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photoluminescence†

Silver nanoclusters: synthesis, structures and

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Metal nanoclusters (NCs) consist of tens to hundreds of metal atoms with a diameter of <2 nm, and have attracted significant attention due to their unique molecule-like properties, such as well-defined molecular structures, explicit HOMO-LUMO transitions, quantized charge and strong luminescence emission. Various robust synthetic protocols have been successfully applied to the preparation of metal NCs. Among metal NCs, Au NCs stay at the frontline of this research, and more structural characteristics, particular optical, catalytic and electronic properties, and related technical applications of Au NCs have been discovered in recent years. By taking guidelines from Au NC research, Ag NCs have recently received increasing attention. In this review article, we first survey recent advances in developing efficient synthetic methods for Ag NCs, highlighting the underlying physical and chemical properties that make the delicate control of their sizes and surfaces possible. In the following section, we discuss recent advances in the structural determination of Aq NCs, such as Aq₂₅(2,4-DMBT)₁₈ (2,4-DMBT: 2,4-dimethylbenzenethiolate), Ag₂₉(1,3-BDT)₁₂ (1,3-BDT: 1,3-benzenedithiolate), and Ag₄₄(SR)₃₀ (R = PhCO₂H₂, PhF, PhF₂ or PhCF₃). Structural determination will help to gain deep insight into the structure-property relationships at the molecular level. In the last part, we highlight some examples of Ag NCs to demonstrate their photoluminescence properties, which offer potential applications as photodetectors and in sensing and bio-imaging. We give a brief outlook on the future development of Ag NCs from the viewpoint of synthesis and applications.

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1. Introduction

Atomically precise metal nanoclusters (NCs) are ultrasmall particles with core sizes below 2 nm, and they are in between the atomic regime and plasmonic metal nanoparticles. 1-7 Such metal NCs exhibit dramatically unique electronic and optical properties, such as molecule-like energy gaps, strong photoluminescence (PL) and high catalytic properties. 8-15 Among metal NCs, noble metal NCs have drawn tremendous attention from the scientific community because of their unique structures and correlation with versatile applications.³⁻⁷ A number of magic size Au and Ag NCs with precise formulas such as $Au_{25}(SCH_2CH_2Ph)_{18}$, $^{16-18}$ $Au_{38}(SCH_2CH_2Ph)_{24}$, $^{19-21}$ and Au_{102} $(SPhCO_2H_2)_{44}^{22}$ as well as $Ag_{25}(2,4-DMBT)_{18}^{23}$ $Ag_{29}(1,3-BDT)_{12}^{24}$ and $Ag_{44}(SR)_{30}$ (R = PhCO₂H₂, PhF, PhF₂ or PhCF₃)^{25,26} are known.

Organic ligands such as thiolates, phosphines, and alkynyls are usually used to cap the surface in order to prevent aggregation and to facilitate the isolation of target Au and Ag NCs. 6,7,27 These ligands not only influence the formation processes of Au and Ag NCs but also determine their structures and thus sizes, shapes and eventual properties.

Among the noble metal NCs reported so far, Ag NCs are particularly attractive because of the unique physical properties of Ag NCs, such as their strong luminescence and ultra-small size. Such properties provide good platforms to construct luminescent probes for bio-imaging and sensing applications. 28,29 However, silver in the zero-valent state is more reactive and easier to oxidize than gold, which makes it more difficult to prepare Ag NCs and investigate their properties as compared with the rather intensively studied gold analogues. Thus, the accessibility of highquality Ag NCs with well-defined size, structure and surface is crucial for both fundamental and applied science.

Recently, a number of efficient strategies have been developed for the synthesis of Ag NCs with tailorable physico-chemical properties, and also in quantities large enough for practical applications. 28,29 With delicate design of synthetic methods such as direct reduction, chemical etching and ligand exchange, many mature processes can be used to prepare high-quality Ag NCs

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with novel and even unprecedented properties. On the other hand, some techniques such as UV-vis absorption spectroscopy, PL emission spectroscopy, electrospray ionization mass spectrometry (ESI-MS), single crystal X-ray crystallography (SC-XRD), etc. have been used to characterize the physio-chemical properties and determine the total structures of Ag NCs, forming a central research direction in nanoscience.²⁸⁻³⁰ The atomically precise nature of their structures enables the investigation of the structure-property relationship, which may further optimize their performance. One of the most important spectroscopic properties is the luminescence, which is particularly useful in biological applications. Tunable PL properties of Ag NCs by controlling the core size and the nature of ligands have been reported during the last five years. 31,32 It is therefore a focus of this review article to provide a detailed discussion on the synthesis, structures and photoluminescent properties of Ag NCs.

In this review article, we first survey the robust synthetic methods such as direct reduction, chemical etching and ligand exchange for high-quality Ag NCs reported during the last five years. Then we discuss recent advances in the determination of the crystal structure of Ag NCs with different sizes and welldefined molecular formulas. In the next section, we highlight some examples relating to the PL properties of Ag NCs. Some factors such as the core size, capping ligand, heterometal atom and temperature governing the PL properties of Ag NCs are addressed. Finally, a brief conclusion and an outlook on the future research challenges for Ag NC research will be provided.

2. Synthesis of Ag CNs

Compared to the synthesis of Au NCs, the synthesis of Ag NCs is more challenging due to their relative susceptibility in solution under atmospheric conditions. Thus, more delicate control is required to synthesize a well-defined composition of Ag NCs. Some successful attempts have been recently reported. 28,29 Some characterization techniques including laser desorption ionization (LDI), matrix assisted laser desorption ionization (MALDI), electrospray ionization (ESI) mass spectrometry (MS), SC-XRD and post-synthetic separation methodologies such as size exclusion chromatography (SEC) and polyacrylamide gel electrophoresis (PAGE) are also used to determine the composition and structures of Ag NCs.³³

The synthesis of Ag NCs can be roughly classified into three categories: direct reduction of silver precursors in the presence of desired ligands, chemical etching and postsynthetic ligandexchange.

2.1. Direct reduction

The direct reduction method has been successfully used to prepare Ag NCs in both organic and aqueous media. This synthetic process includes rapid reductive growth of intermediate Ag NCs and slow size focusing to monodisperse Ag NCs in a reducing agent.³⁴ NaBH₄ is commonly used as the reducing agent to synthesize Ag NCs with a variety of ligands such as thiolates, alkynyls, DNAs, peptides, proteins and polymers. A few Ag NCs,

including thiol-protected Ag NCs (such as Ag₂₅(2,4-DMBT)₁₈²³ and Ag₂₉(1,3-BDT)₁₂²⁴) and alkynyl-protected Ag NCs (such as $Ag_{74}(PhC \equiv C)_{44}^{35}$ and $Ag_{51}(^{t}BuC \equiv C)_{32}^{36}$) have been successfully synthesized by using this method. However, the reduction kinetics with NaBH4 are generally fast and this leads to the formation of polydisperse Ag NCs. Thus, several methods can be used to slow down the reduction kinetics of NaBH4. For example, the solution pH,³⁷ the concentration of reducing agents, 38,39 and the solvent can be used to adjust the reducing capability of NaBH₄. Another efficient way to slow down the reduction kinetics for Ag NC formation is to replace NaBH4 with other mild reducing agents such as formic acid and DMF.41,42 Some other techniques, such as light, 43 ultra-sonication, 44 and electricity, 45 can also be used to create a mild reducing environment for the formation of Ag NCs.

2.2. Chemical etching

Some Ag NCs can also be produced via a chemical etching process, where a relatively larger Ag nanoparticle (NP) is etched to form small Ag NCs. 46-48 Compared to the direct reduction method, there are fewer successful attempts reported involving the chemical etching process, since in general the latter is more time-consuming and often produces Ag NCs at lower yields. Such constraints can be partially addressed by optimizing the etching conditions, including the etching time, reaction temperature, and the ratio of etchant to Ag precursors.

An efficient synthetic protocol requires a mild etching environment that makes possible controlled formation of Ag NCs in the reaction solution. For example, an interfacial etching process was used to digest the as prepared Ag NPs to form two luminescent Ag NCs protected by mercaptosuccinic acid (H₂MSA).⁴⁹ During the reaction, Ag@(H₂MSA) NPs were employed as starting materials and converged to a mixture of Ag₈ and Ag₇ NCs in an aqueous-organic biphasic system, and such a mixture was separated using gel electrophoresis. Another example is the synthesis of the red luminescent Ag₃₈ NC through the etching of large citrate-protected Ag@citrate NPs by adding excess mercaptosuccinic acid.50 During the reaction, there is a disappearance of the plasmon feature at 420 nm, implying that that Ag@citrate NPs were converted to Ag NCs. The route provides nearly pure Ag₃₈ NCs, and no byproducts were detected.

