Low-Temperature Thermal Dissociation of Ag Quantum Clusters in Solution and Formation of Monodisperse Ag2S Nanoparticles

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ABSTRACT: We report the effect of temperature on the stability of glutathione-protected Ag25 clusters. The clusters are stable up to 50 °C. Interestingly, above this temperature, they decompose to yield Ag2S nanoparticles with an average diameter of 3 ± 1 nm, crystallizing in monoclinic acanthite polymorph. Unlike conventional methods of syntheses of Ag2S, where a temperature of ~200 °C is needed, our study shows the possibility of synthesis of Ag2S nanoparticles at much lower temperatures. This is in contrast with silver nanoparticles protected with thiocyanates, which typically give silver and alkyl/aryl disulfide upon thermal activation. The mechanism of cluster decomposition and formation of silver sulphide nanoparticles was investigated using various analytical techniques such as ultraviolet–visible spectroscopy, X-ray diffraction scanning electron microscopy, energy-dispersive analysis of X-rays, transmission electron microscopy, and electrospray ionization mass spectrometry. The monolayer of the cluster undergoes 5–C bond cleavage, as revealed by mass spectrometry. This is somewhat unusual because Ag−S cleavage is expected in view of its lower bond energy.

1. INTRODUCTION

Noble-metal nanoparticles with thiolate protection1−4 have been extensively investigated in the past several years because of their interesting electrical, optical, and chemical properties and due to their possible applications in various fields. Their properties are highly influenced by the medium, nature of the protecting ligand, pH, temperature, and so on, of which temperature is of high importance. Thermal stability of such monolayer-protected nanoparticles, referred to as MPCs (monolayer-protected clusters), previously has been a subject of discussion.5 Thermal desorption of MPCs of gold results in the formation of alkyl disulfide in the gas phase and gold in the solid state, the Au−S bond being stable till 160 °C. Similar decomposition takes place in the case of silver as well.6−8 For example, carboxylates of silver decompose to give metallic silver and carboxylic acid derivatives or radicals upon heating.9 Thermal desorption of thiolate self-assembled monolayers (SAMs) on planar surfaces can also distinguish adsorption sites.10,5b

Noble-metal-derived quantum clusters13 are exciting new materials. They exhibit unique properties due to the confinement of electrons in discrete energy levels. These subnanometer particles having a core of only a few metal atoms can be considered as the smallest analogues of MPCs. Bare cores are inherently unstable because of their high surface energy, which makes them coalesce into larger particles. Such cores could be protected and stabilized with a shell of ligands, and the system as a whole exhibits interesting optical and chemical properties. The ligand shell plays an important role in determining the properties of clusters such as their stability as well as physical and chemical properties.2,14,15 Study of these properties has attracted significant attention in the recent past. Study of applications of nanoclusters has been a subject of interest as well.

Most of the studies in this category of materials have been on gold clusters, especially Au25SG18. (SG is glutathione in the thiolate form, protecting the Au25 core.) Silver clusters are the second most studied systems. These clusters exhibit bright fluorescence with a quantum yield up to 64%.16 Practical applications of clusters are determined by their stability under ambient conditions.17 The stability increases upon going from free to supported to passivated clusters.18 Some of the new areas of research of these materials are: (i) incorporating them in human cells19 as a diagnostic tool,20,21 (ii) fabrication of luminescent patterns,22,23 (iii) catalysis,23,24 (iv) metal ions sensing,25−27 (v) biolabeling,28−30 and (vi) medicine.30

Most of these applications would require an understanding of the thermal stability of the material of interest. We report the experimental results of our study of thermal stability of QCs, taking Ag25SG18 as a model. We find that these clusters undergo thiolate desorption and heterolytic bond cleavages, resulting in the formation of Ag2S nanoparticles at low temperatures. Mechanistic aspects of the reaction were probed with several spectroscopic tools. The only related studies have been on the temperature-dependent optical properties of Au25SR18 in solution,11 but the product of dissociation was not further investigated. It is likely to be Au(1)-thiolates. However, because the chemistry of gold clusters is quite different from that of silver, the products of thermal decomposition may vary for silver clusters. One such example is the heating of aryl-thiolated silver nanoparticles having non-plasmonic optical properties at 90 °C, leading to the formation of...
nearly 100% yield. The yield of the cluster was 66% with respect to AgNO₃.

