

Evolution of Atomically Precise Silver Clusters to Superlattice Crystals

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We report the systematic size evolution of an organic-soluble, atomically precise silver cluster (product 1) of ≈ 0.9 nm diameter to superlattices (SLs). Product 1 converts gradually to more stable plasmonic particles of ≈ 2.9 nm diameter (product 2) and constant heating of the latter at 100 °C leads to crystals composed of self organized nanoparticles or SLs (product 3). Evolution of product 1 to larger nanoparticles was observed by mass spectrometry, while the formation of nanoparticles and crystals was investigated by electron microscopy. The constituent units of products, 1 (m/z of 13.5 k), 2 (mixture of m/z 70 k and 80 k), and 3 (m/z of 148 k) are tentatively assigned to $\text{Ag}_{75}(\text{PET})_{40}$, $\text{Ag}_{530}(\text{PET})_{100}$ (with $\text{Ag}_{561}(\text{PET})_{150}$), and $\text{Ag}_{923}(\text{PET})_{351}$, respectively, where PET refers to 2-phenylethanethiol, the ligand used for protecting the cluster core. Creation of nanoparticle crystals starting from atomically precise clusters points to the synthesis of nanoparticle solids with tunable properties.

Atomically precise clusters of noble metals exhibiting intense luminescence and having distinct absorption characteristics^[1] are said to be the missing link between the atomic and nanoparticle (NP) regimes of matter. Metallic NPs^[2,3] possessing characteristic optical absorption due to plasmon resonance^[4,5] can be converted to clusters exhibiting distinct optical absorption and emission in the visible region, by appropriate chemistry.^[6] NPs having varying morphologies can be annealed to definite, uniform shapes by digestive ripening^[7–11] and such monodisperse particles can self-organize to yield particle crystals or SLs.^[12–17] Refined synthetic methods yielding monodisperse particles can also form self-organized structures directly.^[18] Stacking of NPs into 2D and 3D superstructures and investigating their collective properties are receiving much attention among nanochemists due to diverse applications for the latter.^[19,20]

We show here that atomically precise clusters, consisting of a few tens of atoms can be grown systematically to plasmonic particles, which subsequently yield particle crystals. This methodology can possibly create SLs from particles of any desired size, enabling the creation of designer crystals and consequently varying properties. We show that crystals of plasmonic

nanoparticles are better formed starting from sub-nanometer clusters.

A solid-state route^[21] was used to synthesize atomically precise clusters. Briefly, the method involves grinding the precursors (AgNO_3 and PET) in a mortar and pestle to form silver thiolates. Addition of sodium borohydride in the solid state to this mixture with continued grinding produces well-defined clusters that can be extracted with suitable solvents (details of experimental procedure are outlined in Figure S2, Supporting Information). First, a mixture of AgNO_3 and tetraoctyl ammonium bromide (TOABr) was taken in an agate mortar and ground uniformly. To that, PET was added and ground till the initial yellow color changed to orange (due to the formation of silver thiolate). Reduction was achieved by adding solid NaBH_4 and by constant grinding in ambient air so that the mixture became blackish brown. The product was extracted in ethanol and centrifuged to remove extra thiol in the supernatant and finally the residue was extracted in toluene, which gives a reddish-brown solution. A crucial aspect of the synthesis is the limited supply of water required for the reduction. This was made available from the laboratory air (as NaBH_4 is hygroscopic) and ethanol used for extraction.