2.3. Ligand exchange

The ligand-exchange-induced size/structure transformation process is becoming an important approach in recent years. The peripheral organic ligands have a significant influence on the nuclearity, geometry, bonding and electronic transitions. Depending on the well characterized metal NC species, ligandexchange may be partial or complete, with or without altering the metal core. In 2014, Bakr and coworkers presented a ligandexchange method for the rapid and complete thiolate-forthiolate exchange of Ag₄₄(SR)₃₀.⁵¹ Later, they found that the ligand-exchange conversion of Ag₃₅(SG)₁₈ (SG: glutathionate) into Ag₄₄(4-FTP)₃₀ (4-FTP: 4-fluorothiophenol) is also rapid and direct, while the reverse process proceeds slowly through intermediate cluster sizes.⁵² Meanwhile, the hollow structure

of Ag₄₄(4-FTP)₃₀ is converted to non-hollow Ag₂₅(2,4-DMBT)₁₈ via a disproportionation mechanism with the ligand-exchange method. The reverse reaction between Ag₂₅(2,4-DMBT)₁₈ and 4-FTP results in Ag₄₄(4-FTP)₃₀ by dimerization followed by a rearrangement reaction.⁵³ Recently, the Pradeep group has performed the rapid transformation of Ag₅₉(2,5-DCBT)₃₂ (2,5-DCBT: 2,5-dichlorobenzenethiolate) to other well-known Ag NCs, Ag₄₄(2,4-DCBT/4-FTP)₃₀, Ag₂₅(2,4-DMBT)₁₈ and Ag₂₉(1,3-BDT)₁₂(PPh₃)₄ (PPh₃: triphenylphosphine), by an exchange reaction with diverse thiol ligands.54

Other methods, such as performing the reaction in the solid state or in a gel, can also be used for the synthesis of Ag NCs. For instance, the Pradeep group developed a solid-state method to produce red-emitting thiolated Ag₉(H₂MSA)₇ nanoclusters.⁵⁵ This method can also synthesize thiolated Ag₃₂(SG)₁₉⁵⁶ and Ag₁₅₂(PET)₆₀ (PET: phenylethanethiol),⁵⁷ and selenolateprotected Ag₄₄(SePh)₃₀ NCs.⁵⁸ In addition, Chakraborty et al. applied the gel route to generate thiolated Ag₂₅(SG)₁₈ NCs with strong red emission.⁵⁹ The synthesis of Ag NCs has been summarized in some recent reviews. 28,29

3. Structures of Aq NCs

Based on the reported metal NCs with a fully determined structure, it has been found that the stability and properties of metal NCs are influenced by a number of factors including their compositions, core structures and surface functionalities. Hence, it is crucial to control the sizes and geometric structures of the cores and the interfacial structures. Many Au NCs have been structurally determined by SC-XRD.6,7 In contrast, the number of structurally determined Ag NCs has been limited due to their weaker stability, aerial oxidation, and lower purity. Some examples of structurally solved ligand-protected Ag NCs have been reported. More details about structural details are presented in Table S1 (ESI†). Most of the representative structures of Ag NCs could be considered as being built from basic kernel units such as Ag₄, Ag₆, Ag₇ and Ag₁₃ polyhedrons. On the other hand, peripheral ligands including thiols, phosphines, alkynyls or their combination are used to protect Ag NCs. Here, we categorize the important studies of Ag NCs based on different surface ligands.

3.1. Thiol-protected Ag NCs

Thiol is the most widely used capping ligand in the shape controlled synthesis of Au and Ag NCs. In the reported thiolprotected Ag NCs with a fully determined structure, most of the representative structures could be categorized into the structure with a keplerate Ag icosahedron core and the structure with atoms arranged in a face-center-cubic (FCC) like pattern.

The icosahedron is perhaps the most widely observed structure in metal NCs. The first reported crystal structure of all thiol-protected Ag NCs was that of $Ag_{44}(SR)_{30}$ (R = PhCO₂H₂, PhF, PhF₂ or PhCF₃) in 2013.^{25,26} The single crystal structure suggests the existence of a Ag_{32} kernel and six $Ag_2(SR)_5$ staples. The Ag₃₂ kernel can further be divided into an icosahedral Ag₁₂

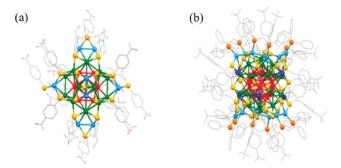


Fig. 1 Total crystal structures of the Aq₄₄(SPhCO₂H₂)₃₀ and the Aq₅₀(TBBM)₃₀-(dppm)₆ nanoclusters. Adapted with permission from ref. 60. Copyright 2017, American Chemical Society.

core and a 20-silver-atom dodecahedral shell (Fig. 1a). By using such Ag₄₄ as seeds, larger size Ag₅₀(TBBM)₃₀(dppm)₆ (TBBM: 4-tert-butylbenzyl mercaptan; dppm: bis(diphenylphosphino)methane) was obtained by Zhu and coworkers.⁶⁰

The structure of Ag₅₀ comprises a Ag₃₂ kernel which is retained from Ag44 surrounded by a dodecahedral Ag20 and two symmetrical Ag₉(TBBM)₁₅P₆ ring motifs (Fig. 1b). Subsequently, the structure of the "golden silver" Ag₂₅(2,4-DMBT)₁₈ NC²³ is found to be essentially identical to that of Au₂₅(SCH₂CH₂Ph)₁₈. ^{16–18} The structure of the Ag₂₅(2,4-DMBT)₁₈ NC has an icosahedral Ag₁₃ kernel which is protected by six dimeric staples (Fig. 2a). The crystal structure of Ag₂₉(1,3-BDT)₁₂(Ph₃P)₄ protected by a dithiol and monodentate phosphine ligand has been solved by Antoine and coworkers.24 The Ag₂₉ cluster has an icosahedral core similar to that of Ag₂₅(2,4-DMBT)₁₈. The icosahedral core Ag₁₃ is protected with a shell consisting of Ag₁₆S₂₄P₄ (Fig. 2b). The shell is composed of four Ag₃S₆ crowns and four Ag₁S₃P₁.

During the past few years, FCC core structures in metal NCs have attracted great attention due to their key roles in understanding the origin of macroscopic FCC metal materials such as gold, silver, copper, etc. 6,61-63 Several FCC-type kernel structures for Ag NCs have been reported thus far.

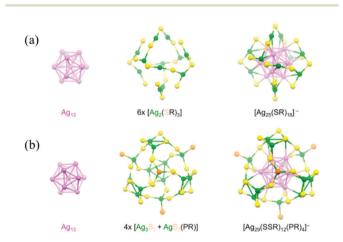


Fig. 2 Core, shell and framework of the Ag₂₅(SPhMe₂)₁₈ and the Ag₂₉(BDT)₁₂(TPP)₄ nanoclusters. Adapted with permission from ref. 6. Copyright 2016, American Chemical Society.

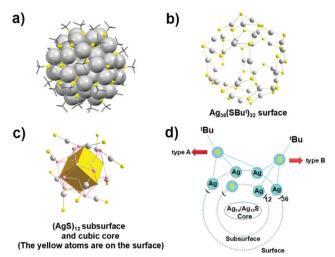


Fig. 3 X-ray structure of $[Ag_{62}S_{13}(S^tBu)_{32}]^{2+}$. (a) The similar frameworks contained in the Ag-QD, Ag-inter, and Ag-NC. (b) $Ag_{36}(S^tBu)_{32}$ shell. (c) Bonding mode of core silver atoms (gray) and sulfur atoms (pink) linked with the shell sulfur atoms (yellow). (d) Two types of ligands. Adapted with permission from ref. 66. Copyright 2016, American Chemical Society.

