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Nanocluster Size Evolution Studied by Mass Spectrometry in Room Temperature $Au_{25}(SR)_{18}$ Synthesis

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Realization of next generation nanodevices will require precise design, controlled synthesis, and isolation of nanomaterials. Toward this effort, progress have been made in the field of molecular gold nanoclusters (<2 nm, <200 atoms).[1−4] These nanoclusters contain a distinct number of core gold atoms and surface thiolate ligands, are of molecular purity that can be grown as single crystals,[5−8] and display interesting optical and electrochemical properties.[3,9] Examples of this class of materials include $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, $Au_{68}(SR)_{34}$, $Au_{102}(SR)_{44}$, and $Au_{144}(SR)_{60}$.[5,6,15,16] Whetten's innovative approach in applying electrospray ionization mass spectrometry (ESI-MS),[10] laser desorption ionization mass spectrometry (LDI-MS),[1] solvent fractionation,[1] electrophoresis,[10] etching,[11] and Raman spectroscopy[12] to the field of gold nanoclusters has led to an explosion of interest in the field. More recent careful studies on high resolution mass spectrometry[13−16] from Murray and Tsukuda groups have unraveled the molecular formulas of these nanoclusters. The theoretical understanding of the structure and bonding has also advanced greatly,[17−22] culminating with the introduction of the superatom complex model.[4] Progress on the synthetic front has been lagging however, still dependent on reliable but tedious solvent fractionation methods.[1] Despite these issues, isolation of highly monodisperse Au_{25}, Au_{38}, and Au_{144} has been reported. $Au_{25}(SCH_2CH_2Ph)_{18}$ has been extracted using acetonitrile.[23,24] $Au_{38}(SC_{12}H_{25})_{24}$ nanoclusters, enriched by excess thiol etching, was extracted from an ∼1:4 toluene/acetone mixture.[15,25] $Au_{144}(SC_6H_{13})_{60}$ has been extracted with either ethanol or a 1:4 toluene/acetone mixture.[15,26] Jin and co-workers have introduced several modifications to achieve Au_{25} in high yield.[27,28] Notably, a one phase synthesis in THF elegantly shows the formation of highly monodisperse Au_{25} nanoclusters (proved by the absorption spectra of the as-prepared nanoclusters) due to "size focusing", eliminating the need for size fractionation.[28] This novel, simple method demystifies the nuances in Au_{25} synthesis and will enable the adoption of Au_{25} by a wider scientific audience. While advances in the "how" and "what" of the material synthesis have been made, little is known about "why" or the underlying phenomenon behind these. Such fundamental understanding is necessary to translate these wet-chemical synthetic methods into complex nanostructures.

We demonstrate the capabilities of MALDI TOF mass spectrometry in studying size evolution in the case of room temperature $Au_{25}(SCH_2CH_2Ph)_{18}$ synthesis. By building on Jin's work,[28] we report a systematic mass spectrometric investigation that unravels the underlying size evolution process that ultimately yields monodisperse Au_{25} nanoclusters. More specifically, at earlier reaction times, a mixture of Au_{25}, Au_{38}, $Au_{\sim44}$, Au_{68}, and Au_{102} is formed and subsequent size evolution leads to the synthesis of highly monodisperse Au_{25}. Besides these revelations, this study emphasizes the importance of MALDI-TOF mass spectrometry as a tool to follow the nanocluster synthesis progress analogous to thin layer chromatography (TLC) or gas chromatography (GC) used in small molecule organic synthesis.

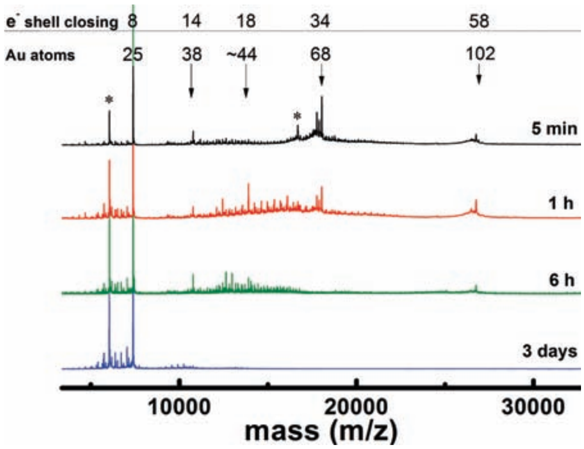

Figure 1. MALDI-TOF mass spectra of the as-prepared nanoclusters using DCTB matrix and operating at threshold laser fluence. Nanocluster synthesis conditions: gold/phenylethanethiol mol ratio 1:6; room temperature; fast stirring (∼500 rpm); reaction solvent, THF. Samples were purified and analyzed at 5 min, 1 h, 6 h, and 3 days. Initially the nanocluster mixture contains Au_{25}, Au_{38}, $Au_{\sim44}$, Au_{68}, and Au_{102}, which over time converges to Au_{25}. Peaks marked by asterisk are fragments.

Briefly, 0.517 g (1.3 mmol) of $HAuCl_4$ was dissolved in 50 mL of THF. 1.05 mL (7.8 mmol) of phenylethane thiol was added under fast stirring (∼500 rpm). After 30 min, when the solution turned colorless, 10 mL of aq. $NaBH_4$ (0.57 g, 15 mmol) were added to the reaction rapidly. The final product and samples at various stages of the reaction were filtered, concentrated, washed with a methanol/water mixture, and extracted with toluene to obtain highly monodisperse Au_{25} and other samples for MS analysis (see Supporting Information).

