

Kinetically Controlled, High-Yield Synthesis of Au₂₅ Clusters

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Noble metal nanoparticles (e.g., Au, Ag) have become one of the most important types of nanomaterials that are being extensively explored in nanoscience and nanotechnology research. Between metal atoms and bulk metals, there are two distinct size regimes of particular interest, that is, the cluster state and the nanocrystal state.^{1,2} Metal nanoclusters (M_n^0 , n = the number of metal atoms in the core) are ideally composed of an exact number of metal atoms (n ranging from several to hundreds of atoms), and their size typically ranges from subnanometer to approximately 2 nm (core diameter). Because of the strong quantum confinement of electrons in this extremely small size regime, electron energy quantization occurs, and such an effect drastically alters the physical and chemical properties of metal clusters, for example, plasmon excitation, which is characteristic of metal nanocrystals, no longer exists in the cluster state.² Small metal clusters behave like molecules and exhibit enhanced catalytic activity, luminescence, and unique charging properties,^{3–11} which make this type of nanomaterial very promising in developing new generations of catalysts, sensors, and optoelectronic devices.

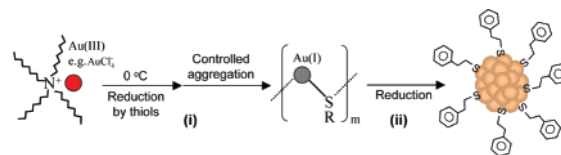
With respect to chemical synthesis of metal nanoclusters, previous work has explored the utility of phosphines and carbonyl ligands for stabilization of metal clusters in solution;^{1–4} several well-defined gold clusters, such as Au₁₁, Au₃₉, and Au₅₅, as well as bimetallic clusters (e.g., Au₁₃Ag₁₂) have been synthesized.^{1,4,7,8} However, a major drawback of phosphine-passivated Au clusters is their lability; these clusters decompose over a period of several days, which greatly limit their practical applications. In recent years, significant advances in nanochemistry have led to the successful synthesis of extraordinarily stable gold clusters (e.g., Au₂₅, Au₁₀₂) using alkyl- or arylthiols as ligands.^{5,12–18}

Despite the remarkable success that has been made in gold cluster syntheses, most synthetic procedures suffer from the production of a mixture of different cluster sizes and, often, the yield for a specific size is quite low; thus the products have to be separated on the basis of techniques such as fractional crystallization, chromatography, and electrophoresis, etc.^{13–16} The difficulty in purifying clusters has become a major obstacle to the practical applications of the cluster materials. Thus, it is highly desirable to develop synthetic strategies that allow for high-yield synthesis of monodisperse metal clusters without the need of nontrivial postsynthetic size separation steps.

We rationalize that by carefully controlling the reaction kinetics of the cluster synthesis reactions, it should be possible to create a specific chemical environment that leads to exclusive formation of one sized clusters and suppresses other sizes. Herein, we report such an example: high yield synthesis of Au₂₅ clusters through kinetic control. It is noteworthy that Au₂₅ clusters have previously been synthesized via a two-phase protocol^{16,17} or conversion of Au₁₁ to Au₂₅.¹⁸ Except for the latter, the reported protocols unfortunately generate a mixture of different sizes.

We choose the two-phase method as our model system to study the reaction kinetics with an aim to control the kinetics toward the

Scheme 1



synthesis of one-sized Au clusters in high yield. This procedure typically involves two steps (Scheme 1): (i) reduction of Au(III) (e.g., HAuCl₄) to Au(I) by thiols, forming an intermediate of Au(I):SR complexes, where R can be alkyl- or arylthiols, and (ii) further reduction of Au(I) to Au(0) by a strong reducing agent (e.g., NaBH₄). We chose phenylethanethiol as the ligands since the bulky phenyl group can provide better steric protection for clusters, as demonstrated in the previous work by Donkers et al.¹⁶ In their work, the yield of Au₂₅ was however quite low, and the product was subject to multiple steps of solvent extraction to remove larger clusters (e.g., an average formula of Au_{~140}).¹⁷

An important discovery from our work is that the kinetics for the formation of Au(I):SR intermediate is very critical for high yield synthesis of Au₂₅ clusters in the two-phase method; specifically, we found that control over the reaction temperature (0 °C) and stirring condition (*slow*) can generate a particular aggregation state of the Au(I):SR intermediates that leads to exclusive formation of Au₂₅ clusters. This low-temperature method successfully eliminates the formation of larger clusters (Au_{~140}) observed previously.^{16,17}