2.3. Thermal Decomposition of the Clusters. The cluster solution was kept in a synthesizer under constant stirring at 80 °C until the color changed from reddish brown to greenish black, which took about 30 h. After cooling, it was centrifuged to get a greenish black residue. The clear supernatant solution was preserved for further characterizations.

2.4. Characterization. Optical absorption spectra were collected in the range 200 to 1100 nm. For room-temperature recordings, a Perkin-Elmer Lambda-25 spectrophotometer was used. For higher temperature recordings, another Perkin-Elmer spectrometer, with an accessory for maintaining sample temperature, was used. Luminescence spectra were recorded using a Jobin Yvon Nano Log spectrofluorimeter. Scanning electron microscopic (SEM) images and EDAX images were obtained using a FEI QUANTA-200 SEM. For measurements, samples were prepared by drop casting on an indium tin oxide (ITO)-coated glass plate and drying in vacuum. The X-ray diffractogram was collected using Cu Kα radiation (λ = 1.5418 Å) in a Bruker AXS D8 Discover diffractometer. Transmission electron microscopy (TEM) measurements were carried out using a JEOL 3011 instrument. Samples for TEM were prepared by dropping the aqueous dispersions on amorphous carbon films supported on a copper grid and drying in an ambient atmosphere. Mass spectra were recorded using a QTrap 3200 instrument with electrospray ionization (ESI). Samples of 20 ppm concentration (in Ag), prepared using 1:1 mixture of CH₂Cl₂/methanol, were electro-sprayed at a flow rate of 10 μL/min and at an ion spray voltage of 5 kV.

2.5. Results and Discussion. The absorption spectrum of freshly prepared clusters in aqueous medium (Figure S1 of the Supporting Information) confirms the formation of Ag₂₅S₁₈ clusters. Unlike larger Ag nanoparticles, which show surface plasmon resonance (SPR) at ~400 nm, Ag₂₅ clusters show molecular-like transitions, as revealed in their absorption spectrum, having (i) a pronounced peak at 478 nm and (ii) two broad peaks at 330, 478, and 640 nm in the UV/vis spectrum of the redispersed sample. The absorption spectrum of the freeze-dried cluster sample was also taken after redispersing the dried powder in water. The features at 330, 478, and 640 nm in the UV/vis spectrum of the redispersed sample indicate the presence of the cluster (Figure S2 of the Supporting Information). The inset in Figure S1 of the Supporting Information shows the TEM image of clusters. No individual cluster is seen in the image because the core dimension is small (<1 nm). Also, such clusters are highly sensitive to electron beam irradiation.

2. EXPERIMENTAL SECTION

2.1. Materials. Silver nitrate (99%), glutathione (GSH, 97%), methanol (GR grade), acrylamide (AR grade), N,N'-methylenebisacrylamide (BIS, AR grade), ammonium persulfate, and N,N,N',N'-tetramethylethylene diamine (TEMED) were purchased from SRL Chemical, India. Other chemicals used were: (1) sodium borohydride (NaBH₄, 99.99%, Aldrich) and (2) ethanol, methanol, and dichloromethane (all HPLC grade, Aldrich). All chemicals were used without further purification.

2.2. Synthesis of Ag₂₅S₁₈. Ag₂₅S₁₈ cluster was prepared by the reductive decomposition of Ag(I)GSH thiolate in gel cavities following a method previously reported from our lab.²¹

\[ \text{AgNO}_3 + \text{GSH} \rightarrow \text{Ag}_25\text{SG}_{18} \]

In brief, a mixture of AgNO₃ and GSH was (in 1:2 molar ratio) dissolved in NaOH solution (45 mg NaOH in 1 mL distilled water) at room temperature and sonicated for a few minutes. A yellow solution of Ag(I)SG complexes was obtained. The mixture was cooled to 0 °C for about 0.5 h. The color of the gel changed from yellow to brown, indicating the formation of clusters within the gel. The dark-brown-colored gel was transferred to a mortar, crushed, and washed many times with methanol to remove excess NaBH₄. The crushed gel was taken, and distilled water was added to extract the cluster into the aqueous medium. The yield of the cluster was 66% with respect to AgNO₃.

