

Controlled Etching of Au:SR Cluster Compounds

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Received: September 10, 1999

When Au:SR cluster compounds ($R = (CH_2)_5CH_3$) with an Au metallic cluster core mass of ~ 14 kDa (~ 75 atoms, 1.1 nm equivalent diameter), are heated in neat dodecane–thiol solution under inert atmosphere, species with smaller Au core masses are formed, presumably by the removal of Au atoms from the outermost surface layer of the cluster's Au core. This process was monitored through laser desorption mass spectrometry, optical absorption spectroscopy, and X-ray diffraction, where all three methods indicate a *substantial* decrease ($> 50\%$, by mass or number of Au atoms) in the size of the cluster compound's inorganic core. The optical absorption spectra and laser desorption mass spectra of the compounds generated by etching are strikingly similar to compounds previously separated without an etching step. The dual function of the thiol as both stabilizing adsorbate and efficient etchant sets this cluster (or nanocrystal) system apart from other metallic and semiconductor systems.

Recently Au:SR cluster compounds, where a metallic Au(0) core is encapsulated by an adsorbate monolayer, such as an alkane thiol ($-SR$), have provided an ideal system for studying large metal cluster compounds (or nanocrystals) with conventional techniques, e.g., NMR,¹ optical spectroscopy,² and IR.³ From extensive studies, it seems the chemical, surface, and interfacial properties of the $-SR$ adsorbate in the Au:SR cluster compounds is analogous in many ways to the extended Au surface self-assembled monolayers (SAMs).^{4,5} At the extended surface layer, formation of SAMs by exposure of Au to thiol solutions has been demonstrated to be accompanied by an etching process, i.e., removal of Au atoms from the outermost surface layer.⁶ Thus, completing this analogy it was evident that Au:SR cluster compounds may be etched by thiols in a controllable manner. Mass spectrometry, optical spectroscopy, and large-angle X-ray diffraction are used to follow the etching process. The laser desorption mass spectrometric analysis monitored the shift in ion abundance to lower mass as the cluster compounds were etched in the thiol solution. The formation of the smaller Au:SR cluster compounds seems to be accompanied by the production of small Au(I)SR oligomer byproducts. After several hours at 70 °C, the primary abundance of negative ions shifted from ~ 14 to ~ 8 kDa. The mass spectra and optical absorption spectra of the starting material (14 kDa) and final products (8 kDa) are nearly identical to cluster compounds, which have been previously prepared and separated *without* an etching process. Large-angle X-ray diffraction of the cluster compounds confirms the decrease in the cluster core diameter. These observations provide the first evidence for a metallic cluster system where the adsorbate unit ($-SR$) can also act as an etchant and illustrate how etching may be the process for the accumulation of specific core sizes in solution.

Refinement of the first reported preparation⁷ of these cluster compounds has been outlined in several reports;^{1–4} however, the smallest cluster size obtainable in appreciable abundance always appeared to give laser desorption mass spectra of

negative ions at ~ 14 kDa. The 14 kDa cluster compound was previously reported as a critical size in the growth of larger cluster compounds,⁸ and does seem to hold a pivotal role in understanding the electronic^{2,8} and structural⁹ properties of this class of materials. Another specific size that has only been separated in very small yield by column chromatographic methods produces laser desorbed negative ions centered at ~ 8 kDa. Both species (14 and 8 kDa) have been studied extensively through mass spectrometry, optical absorption, charging and X-ray diffraction;^{2,8,10} however, no Au:SR cluster compound species has been detected mass spectrometrically between these two masses.

