

Thermally-Induced Formation of Atomic Au Clusters and Conversion into Nanocubes

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Metal and semiconductor nanoparticles are having a major impact on research in materials, chemistry, physics, and biological and environmental sciences.¹ Control over particle size and shape has been achieved for a variety of compositions, e.g., Au, Ag, Pt, Co, and PtFe.^{1–8} Small metal clusters (composed of several to tens of atoms) with robust quantum effects or molecule-like properties (e.g., fluorescence) have also been extensively investigated.^{9–14} Early research on metal clusters was focused on gas-phase beam experiments, including the physical synthesis of clusters (e.g., Na_n, Ag_n) and spectroscopic studies of their structural and electronic properties.¹⁴ However, these gas-phase clusters are typically short-lived and difficult to chemically functionalize for applications such as catalysis or electron microscopy contrast enhancement of biological samples.^{15,16} Therefore, since the 1980s, research has focused on solution-phase chemical synthesis of metal clusters.^{17–19} A number of improved synthetic methods have been reported for the preparation of high-quality, relatively monodisperse, and ligand-stabilized nanoclusters in the form of solution dispersions.^{17–22} Metal clusters, e.g., Au₇₅, Au₅₅, Au₂₈, Au₁₁, and Au₈, as well as differently sized Ag nanoclusters,^{17,22,23} have been synthesized, and their catalytic and photoluminescence properties were extensively studied.^{24–26} These synthetic strategies lead to nanoclusters with greatly enhanced stability and allowed some degree of tailoring of their physical and chemical properties.²⁷ To fully exploit the fascinating properties of metal clusters, it is important to develop new strategies for synthesizing clusters with useful properties and enhanced stability.

This paper reports a facile thermal method in which Au nanocolloids are converted into atomic Au clusters under high-temperature reflux conditions. These clusters show distinct optical properties and extraordinary stability. In addition, they serve as building blocks allowing the synthesis of Au nanocubes.

Au clusters are prepared via a two-step process; the synthesis of ~6 nm (diameter) Au nanocolloids and subsequent conversion into clusters. Au colloids were synthesized via a modification of a literature protocol.²⁸ Briefly, AuCl₃ (30 mg, 0.1 mmol) was dissolved in a solution of didodecyldimethylammonium bromide (DDAB, 20 mM) in anhydrous toluene under inert gas (e.g., N₂). An aqueous solution of NaBH₄ (40 μL, 9.0 M, freshly prepared) was injected into the Au precursor solution under vigorous stirring (see Supporting Information). Au colloids were further passivated with dodecylthiol to enhance their stability. The colloids were precipitated with ethanol and washed with hexane to remove excess DDAB and possible reaction side-products. In the second step, the Au nanoparticles (0.025 mmol in atomic Au) were redispersed in a solution of dodecylthiol (0.4 M) in octyl ether, and the solution was refluxed at ~300 °C for ~50 min. During the initial stages (<10 min), transmission electron microscopy (TEM) shows that

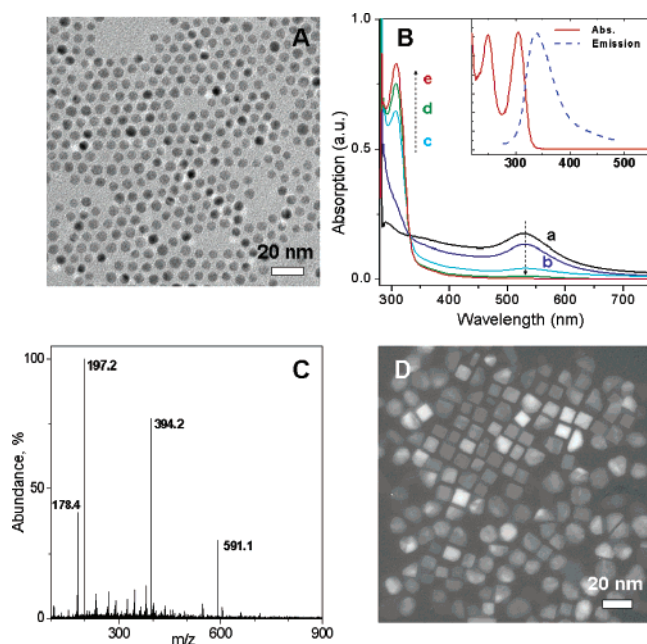


Figure 1. (A) TEM image of Au nanoparticles. (B) Time-dependent UV–vis spectra of the Au colloid under high-temperature reflux (~300 °C), curve *a* = 5 min, *b* = 15 min, *c* = 25 min, *d* = 35 min, and *e* = 55 min. The inset shows the absorption (solid line) and fluorescence spectra (dashed line, excitation = 250 nm). (C) Mass spectrum of Au clusters (note that the *m/z* = 178.4 species is assigned to CH₃(CH₂)₁₀Na⁺ adducts). (D) TEM image of Au nanocubes converted from Au clusters.

only Au nanoparticles with a diameter of 6.0 ± 0.5 nm are present (Figure 1A). The associated UV–vis spectrum shows an absorption peak at 525 nm, which is the plasmon absorption of small Au nanoparticles (Figure 1B, curve *a*). As thermal reflux proceeds, the ruby red color of the Au colloids gradually fades; the absorption at 525 nm decreases, and a new peak at 305 nm develops and grows with time. Finally, the 525 nm absorption completely disappears after ~50 min of reflux (Figure 1B, curves *b*–*e*). Under TEM, Au nanoparticles are no longer observed in the final sample. These observations show that during the high-temperature reflux process, the initial 6 nm Au nanocolloids are converted into ultrasmall clusters that cannot be imaged by TEM due to their extremely small size.