2.3. Synthesis of Ag₅S₁₈ in the gel. A solution of 45 mg NaOH in 1 mL distilled water was added to a mixture of AgNO₃ and GSH, and the mixture was cooled to 0 °C for about 0.5 h. The color of the gel changed from yellow to brown, indicating the formation of clusters within the gel. The dark-brown-colored gel was transferred to a mortar, crushed, and washed many times with methanol to remove excess NaBH₄. The crushed gel was taken, and distilled water was added to extract the cluster into the aqueous medium. The yield of the cluster was 66% with respect to AgNO₃.

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in TEM; they aggregate to form nanoparticles instantaneously upon electron beam irradiation.32,33

Time-dependent absorption spectra of Ag25SG18 cluster were taken at room temperature, which show a gradual decrease in the intensities of the peaks at 330, 478, and 640 nm with time (Figure S3 of the Supporting Information). The peaks at 330 and 640 nm are more sensitive and vanish at a faster rate compared with the prominent peak at 478 nm, which shows reasonable peak intensity even after 90 days. This type of behavior in the absorption spectra is observed for previously reported thiolate protected silver clusters.34 The thermal stability of these clusters was examined by taking UV/vis spectra at several fixed temperatures in the range of 25−85 °C (Figure 1). We see that the peak position remains the same, whereas peak intensities decrease with increase in temperature. Similar to the behavior in the time-dependent spectra, the peaks at 330 and 640 nm vanish very fast compared with the peak at 478 nm. Although there is a decrease in intensity with temperature, clusters seem to be almost stable up to 50 °C, as revealed by the persistence of the peak at 478 nm. Above 50 °C, even the peak at 478 nm decreases at a faster rate, finally showing a featureless spectrum. The decomposition follows first-order kinetics, as revealed by analysis of absorption spectra, shown in Figure S4 of the Supporting Information. One of the products of decomposition is silver sulphide, the presence of which is confirmed by EDAX and XRD. (See Figures 3 and 4.)

**Figure 1.** UV/vis spectra of Ag25SG18 clusters at various temperatures ranging from 25 to 85 °C.

For obtaining the decomposed end product for further characterization, an aqueous solution of clusters was heated to 80 °C for 30 h with constant stirring. The resulting mixture was freeze-dried to get a greenish black solid residue. Figure 2A shows the absorption spectrum of this residue after suspending in water. We see that the peaks, characteristic of clusters, have vanished, and very broad and shallow features are observed. Starting from the beginning of heating at 80 °C, the color of the solution changed from brownish red to a reddish orange and then finally to greenish black, as shown in the photograph (Figure 2A (a−c)). The inset of Figure 2A shows the Jacobian-corrected spectrum of the greenish black residue, where absorption features at ∼340 and ∼770 nm are seen. To amplify less-intense absorption features, we have corrected the data with the Jacobian factor. For this, the experimentally obtained intensities in absorbance as a

**Figure 2.** (A) UV/vis spectrum of product (Ag2S) obtained by complete decomposition of Ag25SG18 clusters. The bottom inset of panel A shows the Jacobian corrected spectrum. The upper inset gives the photographs of clusters in various stages during thermal decomposition. (a) As-synthesized clusters in water. (b) After 20 h of heating at 80 °C. (c) After heating for 30 h at 80 °C. (B) Excitation and emission spectra of Ag25SG18 (i, red trace) and that of the decomposed sample in water at 25 °C (ii, blue trace).
function of wavelength \( I(W) \) have been converted to energy-dependent values \( I(E) = I(W) / (\partial E/\partial W) \alpha I(W) * W^2 \), where \( \partial E/\partial W \) represents the Jacobian factor against wavelength. The onset of absorption is observed at \( \sim 950 \) nm. All of these are attributed to band-edge transitions in silver sulphide nanoparticles. Similar absorption band positions and band profile are seen in the UV/vis spectrum of Ag₂S nanocrystals.³⁵–³⁷,³⁹ The luminescence profile of the as-prepared clusters and of the decomposed sample are shown in Figure 2B. Ag₂S clusters exhibit a red emission peaking at 650 nm when excited with 480 nm radiation. In contrast, the decomposed sample did not show luminescence for the same excitation.

