Facile, Large-Scale Synthesis of Dodecanethiol-Stabilized Au_{38} Clusters[†]

Huifeng Qian,[‡] Manzhou Zhu,[‡] Ulla N. Andersen,[§] and Rongchao Jin*,[‡]

Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, and QB3 Institute, University of California, Berkeley, California 94720

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It has long been a major challenge to achieve synthetic control over size and monodispersity of gold thiolate nanoclusters. Among the reported Au_n thiolate clusters, Au_{38} has been shown to be particularly stable but was only obtained as a minor product in previous syntheses. In this work, we report a bulk solution synthetic method that permits large-scale, facile synthesis of truly monodisperse Au_{38} nanoclusters. This new method explores a two-phase ligand exchange process utilizing glutathione-capped Au_n clusters as the starting material. The ligand exchange process with neat dodecanethiols causes gold core etching and secondary growth of clusters, and eventually leads to monodisperse Au_{38} clusters in high purity, which eliminates nontrivial postsynthetic separation steps. This method can be readily scaled up to synthesize $Au_{38}(SC_{12}H_{25})_{24}$ in large quantities and thus makes the approach and Au_{38} nanoclusters of broad utility.

Metal nanoclusters that are composed of ~10 to hundreds of atoms bridge the gap of small organometallic compounds and nanocrystals.[1] Among precious metals, gold nanoclusters capped by thiolate ligands have attracted a wide variety of research interests due to their extraordinary chemical stability and interesting electronic and optical properties that are fundamentally different than their larger counterparts − gold nanocrystals. Unlike gold nanocrystals whose electronic properties resemble the bulk state, gold clusters with a core diameter less than 2 nm exhibit quantized electronic states due to the quantum confinement effect of electrons. These ultrasmall nanoparticles hold promise for a number of applications such as catalysis,[2−4] biological labeling,[5,6] and as building blocks for nanoscale devices.[7]

With respect to the chemical synthesis of Au_n thiolate clusters (n, the number of atoms), Whetten and co-workers previously synthesized glutathione (G-SH) stabilized gold clusters, $Au_n(SG)_m$, and separated the mixture by polyacrylamide gel electrophoresis (PAGE).[8] The most abundant cluster species separated was determined to be $Au_{28}(SG)_{16}$;[8,9] note that it has recently been corrected as $Au_{25}(SG)_{18}$.[10] Tsukuda and co-workers performed careful isolation and electrospray ionization mass spectrometry (ESI-MS) analysis of isolated Au:SG clusters and identified a range of Au_n cluster species from Au_{10} to Au_{39}.[10] Thus far, Au:SR (where, R = the tail of thiolate) clusters with core masses of 5 kDa (25 atoms), 8 kDa (38 atoms), 14 kDa (~75 atoms), 22 kDa (~101 atoms), and 29 kDa (~140 atoms) have been reported.[11−13] Thiol etching experiments demonstrate that Au:SR clusters with core masses of 5 kDa (Au_{25}), 8 kDa (Au_{38}), and 29 kDa are extraordinarily stable.[12−16] For $Au_{25}(SR)_{18}$ clusters, improved syntheses have been reported in recent years.[17−19] Also, the single crystal structure of $[Au_{25}(SCH_2CH_2Ph)_{18}]^-[TOA]^+$ has been independently determined by Murray[20] and Jin[21a] groups, including the crystal structure of charge neutral $[Au_{25}(SCH_2CH_2Ph)_{18}]^0$ clusters.[21b] Both the anionic and the neutral $Au_{25}(SCH_2CH_2Ph)_{18}$ clusters consist of an icosahedral Au_{13} core and an exterior shell composed of six orthogonal $Au_2(SCH_2CH_2Ph)_3$ motifs.[21] This structure was also theoretically described by Hakkinen et al.[22] Among the extraordinarily stable 5 kDa (Au_{25}), 8 kDa (Au_{38}), and 29 kDa species, the 29 kDa Au:SR clusters (~1.6 nm core size, where R is C4, C6, C12, C18, or benzyl) were found to be predominantly formed in synthesis.[23−25] Recently, Tsukuda et al. improved the synthesis and formulated the composition of the 29 kDa species as $Au_{144}(SR)_{59}$ on the basis of detailed ESI-MS analysis.[26] The 8 kDa species was, however, only obtained in very small quantities as a minor product following column chromatography separation[11,12,26] or a thiol etching method.[13,14,16] Nevertheless, the exact composition of the 8 kDa species has been determined to be $Au_{38}(SR)_{24}$ with ESI-MS.[11−13]

Despite the significant amount of synthetic work that has been done on size and monodispersity control of gold thiolate clusters, most reported methods suffer from the production of a mixture of different sized clusters (except the case of $Au_{25}(SR)_{18}$ clusters), and the clusters of a desired size are often in low yield and small quantities. Thus, to develop bulk solution synthetic methods that offer precise size control of gold thiolate clusters at the atomic level is of critical importance if the full potential of this new type of nanomaterial is to be realized.