Initial extract of the solid state reaction product with ethanol was discarded as it contains excess thiol^[22,23] used in the synthesis along with some clusters. Excess thiol makes smaller clusters unstable and gradually thiolates are formed. Matrix-assisted laser desorption mass spectrum (MALDI MS) of the ethanol extract shows a sharp peak at m/z of 11.8 k (that is, 11 800) and the optical spectrum (corrected by Jacobian factor^[24] shows step-like multiple features at 351 nm, 506 nm and 593 nm, mainly due to the formation of clusters, which is further confirmed by transmission electron microscopy (TEM) (Figure S3, Supporting Information)). The residue upon extraction with toluene (labeled as product 1) yields a characteristic feature at 13.5 k in MALDI MS, along with its dimer at 27 k, with no other features in the entire mass spectrum measured up to 400 k. It is important to note that the mass spectra are measured at threshold laser intensities. A sharp rise and quick fall of the mass spectral features at threshold laser fluence is a characteristic signature of atomically precise clusters.^[25,26] Upon increasing the laser intensity, another threshold is reached where fragmentation commenced yielding lower mass features. Fragmentation increases with increase in fluence and subsequently another threshold is reached beyond which no further fragmentation was observed^[27] (Figure S4, Supporting Information). A small hump arises with increase in fluence at m/z of 78 k along with the 13.5 k peak which suggests the fact that product 1 may be co-existing with another cluster at smaller

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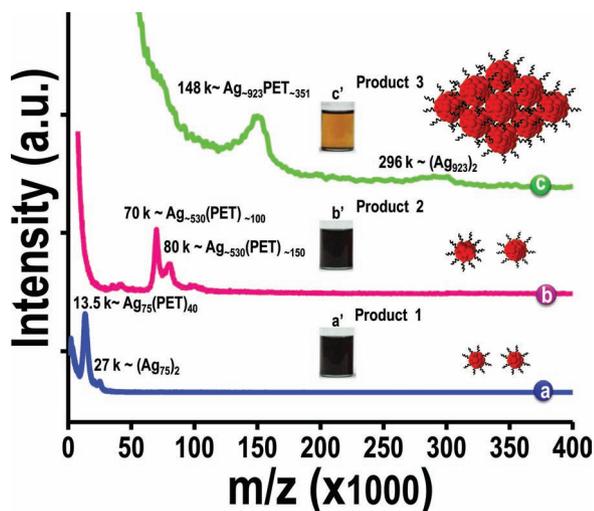


Figure 1. MALDI mass spectra showing the systematic size evolution of product 1 to particle crystals. A sharp peak centered at m/z of 13.5 k (a) obtained by operating at the threshold laser fluence is assigned as $\sim\text{Ag}_{75}(\text{PET})_{40}$ (product 1) with a hump at m/z of 27 k, probably due to the dimer. Product 1 converts to a new plasmonic product 2 (b) with mass of 70 k and a weaker feature at 80 k (tentatively assigned as $\text{Ag}_{-530}(\text{PET})_{-100}$ and $\text{Ag}_{-561}(\text{PET})_{-150}$, respectively). Gradual heating makes assembly of plasmonic product 2 to form SLs with definite periodicity (c) composed of ≈ 923 Ag atoms ($\text{Ag}_{-923}(\text{PET})_{-351}$). Dimer at 296 k is also observed (c). Insets of mass spectra show the corresponding photographs and cartoon representations of the size evolution. In photograph (c'), a black precipitate can be seen, which corresponds to the SL.

concentration, which needs a higher threshold fluence for desorption-ionization. The tentative assignment of 13.5 k would be $\text{Ag}_{75}(\text{PET})_{40}$ which was originally observed by Indranath et al.^[28] and that at 27 k is the dimer of 13.5 k (2×13.5). The clusters kept for one day in refrigerator show a gradual increase in mass. The 13.5 k mass feature disappeared completely after a day. Subsequently two characteristic mass features (Figure 1a) were seen at 70 and 80 k (product 2) suggesting slow size evolution of clusters, which is in agreement with the laser threshold dependence of the 13.5 k feature. These two peaks are tentatively assigned as $\text{Ag}_{-530}(\text{PET})_{-100}$ (similar to the recently reported Au_{530} clusters^[27] and $\text{Ag}_{-561}(\text{PET})_{-150}$). Product 2 upon annealing at 100 °C for 2 h yields a black residue (product 3) and a dark yellow supernatant. Mass spectrum of the residue shows a broad feature centered at 148 k (Figure 1c) with its dimer at 296 k. Further increasing the annealing time, the supernatant becomes colorless indicating complete precipitation. As the cluster size increased, the threshold laser intensity also increases: 1311 for 13.5 k, 1498 for 70 and 80 k and 2000 for 148 k (numbers refer to laser intensity measured in a unitless instrument setting).