The 14 kDa cluster compounds were prepared by a stoichiometric modification of the original preparation⁷ (see Supporting Information). Briefly, the hexanethiol:Au ratio was increased to 3:1 to form a stable polymer (Au(I)SR) starting material. Stopping the reaction after 30 min optimized the yield of cluster compounds with negative ion abundances in the 14 kDa region of the mass spectrum. The resulting material was precipitated with ethanol three times to ensure removal of all reactants and byproducts. Mass spectrometry was used to ensure that the 14 kDa material was produced in largest abundance (Figure 1a). Then the product was dissolved at a concentration of 3 mg/mL in neat dodecanethiol and heated at 70 °C. The heating process was performed under inert atmosphere (N_2 or Ar) to ensure that dodecylsulfonate was not produced by oxidation of the thiol. Under oxygen-rich atmosphere, the production of sulfonates caused the heated product to grow to colloidal gold, as evident from absorption spectra (not shown). At specific times, small amounts of material were removed, precipitated from the thiol solution with excess ethanol, and studied by mass spectrometry, optical spectroscopy, and large-angle X-ray diffraction. The etching process was presumably accompanied by the production of Au(I)SR polymer compounds, as indicated by the quantity of pale-yellow insoluble material formed when the etched product was precipitated from the thiol solution and the increase in relative signal intensity of ions corresponding to small oligomers. The presence of gold in the insoluble material was confirmed by burning the material, which resulted in brilliant Au films, as described previously.¹¹

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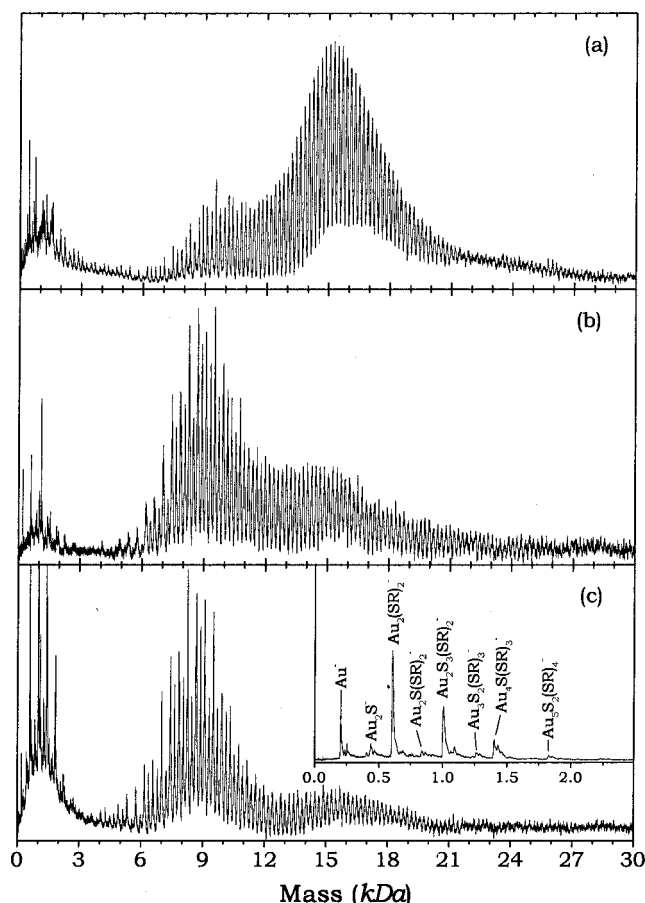


Figure 1. Laser desorption mass spectra of Au:SR cluster compounds as prepared (a), and then heated in neat dodecane thiol for 15 h (b) and for 40 h (c). The spacing between adjacent peaks is consistent with Au_NS_M clusters, where $N \gg M$. The inset in (c) shows the small oligomer ions that are detected in the mass spectra. The intensity of these low-mass ions increases with the amount of time that the clusters are heated in thiol solution.

