Radical-induced core destruction of monolayer-protected metal clusters

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Abstract

Chlorine radicals formed by the UV irradiation of solvents such as CCl_4 react with alkanethiolate-protected gold and silver clusters forming the corresponding metal salts and variously halogenated disulfides. Reaction rates depend on the chain length of the monolayer; whereas the reaction is over within tens of seconds for clusters protected with shorter chain monolayers, those with longer chains need several minutes for complete conversion. © 2001 Elsevier Science B.V. All rights reserved.

As the discovery of alkanethiol protected gold clusters by Brust et al. [1], number of properties of three-dimensional monolayers have been investigated [2]. Molecular interactions between the alkyl chains on each cluster leading to an organized assembly on the cluster surface [3–5], interactions between adjacent clusters resulting in superlattices [6–11], exchange of the protecting ligands with molecules in solution [12], phase transitions of the alkyl chains [13], structural and spectroscopic properties of quantum dot lattices [14–18], electrical transport properties [19], pressure effects [20], electron dynamics [21], electrochemistry [22] etc., have been studied. Apart from the monolayers, the inert core can also exhibit chemistry if treated with sufficiently aggressive reagents [12]. Such reactions will depend on the chemical character of the monolayer cover; it's density and

thickness in addition to the stability of the core itself [12]. These reactions can also probe the physical barrier offered by the monolayer quantitatively. Possible unusual reactivities of the nano-phase materials can be useful in appropriate technologies.

In this Letter, we show that alkanethiol-protected gold and silver clusters dissolved in chlorinated solvents undergo complete degradation upon ultraviolet irradiation. UV exposure leads to the production of chlorine radicals, which penetrate through the monolayer barrier to react with the cluster cores converting them to metal chlorides. Part of the monolayer is also halogenated leading to a mixture of products. The reaction is fast and complete destruction occurs within a few minutes of irradiation and the reaction time is dependent on the monolayer chain length.

Gold and silver clusters with pentanethiol (PT), octanethiol (OT) and octadecanethiol (ODT) protection were prepared by the well established two-phase synthesis method [1]. The Au and Ag clusters

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were of 3 ± 0.5 and 4 ± 0.5 nm average diameter, respectively [11]. The purified clusters were dissolved in various chlorinated solvents such as CCl_4, $CHCl_3$ and CH_2Cl_2 and the solutions were irradiated with a mercury lamp. In a typical experiment, 0.01 g of the Au cluster protected with ODT (called AuODT subsequently, other clusters named similarly) were dissolved in 50 ml of CCl_4 and the solution was irradiated with an 8 W commercial mercury lamp for various times. The solution was taken in a 3 cm diameter glass test tube and a quartz test tube of 2 cm diameter containing the mercury lamp was inserted into it so that the UV radiation passed through the solution. The UV–Vis spectra of 3 ml of the solution, withdrawn at specific intervals, are shown in Fig. 1. The spectra were
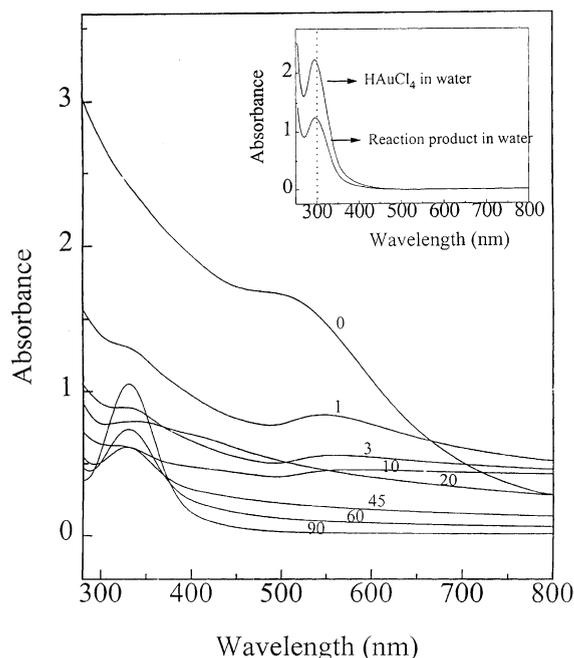
measured with a Varian Cary 5E UV–Vis–NIR spectrophotometer. An abrupt change in color was seen within the first 5 min of irradiation. Gradually, the dark brown solution became colorless which further turned to yellow and after 10 min, no change was visible to the naked eye for a period of 2 h. At present, we do not have an explanation for the formation of colorless Au compounds; the same was observed by Murray and co-workers during the reaction of Au clusters with sodium cyanide which they attributed to the desorption of disulfides [12]. Upon overnight standing, a yellow precipitate settled, which was completely soluble in water and the solution was separated. The CCl_4 solution was colorless. The peak at 295 nm in the UV–Vis spectrum of the water solution is assigned to $AuCl_4^-$ [23]. The peak shape is identical to that of $HAuCl_4$ in water (inset of Fig. 1). Similar experiments were done on PT and OT protected clusters.

