Communication

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J. Am. Chem. Soc., **2007**, 129 (43), 12932-12933• DOI: 10.1021/ja075434+ • Publication Date (Web): 06 October 2007

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Synthesis of ω-Hydroxy Hexathiolate-Protected Subnanometric Gold Clusters

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Studies of thiolated gold clusters of subnanometer dimensions have recently attracted a great deal of interest since, as highlighted by Tsukuda et al.,[1] Murray and Nuzzo et al.,[2a,b] it is recognized now that these materials represent a new boundary between polymers containing low oxidation state metal centers and monolayer-protected gold clusters (MPC).[2c] The reliable synthesis of material with core sizes of subnanometer dimensions using a well-established two-phase technique[3] has been difficult and recent syntheses have employed ligand exchange reactions to replace a triphenylphosphine protecting shell of phosphine-protected Au_{11} clusters by thiols.[2a,b,4]

This Communication reports the synthesis of subnanometer gold clusters using 6-mercapto-1-hexanol (HOC6SH) as capping ligand. This ligand has been recently used to functionalize Au nanoparticles of nm dimensions.[5] The present work attempts to use this ligand to synthesize subnanometer particles. The hydroxyl termination is particularly attractive for two reasons, to test ideas of core size control via ligand shell interactions and for the use of these materials in biological applications. Quantitative high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) has been employed to determine atomic composition. Briefly, nanoparticles were synthesized at low temperatures employing a two-phase method and in the presence of an excess of thiol (S:Au molar ratio of 5:1, Supporting information).[3] The product was purified by column chromatography, and the first low molecular weight fraction eluted has been used in what follows. The IR spectrum shows similar bands to mercaptohexanol (Supporting Information Figure S1) demonstrating that the thiol is a constituent of the ligand shell. The absence of S−H stretching mode vibration provides further evidence that free mercaptohexanol was successfully removed by the purification and that a gold−thiolate bond is formed.

Attempts to measure particle size by mass spectroscopy resulted in sample fragmentation. Figure S2 shows typical results obtained with negative ion laser desorption ionization mass spectrometry using a time-of-flight technique (LDI-TOF, Micromass TOFSPEC, UK). Only peaks corresponding to cluster ions $[Au_n(\text{-S-(CH}_2)_6\text{-O}^-)_{n+1}]$ at low masses were found. Similar results were obtained with matrix-assisted laser desorption/ionization (MALDI, 3,5-dihydroxybenzoic acid as matrix) or electrospray ionization (ESI) mass spectrometry (data not shown). No peaks above 2 kDa (Figure S2) were observed showing that laser damage and high core fragmentation is extensive for these clusters. Similar results were obtained for the other chromatographic fractions.

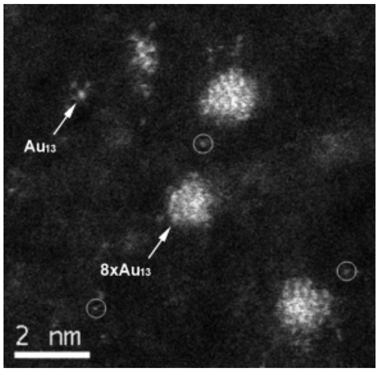

Figure 1. HAADF-STEM image of hydroxyl hexathiolate-protected gold clusters (HOC6 MPCs). The intensity of the images is proportional to the number of gold atoms present in the clusters. Two particles are highlighted and the number of atoms indicated. These were determined from the intensity measured for the entire particle and compared with the intensity from individual atoms in the same image, which can be clearly seen on the carbon support. Several of these have been circled for clarity.

The number of core Au atoms was determined by electron microscopy using HAADF-STEM. This powerful technique is also known as *Z*-contrast (atomic number) imaging since the measured intensity is approximately proportional to the square of the atomic number.[2a,6] The technique is relatively insensitive to sample thickness and defocussing and allows the calculation of the number of atoms present within a particular nanoparticle thus overcoming the limitations of traditional TEM. Because of the large difference in atomic weights, the ligands make a small contribution to the measured intensities.

Figure 1 shows a typical HAADF-STEM image of the $Au\text{-}SC_6\text{-}OH$ gold clusters obtained for the first eluted fraction. A detailed analysis was carried out for four different images (Figure S3a−d) at the same magnification (field of view = 30 nm) to estimate the number of atoms in the nanoparticles by the following method. The intensity of a selected number of particles ($N = 150$) was first measured. The average background intensity from six places in the same image where no particles or atoms were observed was subtracted from each particle intensity to remove contributions from the carbon film. The remaining particle intensity had only contributions from the Au atoms and the ligands. Elemental analysis gave a Au/S ratio of 1.6:1 for the first fraction eluted and between 2.5:1 and 2.6:1 for the fractions containing larger particles. The ligand contributions estimated for the particles intensity was 5.3% and 3.4% for Au_{13} and for the other fractions, respectively. This small contribution was then subtracted, and the number of atoms in each particle was calculated by dividing the resultant intensity by that for a single Au atom intensity obtained by averaging over 6 single atoms in the image with a standard deviation of around 4%. Using this method it is seen that the smallest particles observed contain 13 ± 2 Au atoms as shown in Figure 1. All others clusters contained multiples of this particle size as shown in Figure 2 and indicated in Figure 1, for example, for a $8 \times Au_{13}$ cluster containing 104 atoms. These results suggest that the larger particles observed on the grid are made up of aggregated Au_{13} clusters formed either

