FULL PAPER

Different Silver Nanoparticles in One Crystal: $Ag_{210}(^{i}PrPhS)_{71}(Ph_3P)_5Cl$ and $Ag_{211}(^{i}PrPhS)_{71}(Ph_3P)_6Cl$

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Dedication ((optional))

Abstract: Two pure silver nanoparticles ($Ag_{210}(^{i}PrPhS)_{71}(Ph_3P)_5Cl$ and $Ag_{211}(^{i}PrPhS)_{71}(Ph_3P)_6Cl$ labeled as **SD/Ag210** and **SD/Ag211**, **SD = SunDi**), were found to co-crystallize in forming compound **1**. Single-crystal X-ray diffraction (SCXRD) revealed that they differ by only one $Ag(PPh_3)$. Their four-shell nanoparticles consist of three pure Ag metal shells ($Ag_{19}@Ag_{52}@Ag_{45}$) shielded by a silver-organic $Ag_{89}(^{i}PrPhS)_{71}Cl[Ag(Ph_3P)]_n$. outermost shell. The number (n) of $Ag(Ph_3P)$ is five for **SD/Ag210** and six for **SD/Ag211**. The pseudo-fivefold symmetric Ag nanoparticles exhibit surface plasmon absorption similar to a true metallic state but at the nanoscale. The attributes of this work are i) it exemplifies the important effects of phosphine in stabilizing large silver nanoparticles; ii) it offers a platform to investigate the origin of differences in nanoscale metal materials, even differing by only one metal atom; and iii) it sheds light on the regioselective binding of auxiliary Ph_3P on the surface of silver nanoparticles.

Ligand-protected atomically precise silver and gold nanoparticles have attracted extensive attention in recent years due to their promising optical, photophysical, electronic, and chemical properties.[1] These unique properties are different from their bulk counterparts and are dominated by quantum-size and surface structures. [2] As revolutionized by X-ray crystallography, a large number of gold nanoparticles structures have been fully resolved at atomic-level by Jin, [3] Zhu, [4] Dass, [5] Wang, [6] Wu, [7] Kornberg, [8] Konishi, [9] and Yam[10] groups, among others. However, similar advances in silver nanoparticles have largely lagged behind, with only a few Ag nanoclusters such as Ag_{21}, [11] Ag_{23}, [12] Ag_{25}, [13] Ag_{29}, [14] Ag_{34}, [15] Ag_{44}, [16] Ag_{50}, [17] Ag_{63}, [18] Ag_{74}, [19] Ag_{141},[20] reported and the currently largest system Ag_{374}. [21] This situation is mainly caused by instability and difficult crystallization of silver nanoparticles compared to their gold cousins. Therefore, a systematic study of the crystallization method and assembly strategy of silver nanoparticles is urgent for achieving a deep understanding of the chemical nature of these systems to establish the structure-property correlations. In spite of progress made in structure determination of Ag nanoclusters including both metal core and surface ligand, there remains a great challenge to get high-quality single crystals, especially for nanoparticles larger than 2 nm.

Thiol is the most widely used capping ligand in the shape-controlled synthesis of silver and gold nanoparticles, whereas phosphine normally does not prefer to form large silver and gold nanoparticles. [22] Thus, phosphine was usually used as auxiliary ligand with thiol or alkyl to produce some large metal nanoparticles. [23] According to Bakr, [24] introducing phosphine not only enhanced the yield and stability of silver nanoclusters but also assisted with the growth of high-quality single crystals. However, previous work of Zheng's group mentioned a shrinkage effect of phosphine on the size of as-formed silver nanoparticles**.** [25] The results thus aroused our curiosity on how mixed capping ligands work in terms of their coordination abilities, geometries, selectivities, and steric hindrances on a special metallic region on the surface as well as their effects on the shape and size of the resulting nanocrystals.

