters (Fig. 3a) corroborate the observed color change from yellow **2** to orange **1**. Compared to the solution of reactants, the smaller **2** shows a peak of absorbance increase at 370 nm, whereas larger **1** shows a wide

Fig. 3 UV–Vis spectra for reaction monitoring. **a** UV–Vis spectra of the solution of precursors and the products, **1** and **2**. **b** Increased absorbance of **1** and **2** over the precursors. **c** Time-dependent UV–Vis spectra. **d** Increased absorbance of the reaction solution for synthesizing **1** without adding Ag_2CO_3 . **e** Increased absorbance of the reaction solution for synthesizing **1** with adding 4% amount of Ag_2CO_3 , and **f** Increased absorbance at 330 nm (solid lines) and 370 nm (dash lines) upon time for two parallel reaction solutions with or without adding 4% amount of Ag_2CO_3

Fig. 4 Proposed reaction mechanism. **a** Schematic for constructing hollow cluster **1** through the repeatedly assistance of self-releasable CO₃²⁻ template. **b** Proposed mechanism for the recovery and recycle of CO₃²⁻ template during the formation of **1** and **2**

increase in UV–Vis absorption from 300 to 550 nm (Fig. 3b). Two parallel reactions with and without Ag₂CO₃ were monitored by UV–Vis spectroscopy at 1 h time intervals. As shown in Fig. 3c, the UV–Vis spectra of the reaction solution without Ag₂CO₃ increased obviously upon reaction time. By comparing with the initial spectrum, we derived differential spectra for different reaction time (Fig. 3d), showing an increasing peak at 370 nm in the first 4 h, which corresponds to the formation of **2**. After 5 h, the differential spectra get broader from 300 to 550 nm with a new increasing peak at 330 nm, corresponding to the formation of **2**. For the reaction assisted by Ag₂CO₃, a similar absorption increase was observed by spectroscopy (Fig. 3e and Supplementary Fig. 4), yet with a higher increasing rate upon reaction time. As shown in Fig. 3f, it took approximately 5 h for UV–Vis spectra to increase for 0.08 at 330 nm without introducing Ag₂CO₃, however, accelerated by 4% amount of Ag₂CO₃, it took only 2 h to achieve the similar increase. In fact, the acceleration caused by Ag₂CO₃ could even be reflected by the considerable difference in the rate of color change observed by bare eyes, as shown in Supplementary Fig. 2.

Combining structural analyses and kinetics investigation, we can conclude that the CO₃²⁻ anion acts as a self-releasable template and accelerates the formation process of **1** in a way similar to a catalyst, which is essentially different from the conventional templates that cannot be removed or can only be removed by extra post-synthesis methods^{53–56}. Since the formation processes of supramolecular clusters are usually referred to molecular assembly^{22,28,31}, which mainly involve reversible coordination bonding⁵⁷, we prefer to classify the as-described process in this work as a catalyzed assembly (catassembly) process⁵⁸. The turn over number (TON) is calculated by measuring the amount of **1** over Ag₂CO₃ as 4.8. Catassembly

pathway for forming **1** contains three steps as shown in Fig. 4a, and the proposed mechanism of each step is shown in Fig. 4b.

Compared to *tert*-butyl thiolate and salicylate, CO₃²⁻ has a smaller size and higher negative charge, thus enriching a higher local concentration of Ag⁺ ion for the nucleation of **2**. The chemical equation to form **2** can be derived as Eq. (1).

As shown in Fig. 4b, proton is generated along with the formation of **2**. During the growth from **2** to **1**, the local concentration of proton is further accumulated. As indicated by the single-crystal X-ray analysis, the interaction between the CO₃²⁻ template and the nest structure of **2** is relatively weak. Thus, the CO₃²⁻ template is removed from the nest and becomes free H₂CO₃ when the local proton concentration gets higher during the cluster growth. The free H₂CO₃ further defuses and reacts with AgS^tBu to generate Ag₂CO₃ again. The chemical equation from **2** to **1** can be derived as Eq. (2).

The side products in Eqs. (1) and (2), i.e., HS^tBu and MeO^tBu, were confirmed by the capillary gas chromatography and mass spectrometry analyses of the reaction solution and also the gas phase in the reaction vial (Supplementary Fig. 5). Moreover, if extra Ag₂CO₃ (e.g., 18% molar ratio to AgS^tBu) was introduced into the initial reactants, it would impede the release of CO₃²⁻ from **2** and stop the further growth into **1**. As a result, with adding 18% amount of Ag₂CO₃, the main product of the reaction would become **2**, corroborating the proposed mechanism in Fig. 4b.

Discussion

We have constructed a hollow silver-sulfide cluster with a cat-assembly strategy. Through carefully tracking and analyzing the growth process, we found a carbonate-templated nest-like intermediate, which accelerated the cluster growth in a similar way as catalyst accelerates a chemical reaction. The method to assemble hollow cluster through self-releasable template provides insights into understanding the formation mechanism of other hollow nanoclusters and may facilitate the design and construction of new hollow nanoclusters with various properties.

Methods

Chemicals and materials. Silver oxide (Ag₂O), ammonia (NH₃·H₂O), sodium hydroxide (NaOH), trimethylamine (Et₃N), methanol (MeOH), acetonitrile (MeCN), dichloromethane (DCM), chloroform (CHCl₃), and diethyl ether (Et₂O) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). 2-methylpropane-2-thiol (HS^tBu) was purchased from J&K Chemicals. Silver carbonate (Ag₂CO₃) was purchased from Adamas-Beta, Silver salicylate hydrate (AgC₇H₅O₃·H₂O) was purchased from Alfa-Aesar. AgS^tBu was prepared from the reaction of Ag₂O, HS^tBu in NH₃·H₂O in an ice bath, and further washed in turn with H₂O, MeOH, MeCN, and Et₂O. Other reagents and solvents used without further purification.

