Reactivity of Au$_{25}$ clusters with Au^{3+}

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Abstract

We report the instantaneous decomposition of the small molecular gold cluster, Au$_{25}$SG$_{18}$ (SG-glutathione thiolate) in the presence of externally added chloroaurate ions resulting in the instantaneous formation of the insoluble gold–glutathione polymer. The rate of decomposition, however, was much slower for the metal ions such as Ag$^+$, Fe^{3+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+} and Sr^{2+}. This chemical reactivity is shown to have no direct correlation with the electrochemical potential of the added ions.
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1. Introduction

Chemical reactivity and thermodynamic stability of various metal nanoparticles have been studied extensively. Most of these studies have been on monolayer protected clusters (MPCs), which are typically nanoparticles with diameters larger than 2 nm. Stability of nanoparticles depends on the chemical constitution and the shape of the core as well as the structure and the functionality of the ligands surrounding them [1]. It is reported that gold nanoparticles stabilized by monolayers of arenethiols have less thermodynamic stability than those stabilized by alkanethiols [2]. A temperature-dependent study of alkanethiol capped nanoparticles showed that the stability is directly proportional to the molecular dimension of the ligand. Due to the relevance of nanoparticles in different technological domains, a study of their stability under various environments attracts large attention. Nanoparticles exhibit property changes over time during applications in areas like catalysis, drug delivery, electroanalytical chemistry, etc. Metal nanoparticles are widely used as catalysts due to their large surface-to-volume ratio and they undergo changes in their size and shape during processes [3]. A recent study showed that gold nanoparticles made using phase transfer reagents such as tetraoctylammonium bromide undergo oxidation in air in the presence of halide anions, and therefore, particles must be thoroughly cleaned to avoid particle size growth, oxidation, and precipitation of the nanoparticles [4]. Reaction of ozone with alkanethiol monolayers on gold cluster surface increases disorder in the monolayer assembly which leads to aggregation and consequent precipitation of the clusters [5]. Oxidation of quantum dots such as CdSe when exposed to air results in the reduction of the effective size of the material and quenching of the fluorescence [6]. Quantum dots are also well known for their photo instability.

In the case of molecular clusters in the size regime of 1 nm, the studies are mainly carried out in the gas phase using mass spectrometry [7]. However, there is a lack of detailed investigations of the chemical reactivity and stability of these clusters in the solution phase. This is due to the unavailability of clusters in large quantities. Nowadays various methods have been developed to synthesize molecular clusters in large quantities [8–12]. This opens up a wide platform to study the chemical properties of such clusters in solution.

In this study, the reactivity of Au$_{25}$SG$_{18}$ in the presence of various metal ions was investigated. The cluster is shown to be reactive towards externally added chloroaurate ions. It undergoes a rapid decomposition to insoluble gold–thiolate

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polymer, Au_nSG_m. For other metal ions, no such rapid decomposition was observed. The chemical reactivity is shown to have no direct correlation with the electrochemical potential of the added metal ions. When this study was completed, we came to know of a report which suggested extraordinary stability for $Au_{25}SG_{18}$ in the absence of ions [12]. This is due to the chemical inertness arising from the complete protection of the core by the glutathione ligand.

2. Experimental section

2.1. Methods

2.1.1. Synthesis of glutathione capped gold (Au@SG) clusters

Glutathione capped gold clusters were synthesized according to a reported method [10]. To a 100 mL, 5 mM $HAuCl_4 \cdot 3H_2O$ in methanol, 20 mM GSH was added. The mixture was then cooled to 0 °C in an ice bath for 30 min. An aqueous solution of $NaBH_4$ (25 mL, 0.2 M), cooled at 0 °C, was injected rapidly into this mixture under vigorous stirring. The mixture was allowed to react for another hour. The resulting precipitate was collected and washed repeatedly with methanol through centrifugal precipitation and dried to obtain the Au@SG clusters as a dark brown powder. This is a mixture of small nanoparticles and different clusters.