In this work, we demonstrate a ligand-control strategy to synthesize two colloidal silver nanoparticles (**SD/Ag210** and **SD/Ag211**) which have an intermediate size between previously reported all-thiol protected Ag_{136} and Ag_{374} nanoparticles. [21] **SD/Ag210** and **SD/Ag211** crystallized together in one crystal (denoted as **1**) and have the same pseudo-fivefold symmetry triple-shelled Ag_{116} metallic kernel ($Ag_{19}@Ag_{52}@Ag_{45}$) caged by an outermost Ag_{89}-organic shell, giving an overall Ag_{205} four-shell Russian-Doll motif. Both nanoparticles have the same coatings of 71 $^{i}PrPhS^-$ and one Cl^- ligands, but the Ag_{89} shells are differently capped by five and six $[Ag(Ph_3P)]$ units in **SD/Ag210** and **SD/Ag211,** respectively, which causes the resulting distinct silver nanoclusters**.** This is the first time that two different yet related pure silver nanoparticles co-crystallize into one crystal, although co-crystallization of alloyed nanoparticles $(AuAg)_{267}$ and $(AuAg)_{45}$ driven by magic atomic and electronic shells in one crystal was reported.[26]

1 was synthesized in one-pot by reduction of a mixture of CF_3COOAg, $^{i}PrPhSH$ and Ph_3P in CH_2Cl_2/CH_3OH using $NaBH_4$ at room temperature. The black crystals of **1** containing **SD/Ag210** and **SD/Ag211** were grown by solvent evaporation at room temperature. The synthetic details and basic characterization such as infrared spectra, UV-Vis spectrum, and elements mapping are given in the Supporting Information (SI).

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Despite several attempts, the quality of crystallographic data falls short of routinely accepted and high quality requirements. Accordingly, the quantitative discussions below provide an approximation, thus the given bond parameters should be considered modestly, whereas the core composition and connectivity of Ag_{210} and Ag_{211}, as well as the overall molecular structure of **1** are unambiguously supported by the experimental data and structure optimizations on the DFT calculations. The average molecular structures of **SD/Ag210** and **SD/Ag211** were simultaneously revealed by SCXRD analysis on one crystal (Table S1). They co-crystallized together into triclinic *P*-1 space group with a huge unit cell volume up to 100,000 $Å^3$ and both have a nearly perfect spherical shape (Figure 1) with a diameter of ~ 2 nm excluding the organic shell. The chemical compositions of **1** were identified as $Ag_{210}(^{i}PrPhS)_{71}(Ph_3P)_5Cl$ and $Ag_{211}(^{i}PrPhS)_{71}(Ph_3P)_6Cl$, denoted as **SD/Ag210** and **SD/Ag211**, respectively. The metallic core structures of both share a similar four-shell motif containing the same Ag_{116} kernel caged by the outermost Ag_{89} shell. The main dissimilarity between **SD/Ag210** and **SD/Ag211** is the number of capping $[Ag(Ph_3P)]$ units on the outermost Ag_{89} shell, which causes the resulting differences in the silver nanoclusters in this system. The best expressions for **SD/Ag210** and **SD/Ag211** are $Ag_{19}@Ag_{52}@Ag_{45}@Ag_{89}(^{i}PrPhS)_{71}Cl[Ag(Ph_3P)]_5$ and $Ag_{19}@Ag_{52}@Ag_{45}@Ag_{89}(^{i}PrPhS)_{71}Cl[Ag(Ph_3P)]_6$ respectively.

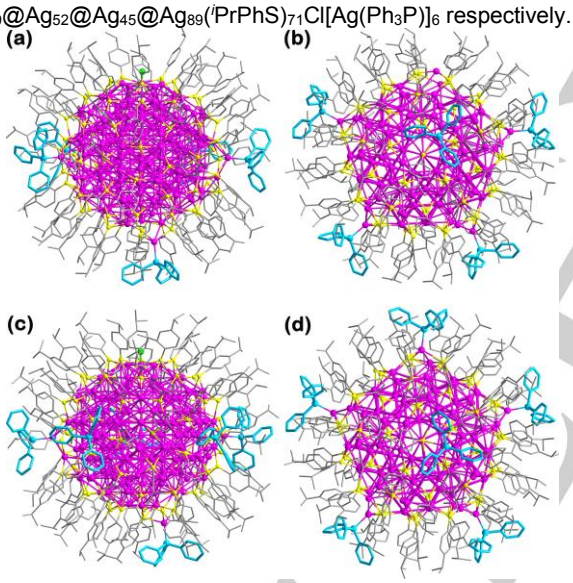

Figure 1. The side and top view of the crystallographic structure of **SD/Ag210** (a and b) and **SD/Ag211** (c and d). (Color legend: Ag: purple; C: gray; S: yellow; Cl: green). All Ph_3P ligands are highlighted in cyan.