In this work, we report a bulk solution synthetic method that permits facile, large-scale synthesis of truly monodisperse $Au_{38}(SC_{12}H_{25})_{24}$ nanoclusters. This new method explores a two-phase ligand exchange process in which glutathione-capped Au_n clusters (a mixture) are utilized as the starting material. Neat dodecanethiol causes gold core etching of the starting material and secondary growth of clusters, ultimately resulting in monodisperse Au_{38} clusters in high purity.

In a typical experiment, the two-phase synthesis of Au_{38} thiolate clusters involves two major steps: i) synthesis of $Au_n(SG)_m$ clusters and ii) two-phase ligand exchange induced growth of Au_{38} clusters from the $Au_n(SG)_m$ mixture (Supporting Information for experimental details). Briefly, the Au:SG clusters were synthesized according to a well established literature method.[8−10,28] The aqueous Au:SG clusters were then subject to ligand exchange using neat 1-dodecanethiol (C_{12}−SH) in a

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* To whom correspondence should be addressed. E-mail: rongchao@andrew.cmu.edu.

[‡] Carnegie Mellon University.

[§] University of California, Berkeley.

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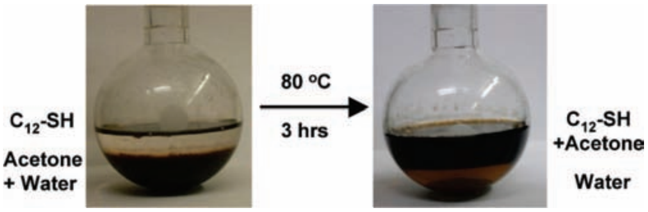

Figure 1. Phase transfer of gold-glutathione clusters from water to dodecanethiol and further conversion to truly monodisperse $Au_{38}(SC_{12}H_{25})_{24}$ clusters.

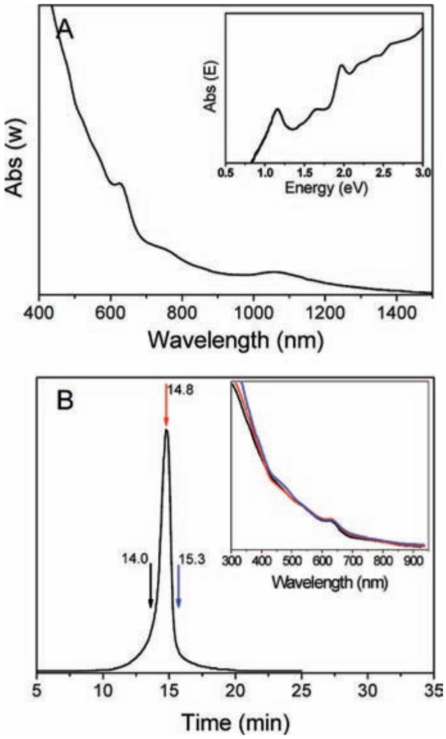

Figure 2. (A) UV−vis spectrum of Au_{38} clusters. The inset shows the absorbance (abs (E)) vs photo energy (eV). The wavelength-dependent absorbance is converted to energy-dependent absorbance according to the equation: $Abs(E) \propto Abs(w) \times w^2$. (B) Typical chromatogram of Au_{38} sample detected by DAD at 630 nm. Inset: UV−vis spectra are obtained by DAD at 14.0 min (black line), 14.8 min (red line), and 15.3 min (blue line).

