Controlling Gold Nanoparticles with Atomic Precision: Synthesis and Structure Determination

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Background and Objective

Gold nanoparticles have drawn significant research and technological interests due to their unique catalytic, optical, and electronic properties. Control of nanoparticles with atomic precision poses major challenges and has long been a major dream of nanoparticle chemists. Atomically precise nanoparticles allow the total structure (metal core plus surface ligands) to be revealed and attain fundamental understanding of the structure (in particular the surface atom arrangement), which is of paramount importance in order to study the catalytic properties of gold nanoparticles and for better design of highly efficient catalysts.

This dissertation focuses on the development of new methodologies for the synthesis of atomically precise gold nanoparticles and structural determination by X-ray crystallography. A universal “size focusing” strategy has been successfully established, which fulfills the major goal of this thesis.

Contributions and Results
1. Developed a universal size-focusing methodology to synthesize atomically precise Au nanoparticles

A new “size focusing” methodology has been developed in my thesis research for the synthesis of atomically precise gold nanoclusters. Using this methodology, a number of molecular purity gold nanoclusters (such as $\text{Au}_{25}(\text{SR})_{18}$, $[\text{Au}_{25}(\text{PPh}_3)_{10}(\text{SR})_5\text{Cl}_2]^{2+}$, $\text{Pd}_1\text{Au}_{24}(\text{SR})_{18}$, $\text{Pt}_1\text{Au}_{24}(\text{SR})_{18}$, $\text{Au}_{36}(\text{SR})_{24}$, $\text{Au}_{40}(\text{SR})_{24}$, $\text{Au}_{55}(\text{SR})_{31}$, $\text{Au}_{144}(\text{SR})_{60}$ and $\text{Au}_{333}(\text{SR})_{79}$) have been made with metal core diameter spanning from 1.0 to 2.2 nanometer.

The major chemical principle involved in the size-focusing methodology is that different sized $\text{Au}_n(\text{SR})_m$ nanoclusters possess vastly different stability, which leads to the survival of the robustest nanoparticle in the harsh size-focusing process, much like natural law—Survival of the Fittest.
Scheme 1. Size-focusing synthesis of atomically precise gold nanoparticles (SG: glutathione).

Figure 1. ESI-MS (left panel) and UV-vis absorption (right panel) spectra of Au_{25}(SR)_{18}, Au_{38}(SR)_{24} and Au_{144}(SR)_{60} nanoclusters, respectively (R: C\textsubscript{2}H\textsubscript{4}Ph).

The key condition for this methodology is to control the size distribution of the starting size-mixed nanoclusters (prior to the size-focusing step). A too broad size distribution would
result in several robust nanoclusters after size-focusing, and isolation of them would be very difficult, albeit in some special cases it might be possible. Therefore, in an ideal situation one would like to control the initial size distribution in a proper range and render it favorable for size focusing into one size of robust nanoclusters. (Scheme 1) After mapping out the important parameters that influence the size distribution of nanoclusters, we chose appropriate conditions for size focusing synthesis of nanoclusters with size control. (Figure 1)

2. Determined the total structure (core and surface) of $\text{Au}_{38}(\text{SR})_{24}$ nanoparticles by single crystal X-ray crystallography

The obtained atomically precise nanoclusters allow for the determination of their total structures (core plus surface). Understanding the total structure, in particular the surface atom arrangement, is of paramount importance in order to study the fundamental properties, for example, the catalytic properties of metal nanoclusters for future design of highly efficient catalysts.$^{12}$ In order to determine the total structure, the growth of single crystals of nanoclusters is the critical step, but unfortunately crystallization of nanoclusters in general has long been a huge challenge. Significantly, the $\text{Au}_{38}(\text{SR})_{24}$ nanoclusters with molecular purity achieved by the size focusing methodology have led to successful crystallization.$^{13}$ The unit cell of $\text{Au}_{38}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}$ crystals surprisingly reveals a pair of enantiomeric nanoparticles (left-handed and right handed). (Figure 2)

Here we choose the left-handed enantiomer for a detailed analysis of its structure. (Figure 3) The particle shows a prolate shape (diameter~ 0.8 nm, length~1.1 nm, Au center-to-center distances). The core of $\text{Au}_{38}(\text{SR})_{24}$ comprises a face-fused biicosahedral $\text{Au}_{23}$ motif (13+13-3=23, inner core or kernel), Figure 3A-B. The fusion of the two icosahedra occurs along a common $C_3$ axis. The rod-like $\text{Au}_{23}$ kernel is structurally strengthened by three monomeric $\text{--SR-Au-RS--}$ staples (Figure 3C). Then, the top icosahedron is further capped by three $\text{--SR-Au-SR-Au-RS--}$ dimeric staples (Figure 3D), which are arranged in a rotative fashion, resembling a tri-blade “propeller”. A similar arrangement of the other three staples is found on the bottom icosahedron, but the bottom “propeller” rotates by ~60° relative to the top one, forming a staggered dual-propeller configuration (Figure 3E). The entire nanoparticle becomes chiral due to the rotative arrangement of the dimeric staples. The chiral structure of $\text{Au}_{38}(\text{SR})_{24}$ is potentially very useful in chiral catalysis, chiral separation, and other applications.
3.3. \( \text{Au}_n(\text{SR})_m \) Catalysts for Selective Oxidation and Hydrogenation Reactions

We have also explored the catalytic applications of the synthesized well-defined \( \text{Au}_n(\text{SR})_m \) nanoparticles in selective oxidation and hydrogenation processes. On the basis of their crystal structures, these Au particles permit a correlation of particle structure with their excellent catalytic properties and an identification of catalytically active sites on the particle; the latter has long been pursued in nanocatalysis, but conventional polydisperse nanoparticles preclude the
identification of active sites and deep understanding of catalysis since the surface structure of polydisperse nanoparticles is impossible to determine. Thus, the atomically monodisperse nanoparticles we have made are expected to significantly advance the catalysis science.

Summary

My doctoral research has successfully establish the first-ever “size focusing” methodology for preparing a series of “perfect” $\text{Au}_n(\text{SR})_m$ nanoparticles with molecular purity. Growth of single crystals has revealed the intriguing chiral structure of $\text{Au}_{38}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}$. The range of sizes attained, including $\text{Au}_{25}(\text{SR})_{18}$, $\text{Au}_{38}(\text{SR})_{24}$, $\text{Au}_{40}(\text{SR})_{24}$, $\text{Au}_{55}(\text{SR})_{31}$, $\text{Au}_{144}(\text{SR})_{60}$, and $\text{Au}_{333}(\text{SR})_{79}$, has explicitly demonstrated the evolution of the structural, optical and electronic properties with the number of gold atoms in the particle. These well defined nanoparticles hold great promise in many applications such as catalysis, optics, and sensing.

Reference