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Review

Mechanistic exploration and controlled synthesis of precise thiolate-gold nanoclusters

Nirmal Goswami, Qiaofeng Yao *, Tiankai Chen, Jianping Xie *

Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117585, Singapore

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ABSTRACT

Well-defined thiolate-gold nanoclusters (generally described as $Au_n(SR)_m$ NCs, where “n” and “m” are the numbers of gold atoms and thiolate ligands (–SR), respectively), comprise a family of ultrasmall particles (<2 nm), which are distinctly different from their large counterparts, plasmonic gold nanoparticles (NPs, >2 nm). They are attracting increasing attention in various areas, including biomedicine, optoelectronics, catalysis, and analytical science, mainly because of their unique molecular-like properties, such as HOMO-LUMO (highest occupied and lowest unoccupied molecular orbital) transitions, quantized charging, and photoluminescence. All of these physicochemical properties are highly sensitive to the size and composition of Au NCs, and thus the ability to control these variables during synthesis is highly important. This review describes recent advances in the precise control of these features during Au NC synthesis, typically via the reduction of Au(I)-SR complexes. First, the formation mechanisms for atomically precise $Au_n(SR)_m$ NCs are explained, which may be decoupled into two stages: 1) generation of intermediate NCs via the reduction of Au(I)-SR complexes (reduction-assisted growth stage), and 2) size evolution of intermediate NCs to form Au NC species with atomic precision (size evolution stage). The size/composition control strategies implemented in the reduction-assisted growth stage are summarized based on this reduction-size evolution mechanism. Details are then given of the regulation strategies with effects in the size evolution stage. Finally, it is shown that balancing the rate of reduction and size evolution may be a unified approach for the facile synthesis (large-scale production, easy preparation, and short reaction time) of $Au_n(SR)_m$ NCs with high control over their size and composition. This concept may facilitate the design and development of large-scale methods for synthesizing stable well-defined Au NCs with advanced functions for use in a wide range of applications in different domains.

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* Corresponding authors.
E-mail addresses: cheyaoq@nus.edu.sg (Q. Yao), chexiej@nus.edu.sg (J. Xie).

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1. Introduction

Metallic gold has been well known for its immense economic value for thousands of years of recorded human history. In addition to its monetary value, nanosized versions of this precious metal have fascinated scientists for centuries and they are now utilized widely in numerous applications [1–3]. Understanding the unusual physical and chemical properties of nanoscale gold compared with bulk gold has led to the emergence of a new area in nanoparticle (NP) research. Indeed, gold NPs (Au NPs) are considered to be of great general interest, as shown by their applications in various fields including catalysis [4,5], sensing [6–8], and biomedical science [9–12]. All these applications have significantly increased the value of gold for the production of functional materials in addition to its current main role in wealth storage.

More recently, a new class of gold nanomaterial has emerged based on the possibility of finding the missing link between gold atoms and Au NPs, which are known as gold nanoclusters (Au NCs) [13–19]. This new class of materials can be differentiated from their larger counterparts, i.e., Au NPs, based on their size and physical/chemical properties [1,20–23]. For instance, Au NCs comprise several to a few hundred Au atoms with a typical size of $\leqslant$2 nm, where the continuous/semi-continuous density of states breaks up into discrete energy levels, thereby leading to a discrete electronic structure and some unique molecular-like properties, such as HOMO-LUMO (highest occupied and lowest unoccupied molecular orbital) electronic transitions [13,24–27], strong photoluminescence [28–36], discrete redox behavior [37], intrinsic magnetism [38–40], and optical chirality [41–44]. By contrast, Au NPs possess a semi-continuous electronic structure with interesting surface plasmon resonance properties. In addition, a distinctive characteristic of Au NCs is their well-defined molecular size and composition, i.e., each Au NC has a precise number of Au atoms and organic ligands. By contrast, the precise structures and compositions of Au NPs are not obvious. All of these unique features make Au NCs suitable for possible uses in a wide range of applications, including optoelectronics [45–47], catalysis [48–54], sensing [55–60], and biomedical science [61–76].