The FCC unit cell comprises 8 vertices and 6 face centers and, hence, a total of 14 atoms in the unit. For example, the crystal structure of an all thiol-protected [Ag₆₂S₁₂(S^tBu)₃₂]²⁺ nanocluster (Ag-NC) shows a complete FCC Ag₁₄ core structure with a Ag₄₈(S^tBu)₃₂ shell configuration interconnected by 12 sulfide ions, which is similar to the $[Ag_{62}S_{13}(S^tBu)_{32}]^{4+}$ (Ag-QD) structure. 64,65 In the center of the Ag₁₄ kernel, there is an octahedral Ag₆ kernel, which is enclosed by eight equilateraltriangle-shaped planes. Of note, the Ag-QD could be electrochemically reduced into the Ag-NC, via an intermediate compound $[Ag_{62}S_{13}(S^tBu)_{32}]^{2+}$ (Ag-inter) (Fig. 3), 66 wherein the Ag₆₂ nanocluster template remained unchanged. It can be seen that the Ag-QD, Ag-inter and Ag-NC have a similar Ag₃₆(S^tBu)₃₂ surface and (AgS)₁₂ subsurface connecting the Ag₃₆(S^tBu)₃₂ surface with the Ag₁₄ (or Ag₁₄S) cubic core.

Recently, Wu et al. reported a new all thiol-protected Ag₄₆S₇(2,4-DMBT)₂₄ nanocluster with FCC structure.⁶⁷ The structure of the Ag₄₆ NC can be viewed as a 38-Ag atom kernel with a sulfur atom in the center, capped by surface motifs including two Ag(2,4-DMBT)₃, six Ag(2,4-DMBT)₂, six 2,4-DMBT, and six sulfido units. The Ag_{38} kernel can further be divided into an octahedral Ag₆ core and a 32-silver-atom tetradecahedron shell (Fig. 4). This tetradecahedron is made up of eight hexagons and six tetragons.

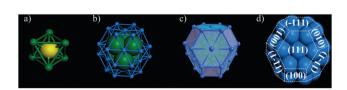


Fig. 4 (a) The central Ag_6 octahedron with a central sulfur; (b and c) the $Ag_6S@Ag_{32}$ kernel; and (d) the crystal facets of the FCC Ag_{38} kernel. S yellow, Ag other colors. Adapted with permission from ref. 67. Copyright 2018, John Wiley & Sons, Inc.

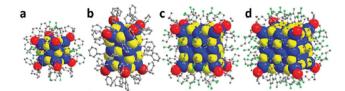


Fig. 5 X-ray structures of Ag cubes: $Ag_{14}(SC_6H_3F_2)_{12}(PPh_3)_8$, $Ag_{23}(PPh_3)_8$ - $(SC_2H_4Ph)_{18}$, $Ag_{38}(SPhF_2)_{26}(P^nBu_3)_8$, and $Ag_{63}(SPhF_2)_{36}(P^nBu_3)_8$. Adapted with permission from ref. 62. Copyright 2019, Royal Society of Chemistry.

Phosphine was usually used as an auxiliary ligand with thiol or alkyl to produce some novel metal NCs. Introducing phosphine not only enhances the yield and stability of Ag NCs but it also assists with the growth of high-quality single crystals. Thiol and phosphine ligands have excellent compatibility in protecting Ag NCs. Zheng et al. reported the single crystal structure of a mixed ligand protected Ag₁₄ cluster in 2012.⁶⁸ As the smallest FCC-type Ag NC reported to date, the Ag₁₄(SC₆H₃F₂)₁₂(PPh₃)₈ cluster contains an octahedral Ag₆⁴⁺ core, which is encapsulated by eight cubically arranged Ag(SC₆H₃F₂)₂PPh₃ tetrahedrons that share one corner between them (Fig. 5a). Another important characteristic of this cluster is that all the thiolate ligands bind to three Ag atoms and no staple motifs are found. Later, a helical FCC structure was observed in the Ag₂₃(PPh₃)₈(SC₂H₄Ph)₁₈ nanocluster (Fig. 5b).⁶⁹ Ag₂₃ has a bioctahedral Ag₁₁ core, which is viewed as two Ag₆ building blocks fused together by vertex sharing. Due to a slight distortion in the vertex-sharing Ag₁₁ core, Ag₂₃ has a chiral structure.

When fusing four of such simple Ag₁₄ FCC cubes together via face sharing, a square like Ag₃₈(SPhF₂)₂₆(PⁿBu₃)₈ metal framework was obtained (Fig. 5c). 70 Further aggregation of another four Ag₁₄ FCC cubes or one more square-like Ag₃₈(SPhF₂)₂₆(PⁿBu₃)₈ gives rise to the cubic-structured Ag₆₃(SPhF₂)₃₆(PⁿBu₃)₈ (Fig. 5d).⁷¹

The Zang group prepared a FCC Ag₁₄ NC protected by facecapping 1,2-dithiolate-o-carborane ligands. Site-specific surface modification of the Ag₁₄ NC with pyridyl-type ligands affords highly thermostable NCs. 72 Moreover, by using a progressively optimized ligand-bridging approach, various 1D-to-3D silver cluster-assembled materials are predesigned and obtained (Fig. 6). This strategy not only greatly improves the stability but also modulates the emission properties of the target materials.

Another series with FCC kernels pertains to the box-like $Ag_{46}(2,5-DMBT)_{24}(PPh_3)_8$ and $Ag_{67}(2,4-DMBT)_{32}(PPh_3)_8$ NCs.⁷³⁻⁷⁵ The crystal structure of Ag₆₇(2,4-DMBT)₃₂(PPh₃)₈ was reported by Alhilaly et al.75 The Ag₆₇ structure consists of a Ag₂₃ kernel protected by a layer of Ag44S32P8 arranged in the shape of a box (Fig. 7). Unlike the common Ag₁₃ icosahedron geometry, the Ag₂₃ kernel was formed through a cuboctahedron sharing opposite square faces with two Ag₈ crowns and then capped by two silver atoms at the open crown positions. This crowning of the Ag₁₃ cuboctahedron leads to the box-shape growth of the Ag₆₇ cluster. The entire cluster is stabilized by 8 AgS₃P motifs and 8 bridging thiolates. Of note, after removing a block of the Ag₂₁(SR)₈ unit from Ag₆₇(SR)₃₂(PPh₃)₈, a box-like structure of Ag₄₆(SR)₂₄(PPh₃)₈ was predicted. Experimentally, the Ag₄₆(2,5-DMBT)₂₄(PPh₃)₈ NC has



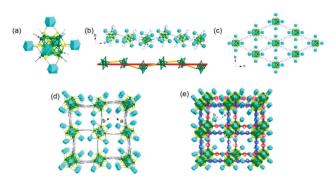


Fig. 6 Structural represention of the (a) 1,2-dithiolate-o-carboranecapped Ag₁₄ NC; (b) 1D helix; (c) 2D grid network; (d) 3D porous framework and (e) 2-fold interpenetrated porous 3D frameworks. Adapted with permission from ref. 72. Copyright 2018, American Chemical Society.

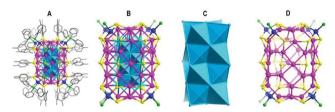


Fig. 7 (A) Total structure of Ag₆₇(SPhMe₂)₃₂(PPh₃)₈. (B) The structure of Ag₆₇S₃₂P₈ obtained by disconnecting carbon atoms in A. (C) Ag₂₃ metal core. (D) The structure of the NC without the Ag23 metal core, i.e., Ag₄₄(SPhMe₂)₃₂(PPh₃)₈. Adapted with permission from ref. 75. Copyright 2017, American Chemical Society.

recently been synthesized and crystallized (Fig. 8). 73,74 Ag₄₆ has a Ag₁₄ core with a FCC structure which is protected by a $Ag_{32}S_{24}P_8$ shell.

The $Ag_{40}(2,4-DMBT)_{24}(PPh_3)_8$ and $Ag_{46}(2,5-DMBT)_{24}(PPh_3)_8$ NCs share the same shell of Ag₃₂S₂₄P₈, while the metal cores are arranged into different types (Fig. 8).73,74 In contrast to the Ag₄₆ nanocluster, Ag40 presents a newly found loose Ag8 core with a simple-cubic structure. Interestingly, a cavity exists between the Ag₈ core and the inner layer of the protecting shell, but no such cavity exists in Ag₄₆. In Zhu's work, they successfully transformed Ag₄₀ to Ag₄₆ via a ligand exchange strategy.⁷³ Notably, the intermediate Ag nanocluster, [Ag₄₃(2,5-DMBT)₂₅(PPh₃)₄], was also obtained.73 The framework of Ag43 has a two-shelled Ag12@Ag20 core, which is protected by four kinds of units, including Ag₂S₅P, Ag₄S₈P, Ag₂S₄P and Ag₃S₆P, and two S bridge bonds were found on the surface of this nanocluster.