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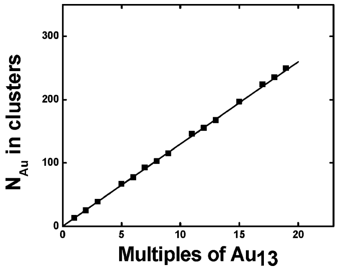

Figure 2. Dependence of the average number of atoms of Au per cluster (N_{Au}) on multiples of the number of Au_{13} subunits calculated from the HAADF-STEM images the analysis of 150 particles. The solid line corresponds to a slope of 13.

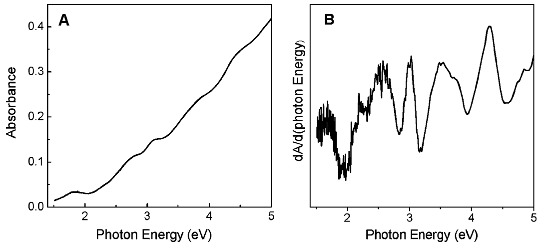

Figure 3. Absorption spectra (A) and derivative spectra (B) of a solution of $Au-SC_6OH$ nanoparticles in ethanol.

during drying of the sample on the grid or more likely, due to electron-beam-induced structural changes during measurement.[7]

The Au_{13} core size corresponds to a closed shell core structure as recently described[1c,8] and synthesized by exchange of dodecanethiol with phosphine−halide gold clusters by Nuzzo et al.[2b] A similar Au/ligand composition ($Au_{13}(SC_6OH)_8$, 1.6:1 Au:S ratio from elemental analysis) has also been observed in the present work. Although a possible structural model for the $Au_{13}(SC_6OH)_8$ cluster could be cuboctahedron,[8a] Nuzzo et al. concluded that subnanometric Au_{13} clusters adopt an icosahedral structure.[2b]

Figure 3A shows the absorption spectra of the purified clusters. Discrete electronic transitions are observed, and the fine structure of the spectra is more easily visualized in the derivative spectra (Figure 3B). The absorption bands are associated with interband transitions from the Au $5d^{10}$ levels to the unoccupied Au $6(sp)^1$ band[9] although metal−ligand charge transfer can also contribute to the fine details of the spectra.[8a] The absorbances observed are in good agreement with the results of Murray at al.[2a] for Au_{13}. It is noteworthy that the spectra does not correspond to that of a Au(I) polymer[1a] and therefore is that of metallic clusters, similar to previous reports.[2a,b] Tsukuda et al. [1a,b] recently proposed a selective stabilization of small-sized Au clusters by considering that for small size cores, interactions within the thiolate ligand shell have a significant influence on the stability of the nanoparticles. In our case, the observation of the formation of a Au_{13} fraction indicates not only stabilization by hydrogen bonding in the ligand shell but also a restriction of core growth due to the insolubility in both the aqueous and the organic phase of this fraction. This provides a channel for the subtraction of growing clusters of particular dimensions during the course of reaction. Besides inhibition by thiol passivation, the low reaction temperature provides additional control of core growth. Because of their hydrophilic properties, the hydroxyl-terminated nanoparticles described here are easily dispersed from their ethanol solution into water containing 2% ethanol. However, the material was insoluble in the aqueous phase during synthesis. Surprisingly, it was found that a small concentration of electrolyte (~0.01 M $NaClO_4$) was sufficient to cause precipitation. The reason for this effect is unclear, and further work is required to clarify this matter. As previously mentioned, solubility in aqueous media is an important feature since there is great interest in the use of MPCs in biological applications.[10] In addition, the OH termination is very convenient for further functionalization chemistry.[5]

To summarize, we have demonstrated a synthesis of subnanometer gold clusters passivated by a hydrophilic thiol using a simple two-phase reaction. HADDF-STEM reveals that the core is composed of 13 ± 2 atoms and that the larger sizes observed during imaging are formed by multiples of this basic building block, probably as a result of electron beam damage.

Acknowledgment. The authors are grateful to the European Union (DYNAMO project) for their financial support. J.M.A. acknowledges a postdoctoral fellowship from Fundación Ramón Areces.

Supporting Information Available: Experimental section, Figures S1, S2, S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA075434+