Direct confirmation of the formation of Ag₂S nanoparticles is obtained from the XRD pattern (Figure 3) of the solid product. The pattern shows prominent peaks corresponding to diffraction from (111), (−111), (112), (−103), (−023), (−123), and (−213) crystal planes of room temperature modification (Acanthite, monoclinic) of Ag₂S³⁸ (JCPDS file no: 14-0072, inset of Figure 3.). Acanthite is stable at temperatures <176°F.³⁹,⁴⁰ The other phases of Ag₂S, such as body-centered cubic (argentite) and face-centered cubic (high argentite) forms, exist at high temperatures. These phases are not present in the present system. The absence of silver nanoparticles and silver thiolate is confirmed by XRD as well. This XRD taken for the decomposed sample is different from that of the parent Ag₂S₁₈ cluster, which shows a broad peak at 36° (2θ) (Figure S5 of the Supporting Information). Slightly broader peaks observed in our diffraction pattern of the decomposed sample as compared with that of well-crystallized samples are ascribed to the smaller grain size of the former.

EDAX of the final solid (Figure 4A) shows the atomic ratio of Ag:Sn in the final product to be 2:1, as expected for stoichiometric Ag₂S. Figure 4B gives the SEM image of the product. Figure 4C,D is the EDAX image collected using Ag Lα and S Kα, respectively. Peaks of other elements such as O, Si, Sn, and Ca are also present in the EDAX spectrum, which are due to elements present in the ITO-coated glass plate.

The shape and distribution of Ag₂S nanoparticles were studied by TEM (Figure 5). Monodispersed spherical nanoparticles with a mean diameter of 3 ± 1 nm are seen in the images. Aggregation is expected because of the lack of surface protection. The large number of aggregates seen in the image is due to high particle concentration in the solution used for analysis. The Ag₂S nanoparticles formed in the present study are very small in size in comparison with that of Ag₂S nanoparticles synthesized by previously reported methods, employing other wet chemical routes, the minimum mean diameter reported being ~8 nm. Although XRD revealed the presence of distinct lattice planes, TEM images did not show them because particles are very small. Thermal decomposition of Ag₂S₁₈ clusters at comparatively high temperatures (∼80 °C) for long time seems to favor the breaking of sulfur–carbon bond (S–C bond) of the thiol ligand rather than the silver–sulfur bond (Ag–S bond). The organic Appendix A

Figure 4. (A) EDAX spectrum of the residue left after decomposition of Ag₂S₁₈ clusters. (B) Its SEM image and EDAX images collected using Ag Lα (C) and S Kα (D).

Figure 5. TEM image of the decomposed sample showing nanoparticles. Inset shows the image of a single nanoparticle at a higher magnification.
moieties formed after dissociation go to the solution, leaving stable Ag₂S. The presence of desulphurized organic entities of GSH was confirmed by ESI MS of the supernatant solution left after the removal of the solid product (Figure 6A). Only the significant portion of the mass spectrum is shown in Figure 6A.

Figure 6. (A) Portion of negative ion ESI MS of the supernatant solution left after the removal of solid products obtained after decomposition of Ag₂S⁵GSH₁₆. (B) Scheme showing the possible fragmentation path for glutathione molecules bonded to the Ag core.

Schematics shown in Figure 6B give the possible bond cleavage schemes of GSH upon temperature-induced decomposition application. The fragmentation results in two kinds of products: (i) a desulphurized GSH (as in scheme (a)) and (ii) two asymmetric fragments of SGH (as in schemes (b) and (c)). Mass
spectrum, taken in the negative mode, shows a peak at m/z 272, which we assign to desulphurized species. The peak at m/z 306 is assigned to reduced GSH. We can also see a number of small fragments of GSH in the mass spectrum. The formation of some prominent fragments is explained through the scheme presented in Figure 6B. Peaks appear at the calculated positions for GSH. For example, the peak due to the first fragment (in scheme (b)) is at m/z 129, and that at m/z 143 (in scheme (c)) can be attributed to the removal of neutral pyroglutamic acid from desulphurized species. A peak at m/z 198 (Figure 6A) is due to the presence of the second fragment in which proton is replaced by a Na+, that is present in the medium. The peak at m/z 254 is due to the species formed by the loss of one water molecule from the desulphurized GSH species. Along with these peaks, there are some peaks originating from a small amount of acrylamide gel still remaining in solution (for example, the peak at m/z 224). The mass spectrum in the positive ion mode also shows all of these peaks (not shown here). The mass spectrum collected for GSH alone, in the negative mode, also shows similar peaks at corresponding m/z values (Figure S6 of the Supporting Information), which further justifies our result.