Recently, Zheng and coworkers reported a detailed structural and spectroscopic characterization of Ag₄₀(DMBT)₂₄- $(PPh_3)_8H_{12}$ $(Ag_{40}H_{12})^{.76}$ In contrast to the Ag_{40} NC, the metal framework of Ag₄₀H₁₂ also consists of identical Ag₈@Ag₃₂S₂₄P₈. Based on a detailed analysis of the structural features and ¹H and ²H NMR spectra, the positions of the 12 hydrides were determined to be residing on the 12 edges of the cubic core.

Among thiolate protected metal NCs, chiral thiolate protected metal NCs with different electronic configurations are of great importance in nanoscience and nanotechnology owing to their chiro-optical properties and applications in asymmetric drugs,

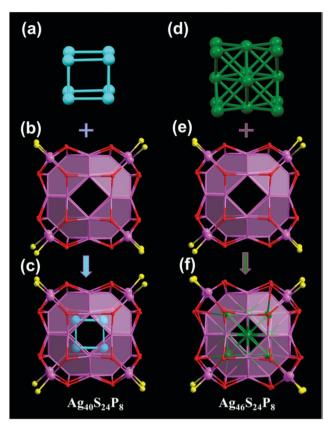


Fig. 8 Core, shell and framework of Ag₄₀(2,4-DMBT)₂₄(PPh₃)₈ and Ag₄₆(2,5-DMBT)₂₄(PPh₃)₈. Adapted with permission from ref. 73. Copyright 2018, American Chemical Society.

sensors, and catalysts. For example, a range of structures and properties of chiral thiolate protected Au NCs including ${\rm Au}_{20}({\rm SPh}^t{\rm Bu})_{16},^{77}~{\rm Au}_{28}({\rm SPh}^t{\rm Bu})_{20},^{78}~{\rm Au}_{38}({\rm SCH}_2{\rm CH}_2{\rm Ph})_{24},^{21}~{\rm Au}_{102} (p{\rm -MBA})_{44},^{22}$ and ${\rm Au}_{133}({\rm SPh}^t{\rm Bu})_{52},^{79}$ have recently been studied.

We herein highlight recent findings on chiral thiolate-protected Ag NC clusters. A few chiral thiolate protected Ag NCs such as $Ag_{16}(dppe)_4(SPhF_2)_{14}$ (dppe: 1,2-bis(diphenylphosphino)ethane), 80 Ag₃₂(dppe)₅(SPhCF₃)₂₄, ⁸⁰ Ag₃₂(dppm)₅(SAdm)₁₃Cl₈, ⁸² Ag₄₅(dppm)₄-(S^tBu)₁₆Br₁₂, 82 and Ag₃₃(SCH₂CH₂Ph)₂₄(PPh₃)₄83 have been characterized by SCXRD, in which all the surface organic ligands are

In 2003, Zheng et al. reported two chiral AgNCs, Ag₁₆(dppe)₄- $(SPhF_2)_{14}$ and $Ag_{32}(dppe)_5(SPhCF_3)_{24}$, ⁸⁰ which are protected by achiral diphosphine and thiolate ligands. The clusters have core-shell structures with a multinuclear Ag unit encapsulated in a shell containing a Ag(i)-thiolate-diphosphine complex. In Ag₁₆(dppe)₄(SPhCF₂)₁₄, a Ag₈ core is encapsulated in a shell of Ag₈(dppe)₄(SPhCF₂)₁₄, while the structure of Ag₃₂(dppe)₅(SPhCF₃)₂₄ shows that it possesses a Ag₂₂ core protected by one Ag₆(dppe)₃-(SPhCF₃)₁₂, two Ag₂(dppe)(SPhCF₃)₄ and four (SPhCF₃) units. As shown in Fig. 9, both Ag_{16} and Ag_{32} conform to C_2 symmetry, and their chirality is caused by the asymmetric arrangements of the tetrahedral [AgS₃P] coordination units on the surface.

As a further development, the synthetic recipe of Ag₁₆ and Ag₃₂ was modified by replacing dppe with dppp (1,3-bis(diphenyphosphino)propane). A pair of optically pure enantiomers

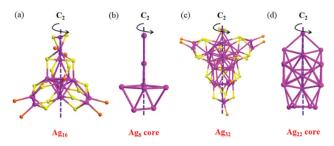


Fig. 9 Core and framework of $Ag_{16}(dppe)_4(SPhF_2)_{14}$ and $Ag_{32}(dppe)_5$ -(SPhCF₃)₂₄ NCs. Adapted with permission from ref. 27. Copyright 2018, American Chemical Society.

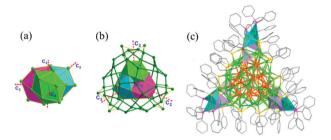


Fig. 10 Core, shell and overall structures of Ag₇₈(dppp)₆(SPhCF₃)₄₂. Adapted with permission from ref. 82. Copyright 2017, American Chemical Society.

Ag₇₈(dppp)₆(SPhCF₃)₄₂ (R/S-Ag₇₈) were synthesized.⁸¹ The molecular architecture of the R/S-Ag78 NCs can be described as a Ag@Ag₂₁@Ag₄₄@A_{g12}(dppp)₆(SPhCF₃)₂₄(SPhCF₃)₁₈ core-shell structure (Fig. 10). The Ag@Ag $_{21}$ kernel displays D_3 symmetry and can be described as three mutually inter penetrating icosahedra. The 3-fold axis and three 2-fold axes pass through the center Ag atoms. The Ag@Ag21 kernel is encapsulated in a Ag44 shell whose structure can be rationalized. The predetermined chirality in the Ag₇₈ cluster originates in the chiral arrangement of the surfaceprotecting units.

Two multi-ligand-protected chiral Ag NCs, Ag₃₂(dppm)₅-(SAdm)₁₃Cl₈ and Ag₄₅(dppm)₄(S^tBu)₁₆Br₁₂, have been synthesized and structurally characterized (Fig. 11).82 Ag₃₂ possesses an achiral Ag₁₃ icosahedral kernel, and Ag₄₅ also has an achiral core of 23 Ag atoms, but the cores are protected by chiral shells, Ag₁₉S₁₃C₁₈P₁₀ and Ag₂₂S₁₆P₈Br₁₂, respectively. It is interesting to note that the coplanar fusion of Ag₁₃ units into Ag₂₃ constitutes the metal core of the Ag₄₅ nanocluster.

Remarkably, the asymmetric distribution of the three types of ligands (thiolate, phosphine, and halogen) on the cluster surface induces chirality that can transfer from the ligand shell to the inner metal core, thereby resulting in an intrinsic chiral structure.

Very recently, Chen et al. discovered a new chiral crystal structure of the Ag₃₃(SCH₂CH₂Ph)₂₄(PPh₃)₄ NC (Fig. 12).⁸³ The Ag₃₃ nanocluster contains a Ag₁₃ icosahedral core and a chiral shell of Ag₂₀S₂₄P₄ composed of -SR-Ag-SR- motifs and -Ag-P terminals. Pd(PPh₃)₄ played a crucial role in the formation of Ag₃₃ but not by replacing silver atoms to form alloys.

The shell-by-shell mode is the most common growth mode for nanoparticles, as reflected in different-size spherical nanoparticles.

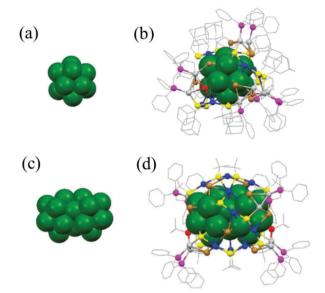


Fig. 11 Core and overall structures of Ag₃₂(dppm)₅(SAdm)₁₃Cl₈ and Ag₄₅(dppm)₄(S^tBu)₁₆Br₁₂ NCs. Adapted with permission from ref. 81. Copyright 2017, Royal Society of Chemistry.

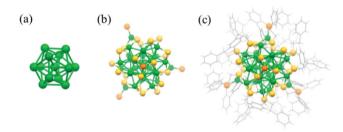


Fig. 12 Core, shell and framework of $Ag_{33}(SCH_2CH_2Ph)_{24}(PPh_3)_4$. Adapted with permission from ref. 83. Copyright 2019, American Chemical Society.