two-phase system as shown in Figure 1. According to the previous work by Tsukuda et al.,[10] the as-prepared Au:SG clusters contain a mixture of Au_n clusters ranging from Au_{10} to Au_{39}. It has also been found that in the presence of excess G-SH and at 55 °C, Au_n clusters with $n < 25$ were oxidized to Au(I)−SG complexes, whereas Au_n clusters with $n \geq 25$ were converted to $Au_{25}(SG)_{18}$ clusters.[15] In our work, we use C_{12}−SH (insoluble in water, i.e., a two-phase system) to effect core etching of Au:SG clusters during the course of the two-phase ligand exchange process and finally attain highly pure $Au_{38}(SC_{12}H_{25})_{24}$ clusters. It is worth noting that Shichibu et al. previously explored a ligand-exhange approach to the synthesis of $Au_{25}(SG)_{18}$ clusters from phosphine-capped Au_{11} clusters.[27]

A key to our new synthetic approach is to effect an efficient phase transfer of Au:SG clusters from the aqueous solution to the C_{12}−SH phase (neat C_{12}−SH). We found that the Au:SG clusters cannot be directly transferred into the C_{12}−SH phase due to a surface tension issue; hence, acetone was added to the water/C_{12}−SH two-phase system to reduce the surface tension[29] and prompt phase transfer of Au:SG clusters from water to the C_{12}−SH phase. The ratio of water to acetone was found to influence the phase-transfer efficiency. The optimal water to acetone ratio was determined to be 1.0−1.5. More acetone results in precipitation of Au:SG clusters (black precipitate forms at the water/C_{12}−SH interface), whereas less acetone slows down the phase-transfer rate. Figure 1 shows the phase transfer of Au:SG clusters from water to C_{12}−SH. The water phase is initially at the bottom of the flask and the C_{12}−SH phase forms the upper layer of the mixture. Prior to the phase-transfer reactions, gold clusters are solely protected by G-SH, which makes them only soluble in water. After the solution was vigorously stirred for ∼3 h at 80 °C, gold clusters were almost completely transferred to the C_{12}−SH phase (Figure 1, right). During this process, gold-cluster core etching by C_{12}−SH and secondary growth of clusters are expected to occur, which ultimately results in monodisperse $Au_{38}(SC_{12}H_{25})_{24}$ clusters (vide infra).

The Au clusters in the C_{12}−SH phase were isolated after the two-phase reaction process was completed. The excess C_{12}−SH was removed by washing the solution with methanol several times. To isolate Au_{38} clusters, toluene was used to extract the Au_{38} clusters (Figure S1 of the Supporting Information for the absorption spectrum of the extracted clusters). The residue is poorly soluble in typical organic solvents (e.g., toluene or CH_2Cl_2, etc.), which is possibly Au(I)−SC_{12} polymers because Au(I)−SC_{12} polymer tends to form in thiol etching processes[14] and has a poor solubility in organic solvents. To confirm that, we characterized the residue by thermal gravimetric analysis (TGA) and found that the weight loss is 50.3% (Figure S2 of the Supporting Information), consistent with the calculated organic content (50.5%) of Au(I)−SC_{12} polymer.

To further increase the purity of Au_{38} clusters, a mixed toluene/acetone (1:5 v:v) solvent was used to extract Au_{38} clusters from the crude product. The UV−vis spectrum of as-isolated Au_{38} clusters shows a stepwise, multiple-absorption band spectrum (part A of Figure 2), which is typical of gold thiolate clusters. The spectrum is almost superimposable with previously reported $Au_{38}(SR)_{24}$ optical spectrum.[11−13] The optical band edge energy is ∼0.9 eV, and there is a prominent peak centered at 625 nm (2.0 eV). Other distinct peaks are at 1060 nm (1.17 eV), 755 nm (1.64 eV), and less intense ones at 2.2, 2.4, and 2.6 eV (part A and inset of Figure 2).

Size-exclusion chromatography was used to further confirm the purity of the as-prepared Au_{38} clusters. A diode array detector (DAD) in situ monitors the UV−vis spectra of eluted Au clusters. Part B of Figure 2 shows one single symmetric peak; the inset shows the spectra (190−950 nm) corresponding to the eluted components at 14.0 min (left side of the peak), 14.8 min (the peak position), and 15.3 min (right side of the peak), respectively. The three spectra are indeed superimposable, which confirms high purity of the as-prepared Au_{38} clusters.