2.1.2. Synthesis of $Au_{25}SG_{18}$

$Au_{25}SG_{18}$ was synthesized from the prepared Au@SG clusters by ligand etching. The Au@SG clusters prepared as described in Section 2.1.1 were dissolved in 25 mL water. GSH was added (20 mM) and stirred at 55 °C. The reaction was monitored by optical absorption spectroscopy. Heating was discontinued when the absorption features of $Au_{25}SG_{18}$ appeared in the UV–vis spectrum. This typically took 12 h. The solution was centrifuged and methanol was added to the supernatant to precipitate the cluster. The precipitate was dried to obtain $Au_{25}SG_{18}$ clusters in the powder form. The etching may also be done at room temperature.

2.1.3. Reaction of $Au_{25}SG_{18}$ clusters with metal ions

The cluster (250 μg per mL) of pH 3.3 was allowed to interact with 50 μM of metal ions ($AuCl_4^-$, Ag^+, Fe^{3+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+} and Sr^{2+}) separately. The solution was stirred and monitored by optical absorption spectroscopy. The starting materials used for the various ions were $HAuCl_4 \cdot 3H_2O$, $AgNO_3$, $FeCl_3$, $CuCl_2 \cdot 2H_2O$, $NiCl_2$, $CdCl_2 \cdot H_2O$, $ZnBr_2$ and $SrCl_2.6H_2O$. They were obtained from a variety of sources such as Sigma Aldrich, CDH (P) Ltd., India, HiMedia Laboratories Pvt. Ltd., India and SD-Fine Chemicals Ltd., India.

3. Instrumentation

UV–vis spectra were measured with a Perkin Elmer Lambda 25 instrument in the range of 200–1100 nm. The FT-IR spectra were measured with a Perkin Elmer Spectrum One instrument. KBr crystals were used as the matrix for preparing the samples. High resolution transmission electron microscopy of clusters was carried out with a JEOL 3010 instrument. The microscope was operated at 200 keV to reduce beam-induced damage. The samples were drop casted on carbon coated copper grids and allowed to dry in ambience. The FT-NMR measurements were done with a JEOL 300 MHz instrument. The solvent used was D_2O.

4. Results and discussion

The formation of $Au_{25}SG_{18}$ was confirmed by various spectroscopic techniques including optical absorption, infrared, NMR and TEM. Fig. 1A shows the UV–vis absorption spectrum of Au_{25}, showing the characteristic absorption features due to the intraband transitions (from the HOMO 6s to the LUMO 6s/6p orbitals) in the visible region and the interband transitions (transitions from the Au–S bonding or Au 5d orbitals to the unoccupied Au 6s/6p orbitals) in the ultraviolet region [10]. FT-IR spectra (Fig. 1B) show that the peak at 2526 cm^{-1}, which correspond to the S–H stretching vibration of glutathione, disappears in the Au_{25} clusters (marked with arrow) proving the binding of glutathione to the cluster surface. HRTEM image of the cluster (Fig. 1C) shows faint spots (marked with circles) of average diameter 0.7 nm. The sub-nanometer clusters are extremely sensitive to the electron beam and result in aggregation to yield larger nanoparticles upon longer exposure. The ^1H NMR of pure glutathione and $Au_{25}SG_{18}$ clusters is measured in D_2O. The resonances are labeled in Fig. 1D. There is one-to-one correspondence between the two spectra, except that the βCH$_2$resonance (labeled as C) disappears completely in the cluster which is expected as it is close to the cluster surface. All the observed resonances have been broadened in view of their faster relaxation.

The reactivity of $Au_{25}SG_{18}$ with various transition metal ions was studied. The metal ions selected were $AuCl_4^-$, Ag^+, Fe^{3+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+} and Sr^{2+}. It was found that when $AuCl_4^-$ ions were added to the cluster solution, the cluster underwent almost an instantaneous decomposition. The dissociation of the cluster was slow in the presence of other ions. The product of the reaction was assumed to be the insoluble gold–glutathione coordination polymer Au_nSG_m. Fig. 2 shows the optical absorption spectra of $Au_{25}SG_{18}$ cluster, the reaction product (measurement started within 5 s after the addition of Au^{3+}, it took 2 min for the measurement itself) and Au_nSG_m coordination polymer prepared separately according to the proportion of gold and thiol present in the reaction product. Inset of Fig. 2 is a schematic of the cluster decomposition reaction.