Along with this gradual mass evolution, systematic change is observed in the optical absorption spectra (as seen in Figure 2). Characteristic absorption in the higher wavelength region is observed for nanoclusters. Product 1 shows a band at 480 nm along with a hump at 425 nm (Figure 2a) which closely resembles the Ag_{75} cluster feature, reported from our group.^[25] At smaller core sizes, the spectrum shows distinct features in the higher wavelength region as in $\text{Ag}_{7,8}$, Ag_9 , etc. The spectrum of

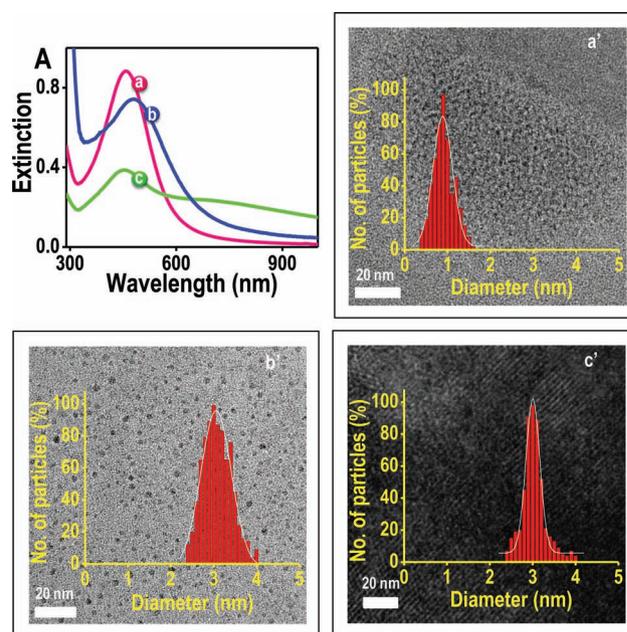


Figure 2. A) UV/Vis spectrum of product 1 showing a band at 480 nm along with a small hump at 425 nm (a), which gradually evolves to plasmonic product, 2 (b). After 2 h of heating of product 2 we obtained a residue that was dispersed in toluene and gives a less intense 455 nm peak with a broad peak around 700 nm (c). This is due to the gradual assembly of product 2 to form SLs. Broad background is in agreement with this. The TEM images and the corresponding size distribution of product 1, product 2 and product 3 (a', b', c') and their Gaussian fits further confirm evolution of clusters.

Ag_{75} evolves to a single plasmonic feature at 458 nm (Figure 2b) which is further confirmed from TEM images. This implies the formation of bigger NPs. The spectrum of a dispersion of product 3 shows the plasmonic feature at 455 nm but with a higher wavelength band, characteristic of aggregates and is attributed to interplasmon coupling.^[29] The characteristic 458 nm feature is identical to the plasmon absorption spectrum of PET protected NPs (Figure S5, Supporting Information). The TEM image of product 1 shows uniform size distribution ($0.9 \text{ nm} \pm 0.2 \text{ nm}$) but, product 2 shows a broad size distribution ($2.9 \text{ nm} \pm 0.4 \text{ nm}$) and product 3 shows uniform size distribution ($3.4 \text{ nm} \pm 0.2 \text{ nm}$), which is a requirement of SL formation.