In Fig. 2, we compare the reactivities of the clusters studied. The intensity of the plasmon loss feature at 530 nm [24] was taken as a measure of the reactivity. An exponential function is used to fit the data. The curves suggest a first-order reaction.

Fig. 1. UV–Vis spectra of an octadecanethiol-protected Au cluster solution in CCl_4 during UV irradiation. Time in minutes is indicated in the figure. At every stage of the reaction, 3 ml of the reaction mixture was withdrawn and the spectra were taken. Note the appearance of the peak at ~325 nm. The peak at 530 nm is due to the surface plasmon absorption of Au. Changes in the plasmon peak and shift in the base-line are due to the chemical changes occurring in the cluster. The inset compares the spectra of $HAuCl_4$ in water with that of the water soluble reaction product.
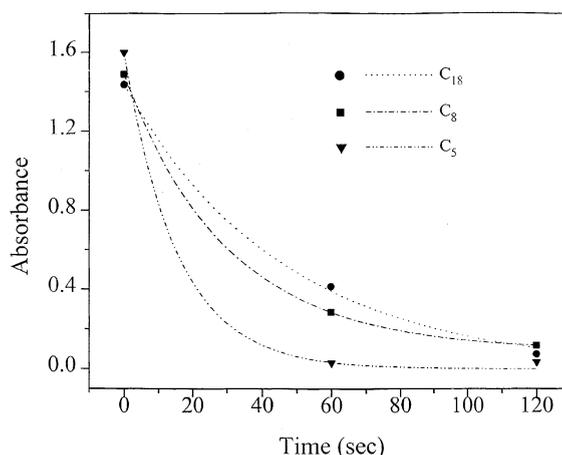

Fig. 2. A comparison of the reactivities of the chlorine radical reaction with the cluster core for different protecting molecules. Reactivity is monitored by the reduction in intensity of the plasmon loss feature. A first-order fit is used (the dotted lines). Note that at zero time, the intensity of the plasmon loss feature for all samples were almost the same indicating nearly similar concentrations. The intensity falls of rapidly in the order AuPT > AuOT > AuODT. Reaction rate is calculated using the first-order rate equation.

Reaction rate constants were calculated to be 2.0×10^{-2}, 2.7×10^{-2} and 6.6×10^{-2} s^{-1} for Au-ODT, AuOT and AuPT, respectively. The reaction rate is significantly larger for the smallest chain length and is almost the same for larger chain lengths ($n \geqslant 8$). Since the cluster dimension, the type of interaction of the monolayer with the cluster, etc., are largely the same in all these cases, the time required for the radical to diffuse through the monolayers appears to be the principal factor determining this change. Whereas monolayers with $n \geqslant 8$ are solid-like, they are liquid-like for shorter chains; explaining the difference in rates. Thus the species involved in the core destruction are produced outside the cluster. The same reaction was conducted in other chlorinated solvents such as CHCl$_3$ and CH$_2$Cl$_2$ where identical processes were observed.