This growth mode allows the isotropic three-dimensional expansion of the particle size and is expected to apply to the structures of giant nanoclusters. Indeed, this mode has been observed in many metal NCs.6,61 The Zheng and Jin groups solved the crystal structures of a series of plasmonic twinned silver nanoclusters, such as Ag₁₃₆(SPh^tBu)₆₄Cl₃Ag_{0.45}, ⁸⁴ Ag₁₄₁X₁₂- $(SAdm)_{40}$ (X = Cl, Br, I and SAdm = 1-adamantanethiolate), 85 $Ag_{146}Br_2(SPh^iPr)_{80}$, ⁸⁶ $Ag_{206}(SCy)_{68}F_2Cl_2$ (Cy: cyclohexanethiolate), ⁸⁷ and Ag₃₇₄(SPh^tBu)₁₁₃Br₂Cl₂, 84 which can be described as 5-fold twinned cores enclosed within related structurally distinctive Ag-SR complex shells (Fig. 13).

These large nanoclusters follow the shell-by-shell growth mode, in which a Ag₇ or Ag₁₉ innermost kernel and corresponding growth modes have been observed. For the Ag₇-kernel based nanoclusters, Ag₁₄₆Br₂(SPhⁱPr)₈₀ can be dissected into Ag₇ (kernel)@Ag₃₂ (1st shell)@ Ag_{12} (2nd shell) $Ag_{95}Br_2(SPh^iPr)_{80}^{86}$ and $Ag_{206}(SR)_{68}F_2Cl_2$ follows a Ag₇ (kernel)@Ag₃₂ (1st shell)@Ag₇₇ (2nd shell)@ Ag₉₀(SCy)₆₈F₂Cl₂ (motif shell) configuration.⁸⁷

For the Ag₁₉-kernel based nanoclusters, Ag₁₄₁(SAdm)₄₀-(Cl/Br/I)₁₂ displays a Ag₁₉ (kernel)@Ag₅₂ (1st shell)@Ag₇₀-(SAdm)₆₈F₂Cl₂ (motif shell) three-shell configuration⁸⁵ and

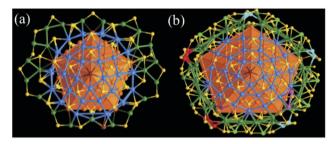


Fig. 13 (a) The shell of Ag_{136} with the bowl-like half J73 related [Aq₃₀(SPh^tBu)₁₅Cl] caps highlighted in blue; and (b) the shell of Aq₃₇₄ with key structure elements highlighted in different colors. Adapted with permission from ref. 84. Copyright 2016 Nature Publishing Group.

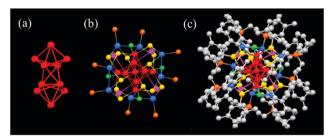


Fig. 14 Core, shell and overall structures of Ag₂₂(dppe)₄(2,5-DMBT)₁₂Cl₄. Adapted with permission from ref. 89. Copyright 2019, American Chemical

 $Ag_{210}/_{211}(SPh^{i}Pr)_{71}(PPh_{3})_{5/6}Cl$ exhibits a Ag_{19} (kernel)@ Ag_{52} (1st shell)@Ag₄₅ (2nd shell)@Ag₈₉(SPhⁱPr)₇₁Cl&(Ag-PPh₃)_{5/6} (motif shell) four-shell configuration.88

Unlike the shell-by-shell growth mode in larger metal NCs, many smaller structures have been found to be assembled from small polyhedrons.⁶ For instance, the structure of Ag₂₂(dppe)₄(2,5-DMBT)₁₂Cl₄ exhibits a Ag₁₀ kernel, which is composed of two Ag₅ units having distorted trigonal bipyramidal geometry (Fig. 14). The Ag_{10} core is protected by a $Ag_{12}(dppe)_4(2,5-DMBT)_{12}Cl_4$ shell, which is formed by four Ag₂SP₂Cl and four AgS₂ staple motifs.⁸⁹ The Ag₂₂ cluster exhibits crystallization-enhanced PL.

3.2. Alkynyl-protected Ag CNs

Beyond thiolate ligands, the alkynyl ligand has been employed for the synthesis of a number of coinage metal clusters. 90-92 Recently, some alkynyl-protected Ag NCs have been identified, and they exhibit good stability and crystallizability. For example, Zhang et al. and Xie et al. exhibited the structures of two all alkynyl-protected Ag NCs, Ag₇₄(PhC = C)₄₄ and $Ag_{51}(^{t}BuC \equiv C)_{32}$, respectively. ^{35,36} Their crystal structures both contain three-shell structures. The crystal structure of Ag74 possesses a Ag₄ tetrahedron inner core, which is surrounded by the second Ag₂₂ shell (Fig. 15).³⁵ The outermost shell consists of 48 Ag atoms that are enclosed into 12 pentagons and 56 triangles. However, when the phenylacetylene is replaced by tert-butylethynide, the Ag₅₁ NC is prepared. The crystal structure of Ag₅₁ displays a Ag@Ag₁₄@Ag₃₆ three shell structure, which is capped by 32 tert-butylethynide ligands on the surface (Fig. 16).36

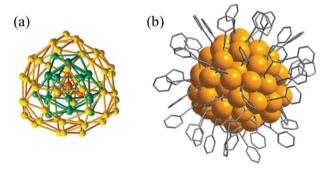


Fig. 15 (a) The Ag₇₄ core; and (b) overall structure of Ag₇₄(PhC \equiv C)₄₄. Adapted with permission from ref. 35. Copyright 2017, American Chemical Society

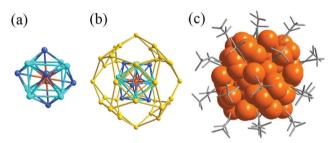


Fig. 16 (a) The Ag@Ag₁₄ core; (b) the structure of the Ag@Ag₁₄@Ag₃₆ shell; and (c) overall structure of Ag₅₁(^tBuC = C)₃₂. Adapted with permission from ref. 36. Copyright 2018, Royal Society of Chemistry.

Aside from all alkynyl-protected Ag NCs, alkynyl and auxiliary ligand co-protected Ag NCs have been obtained. In 2017, Wang et al. reported two Ag NCs, $Ag_{19}(dppm)_3(PhC \equiv C)_{14}$ and $Ag_{25}(dpppe)_3(MeOPhC \equiv C)_{20}$ (dpppe: 1,5-bis(diphenylphosphino)pentane), which are protected by both alkynyl and phosphine ligands (Fig. 17). 93 They have D_{3h} symmetry with a centered anticuboctahedral Ag₁₃ kernel extended by three Ag₂ motifs and three tetrahedral Ag₄ motifs, respectively. Later, they obtained two Ag NCs containing the protection of thiacalixarenes, $Ag_{34}(BTCA)_3(^tBuC \equiv C)_9(tfa)_4(CH_3OH)_3$ and $Ag_{35}(H_2BTCA)_2(BTCA)_3(CH_3OH)_3$ $(^tBuC \equiv C)_{16}$ (H₄BTCA: 4-tert-butylthiacalix[4]arene and tfa: trifluoroacetate). 94,95 The Ag₃₄ and Ag₃₅ NCs have a centered icosahedral Ag@Ag₁₂ kernel that is surrounded by 21 and 22 peripheral silver atoms (Fig. 18), respectively. Surrounding

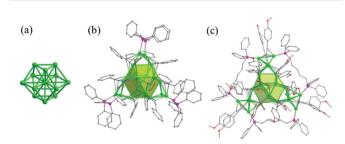


Fig. 17 (a) The Ag_{13} anticuboctahedron kernel; and (b and c) overall structures of $Ag_{19}(dppm)_3(PhC \equiv C)_{14}$ and $Ag_{25}(dpppe)_3(MeOPhC \equiv C)_{20}$. Adapted with permission from ref. 93. Copyright 2017, Royal Society of Chemistry.

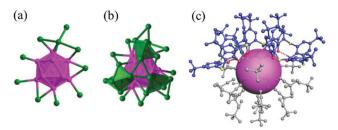


Fig. 18 X-ray structure of Ag₃₅(H₂BTCA)₂(BTCA)(^tBuC≡C)₁₆. (a) Position of 10 peripheral Ag atoms (green) held by thiacalixarene ligands onto the Ag₁₃ core (pink); (b) position of 12 peripheral Ag atoms (green, triangular prisms) capped by alkynyl ligands; and (c) side views of the position of surface ligands with respect to the Ag₃₅ core. Adapted with permission from ref. 95. Copyright 2015. American Association for the Advancement of Science.

protection for Ag₃₅ is provided by three thiacalixarene ligands and 16 alkynyl ligands, while Ag₃₄ is protected by four kinds of ligands, including three BTCA, nine alkynyl ligands, four tfa, and three methanol solvent ligands.