The characteristic absorption features of the $Au_{25}SG_{18}$ cluster, due to the intraband transitions in the visible region and the interband transitions in the ultraviolet
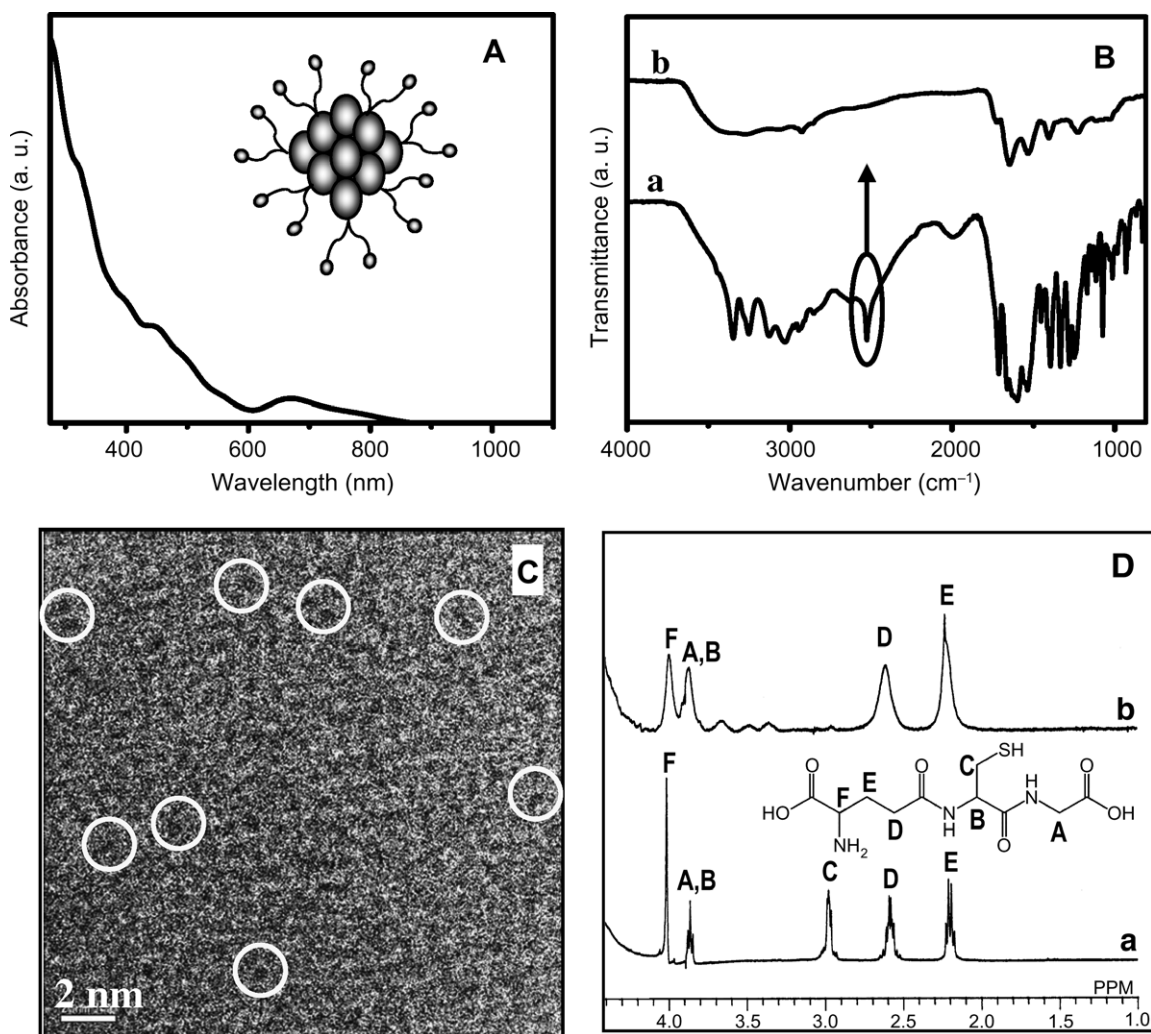
Fig. 1. (A) UV–vis absorption spectrum of $Au_{25}SG_{18}$ showing the characteristic features. (B) FT-IR spectra of (a) glutathione and (b) $Au_{25}SG_{18}$. The peak at 2526 cm^{-1}, which correspond to the S–H stretching vibration, disappears in the $Au_{25}SG_{18}$ clusters. (C) HRTEM image of the cluster showing faint spots (marked with circles) of average diameter 0.7 nm. (D) ^1H NMR of (a) pure GSH and (b) $Au_{25}SG_{18}$ in D_2O. The resonances are labeled. A schematic of the cluster is presented in the inset (A).