Due to the similar four-shell structures in **SD/Ag210** and **SD/Ag211**, we discuss the structural features using **SD/Ag210** as representative. The anatomy of the Ag_{205} core is depicted in Figure 2. The innermost shell is Ag_{19} comprised of three vertex-shared pentagonal bipyramidal decahedra (Figure 2a and 2b) and the total height is 8.74 Å. Alternatively, the Ag_{19} core can be built from two interpenetrated elongated pentagonal bipyramids (J_{16}, one of the Johnson solids, Figure S1) with 10 silver trigons and 5 silver tetragons. [27] This Ag_{19} core is different from that found in Ag_{141}, which has interpenetrating bi-icosahedra with 30 silver trigons on the surface. [20] This difference is mainly caused by the face-to-face arrangement of three Ag_5 pentagons in the Ag_{19} shell of **SD/Ag210**, whereas adjacent Ag_5 pentagons are arranged in a staggered fashion in the Ag_{19} core of Ag_{141} (Figure S2). The Ag_{19} core is caged by the second Ag_{52} shell also in an elongated pentagonal bipyramid configuration (Figure 2c and 2d). This Ag_{52} shell contains two single Ag atoms as vertexes, two small Ag_5 and four larger Ag_{10} pentagons. It has the same count of silver atoms as the 2nd shell in Ag_{141} but differs in the staggered fashion between adjacent pentagons. It can also be seen as a longer version of the Ag_{42} shell observed in Ag_{374} (Figure S3). [21] The Ag_{52} shell is encircled by a 45-atom opened pentagonal cylinder (Figure 2e and 2f), which is a reduced version of the Ag_{60} pentagonal cylinder in Ag_{374}. The inner three shells constitute a fivefold twinned Ag_{116} kernel, which is encapsulated by the outmost Ag_{89} shell **(**Figure S4**)**. The Ag_{89} shell is comprised of one complete 15-silver pentagonal cupola (J_5) and one incomplete 14-silver pentagonal cupola (J_5) missing a corner, which cap the Ag_{60} pentagonal cylinder up and down (Figure 2g and 2h). The Ag_{89} shell encloses the $Ag_{19}@Ag_{52}@Ag_{45}$ shells inside in a concentric fashion (Figure 2i and 2j) to form the final four-shell Ag_{205} nanocluster**.** This 4th Ag_{89} shell is extremely similar to the 3rd Ag_{92} shell in Ag_{374} but with two apical silver atoms and one silver atom on the top pentagon missing. Two apical sites in the Ag_{89} shell are occupied by one Cl^- ion and one $^{i}PrPhS^-$ ligand, respectively (Figure S5). The Cl^- ion should be sourced from CH_2Cl_2 solvent used.[21] The average Ag···Ag distances in the four shells (Table S2-S5) from inner to outer are 2.867, 2.883, 2.857, 3.047 Å, respectively. The average Ag···Ag distances between 1st and 2nd, 2nd and 3rd, 3rd and 4th shells are 2.864, 2.848, 2.912 Å, respectively (Table S6).

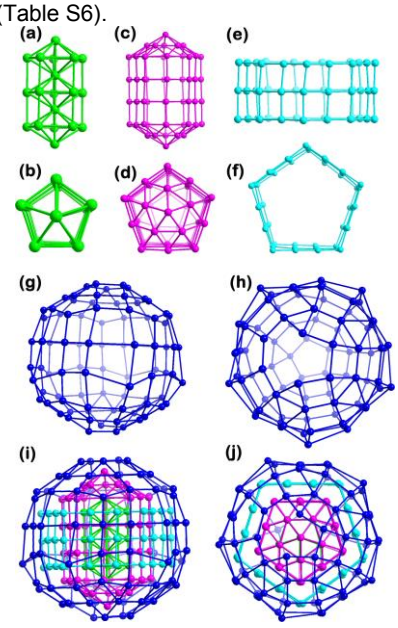

Figure 2. Four-shell structures in **SD/Ag210**. Side and top views of Ag_{19} shell (a and b), Ag_{52} shell (c and d), Ag_{45} pentagonal cylinder (e) and (f), the outmost Ag_{89} shell (g and h) and the total $Ag_{19}@Ag_{52}@Ag_{45}@Ag_{89}$ four-shell structure (i and j).