Synthesis of Ag₅₆S₁₂(SC₄H₉)₂₀(O₃H₅C₇)₁₂ (1**).** Mixed acetonitrile, dichloromethane and methanol (1:1:1, 75 mL) was added 3.7 mg Ag₂CO₃, 306.1 mg AgC₇H₅O₃·H₂O, and 892.2 mg AgS^tBu. Under ultrasound condition, a white suspension was formed and further refluxed under nitrogen at 80 °C with a balloon for 5 days. The reaction solution changed from colorless to yellow and finally to orange, after cooled to room temperature, orange-red solution and orange solids were obtained. The solution was further concentrated by evaporation to generate more orange solids. Orange solids were collected, and then washed with diethyl

ester (50 mL, twice) and dissolved in 30 mL dichloromethane. To this dichloromethane solution, mixed acetonitrile and methanol (1:1, 15 mL) was added to give the orange powder of **1** (633.2 mg, yield 89.7% based on $\text{AgC}_7\text{H}_5\text{O}_3\cdot\text{H}_2\text{O}$). Anal. Calcd. for **1**: $\text{Ag}_{56}\text{S}_{12}(\text{SC}_6\text{H}_5)_{20}(\text{O}_3\text{H}_5\text{C}_7)_{12}$: C, 19.989; H, 2.455. Found: C, 20.279; H, 2.367. IR spectrum of **1** is shown in Supplementary Fig. 6a.

Synthesis of $(\text{CO}_3)\text{Ag}_{33}\text{S}_3(\text{SC}_6\text{H}_5)_{16}(\text{O}_3\text{H}_5\text{C}_7)_9$ (2**).** Mixed acetonitrile and methanol (1:1, 9 mL) was added 25.6 mg Ag_2CO_3 , 102.8 mg $\text{AgC}_7\text{H}_5\text{O}_3\cdot\text{H}_2\text{O}$, and 137.9 mg AgS^tBu . Under ultrasound condition, a white suspension was formed and further refluxed under nitrogen at 80 °C for 7 h. To the cooled reaction solution was added 10 mL diethyl ether, after filtered, the yellow filtrate was dried and gave yellow powder of **2** (194.2 mg, yield 91.6% based on AgS^tBu). Anal. Calcd. for **2**: $(\text{CO}_3)\text{Ag}_{33}\text{S}_3(\text{SC}_6\text{H}_5)_{16}(\text{O}_3\text{H}_5\text{C}_7)_9(\text{CH}_3\text{CN})_3(\text{H}_2\text{O})_9$: C, 24.158; H, 3.268; N, 0.631. Found: C, 23.929; H, 3.064; N, 0.631. IR spectrum of **2** is shown in Supplementary Fig. 6b.

Kinetic measurements for the reaction accelerated by Ag_2CO_3 . In a 20 mL headspace bottle, mixed acetonitrile and methanol (1:1, 5 mL) was added into 2.9 mg Ag_2CO_3 , 40.3 mg $\text{AgC}_7\text{H}_5\text{O}_3\cdot\text{H}_2\text{O}$ and 109.2 mg AgS^tBu . Under ultrasound condition, a white suspension was formed. Then 10 mL chloroform was added, the suspension dissolved and gave a colorless transparent solution. The reaction vial was tightly sealed and stirred in an oil bath at 80 °C. At 1 h time intervals, the reaction solution (50 μL) were drawn out and injected into 5.00 mL chloroform. The diluted solutions were immediately refrigerated in a refrigerator at 4 °C for the latter UV-Vis characterizations. The spectra of refrigerated solutions did not change after being kept in liquid nitrogen for more than 24 h.

Kinetic measurements for the reaction without adding Ag_2CO_3 . In a 20 mL headspace bottle, mixed acetonitrile and methanol (1:1, 5 mL) was added into 40.3 mg $\text{AgC}_7\text{H}_5\text{O}_3\cdot\text{H}_2\text{O}$ and 110.4 mg AgS^tBu . Following treatment was exactly the same as the above reaction accelerated by Ag_2CO_3 .

General characterization. UV-Vis absorption spectra were collected on an Agilent Cary 5000. Fourier-transform infrared spectroscopy (FT-IR) spectra were collected from KBr pellets in the range of 4000–400 cm^{-1} with a Nicolet AVATAR FT-IR 380 spectrometer. Nuclear magnetic resonance (NMR) data were collected on a Bruker Avance II spectrometer (600 MHz). GC-MS analyses were performed on Shimadzu GC-2010 MS with a capillary column (Rtx-5MS). X-ray crystallography is detailed in Supplementary Note 1 and Supplementary Data 1.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request. The X-ray crystallographic coordinates for structures reported in this Article have been deposited at the Cambridge Crystallographic Data Center (CCDC), under deposition number CCDC 1825401 and 1825402. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/data_request/cif. All other data associated with this study are available from the authors upon reasonable request.

Received: 13 June 2018 Accepted: 27 November 2018

Published online: 21 December 2018

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Acknowledgements

We thank Mr. Kuang-Yu Wang at Peking University for assistance in experiments. This work was supported by National Natural Science Foundation of China (21473139, 21631007, 91227111, and 91427304).

Author contributions

Q.W. and Z.T. supported and guided the whole experiment. Y.W. drafted the manuscript. Z.N. proposed the research direction, conducted the synthesis and characterization of the clusters. Z.C. gave some advice for the kinetics study and S.Y. picked the single crystals of the clusters.

Additional information

Supplementary information accompanies this paper at <https://doi.org/10.1038/s42004-018-0102-3>.

Competing interests: The authors declare no competing interests.

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