The as-prepared Au_{38} clusters were also analyzed by laser desorption ionization (LDI) mass spectrometry. In previous work, the formula of Au_{38} clusters has been determined to be $Au_{38}(SR)_{24}$.[13,30] The LDI mass spectrum (negative mode) of the Au_{38} clusters is shown in part A of Figure 3. A broad peak centered at ∼8.2 kDa was observed. The 8.2 kDa peak mass corresponds to $[Au_{38}S_{24}]^-$. The broadness of the mass peak is due to fragmentation of the $[Au_{38}S_{24}]^-$ ions as well as a series of recombination processes of the fragments in gas phase. Unlike the previous work in which the Au_{38} clusters were found to always coexist with the Au_{144} clusters.[13] Herein, our new synthetic approach does not involve or generate Au_{144} clusters, which greatly improves the purity of Au_{38} clusters.

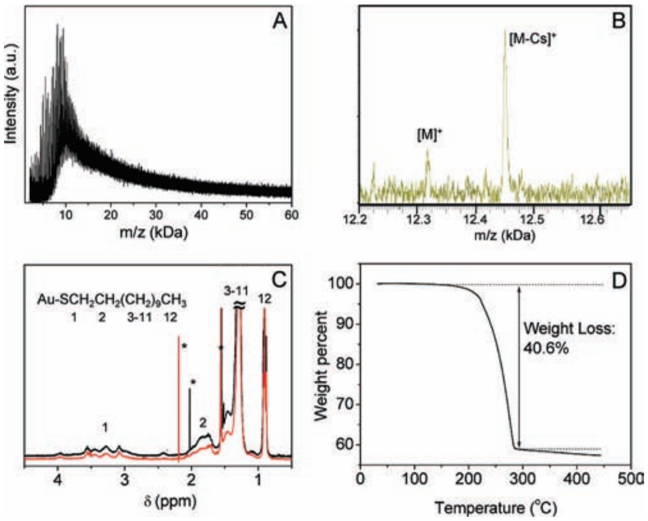

Figure 3. (A) LDI mass spectrum and (B) ESI mass spectrum of $Au_{38}(SR)_{24}$ clusters, (C) NMR of $Au_{38}(SR)_{24}$ prepared from ligand exchange (black line) and $Au_{38}(SC_{12})_{24}$ prepared by literature procedure (red line).[13] The asterisks indicate the peaks from residual solvents. (D) TGA of $Au_{38}(SR)_{24}$ clusters.

Because our synthesis of Au_{38} clusters involve two types of thiol ligands (G-SH and $C_{12}-SH$), it is important to find out whether the final Au_{38} clusters possess a mixed ligand shell or sole dodecanethiolates. Given that the Au_{38} clusters are only soluble in the organic phase (toluene, CH_2Cl_2, etc.), the ligand shell of as-prepared Au_{38} clusters may be only dodecanethiolates. To determine the exact ligand composition, we have performed electrospray mass spectrometry (ESI-MS), nuclear magnetic resonance (NMR), and thermogravimetric analysis (TGA).

Part B of Figure 3 shows the ESI-MS result of the Au_{38} clusters. The peak at m/z 12 451 corresponds to the adducted species $Au_{38}(SR)_{24}Cs^+$. After subtracting Cs^+, the m/z 12 318 indeed matches the formula $Au_{38}(SC_{12}H_{25})_{24}$. This is further confirmed by observing the intact cluster ion signal at m/z 12,318 (part B of Figure 3). These results show that the ligand exchange process between $C_{12}-SH$ and G-SH on the Au cluster surface is thorough, which can be attributed to three reasons. First of all, a large excess of $C_{12}SH$ was used (the ratio of $C_{12}SH/GSH$ $\sim$ 45). Second, the high temperature (80 °C) accelerates the ligand exchange process and tends to drive the process to completeness. Third, the highly hydrophilic GSH ligand would be difficult to enter the $C_{12}SH$ phase where Au_{38} clusters are formed. The pure ligand composition of the Au_{38} clusters was also confirmed by NMR analysis. We prepared and isolated $Au_{38}(SC_{12}H_{25})_{24}$ clusters following a literature procedure,[13] albeit the yield is very low. The ^1H NMR spectra of these two types of Au_{38} clusters are indeed almost identical (part C of Figure 3), which confirms that no GSH ligands should exist in the final Au_{38} clusters prepared by our two-phase exchange approach. In both NMR spectra, significantly broadened peaks (compared to free ligands) were observed, similar to previous report.[23] A set of broad peaks in the 2.8−4.1 ppm range are tentatively assigned to the H1 position (part C inset of Figure 3). The peaks in the 1.6−2.1 and 1.1−1.6 ppm range are assigned to H2 and H3−11, respectively. Finally, the triplet at ~0.9 ppm is assigned to the C12 position. TGA analysis also indicates that the Au_{38} cluster composition should be $Au_{38}(SC_{12}H_{25})_{24}$, as shown in part D of Figure 3; the weight loss of $Au_{38}(SC_{12}H_{25})_{24}$ clusters prepared by the ligand exchange approach is 40.6%, which is very close to the theoretical value (39.2%).