region were quenched immediately after the addition of $AuCl_4^-$ ions. The solution became colorless and a white material was precipitated after 10 min. There was no characteristic peak in the UV–vis spectrum. This eliminates the possibility of Au^{3+}, which has a characteristic absorption at 330 nm in water. The only other possibility is Au(I) which in the presence of glutathione will be in the form of Au(I)glutathione complex. To check the characteristic features of the complex, Au(I)glutathione complex was prepared separately by calculating the amount of gold and glutathione present in the reaction product. This polymeric material does not show any characteristic feature. Au(I) is not expected to have any characteristic absorption feature. However, the nature of the polymer formed in the reaction and that from the ionic precursors is not the same and larger scattering in the case of the former is observed, presumably because the extent of polymerization is different and longer polymer chains contribute to scattering. It may be mentioned that the formation of the white precip-

itate and the absence of any specific absorption feature suggests that no nanoparticles or clusters are present.

To check whether externally added gold ions were consumed during the decomposition of the cluster, the absorption feature of $AuCl_4^-$ (50 μM) was monitored upon the addition of $Au_{25}SG_{18}$ in steps. As the reaction progressed, Au^{3+} intensity decreased systematically. Fig. 3 depicts the intensity variation which confirms that externally added gold ions are utilized during the reaction. Inset of Fig. 3 depicts the progress of the reaction in the reverse direction; i.e., when Au^{3+} was systematically added to $Au_{25}SG_{18}$ (250 μg per mL) in steps. The gradual disappearance of Au_{25} features is evident as the concentration of Au^{3+} increases and finally all the features of the cluster disappear as the final concentration of Au^{3+} in the solution reaches 50 μM.

The decomposition of the cluster with different metal ions was monitored. Ions with different reduction potentials were selected for this. The reduction potentials of
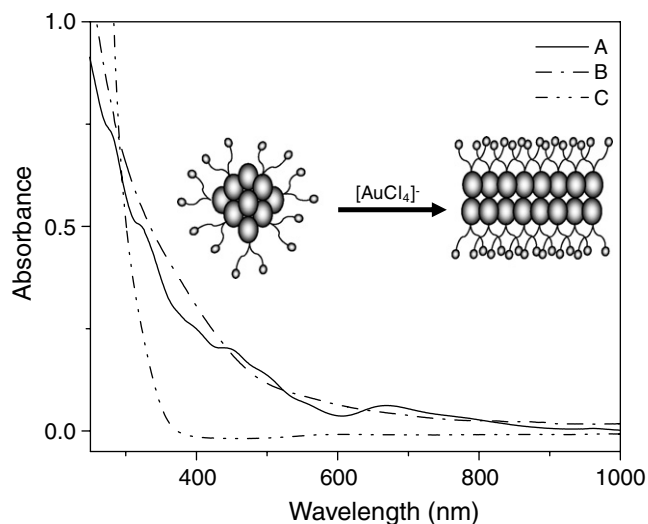
Fig. 2. Optical absorption spectra of (A) $Au_{25}SG_{18}$ cluster, (B) after adding 50 μM $AuCl_4^-$ ions to the cluster and (C) the synthesized Au(I)SG polymer. The scheme (inset) represents the dissociation of the $Au_{25}SG_{18}$ cluster.
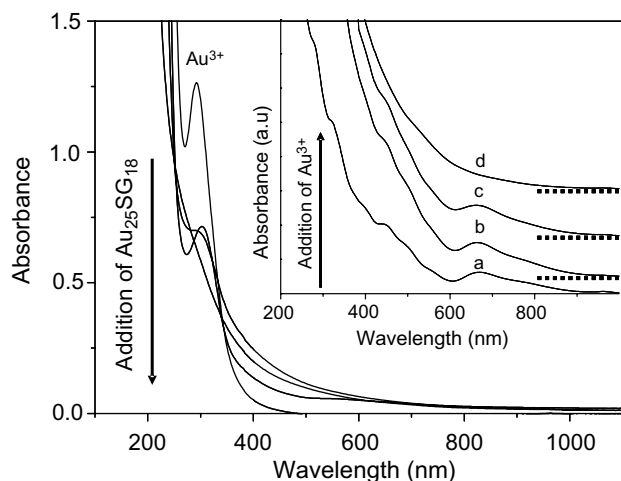