The synthetic chemistry of thiolate-gold NCs (thiolate-Au NCs) has been explored the most often among all the metal NCs [77–106]. In particular, the design of efficient protocols for synthesizing thiolate-gold NCs with atomic precision has been a key task in this field during the past two decades [79,107–122]. The method developed by Brust et al. (Brust-Schiffrin method) for the synthesis of small-sized Au NPs (1–3 nm) using organic thiols as ligands in a two-phase method has been a particularly important advance [123]. Due to its simplicity, this method has been used widely by the research community and it has affected the subsequent development of thiolate-Au NCs with well-defined sizes and compositions. This method has been used successfully to prepare ultrasmall thiolate-Au NCs, and it is now possible to determine their precise size and composition using a number of high-resolution analytical techniques, such as laser desorption ionization (LDI) and matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) [17,124–130]. An important example is the preparation of a mixture of water soluble thiolate-Au NCs using a modified Brust-Schiffrin method and the subsequent isolation of nine Au NC species by gel electrophoresis [131]. The exact composition of these nine Au NC species was determined by electrospray ionization-mass spectrometry (ESI-MS). The physicochemical properties of thiolate-Au NCs are highly sensitive to their size and composition, so they are often represented by the molecular formula of $Au_n(SR)_m$, where n and m are the numbers of Au atoms and thiolate ligands (–SR), respectively.

However, thiolate-Au NCs synthesized by Brust-Schiffrin method are usually polydisperse in size and they require post-synthetic separation, which is laborious and infeasible during large-scale production. To address this problem, a unique size-focusing strategy was introduced recently, which allows the most thermodynamically stable Au NC species to be obtained from a mixture of NCs [132,133]. In recent years, many advances have been achieved in this field, as shown by the production of a series of atomically precise Au NCs with different core sizes and compositions, e.g., some representative thiolate-Au NCs are $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, $Au_{40}(SR)_{24}$, $Au_{64}(SR)_{32}$, $Au_{99}(SR)_{42}$, $Au_{102}(SR)_{44}$, $Au_{130}(SR)_{50}$, $Au_{133}(SR)_{52}$, and $Au_{144}(SR)_{60}$ [107,134–142].

In addition to the methodological development of Au NCs with precisely controlled sizes and compositions, fundamental studies of the underlying chemistry that governs these synthetic methods have been equally important. Recent advances in the synthetic chemistry of thiolate-Au NCs have shown that the production of atomically precise $Au_n(SR)_m$ NCs via the reduction of Au(I) complexes typically involves two steps: 1) kinetically controlled reduction of Au(I) complexes, where $Au_x(SR)_y$ NCs are formed with different sizes (x, y); and 2) thermodynamically controlled size-focusing of different size intermediate $Au_x(SR)_y$ NCs, thereby leading to the survival of a specific Au NC (most stable species). Based on this two-step scheme, the rational design of Au NCs (with uniform and tunable attributes, e.g., size and composition) might be possible by carefully tailoring the chemistry in each step.

This review describes recent advances in our understanding of the formation of thiolate-Au NCs based on the two-step scheme mentioned above. According to this understanding of the detailed synthetic chemistry involved in each step, it is possible to analyze the synthetic strategies that are effective in each step, thereby obtaining atomically precise Au NCs. First, a summary is provided of the strategies employed to control the size and structure of Au(I) complexes, as well as their reduction kinetics during the formation of intermediate $Au_x(SR)_y$ NCs with narrow size and composition distributions. Next, a detailed discussion is given of the strategies that can effectively modulate the size and composition of intermediate $Au_x(SR)_y$ NCs to yield desirable atomically precise $Au_n(SR)_m$ NC species. Finally, it is shown that balancing the reduction-assisted growth and size evolution of thiolate-Au NCs might facilitate the large volume production of thiolate-Au NCs with atomically precise sizes and compositions. Many (if not all) of the material properties of thiolate-Au NCs are highly sensitive to their size and composition, so this review focuses on the ability to control the design (i.e., uniform and tailorable) of the size and composition of thiolate-Au NCs.