It is worthy of comparing our two-phase exchange approach with previous work;[12−14] the latter has demonstrated that Au_{38} clusters were formed during the etching process of large Au clusters (14 kDa)[14] or a mixture of 14, 22, and 29 kDa Au clusters.[12,13] The 22 and 29 kDa Au clusters were found to coexist with Au_{38} clusters even after reaction with neat $C_{12}-SH$ for 24 h. To obtained pure Au_{38} clusters, Tsukuda et al. used recycling size exclusion chromatography[12,26] or a complicated solvent extraction method[13] to isolate 8, 22, 29 kDa Au clusters. This time-consuming procedure requires significant effort to obtain pure Au_{38} in bulk quantities. In our work, we use an $Au_n(SG)_m$ mixture (n = 10−39) as the starting material to prepare Au_{38} by ligand exchange with neat $C_{12}-SH$. Analogous to the reaction between excess GSH and small Au:SG clusters,[15] those small, relatively unstable Au:SG clusters would decompose to form $Au(I)-SC_{12}$ complexes and only the thermodynamically stable Au_{38} clusters survive the rather harsh thiol etching reaction at 80 °C. It is interesting that we did not observe Au_{25} cluster formation in the exchange reaction with neat thiols at high temperature (80 °C), albeit Au_{25} clusters are very stable under mild environment due to their highly symmetric and stable structure.[21] A similar observation (i.e., not observing Au_{25} cluster formation) has been noticed by Quinn et al.[16] In our procedure, the Au_{38} clusters are the sole cluster species after ligand exchange with neat $C_{12}-SH$. The extraordinary stability of $Au_{38}(SR)_{24}$ clusters at elevated temperatures (e.g., 80 °C) should account for the favorable growth of highly pure Au_{38} clusters from the $Au_n(SG)_m$ mixture in the two-phase exchange process.

The above results exclusively demonstrate that the Au_{38} clusters prepared by the ligand exchange process are $Au_{38}(SC_{12}H_{25})_{24}$ in high purity, which is of critical importance for practical applications such as catalysis and biological labeling. This method allows easy scale-up for synthesizing $Au_{38}(SC_{12}H_{25})_{24}$ in large quantities, which makes this synthetic approach and Au_{38} clusters of broad utility. The crystal structure of $Au_{38}(SR)_{24}$ cluster is still unknown, but several groups have done theoretical calculations[30−34] and predict that $Au_{38}(SR)_{24}$ has 22 to 26 Au atoms as a core and mixed $Au(SR)_2$ and $Au_2(SR)_3$ motifs as protecting groups.[13,33,34] This prediction is based upon some empirical structural rules learned from the single crystal structures of $Au_{102}(p\text{-MBA})_{44}$ (p-MBA= p-mercaptobenzoic acid)[35] and $[Au_{25}(SCH_2CH_2Ph)_{18}]^-[TOA]^+$ [20,21] reported recently.

In summary, we have developed a facile method for synthesizing $Au_{38}(SC_{12}H_{25})_{24}$ clusters in high purity and yield via ligand exchange reactions of Au:SG clusters with neat $C_{12}SH$ in a two-phase reaction system. A key to this approach is the use of acetone to effect phase transfer of Au:SG clusters from the water phase to the neat $C_{12}SH$ phase. Surprisingly, the ligand shell of Au_{38} clusters was found to be sole dodecanethiolates, rather than a mixed ligand shell of dodecanethiolates and glutathionates. The exact formula of the as-prepared Au_{38} clusters is determined to be $Au_{38}(SC_{12}H_{25})_{24}$ based upon ESI-MS, NMR, and TGA analyses. The crystal structure of $Au_{38}(SR)_{24}$ cluster is yet to be unraveled.

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Supporting Information Available: Detailed information about the synthesis and characterization of $Au_{38}(SC_{12}H_{25})_{24}$, and supporting figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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