In a typical experiment (see Supporting Information for details), gold salt (HAuCl₄·3H₂O, 0.4 mmol) was phase-transformed from the aqueous to organic (toluene) with the aid of tetraoctylammonium bromide (TOAB); the solution was then cooled down to 0 °C (ice-bath), and subsequently, phenylethanethiol (0.17 mL) was added to the cold Au(III) solution; magnetic stirring was reduced to a very low speed (~30 rpm). The solution color changed from deep red to faint yellow over a period of ~5 min, indicating reduction of Au(III) to Au(I) by phenylethanethiols (Scheme 1). For the next stage, aggregation of Au(I):SR (R = CH₂CH₂Ph, same below) occurred, and the solution gradually turned from faint yellow to clear over a period of ~1 h. Note that both the low temperature and slow stirring conditions are critical for the formation of particular aggregates (see light-scattering measurements below) of Au(I):SR intermediates that lead to Au₂₅ in high yield in the second reduction step (Scheme 1). After the formation of Au(I) aggregates (~1 h), stirring was changed to fast (~1100 rpm) and NaBH₄ (aqueous) was immediately added. The growth of gold clusters was allowed to proceed overnight. Significantly, under the experimental conditions explored (0 °C and very slow stirring), the Au(I):SR aggregates lead to exclusive formation of Au₂₅ clusters. The final crude products, *without* any purification, already show distinct absorption bands at 670, 450, and 400 nm (Figure 1A and Figure S1), which are characteristic of Au₂₅ clusters,^{16–19} indicating high yield synthesis of Au₂₅ clusters (40% Au atom basis). Mass

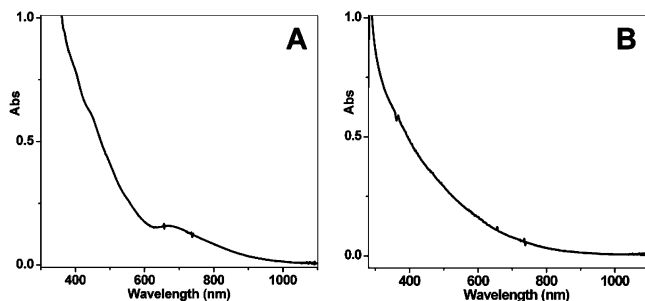


Figure 1. UV-vis spectrum of the final crude products (A) prepared by the low-temperature method and (B) by the room-temperature protocol.

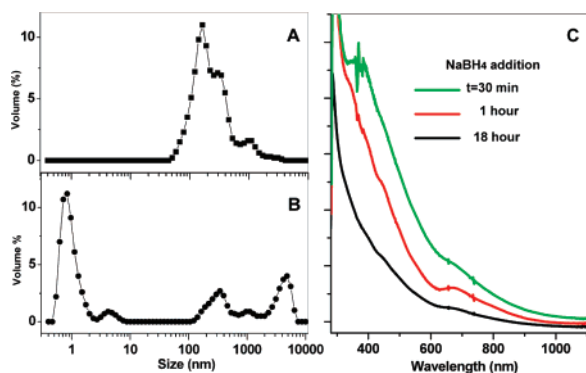


Figure 2. DLS spectra of Au(I):SR intermediates formed at (A) 0 °C and (B) room temp; (C) UV-vis spectra of the final colloids showing the effect of Au(I):SR aggregation time on the yield of Au₂₅.

spectrometry and thermogravimetric analyses confirmed that the as-prepared clusters are Au₂₅ (Figures S2–S4).

In contrast, the Au(I):SR aggregates formed at room temperature led to a low yield of Au₂₅ clusters (8% Au atomic basis), evidenced by a featureless decaying spectrum of the final crude products (Figure 1B), similar to previous observation.¹⁶ The low yield is because a major amount of Au(I):SR was converted to larger Au clusters (Au_{~140}) as previously determined by Murray and co-workers.^{16,17}

Compared to the room-temperature method, our major improvement is that the aggregation process of Au(I):SR intermediates was carried out under controlled conditions (0 °C and slow stirring), which leads to Au₂₅ formation and successfully eliminates the formation of other sizes. Interestingly, fast stirring was found to disrupt the formation of the peculiar Au(I):SR aggregates and the Au₂₅ yield was lower. These results demonstrated the importance of kinetic control over the Au(I):SR formation in order to achieve high yield synthesis of Au₂₅ clusters.