We have performed the reaction in other solvents such as toluene, where we did not see the formation of AuCl$_4^-$ whereas the aggregation and subsequent deposition of cluster on the quartz tube was observed. The reaction product was analyzed with IR and found that the sulfur end of the monolayer had undergone oxidation. This is attributed to the ozonolysis of the monolayer as a result of UV-irradiation [25]. Dissolved oxygen from toluene might have converted to ozone and reacted with the sulfur. This experiment confirms the role of chlorine radical (see below) in the reaction.

The organic liquid left behind after the removal of gold chloride was dried and the product was analyzed by infrared spectroscopy. Spectra were measured with a Bruker IFS 66v FT-IR spectrometer and samples were prepared in the form of pressed KBr pellets. All spectra were measured with a resolution of 4 cm^{-1} and were averaged over 100 scans. The spectrum showed a signature of disulfide at 540 cm^{-1} [26]. The spectra also showed features due to C—Cl vibrations at 778 cm^{-1} [26]. The spectra also showed carbonyl stretches, indicating the involvement of oxygen. Irradiation conducted in CCl$_4$ after repeated freeze-pump–thaw cycles to remove dissolved gases also showed the carbonyl features. In order to understand the process in more detail, free thiol solutions in CCl$_4$ were irradiated with UV and the products were analyzed by IR, which also gave

similar features except that due to the disulfide. The radical reaction product with the thiol (or cluster) is a complex mixture. As reported earlier, variously halogenated products are possible upon UV irradiation of hydrocarbons in CCl$_4$ [27].

In order to confirm the presence of chlorine, we performed mass spectral analysis which showed the chlorine patterns. Further, qualitative elemental analysis confirms the presence of chlorine in the reaction products.

Identical experiments were conducted with silver clusters, where a band at 280 nm attributable to Ag$^+$ was observed [24]. The solid powder precipitated was washed repeatedly with CCl$_4$ and water and was subjected to X-ray powder diffraction, which showed reflections of AgCl. We found the reaction to be faster compared to gold. Monolayer undergoes partial chlorination and desorbs as disulfides as in the case of gold.

We explain the observed process in the following fashion. Upon UV irradiation, carbon tetrachloride is dissociated into Cl$^{\cdot}$ and CCl$_3^{\cdot}$ [28]. Driving force for the reaction is the resonance energy of CCl$_3^{\cdot}$ [28]. Chlorine radical diffuses through the monolayer and reaches the surface of the cluster. Reaction with the Au core leads to the formation of AuCl$_3$, which is converted into AuCl$_4^-$ in presence of excess chlorine and as a result, desorption of the thiol takes place, which appears to be in the form of disulfide, as seen in desorption experiments [11]. Part of the alkyl chain also gets chlorinated during this process. As the chain length of the thiol increases, it takes more time for the chlorine radicals to reach the Au core. It may be noted that diffusion of molecules through the hydrocarbon matrix is fast [29] so that many radicals reach the core before reacting with the monolayers. Proposed reaction is as follows:

$$CCl_4 \xrightarrow{hv} Cl^{\cdot} + CCl_3^{\cdot}$$

$$zCl^{\cdot} + Au_n(SC_xH_{2x+1})_m \rightarrow nAuCl_4^- + mC_xH_{2x+1}SCl_y$$
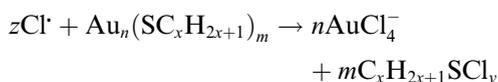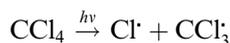
where n is the number of gold atoms present in a cluster, which is determined by the geometry of the cluster. The product C$_x$H$_{2x+1}$SCl$_y$ is a complex mixture, in accordance with mass balance. It

is possible that CCl_3 also takes part in the reaction.

It is important to compare this process with the reaction of self-assembled monolayers (SAMs) on two-dimensional surfaces with ozone. Schoenfisch and Pemberton [30] suggested the penetration of ozone through the monolayer on Au and Ag surfaces. Their results suggested the formation of sulfonates at the head group. Similarly, UV irradiation of alkanethiolate SAMs on Au in air has been shown to form sulfonates [25]. UV photopatterning of SAMs also has been reported [31]. In all these experiments, penetration of ozone through the monolayer is suggested to be the reason for the formation of sulfonates. We did not observe any sulfonates possibly because of the fast diffusion rate of chlorine radical than atomic oxygen or ozone, which also could be formed during the UV irradiation. The oxygen radicals may have reacted with the tail groups to form carbonyls. Since the chlorine radical is more reactive than ozone, reaction with gold surface also takes place.