Very recently, Wang et al. solved the crystal structure of a large alkynyl and halide protected silver NC, (C7H17ClN)3-[Ag₁₁₂Cl₆(ArC=C)₅₁]. ⁹⁶ The cluster exhibits a four concentric coreshell structure Ag₁₃(a)Ag₄₂(a)Ag₄₈(a)Ag₉, and four types of alkynyl-Ag binding modes are observed. Chloride is found to be critical for the stabilization and formation of the Ag NC. Another interesting case is $Ag_{48}(^{t}BuC \equiv C)_{20}(CrO_{4})_{7}$, which is co-capped by CrO_{4}^{2-} and ^tBuC≡C⁻ ligands. ⁹⁷ The pseudo-5-fold symmetric metal skeleton of Ag48 shows a core-shell structure composed of a Ag23 cylinder encircled by an outer Ag₂₅ shell (Fig. 19). The involvement of both organic and inorganic protection is a new path for synthesizing Ag NCs and controlling the formation and structure.

Another interesting case is $Ag_{48}(^{t}BuC \equiv C)_{20}(CrO_{4})_{7}$, which is co-capped by CrO₄²⁻and ^tBuC = C⁻ ligands.⁹⁷ The pseudo-5fold symmetric metal skeleton of Ag48 shows a core-shell structure composed of a Ag₂₃ cylinder encircled by an outer Ag₂₅ shell (Fig. 19). The involvement of both organic and inorganic protection is a new path for synthesizing Ag NCs and controlling the formation and structure.

3.3. Other ligand-protected Ag NCs

It is an effective strategy to obtain new functional metal nanoclusters by using ligands beyond the conventional ones.

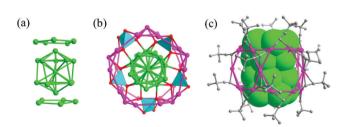


Fig. 19 X-ray structure of $Ag_{48}(^{t}BuC \equiv C)_{20}(CrO_{4})_{7}$. (a) Formation of the Ag_{25} shell by capping two silver pentagons on the Ag_{13} Ino decahedron on the top and bottom; (b) top view of the coordination of five equatorial ${\rm CrO_4}^{2-}$ anions linking the ${\rm Ag_{23}}$ cylinder and ${\rm Ag_{25}}$ shell; and (c) side view of the Ag₂₃ cylinder encircled by the outer [Ag₂₅(t BuC \equiv C)₂₀] shell. Adapted with permission from ref. 97. Copyright 2019, American Chemical Society.

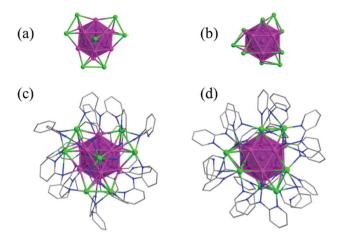


Fig. 20 View of the Ag_{21} kernel (a) and the Ag_{22} kernel (b); and total structures of $A_{q21}(dpa)_{12}$ (c) and $Ag_{22}(dpa)_{12}$ (d) showing the Ag_{13} polyhedron. Adapted with permission from ref. 101. Copyright 2019, Nature Publishing Group.

For example, Liu et al. successfully synthesized and determined the structures of $Ag_{20}\{E_2P(OR)_2\}_{12}$ and $Ag_{21}\{E_2P(O^{i}Pr)_2\}_{12}$ (E = S, Se). 98-100 The Ag₂₀ and Ag₂₁ NCs have a Ag-centered Ag₁₃ icosahedral kernel with 7 and 8 capping Ag atoms and 12 dichalcogeno ligands.

Recently, Wang et al. reported two homoleptic amidoprotected Ag NCs Ag₂₁(dpa)₁₂ and Ag₂₂(dpa)₁₂ (dpa: dipyridylamido).101 The Ag21 and Ag22 NCs consist of a centeredicosahedron Ag₁₃ core wrapped by 12 dpa ligands (Fig. 20). The flexible arrangement of the N donors in dpa facilitates the solvent-triggered reversible interconversion between Ag21 and Ag₂₂ due to their very different solubility.

The Wang group successfully prepared and characterized a Ag NC protected by phosphine and halide, Ag₁₅(Ntriphos)₄Cl₄ (N-triphos: tris((diphenylphosphino)methyl)amine). 102 The Ag₁₅ cluster has a hexacapped body-centered cubic framework which is consolidated by four tripodal N-triphos ligands, in which one Ag atom occupies the center of the Ag₈ cube, while the six square faces of this Ag₈ cube are capped respectively by one Ag atom (Fig. 21). Our group recently reported three oxometalate and phosphine ligand co-protected Ag NCs, Ag₂₈(dppb)₆(MoO₄)₄

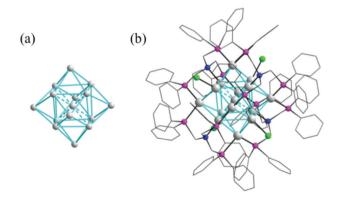


Fig. 21 (a) The core of Ag_{15} in a hexacapped bcc arrangement; and (b) X-ray structure of [Ag₁₅(Ntriphos)₄(Cl₄)]³⁺. Adapted with permission from ref. 102. Copyright 2017, Royal Society of Chemistry.

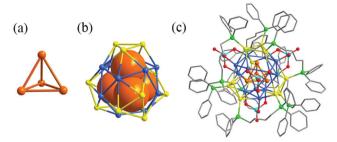


Fig. 22 (a) View of the Ag₄ inner core; (b) the structure of the two-shell $Ag_4@Ag_{24}$; and (c) total structure of $Ag_{28}(dppb)_6(MoO_4)_4$. Adapted with permission from ref. 103. Copyright 2020, Royal Society of Chemistry.

(dppb: 1,4-bis(diphenylphosphino)butane), Ag₂₈(dppb)₆(WO₄)₄ and Ag₃₂(dppb)₁₂(MoO₄)₄(NO₃)₄. Each cluster comprises a double shell Ag₄@Ag₂₄ core covered by 4 oxometalates (Fig. 22). Two similar Ag₂₈ cores of our clusters are observed in the $Cu_{12}Ag_{28}(2,4\text{-DCBT})_{24} \quad and \quad Cd_{12}Ag_{32}(SePh)_{36} \quad clusters, \\^{104,105}$ however with vividly different metal and ligand compositions, electronic charges, and surface structures.

In 2019, the Suzuki group prepared a unique ultrastable Ag NC with a C-shaped {Si₂W₁₈} building unit (Fig. 23). ¹⁰⁶ The Ag₂₇(Si₂W₁₈O₆₆)₃ cluster was assigned to five octahedral {Ag₆} clusters and three bridging Ag atoms, and it was surrounded by C-shaped {Si₂W₁₈} through direct Ag-O-W bonds. Recently, Sun et al. also reported a series of silver NC based POMs, such as $Ag_{10}@(Mo_7O_{26})_2@Ag_{70}(MoO_4)_2(S^iPr)_{36}(CF_3SO_3)_{16}(DMF)_6, Ag_{10}@$ $(MoO_4)_7$ $(SPh^tBu)_{33}$ $(mbc)_{18}$ $(DMF)(H_2O)_2$, $(MoO_4)_7 @Ag_{56} (MoO_4)_2 (S^i Pr)_{28} (CF_3 SO_3)_{14} (DMF)_4.^{42,107-109} \ \ These$ large Ag NCs follow the shell-by-shell growth mode, in which a Ag₆ or Ag₁₀ innermost kernel and corresponding growth modes have been observed. For example, in the innermost region of Ag_{10} (Mo_7O_{26})₂ (Ag_{70} (MoO_4)₂ (S^iPr)₃₆ (CF_3SO_3)₁₆ (DMF)₆, an unusual FCC-structured Ag₁₀ nanocluster is locked by a pair of $Mo_7O_{26}^{10-}$ anions to form an inner $Ag_{10} @ (Mo_7O_{26})_2$ core which acts as a template to support the outer Ag₇₀ nanocluster to form a final three-shell Ag₁₀@(Mo₇O₂₆)₂@Ag₇₀ nanocluster (Fig. 24).