Fig. 3. Optical absorption spectra showing the decrease in the intensity of $AuCl_4^-$ peak proving that gold ions added are used up and the small cluster is converting to the $(Au–SG)_m$ polymer. Inset shows the progress of the reaction when Au^{3+} is added to $Au_{25}SG_{18}$ (a: Au_{25} alone, b, c and d: Au_{25} in the presence of 10, 25 and 50 μM of Au^{3+}, respectively).

the ions decrease in the order, Ag^+ (+0.80 V) > Fe^{3+}(+0.77 V) > Cu^{2+}(+0.34 V) > Ni^{2+}(−0.23 V) > Cd^{2+}-(−0.40 V) > Zn^{2+}(−0.76 V) > Sr^{2+}(−2.89 V). If the reduction potential plays any significant role, then the cluster should be most reactive with silver ions because of the highest potential, and least reactive with strontium ions because of the lowest potential among the selected ions. However, such a regular trend was not observed as shown in Fig. 4, which presents the spectra of the mixture when metal ions (50 μM each) were incubated with the cluster (250 μg per mL). The cluster was most reactive in the presence of silver ions but least reactive in the presence of copper ions. In the presence of silver ions the cluster

decomposed in 1 h. On the other hand the cluster was stable for days in the presence of copper ions. This suggests the insignificant role of reduction potential.

This kind of reactivity was not seen in metallic nanoparticles. We conducted the same experiment with citrate capped gold nanoparticles having diameters of 15 nm and 4 nm. Both the particles retained their absorption features after incubation with [$AuCl_4^-$] ions. This shows that metal nanoparticles have better stability as compared to the molecular clusters. However, anisotropic particles such as gold nanorods are unstable in the presence of excess Au^{3+} [13]. As these nanoparticles are not the right systems to compare the reactivity, we conducted the experiments with glutathione protected gold nanoparticles of 2 nm diameter. They are also stable of the order of weeks in the presence of added Au^{3+}.

To confirm the formation of gold–glutathione polymer due to the decomposition of the cluster by chloroaurate ion, gravimetric analysis was done. The polymer formed in the reaction (Compound A) and the polymer synthesized by taking equivalent amount of gold and glutathione (Compound B) were analysed. To measure the gold content, both the samples were heated to 1000 °C to exclude the organic part. The weight of gold formed was comparable in both the samples. This observation was further confirmed by absorption spectroscopy (Fig. 5) by converting gold to tetrachloroaurate ion. Both the samples exhibited Au(III) features and the intensity variations were within acceptable limits. Data from the gravimetric analysis are presented in the inset of Fig. 5. The polymer formed has a composition of Au_3SG_2 (gold/thiol molar ratio was 1.5). Such non-stoichiometric thiolates are known. Thiolates with stoichiometry other than 1:1 (gold:thiol) are most often the precursor species for the formation of nanoparticles [14]. In the presence of excess Cl^-, coordinating halide ions are likely to be present to maintain the charge balance.