For **SD/Ag210** and **SD/Ag211**, the outermost Ag_{89} shell is similarly capped by 71 $^{i}PrPhS^{-}$ (3 μ_2, 51 μ_3, and 17 μ_4) and one Cl ion (Figure 3a and 3b). The Ag-S bond lengths are in the range of 2.367-2.966 Å However, the Ag_{89} shells in **SD/Ag210** and **SD/Ag211** were ligated additionally by five and six [Ag(Ph_3P)] units, respectively. In **SD/Ag211**, five [Ag(Ph_3P)] units ligated the nanoparticle at the equatorial region perpendicular to the 5-fold axis and the sixth [Ag(Ph_3P)] unit capped the polar site (Figure 3c). However, the one missing [Ag(Ph_3P)] unit in **SD/Ag210** occurred at the equatorial region (Figure 3d). The average Ag−P bonds are 2.429 and 2.467 Å for **SD/Ag210** and **SD/Ag211**, respectively. All Ag···Ag contacts between [Ag(Ph_3P)] units and the Ag_{89} shell are longer than 3 Å, indicating loosely ligated [Ag(Ph_3P)] units on the surface.

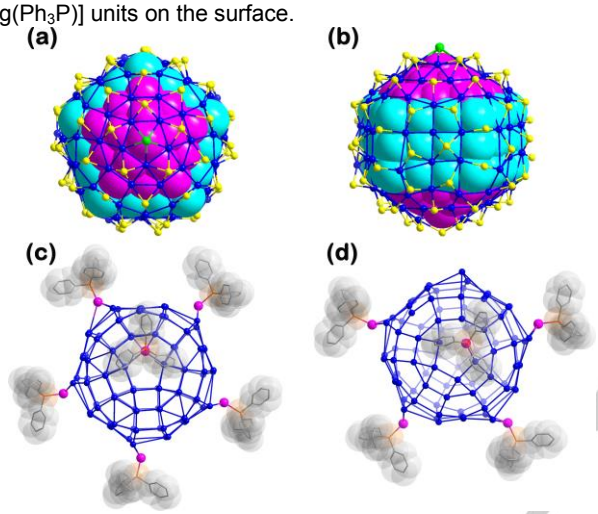

Figure 3. (a) and (b) Top and side views of thiol ligands and one Cl^- ligand on the surface of the Ag_{89} shell. Color legend: S: yellow; Cl: green; the rest: Ag. All carbon atoms are omitted for clarity. (c) The ligation of six [Ag(Ph_3P)] units on the Ag_{89} shell of **SD/Ag211**. (d) The ligation of five [Ag(Ph_3P)] units on the Ag_{89} shell of **SD/Ag210**. The silver atoms bonded to Ph_3P are shown in pink and all Ph_3P ligands are drawn in space-filling mode.

Based on the above structure analysis and comparison, we found the structures of shell, sequences of shells, and the surface ligand ligation are different from previously reported Ag nanoparticles such Ag_{141} and Ag_{374} (Figure S6). We also noted a very recently reported [$Ag_{206}(RS)_{68}X_4$] (RSH = cyclohexanethiol; X = F or Cl) [28] which has a very similar four-shelled structure to **SD/Ag210** and **SD/Ag211** but without the outer [Ag(Ph_3P)] units (Figure S7). Another important difference between them occurs in the 4th shell (consisting of Ag_{89} *vs.* Ag_{90}), in which a pentagon missing a corner and a complete pentagon are observed perpendicular to the 5-fold axis in **SD/Ag210** or **SD/Ag211** and [$Ag_{206}(RS)_{68}X_4$], respectively (Figure S8). By comparison, the introduction of the bulkier Ph_3P ligand plays an important role in controlling the structure and composition of **SD/Ag210** and **SD/Ag211**. The Ph_3P ligand yields a dragging effect due to steric repulsion that pulls the surface silver atom bonded to it far away from the inner shell, creating protuberances on the surface.

The crystals of **1** are readily dissolved in CH_2Cl_2 to give a brown solution. As shown in Figure 4, **1** shows a strong UV absorption band centered at 464 nm, similar to the surface plasmonic absorption band of metallic Ag nanoparticles. [29] This absorption wavelength is shorter than that of Ag_{374} (465 nm) but longer than for Ag_{136} (450 nm) and Ag_{141} (460 nm), which coincides with the basic rule that as the size of nanoparticles becomes larger the surface plasmon absorption peak shifts to longer wavelengths. [30]

In order to deeply understand the above optical properties, we also calculated absorption spectra, density of states (DOS) and the major occupied-virtual transitions using time-dependent density functional theory (TD-DFT) for simplified models of **SD/Ag210** and **SD/Ag211**. Three different ligands (hydrogen, vinyl and phenyl) were considered for the R groups in RS^- whereas phosphine groups were modelled as PH_3 in all calculations. The details are given in Supporting Information. Based on these calculations result, we well correlated the molecular structure and electronic structures and explained the stabilization origins of such large clusters.