In contrast to other ligand protected Ag NCs, DNA templated Ag NCs (DNA-Ag NCs) have received much interest, attributable to the photophysical properties including high quantum yield, excellent brightness, photostability, and tunable emission colors from visible to near IR. 110-118 The structures and optical properties of DNA-Ag NCs are regulated by the sequences or

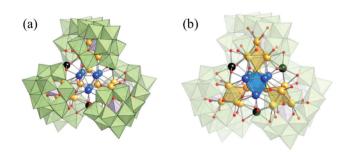


Fig. 23 X-ray structure of $Ag_{27}(Si_2W_{18}O_{66})_3$. Adapted with permission from ref. 106. Copyright 2019, American Chemical Society

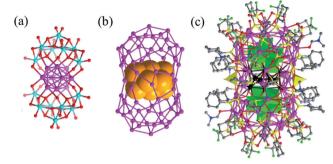


Fig. 24 (a) The Ag_{10} bioctahedron locked by a pair of $Mo_7O_{26}^{10-}$ anions; (b) the Ag_{10} bioctahedron (claybank space-filling balls) residing in the Ag_{70} shell; and (c) overall structure of $Ag_{10}@(Mo_7O_{26})_2@Ag_{70}(MoO_4)_2(S^iPr)_{36}$ -(CF₃SO₃)₁₆(DMF)₆. Adapted with permission from ref. 107. Copyright 2019, Royal Society of Chemistry.

secondary structures of DNA scaffolds that possess different binding affinities to Ag NCs. The first example of DNA-Ag NCs was discovered by Dickson and co-workers in 2004, 119 where a 12-base scaffold of 5'-AGGTCGCCGCCC-3' was employed as the template to direct the assembly of silver ions, and then reduced by NaBH₄ to form Ag NCs in aqueous solution at room temperature. By choosing DNA templates with various sequences and lengths, many types of fluorescent DNA-Ag NCs were prepared. 110-123 Mass spectrometry reveals that the sequence and length of DNA scaffolds could play an important role in determining the size of Ag NCs. In addition to the size, the DNA conformation and the oxidation state of Ag NCs are other factors that modulate the structures and optical properties.

The secondary structure of DNA scaffolds has also important influences on the structure and optical properties of DNA-Ag NCs. Secondary structures such as hairpin, i-motif and G-quadruplex have been made in creating DNA-Ag NCs. For example, DNA-Ag NCs can be prepared by using hairpins with a C-loop of 3 to 12 cytosines, which contained different numbers of silver atoms and showed different fluorescence. 120-122

Li et al. synthesized fluorescent DNA-Ag NCs with i-motif DNA, and such NCs display an emission wavelength range over green to NIR. 123 By using a G-quadruplex DNA sequence, Wang et al. synthesized dual-emissive DNA-Ag NCs possessing high thermo-stability. 124 To better understand the properties and applications of DNA-Ag NCs, readers are also recommended to refer to recent reviews. 125-134

4. Optical properties of Ag NCs

4.1. UV-vis absorption

Surface plasmon resonance (SPR) is the most prominent feature in the UV-vis absorption spectra of Ag NPs due to their distinct optical absorption. 135-138 The SPR peak of Ag NPs is typically located at about 400 nm. In contrast, Ag NCs generally show several distinct absorption peaks in the UV-vis region. The optical absorptions of Ag NCs and Ag NPs are distinctively different, with different origins and different peak locations. Such data can be used to confirm the successful synthesis of Ag

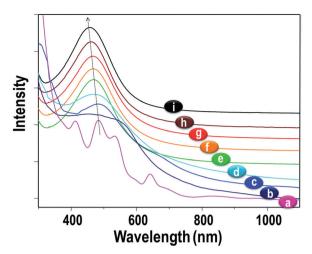


Fig. 25 UV-vis absorption spectra of thiol-protected Ag₄₄ [a], Ag₅₅ [b], $Ag_{\sim 75}$ [c], $Ag_{\sim 114}$ [d], Ag_{152} [e], $Ag_{\sim 202}$ [f], $Ag_{\sim 423}$ [g], $Ag_{\sim 530}$ [h] and Ag NPs [i]. Reproduced with permission from ref. 140. Copyright 2014, Royal Society of Chemistry.

NCs and the transformation of small Ag NCs into large plas-

The surface ligands and cluster size can affect the optical absorption of Ag NCs (Table S2, ESI†). For example, thiolprotected Ag₂₋₈ NCs showed discrete absorption peaks in their UV-vis absorption spectra. 139 The UV-vis spectra of thiolprotected Ag NCs, such as Ag₄₄(4-FTP)₃₀, Ag₅₅(PET)₃₁, Ag₇₅(PET)₄₀, $Ag_{114}(PET)_{46}$, $Ag_{152}(PET)_{60}$, $Ag_{202}(BBS)_{70}$, $Ag_{423}(PET)_{105}$, Ag₅₃₀(PET)₁₀₀, show multiple features up to Ag₁₁₄ and, from Ag₁₅₂ onwards, only one absorption peak at 460 nm (Fig. 25).

The change of the protecting ligands and cluster size, which affect the behavior in the excited state, results in an alteration of the electronic transition. 140 Insight into the modulation of the PL properties and the relaxation from the excited state is provided in the following sections.

4.2. Photoluminescence

PL is amongst the most intriguing and fascinating properties of nanomaterials due to the scope in diverse applications. Ag NCs excited from the ground state release extra energy before returning back to the ground state, which gives rise to PL. However, Ag NCs normally display low quantum yield (QY), and some fundamental issues related to the PL properties of Ag NCs are still indistinct. The PL of Ag NCs can be dictated by the cluster size, protecting ligand, and heterometal atom. Moreover, the valence electron count, oxidation state of the metal, crystal structure, temperature, and pH are crucial to regulate the PL behavior. 31,32

4.2.1. Influence of peripheral ligands. In 2001, Dickson 141 reported bright PL from individual Ag NCs, which accelerated research into metal NCs stabilized with various ligands such as thiols, phosphines, alkynyls or their combination. These peripheral ligands have been proved to have a profound influence on the PL of NCs. With the revelation of different PL behavior in Ag NCs, the effect of the functional groups in the capping ligands has been realized. For example, the C₁₂H₆O₂NCH₂CO₂

ligand Ag₂₀ nanocluster showed green emission around 513 nm with a high PL QY of 6.36% at room temperature. However, the fluorescence was completely quenched in terms of the substitution of the C₁₂H₆O₂NCH₂CO₂ ligand with NO₃ or other ligands. The NIR emission of [Ag₂₉(BDT)₁₂(PPh₃)₄]³⁻ NCs increases 30 fold when monophosphine ligands are replaced by diphosphines with increased chain length. 143

The ligand effect on the PL of a Ag₆₂ nanocluster template has been investigated. The tetracationic silver nanocluster $[Ag_{62}S_{13}(S^tBu)_{32}]^{4+}$ (Ag-QDs) has been reported with intense red emission at 613 nm (solution) and 621 nm (solid state). 65 Later, Zhu et al. reported the crystal structure of [Ag₆₂S₁₂(S^tBu)₃₂]²⁺ (Ag-NCs), 64 which can be regarded as $[Ag_{62}S_{13}(S^tBu)_{32}]^{4+}$ lacking the innermost S ligand. The PL intensity of the Ag-NCs was much weaker than that of the Ag-ODs due to the difference in the valence electron count. The 4 free valence electrons in the Ag-NCs cause luminescence quenching as the LMCT process (ligand-tometal charge transfer) gets hindered, while the Ag-QDs exhibit intense PL owing to the absence of free valence electrons. Interestingly, the Ag-QDs could be electrochemically reduced into Ag-NCs, via an intermediate NC, Ag-inter. 66 Though the structural integrity of the parent Ag₆₂ remains unaltered, the PL intensity of the Ag-inter displayed a 2-fold enhancement relative to the Ag-NCs, and it was still far below the intensity of the Ag-QDs (Fig. 26).

4.2.2. Tuning of the emission with the core size. Etching of silver NPs at the water-toluene interface with MSA ends up with a crude mixture of Ag₇ and Ag₈ NCs. After separation by gel electrophoresis, the Ag₇ NCs display bluish green emission at 440 nm while weak red emission at 650 nm is observed in the Ag_8 NCs. ⁴⁹ In 2003, Zheng *et al.* reported the $Ag_{14}(SC_6H_3F_2)_{12}(PPh_3)_8$ NC with yellow luminescence.⁶⁸ The comparatively large NCs, $Ag_{16}(dppe)_4(SC_6H_3F_2)_{14}$ and $Ag_{32}(dppe)_5(SC_6H_3CF_3)_{24}$, exhibit only a prominent emission peak at 440 nm.80 More information about the PL of Ag NCs with various core sizes is given in Table S2 (ESI†).