The mass spectra^{12a} of the initial product from the ambient condition reaction and the subsequent etching experiments are shown in Figure 1. The initial product mass spectrum (Figure 1a) is similar to that previously reported from the 14 kDa cluster compounds by Reilly et al.;¹³ however, lower mass ions were present in the mixture, as prepared. Upon heating (progressing from Figure 1a to Figure 1c in time), the relative abundances for the groupings of peaks changed from $\sim 90\%$ 14 kDa to only $\sim 20\%$ 14 kDa, with most of the mass concentrated in the 8 kDa region. All ions seen in the negative ion mass spectra of the Au:SR cluster compounds have spacings that correspond to ions containing only Au and S, with no trace of the hydrocarbon content. The abundance of $[\text{Au}_N\text{S}_M]^-$ ions is indicative of selective cleaving of the S–C bond that has been previously observed independently in three laboratories on Au:SR cluster compounds with 28,¹⁴ 14,¹³ and 8 kDa¹⁵ core mass. Selective cleavage of S–C bonds has also been observed in UV¹⁶ and electron beam damage¹⁷ of self-assembled monolayers formed from alkane thiols. Although fragmentation is quite extensive, the abundances measured mass spectrometrically have been previously shown to correspond well with other independent types of measurements of the cluster core size, e.g., X-ray diffraction and TEM.^{9,10,18} The Au:SR cluster compounds which produce ions in the 8 kDa and 14 kDa mass ranges have been studied previously as separated compounds (not etched), with well-defined large-angle X-ray diffraction patterns and optical absorption signatures.^{2a}

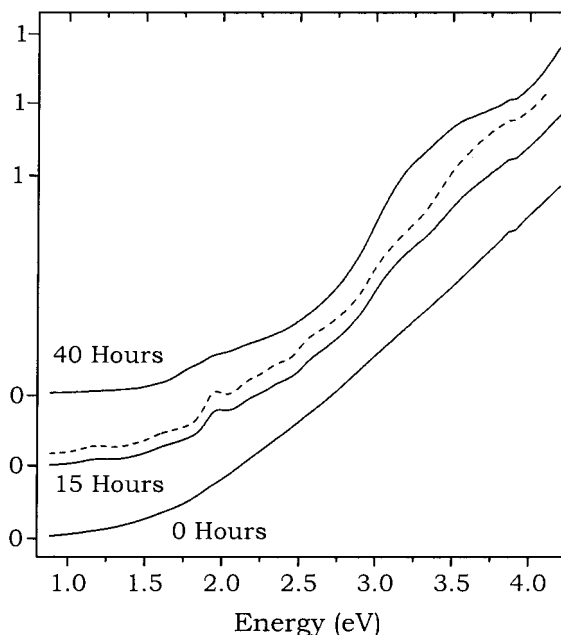


Figure 2. Optical absorption spectra for the Au:SR cluster compounds as prepared (lower curve), and then heated in dodecane thiol for 15 h (middle) and for 40 h (upper curve). The dotted absorption spectrum was obtained on an 8 kDa cluster compound that was separated in small yield using column chromatography.^{2a} The spectrum for the cluster produced from heating for 40 h is strikingly similar to those obtained on smaller clusters (~ 6 kDa core mass) produced using glutathione.²⁰

The large-angle XRD data^{12c} was used to verify changes in size of the Au:SR core. The approximate cluster core diameter is inversely proportional to the width of the peak in reciprocal space (Δs , where $s = 2\sin\theta/\lambda$) by the Debye–Scherrer formula ($D \approx 0.9/\Delta s$). Although this formula alone cannot be used to precisely determine nanocrystal size, variations in Δs can be used to detect changes in relative Au cluster core size. In the large-angle region, peak widths increased with the amount of time that the cluster compounds were heated in thiol. The full width at half-maximum (Δs) of the Au (111) peak (See Supporting Information, Figure S1) changes from 1.07 nm^{-1} for the reaction product (no heating) to 1.22 nm^{-1} at 15 h; however, a small difference was seen between 15 and 40 h. The widening of the Au(111) peak seen after heating the cluster compound in neat thiol was also accompanied by a slight shift in the peak apex to lower s values, indicating a slight dilation of the cluster core. Thus, XRD data is consistent with the mass spectral analysis, indicating a general trend of decreasing cluster size during the heating process.