From the above observations it is found that the molecular cluster $Au_{25}SG_{18}$ shows an unusual chemical reactivity in the presence of externally added transition metal ions. The decomposition of the cluster core in the presence of these ions can be explained as follows. Out of the 25 gold atoms in the $Au_{25}SG_{18}$ cluster, 18 atoms are in +1 oxidation state on which 18 glutathione molecules are bound and seven atoms are in zero oxidation state. When the cluster is allowed to interact with [$AuCl_4^-$], electrons in the cluster core reduces $AuCl_4^-$ ions to $AuCl_2^-$ ions. Due to this, the cluster geometry destabilizes and decomposes to non-stoichiometric gold–glutathione coordination complex. As ligand exchange of gold clusters and monolayer protected clusters [15] is known, it is expected that the –SG ligands can be detached to form the more stable thiolate. However, the exact nature of the intermediate is not known from the current studies. It appears that the electron transfer from the cluster as a whole does not occur as the resulting [$Au_{25}SG_{18}$]$^+$ may be stable. We note that [$Au_{25}(SC_6H_{13})_{18}$]$^+$ is stable [16]. However, the stability of such charged clusters in the presence of Au^{3+} has not been
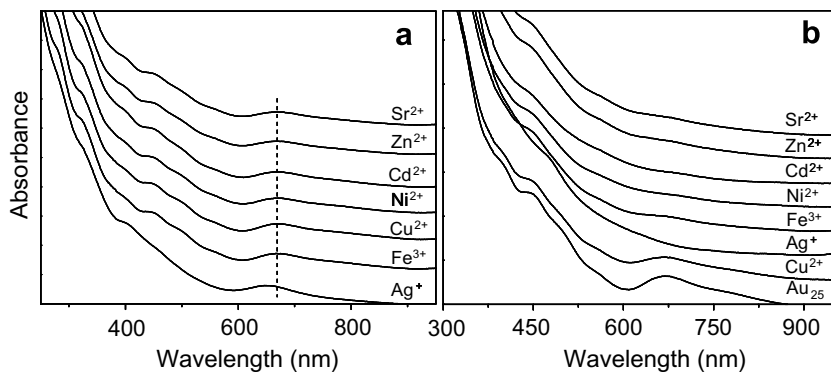
Fig. 4. Optical spectra showing the reactivity of the cluster in the presence of various metal ions. (A) Immediately after adding metal ions and (B) after two days of incubation. Note that, the cluster is most stable in the presence of Cu^{2+}.
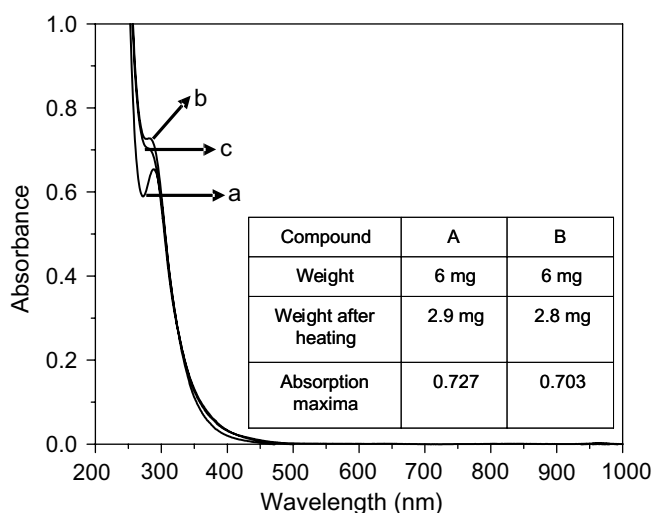

Compound	A	B
Weight	6 mg	6 mg
Weight after heating	2.9 mg	2.8 mg
Absorption maxima	0.727	0.703

Fig. 5. Optical spectra showing the features of $AuCl_4^-$ ions: (a) known concentration of $AuCl_4^-$, (b) and (c) $AuCl_4^-$ prepared from A and B. Data of the various analyses are given in the table.

reported. The specificity of this reaction to Au^{3+} may be because of the affinity of gold towards glutathione. As more gold ions are supplied, the bound glutathione ligands of the Au_{25} cluster may bind with gold ions and subsequently the cluster core collapses.

In conclusion, the molecular cluster, $Au_{25}SG_{18}$ undergoes a rapid decomposition to Au–SG polymer in the presence of Au^{3+}. The net reaction can be represented as an electron-transfer process as in effect seven gold atoms go to the Au(I) state. However, such a fast decomposition does not happen in the presence of other ions added. The formation of insoluble gold–glutathione complex was confirmed by gravimetric analysis. We believe that this work is important as it shows the reactivity of $Au_{25}SG_{18}$ in the presence of metal ions and one can take precautions when the cluster is used for further applications. While complete decomposition to thiolate polymers occurs in the case of Au_{25}, such decomposition is not observed for Au nanopar-

ticles with –SG protection. We note that this reactivity of Au_{25} does not suggest that it is unstable in comparison to the neighboring clusters. We note that Au_{25} is far more stable than other clusters of this class [12] and this is the principal reason for its formation in the etching reaction. It is worth mentioning that $Au_{25}SG_{18}$ reacts with excess glutathione to form thiolates.

Acknowledgments

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