4.2.3. Influence of the doped atoms. Doping with foreign metal atoms in Ag NCs has been proved to be an effective method for the modulation of the geometric and electronic structures, and thus could be used to tune the PL (Fig. 27).

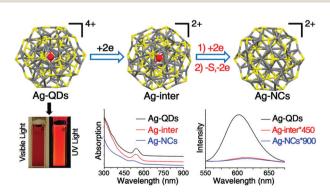


Fig. 26 Schematic illustration of the structural transformation on the basis of a Ag_{62} nanocluster template from Ag-QDs to Ag-inter, and then to Ag-NCs; (bottom-left) digital photographs of Ag-QDs under visible and UV light; and (bottom-middle and -right) UV-vis and PL spectra of Ag-QDs, Ag-inter, and Ag-NCs. Reproduced with permission from ref. 31. Copyright 2019, Royal Society of Chemistry.

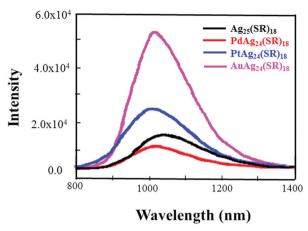


Fig. 27 PL spectra of $MAg_{24}(SR)_{18}$ (M = Ag/Pd/Pt/Au) NCs in the crystal state. Reproduced with permission from ref. 148. Copyright 2017, American Chemical Society.

The optical, electrochemical, and catalytic properties of metal NCs $M_1Ag_{24}(SR)_{18}$ (M = Ag, Au, Pd, Pt) have been systematically characterized. 23,144-148 For example, Bootharaju et al. demonstrated the PL property enhancement of Ag₂₅(SPhMe₂)₁₈ doped with Pd or Au. Due to the stabilization of the charges in the LUMO of the alloy cluster akin to $Au_{25-n}Ag_n$ NCs, the luminescence of the Ag₂₅ cluster is enhanced by a factor of 25 upon doping with gold atoms. 144 Wu et al. investigated the PL property of M@Ag₂₄(DMBT)₁₈ (M = Ag, Pd, Pt, Au) in both crystal and solution phases. 148 A blue shift of the PL with the doping of Ag₂₅(DMBT)₁₈ by Pd/Pt/Au heteroatoms is observed. The sequence of the PL intensity PdAg₂₄(DMBT)₁₈ < Ag₂₅(DMBT)₁₈ < $PtAg_{24}(DMBT)_{18} < AuAg_{24}(DMBT)_{18}$ is exactly related to the electron affinity of the core atom (Fig. 28).

Ag₂₉(S₂R)₁₂(PPh₃)₄ is another fluorescent Ag NC which has been studied in the context of doping. The PL characteristic of

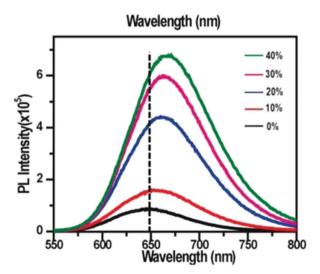


Fig. 28 PL spectra of Ag₂₉ and Au doped Ag₂₉ NCs with different amounts (mmol%) of Au. The inset shows digital photographs under a UV lamp (365 nm). Adapted with permission from ref. 150. Copyright 2016, John Wiley & Sons, Inc.

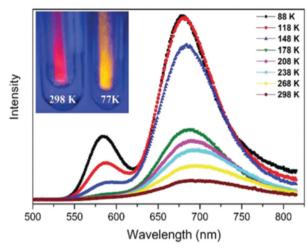


Fig. 29 Effect of temperature on the PL of Ag₁₈ in the solid state at 440 nm excitation. Adapted with permission from ref. 130. Copyright 2017, Royal Society of Chemistry.

the Ag₂₉(S₂R)₁₂(PPh₃)₄ NC has been tuned by doping such a NC with Au/Pt ions. The introduction of the Au or Pt heteroatoms improves the PL intensity relative to the homo-silver Ag₂₉ NC. Bootharaju et al. reported the enhancement of the PL intensity in doped PtAg₂₈(BDT)₁₂(TPP)₄ compared to homo-silver Ag₂₉NCs. 149 Soldan et al. prepared metal NCs Ag_{29-x}Au_x(BDT)₁₂(TPP)₄ and demonstrated that the emission maxima are red shifted from 658 nm (10% Au) to 668 nm (40% Au) with an increase in the Au concentration (Fig. 28).150

4.2.4. Influence of the surrounding environment. Apart from the core size and protecting ligand, the PL behavior of Ag NCs is altered by different external factors such as temperature, solvent, pH etc. For example, the temperature-dependent PL properties of a series of Ag NCs were reported by the Sun group. 107,151-159 Some Ag NCs exhibited higher PL intensities at low temperature, but the emission wavelengths were little changed. However, the emission maximum of the Ag₁₈₀ NC shifts from 723 nm to 623 nm with lowering of the temperature from 293 K to 93 K.131 The Ag18 NC displays an emission wavelength change from red emission (700 nm) to yellow (550 nm) when the temperature of the Ag₁₈ NC was reduced (Fig. 29). 155 Of note, PL intensity enhancement and emission wavelength shifts for nanocluster-based networks have also been researched by the Zang group. 72,160-165

Solvents can also influence the PL properties of NCs, although to a lesser degree than that seen in metal complexes. Silver NCs, being composed of diverse functional groups in the surface ligand, often display solvent specific optical behavior. The nature of the solvent (polarity, protic or aprotic, coordinating or non-coordinating) controls the electronic properties, which eventually influence the emission of Ag NCs. 92,101,148 Xie et al. evaluated the solvatochromism of the $Ag_{51}(^{t}BuC \equiv C)_{32} NC.^{92} As$ the solvent polarity increased from less polar dichloromethane to highly polar methanol, the emission peaks of Ag₅₁ are gradually red-shifted from 436 to 656 nm, exhibiting a remarkable bathochromic effect (Fig. 30).

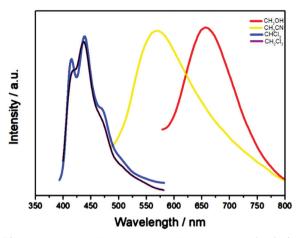


Fig. 30 Emission bands of Ag₅₁ in solvents of varying polarity, CH₂Cl₂ (purple line), CHCl₃ (blue line), CH₃CN (yellow line) and CH₃OH (red line). Adapted with permission from ref. 92. Copyright 2018, Royal Society of Chemistry.

Ag NCs feature tunable luminescence properties, photostability and a biocompatible nature, and have enthralled the scientific community for their applicability in versatile applications such as optoelectronics, catalysis, bio-sensing, and bio-imaging. 6,7,12,13,29,31 More studies are required to explore new applications of Ag NCs. Further development of multi-photon excitation microscopy in Ag NCs calls for more efforts. More Ag NCs with visible range absorption still need to be developed in photovoltaic applications. Biological applications such as bio-sensing and bio-imaging demand hydrophilic Ag NCs with very high PLQY, while catalytic applications need structurally precise Ag NCs.

5. Conclusions

We have summarized significant advances in the field of Ag NCs such as synthesis, structure, and PL properties. For instance, a number of efficient synthetic strategies including direct reduction, chemical etching, and ligand exchange have been developed to produce Ag NCs. Some high-resolution analytical techniques have emerged as powerful tools to characterize Ag NCs, including UV-vis, PL, ESI-MS, SC-XRD, etc. Such techniques have been used to determine the chemical properties and crystal structures of Ag NCs. The crystal structures of Ag NCs eventually control the electronic transition and physical properties. The PL properties of Ag NCs are modulated by the valence state, electronic structure, functional groups and doping heteroatoms. Some parameters of the surroundings such as temperature and solvent also tune the PL properties of Ag NCs.

However, although we have witnessed remarkable progress in the study of Ag NCs, some challenging issues still remain. For example, efficient synthetic strategies for high-purity Ag NCs in the aqueous phase are still lacking. Strategies for increasing the PL quantum yield and tuning the PL colors of nanoclusters are to be devised. Much more effort is needed to further explore promising luminescent probes for a wide spectrum of bio-imaging and bio-sensing applications.

Conflicts of interest

There are no conflicts to declare.

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