Since optical absorption spectral features of Au:SR cluster compounds are derived from the delocalized electronic states of the Au core,² the optical spectra of smaller cluster compounds is highly sensitive to the size (and geometry) of the metallic core of the cluster assembly.¹⁹ Thus, variations in the features of the optical absorption spectra (energy of absorption onset, spectral minima and/or maxima) of the Au:SR cluster compounds can be used to determine changes in the cluster's Au core. In correlation with the mass spectral and X-ray diffraction data, the optical absorption spectra^{12b} of the Au:SR cluster compounds evolved as the compounds were heated in neat thiol (Figure 2). The initial absorption spectrum is identical to those obtained on purified 14 kDa cluster compounds² (lower curve), showing very little structure, the absence of a plasmon absorption band, and a distinct absorption onset at $\sim 1.6 \text{ eV}$. After heating the neat-thiol/cluster solution for 15 h, the absorption spectrum of the etched material is now identical to that of the previously reported 8 kDa cluster compounds (middle curve).

Upon further heating to a total time of 40 h, the spectrum becomes similar to spectra observed with certain Au:SG (GSH = glutathione) cluster compounds that have been electrophoretically separated, and have masses slightly lower than 8 kDa.²⁰ Thus, the optical spectra not only correlate with the other independent measurements (MS and XRD), it also suggests that certain Au cores are produced during the etching.

Here, we have shown that the inorganic core size of the 14 kDa cluster compounds can be decreased by etching in neat thiol. This process was monitored through mass spectrometry, optical absorption spectroscopy, and X-ray diffraction, where all three methods indicate a substantial decrease (>50%, by mass or number of Au atoms) in the size of the cluster compound's inorganic core. The mass spectrometry and X-ray diffraction provide direct compositional evidence that the core size has decreased during the etching process. The absorption spectra of the cluster compounds show that the Au:SR cluster compounds generated by etching are the same as those previously separated without thiol etching. In addition, the increased structure observed in the optical absorbance spectra of the "etched" species indicates that this process may be monitored (roughly) through spectroscopic means.

While the exact mechanism for the etching process is still unknown, a plausible mechanism for the mass loss of cluster and mass gain of polymer (Au(I)SR) compounds is one in which stable, smaller oligomers of the Au(I)SR polymer compounds are generated. Similar oligomers with only 2–6 monomers have been detected through mass spectrometry,²¹ and other methods involved in the studies of Au(I)SR anti-rheumatoid arthritis drugs. This would account for both the mass loss seen in the cluster compounds and the increased signal intensity of (AuSR)_N negative ions in the mass spectra of the heated samples.

Formation or preparation of cluster assemblies is usually considered to be dominated by unidirectional, irreversible processes, namely nucleation and growth, although some local reversibility may be evident. An efficient competitive disintegration process, such as an etching reaction, is needed to attain global reversibility and thermodynamic control of cluster size and structural forms. Besides the evident desirability for control of cluster properties, this condition permits an enormous simplification for theory, because the thermochemical parameters are directly accessible. In earlier reports on Au:SR cluster compounds,^{2,8,18} the action of an efficient reverse process, such as etching, has been inferred from the distribution of cluster sizes and properties obtained, without direct evidence for a separate process. Thus, the dual function of a thiol as both stabilizing adsorbate and efficient etchant is integral to the control afforded to this process and, so far, sets this cluster (or nanocrystal) system apart from other metallic and semiconductor systems.

Acknowledgment. We graciously thank Dr. Angus Wilkinson for the use of the X-ray diffractometer and Marat Shafigullin for performing the X-ray diffraction experiments. In addition, we thank Dr. Laren Tolbert for the use of the UV–vis–NIR instrument. This work was funded by NSF and Georgia Tech Research Foundation.

Supporting Information Available: Synthetic details for the high-yield preparation of 14 kDa Au:SC6 cluster compounds and large-angle ($s = 3$ to 6.5 nm^{-1}) X-ray diffraction patterns for the compounds discussed in the text.

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