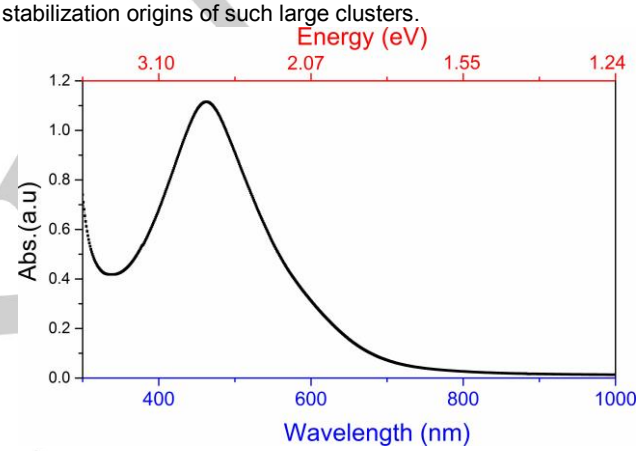

Figure 4. The ultraviolet–visible absorption spectrum of crystals dissolved in CH_2Cl_2 containing both **SD/Ag210** and **SD/Ag211**.

In conclusion, we successfully isolated two colloidal silver nanoparticles with more than 200 metal atoms using $^{i}PrPhSH$ and Ph_3P as co-capping ligands co-crystallizing within one solid. The two silver nanoparticles share the same Russian-doll $Ag_{19}@Ag_{52}@Ag_{45}@Ag_{89}$ four-shell motif that is covered by the same counts of $^{i}PrPhS^-$ and Cl^- ligands but a different number of [Ag(Ph_3P)] units. With these two comparable structures in one crystal, the origin of differences in nanoparticles, even differing in only one metal atom, was well recognized by resolving their structures, which also widened our general knowledge that the single crystals of nanoparticles represent absolutely atomically mono-dispersion. These Ag nanoparticles behave in a true metallic state at the nanoscale with a fivefold symmetry structural feature and surface plasmon resonance absorption. The results not only elucidated important effects of the auxiliary phosphine ligand in the controlled synthesis of metal nanoparticles but also shed light on the regioselective binding of auxiliary Ph_3P on the surface of silver nanoparticles.

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Keywords: silver nanoparticles • alkyne • core-shell • surface plasmon • co-crystallization

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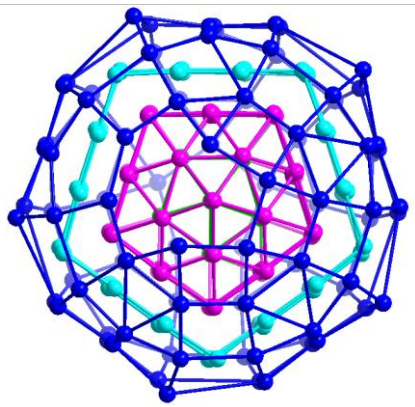
Entry for the Table of Contents (Please choose one layout)

Layout 1:

Rare co-crystallization of two different silver nanoparticles, $Ag_{210}(^{i}PrPhS)_{71}(Ph_3P)_5Cl$ and $Ag_{211}(^{i}PrPhS)_{71}(Ph_3P)_6Cl$, having pseudo-fivefold symmetry 'Russian Doll' onion structure in one crystal and exhibiting strong red surface plasmon absorption.		*Jun-Yan Liu,[a] Fahri Alkan,[b] Zhi Wang,[a] Zhen-Yi Zhang,[c] Mohamedally Kurmoo,[d] Zier Yan,[e] Quan-Qin Zhao,[a] Christine M. Aikens,*[b] Chen-Ho Tung,[a] and Di Sun*[a]* ***Page No. – Page No.*** **Different Silver Nanoparticles in One Crystal: $Ag_{210}(^{i}PrPhS)_{71}(Ph_3P)_5Cl$ and $Ag_{211}(^{i}PrPhS)_{71}(Ph_3P)_6Cl$**