The residue upon closer examination in TEM shows a periodic array of NPs of 3.4 nm core size (Figure 3A). The average size of these particles increased from product 2 (2.9 nm) to product 3 (3.4 nm). The improved monodispersity is suggested to be due to core size growth in clusters, similar to digestive ripening upon heating. In the TEM image presented, the (110) plane of the SL crystal is projecting towards the viewer. The image reveals that no further growth of the NPs occurs in the SL crystal. The constituent silver NPs are stacked in a *fcc* pattern rather than *hcp* in the 3D array. The crystals show preferential (111) (Figure 3A, a') orientation as expected from a majority of hexagonal or diamond-like morphologies (Figure 3B, C).

The (111) plane of the SL yields a characteristic hexagonal Fourier transform indicating extended periodicity in the

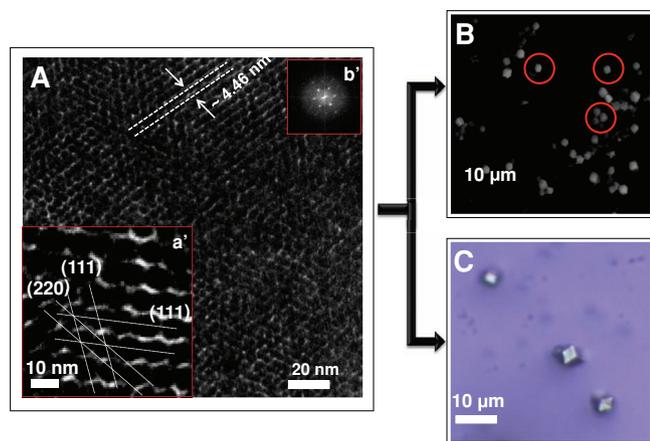


Figure 3. A) TEM image of superlattice formed after 2 h of heating of the plasmonic product **2**. Inset (a') shows an expanded view of the hexagonal array of the NPs with (111) and (220) facets which confirms the periodic arrangement of superlattices (SLs). Inset (b') shows the characteristic hexagonal FFT pattern from the same area emphasizing periodic arrangement of NPs. The SEM image (B) shows that they are hexagonal crystals with sharp edges and C) shows the optical image of the same which further confirms the formation of SL crystals.

material (Figure 3A,b'). This core size of 3.4 nm is in agreement with a cluster of ~ 923 atoms, suggested by the mass spectrum. As expected, the crystals in SEM show well-defined facets (Figure 3B). It suggests that each facet has hexagonal plate-like morphologies which confirm the periodic arrangement of the NPs. The residue gave shiny crystals under an optical microscope (Figure 3C). The corresponding TEM image of dark yellow supernatant (obtained after 2 h heating of product **2**) shows a uniform size distribution with a size of 2.4 ± 0.4 nm (Figure S6, Supporting Information) and optical absorption spectrum shows a broad SPR band at 455 nm.

Elemental analysis of the SL by EDAX shows Ag and S at 2.5:1 ratio in agreement with the composition (Figure S7, Supporting Information), $\text{Ag}_{-923}(\text{PET})_{-351}$. No other elements (other than C) were seen in significant concentration. These support the formation of particle crystals of atomically precise NPs. The inter-particle distance observed is 5.48 nm (Figure S8, Supporting Information), which is smaller than twice the distance of the clusters (including PET shell and the core, i.e., 5.82 nm). This suggests interdigitation of the monolayers during the formation of SLs.^[30]

In summary, we have demonstrated the transformation of atomically precise clusters to NPs and the latter's subsequent conversion to SLs. Although systematic size evolution is studied here with MALDI MS, experiments with electrospray ionization mass spectrometry (ESI MS), small-angle X-ray scattering (SAXS), and dynamic light scattering (DLS) can reveal the dynamics of size evolution in solution and such studies are important to understand the events in solution. The present study, in conjunction with other reports of clusters suggests the possibility of creating SLs of varying core sizes starting from well-defined clusters. This will enable the creation of designer crystals of metals with varying properties as particle growth can be controlled at various stages.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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