Figure 1 shows the composition of the as-prepared gold nanoclusters as followed by MALDI-TOF mass spectrometry. The synthesis is performed in a gold/thiol ratio of 1:6 in tetrahydrofuran under room temperature and fast stirring (∼500 rpm) conditions. At earlier reaction times, ∼5 min, larger nanoclusters such as Au_{102} and Au_{68} are dominant. After 6 h the larger nanoclusters seem to decrease in intensity and smaller clusters such as Au_{25} and Au_{38} seem to be dominant. After 3 days, the reaction mixture contains primarily Au_{25} nanoclusters. Clearly, the room temperature synthesis of Au_{25} nanoclusters is not due to better control over the nucleation stage. After 5 min, the reaction yields a mixture of nanoclusters, which over time is converted into the more stable Au_{25} species. The synthesis yielded the identical final product, Au_{25} nanoclusters,

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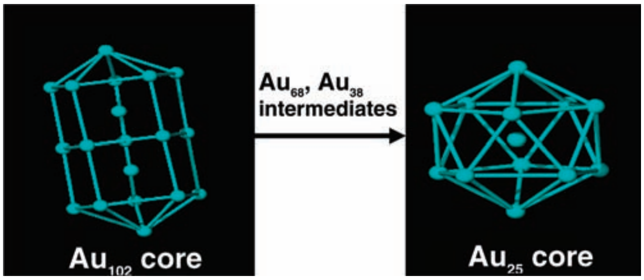

Figure 2. Partial inner cores of $Au_{102}(SC_6H_4COOH)_{44}$ and $Au_{25}(SCH_2CH_2Ph)_{18}$ nanoclusters (19 atom fused double dodecahedron and 13 atom icosahedron, respectively) taken from experimental X-ray diffraction crystal structures.[5,6] The thiolate groups and outer Au atoms are omitted to compare the similarities of the innermost core.

when performed at 0 °C or slow stirring or with hexanethiol. In passing we would like to note the clear presence of an ~13.5 kDa species (represents the total molecular weight including the gold core and the ligands) previously assigned to $Au_{44}(SR)_{28}^{2-}$ species,[29] with an expected 18 atom electron shell closure.[4]

It is well-known that Au_{25} nanoclusters possess exceptional stability.[30] The fact that all the clusters Au_{102}, Au_{68}, and Au_{38} converge toward Au_{25} suggests that the core size of the nanoclusters is reduced by some attrition and not by a growth process. While the formation of Au_{25} from smaller gold phosphine clusters, Au_{29}:SG, Au_{33}:SG, and Au_{39}:SG, has been reported,[30,31] etching of larger clusters such as Au_{68} and Au_{102} to form Au_{25} has not been previously reported.

Does the apparent interconversion of core sizes involve a simple etching[11] of outer layers to result in Au_{25}? Or is there a significant structural reconstruction during this process? Comparing the inner cores of the two structurally characterized nanoclusters will address some of these questions. Figure 2 shows the partial inner core of the Au_{102} and Au_{25} nanoclusters structure with 19 atom fused double-dodecahedron and 13 atom icosahedron structures, respectively. (Note that the innermost core of the Au_{102} nanocluster is a 7 atom decahedron and the second outermost core is a 39 atom dodecahedron. The partial 19 atom core is shown here for comparison purposes.) A cursory observation gives the impression that the 13 atom icosahedron/Au_{25} core is a simple subset of the 19 atom structure obtained by deletion of 6 atoms at one end. However, the axis of the upper half of the structure has to be rotated by 36° to obtain the 13 atom icosahedron. This involves significant structural reconstruction of the cores, possibly through Au_{68} and bi-icosahedral Au_{38} intermediates.[22] It is intriguing that the cores of 38, 68, and 102 will *all* reconstruct to the Au_{25} core.

A brief explanation of the observed size evolution starts with the reaction $6\ RS{-}H + Au(III) \rightarrow [Au(I)SR] + RS{-}SR + 3\ RS{-}H$, where the stoichiometric byproducts (oxidized and reduced forms of thiolate) are indicated. Addition of excess $NaBH_4$ leads to rapid reduction of [Au(I)SR] to Au(0), in the form of a gold nanocluster mixture (see Figure 1, 5 min), releases additional reduced thiolate (RSH or $RS-$), and also reduces the original $RS{-}SR$ byproduct. The larger gold thiolate nanoclusters detected at earliest times are the stable products of this rapid initial stage. Then, in a slow subsequent stage, the large excess of free reduced thiols gradually converts to a mixture of oxidized ($RS{-}SR$) and reduced forms. This concentrated mixture is capable of carrying out the oxidative etching of Au(0) from the large clusters and results in the smaller sizes detected (eventually leading to monodisperse Au_{25} nanoclusters), along with the regeneration of soluble and insoluble [Au(I)SR] species.[11,32]

We reiterate Whetten's emphasis[1] on the importance of nanocluster mass spectrometry,[33,34] showing that MALDI-MS, suitable for mixtures, is an indispensable tool in probing the mechanism of nanocluster synthesis enabling positive identification of nanoclusters. The size evolution of a mixture of larger clusters (Au_{102}, Au_{68}, and Au_{38}) to form highly monodisperse Au_{25} nanoclusters is demonstrated and probably involves Au(I) thiolate. A mass spectrometry based study to probe the dependence of thiol/gold ratio, temperature, solvent, O_2/N_2 reaction conditions, and other reaction parameters is currently underway.

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Supporting Information Available: Detailed synthetic procedure and expanded mass spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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