Figure 7 shows the MS/MS spectrum of the peak at m/z 272. MS/MS gives major fragment peaks at m/z 129, 143, 210, and 253. The formation of these fragments is explained in Figure 6. Peaks at m/z 152 and 165 are assigned, respectively, to species formed by the replacement of protons in fragments, m/z 129 and 143 by Na+.

The mechanism of formation of silver sulphide nanoparticles is not well understood. Here we present our tentative suggestions for the formation of Ag2S upon thermal decomposition of silver quantum clusters.

There are two possible routes for the dissociation of thiolates on cluster surfaces, as shown in Scheme 2. In the first case, the organic moiety, devoid of sulfur, leaves the cluster surface, resulting in silver sulphide nuclei of the form Ag25S12; subsequently, these aggregate to form Ag2S nanoparticles (Route 1). Assuming the structure of Ag25SG18 to be similar to that of Au analogue, there could be SG ligands directly bonded to the core along with bridged ligands. Probably, it is these bridged species that are thermally less stable, and they get desorbed with activation. This desorption could explain the presence of anionic GSH seen in the mass spectrum of the solution. MALDI mass spectra of such clusters, where Au25SR12 fragments were observed, also support this view. Analogous entities existing in solution might have undergone thermal cleavage, leading to Ag25S12. We note that the Ag to S ratio, 25:12, is very close to the ideal ratio, 25:12.5, needed for the formation of stoichiometric Ag2S. The extent of nonstoichiometry due to lower sulfur content, if it exists, would be very small. The organic moieties go to the supernatant solution as previously described. In the second case, Ag(I) thiolates are formed by thermal decomposition of the cluster and eventually Ag2S nanoparticles formed by continuous heating (Route 2). Route 2 may be better feasible thermodynamically because the formation of thiolates is commonly seen from such clusters. Thiolates, once formed, can have two possible cleavages, namely, at the Ag−S bond (eq 1) and at the C−S bond (eq 2).

\[
\begin{align*}
2R-S-Ag & \rightarrow 2Ag + R-S-S-R \\
2R-S-Ag & \rightarrow 2Ag_2S + R-S-R
\end{align*}
\]

The changes in enthalpy of formation for the two reactions were calculated.

\[
\Delta H_f = \Delta f H^\circ(R-S-S-R) + \Delta f H^\circ(Ag) - 2\Delta f H^\circ(R-S-Ag)
\]
These prototypical reactions represent the formation of silver nanoparticles or Ag$_2$S nanoparticles. The enthalpy of formation of Ag$_2$S is $\Delta H_f = -32.6$ kJ/mol. The possible entities upon heating, R-S- and R-S-R, were taken to be dimethyl sulphide and dimethyl disulphide, respectively, and the corresponding values of enthalpy of formation of R-S- are $\Delta H_f = -65.3$ and $\Delta H_f = -62.6$ kJ/mol.$^{14}$

3. CONCLUSIONS

In summary, temperature-dependent studies were performed on silver quantum clusters, which exhibit distinct nonplasmonic features in their absorption spectrum. Results presented here suggest that thermal decomposition of these quantum clusters follows a mechanism that is significantly different from that of their larger analogues, namely, nanoparticles. Whereas the direct desorption of disulphide, resulting in the formation of bulk silver, is seen in the case of nanoparticles, C=S bond cleavage occurs in quantum clusters, resulting in the formation of silver sulphide nanoparticles. The difference in ligand binding strength is manifested in the observed product. We have used spectroscopic studies to understand an approximate chemical reaction for the process. An extension of the study to diverse quantum clusters in different media may lead to new products of different morphologies.

ASSOCIATED CONTENT

Supporting Information

Preliminary confirmation of cluster formation through UV/vis profile and a TEM image, time-dependent UV/vis spectra of Ag$_{32}$S$_{18}$ quantum cluster, and kinetics of decomposition. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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