We have performed the reaction in gas phase also. A thin film of the cluster was deposited on the inner side of a glass tube by slow evaporation of a solution and was irradiated with UV light; the lamp (8 W) was kept inside the glass tube. After evacuation of the tube – whose inner walls were coated with the clusters – to 10^{-6} Torr, CCl_4 vapors were admitted at a pressure of 0.1 Torr. The UV irradiation was performed at room temperature for several minutes. We observed that pentanethiol-protected clusters undergo coalescence leading to the formation of a gold mirror on the glass tube within 30 min of UV exposure. Fig. 3 shows the XRD patterns of the sample before and after UV exposure. The formation of bulk metal is clear from the pattern. The broad peak shape of the cluster (pattern a) is due to smaller particle size. This suggests desorption of thiolates from the cluster surfaces as a result of UV irradiation and subsequent aggregation. Earlier studies of photooxidation of alkanethiol monolayer on planar Ag surfaces suggest the possibility of C—S bond scission [32] and subsequent monolayer desorption. Difference between the solution and solid-state reactions appear to be due to the difference in the number densities. In gas phase, the amount of
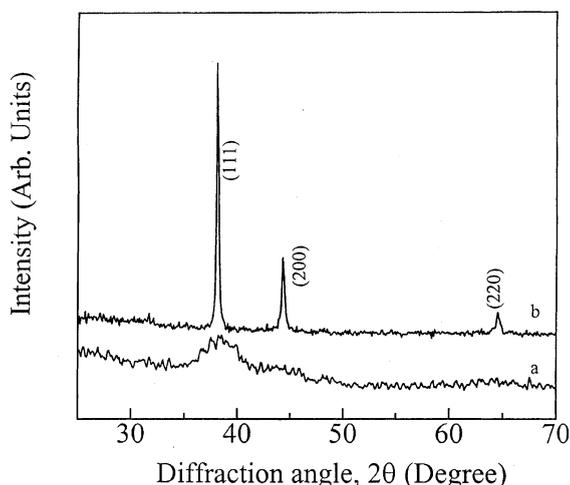

Fig. 3. XRD pattern of Ag–PT samples: (a) before and (b) after the gas phase reaction. The narrowing of the bulk reflections is indicative of the formation of bulk metal.

$Cl^.$ formed will be less compared to that in the solution phase, which makes the unprotected clusters to aggregate rather than react.

We observed chain length dependence as well. The same reaction carried out with octadecanethiol protected clusters did not result in a gold mirror at room temperature but aggregation leading to the formation of larger clusters was seen. The dark brown clusters become violet in color and a red shift of the plasmon band was observed in the UV–Vis spectrum. Decrease in width of the peak is observed in XRD, which indicates aggregation. However, UV irradiation when conducted at 423 K showed the formation of gold mirrors. Note that this temperature is below the desorption temperature of SAMs (543 K) [3]. This radical assisted desorption and subsequent coalescence of clusters was seen in both OT and ODT protected clusters. We have done the heating experiment at various conditions like absence of UV light, absence of chlorinated solvents etc. All these experiments resulted in the aggregation of clusters, not the formation of gold mirror. This confirms that desorption and aggregation of the clusters are radical assisted.

In conclusion, monolayer-protected Au and Ag nanoclusters react with carbon tetrachloride in presence of UV light resulting in complete degradation of the metal core. The reaction leads to the

formation of $AuCl_4^-$ and partially chlorinated disulfides. Even though the chemistry of monolayers has been explored in greater detail, radical mediated core destruction is reported for the first time. More details of the mechanism are currently under investigation. The observed chemistry suggests a methodology for the disposal of chlorocarbons using metal nanoclusters.

Acknowledgements

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