The as-prepared ultrasmall Au clusters are characterized by mass spectrometry. Whetten and co-workers have shown that Au clusters passivated with alkanethiols can be directly analyzed with laser desorption/ionization mass spectrometry in the absence of matrix molecules.²⁶ Following this method, the as-prepared Au cluster sample (diluted with hexane in a 1:2 ratio) was deposited on a steel plate without matrix molecules and, after drying, analyzed with a MALDI mass spectrometer. Laser (337 nm) irradiation results in desorption and ionization of clusters due to the breaking of S–C

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and Au–S bonds.²⁹ Three major peaks are observed in the mass spectrum (Figure 1C). All the peaks are singlets, and their mass/charge ratios ($m/z = 197.2, 394.1, 591.5$, respectively) are assigned to Au monomers ($\text{Au}^+ = 197$, isotope abundance 100%), dimers ($\text{Au}_2^+ = 394$), and trimers ($\text{Au}_3^+ = 591$). No larger clusters are detected when scanning the spectrum over a wide mass range (10–100 000 Da). Taken together with the spectroscopic data (see next paragraph), the clusters prepared from Au colloids are most probably molecular Au trimers, i.e., $\text{Au}_3(\text{SC}_{12}\text{H}_{25})_3$. The monomers and dimers observed in the mass spectrum may result from laser-induced dissociation of the parent trimer ions, namely, $\text{Au}_3^+ \rightarrow \text{Au}_2^+ + \text{Au}$, $\text{Au}_2^+ \rightarrow \text{Au}^+ + \text{Au}$ as previously observed.³⁰ There could be two possible geometrical isomers for Au trimers: linear and planar triangular structures. Bauschlicher et al.³¹ concluded that gas-phase ligand-free $\text{Au}_{3(\text{g})}$ should adopt the triangular structure by careful comparison of the experimental electron affinity data of $\text{Au}_{3(\text{g})}$ with simulations of linear and planar isomers. Therefore, we propose that the present solution-phase Au trimers should adopt a triangular configuration, albeit the possibility of ligand-induced structural change of the clusters may occur.

Previous gas-phase absorption measurements of bare Au trimers established that $\text{Au}_{3(\text{g})}$ shows transitions at 302, 285(292), and 258 nm.^{32,33} Solution-phase Au trimers show transitions at 305 and 250 nm (measured in hexane, cutoff wavelength 220 nm). The 305-nm absorption (Figure 1B inset, solid line) should correlate with the 292 nm transition of bare $\text{Au}_{3(\text{g})}$ clusters when accounting for the solution dielectric-induced spectral red-shift. Photoexcitation of either the 305 or 250 nm absorption band of the clusters leads to strong fluorescence emission centered at 340 nm (Figure 1B inset, dashed line). The Au clusters are highly luminescent with both states having the same emission spectrum, indicating an efficient non-radiative decay of the 250 nm state to the 305 nm-associated state. Therefore, the optical transitions at 305 and 250 nm are both assigned to Au trimers. The long-wavelength (470 nm) absorbance reported in ref 32 is attributed to aggregates/larger cluster in a more recent paper.³³ Therefore, no such absorption is expected for a pure Au trimer sample, consistent with our observation.

The as-prepared Au_3 clusters show extraordinary stability, as evidenced by the lack of observable degradation in two months monitored by UV–vis spectroscopy. This great stability of the Au clusters is partly due to the alkanethiol ligands.

Another striking feature of the atomic Au clusters prepared here is that they can serve as building blocks allowing the synthesis of Au nanocubes on a substrate. To demonstrate this, a diluted cluster solution was deposited onto a carbon film-coated TEM grid. When the substrate was heated on a hotplate at ~ 100 °C for a few minutes, Au nanocubes formed (average lateral dimension ~ 10 nm, Figure 1D). Note that when the cluster solution was heated in a flask, formation of Au nanocubes was not observed. Therefore, the growth of Au nanocubes must involve a nonequilibrium and surface-assisted nucleation/growth process. Conditions, structures formed, and proposed growth mechanism(s) are described elsewhere.³⁴ Femto-second laser two-photon interferometric fluorescence and pump–probe measurements³⁵ will be carried out to establish the electron dynamics of the clusters.

Acknowledgment. This work was supported by the University of Chicago MRSEC (#DMR0213745), NSF (#CHE0317009), and the Consortium for Nanoscience Research. We acknowledge the

NSF for an MRI grant (CHE 0216492) that aided this research. We thank Prof. Norris for use of a UV–vis spectrometer, Prof. Lee for use of a hood for synthesis, and Dr. Qin for assistance in MS analysis.

Supporting Information Available: Detailed experiments for the synthesis of Au nanoparticles and clusters (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA0482482