To gain further insight into the kinetic control process, in particular, how the aggregation state of Au(I):SR intermediates correlate with high-yield of Au₂₅ clusters, we have performed dynamic light scattering (DLS) measurements on the Au(I):SR intermediates. DLS measurements showed that the Au(I):SR formed at 0 °C and under very slow stirring condition is predominantly distributed in a range of 100–400 nm (nominal hydrodynamic diameter) (Figure 2A), while the Au(I) intermediates formed at room temperature show multiple distribution peaks (<2 nm, 100–400 nm, and >1 μm (note that the large aggregates formed at room temperature are beyond the DLS spectral range; they precipitate, visible to naked eye)). These results clearly show that the two synthetic protocols lead to major differences in size and possibly internal structures of the Au(I):SR aggregates. Odriozola et al. have reported a type of lamellar structure of Au(I):S-Glutathione species.²⁰ In our case, however, further structural analysis of the

Au(I):SR aggregates was not successful because of their metastable nature and difficulty in separation (e.g., removing TOAB); in situ small-angle X-ray diffraction analysis of the Au(I) aggregates is to be pursued. We rationalize that the 100–400 nm Au(I):SR aggregates break up after NaBH₄ reduction and self-assemble into Au₂₅ clusters; predominant formation of Au₂₅ clusters may also be related to their extraordinary stability.¹⁵ We have further investigated the effect of Au(I):SR aggregation time on the final Au₂₅ yield. NaBH₄ solution was added at different times to reduce the Au(I) aggregates to gold clusters. The UV-vis spectra for the final products (Figure 2C) showed that an optimum aggregation state of Au(I):SR indeed exists; the highest yield was achieved at ~1 h of the Au(I):SR aggregation process.

In summary, we have developed a facile, low-temperature method for synthesizing Au₂₅ clusters in high yield via controlling the kinetics of the formation of Au(I):SR intermediates. An important finding from this work is that the aggregation state of the Au(I):SR intermediate species is critical for subsequent growth of monodisperse gold clusters. This method is promising and has been extended to the synthesis of gold clusters of other sizes by carefully tuning the reaction kinetics.

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Supporting Information Available: Experimental details, ESI, MALDI-TOF, and TGA data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Schmid, G., Ed. *Clusters and Colloids*; VCH: Weinheim, Germany, 1994.
- (2) Kreibitz, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer-Verlag: New York, 1995.
- (3) de Silva, N.; Dahl, L. F. *Inorg. Chem.* **2005**, *44*, 9604.
- (4) Teo, B. K.; Shi, X.; Zhang, H. *J. Am. Chem. Soc.* **1992**, *114*, 2743.
- (5) Link, S.; Beeby, A.; FitzGerald, S.; El-Sayed, M. A.; Schaaff, T. G.; Whetten, R. L. *J. Phys. Chem. B* **2002**, *106*, 3410.
- (6) Wang, G.; Huang, T.; Murray, R. W.; Menard, L.; Nuzzo, R. G. *J. Am. Chem. Soc.* **2005**, *127*, 812.
- (7) Bertino, M. F.; Sun, Z.-M.; Zhang, R.; Wang, L.-S. *J. Phys. Chem. B* **2006**, *110*, 21416.
- (8) Woehle, G. H.; Warner, M. G.; Hutchison, J. E. *J. Phys. Chem. B* **2002**, *106*, 9979.
- (9) Zheng, J.; Petty, J. T.; Dickson, R. M. *J. Am. Chem. Soc.* **2003**, *125*, 7780.
- (10) Jin, R.; Egusa, S.; Scherer, N. F. *J. Am. Chem. Soc.* **2004**, *126*, 9900.
- (11) Yang, Y.; Chen, S. *Nano Lett.* **2003**, *3*, 75.
- (12) Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.; Kornberg, R. D. *Science* **2007**, *318*, 430.
- (13) Schaaff, T. G.; Knight, G.; Shafiqullin, M. N.; Borkman, R. F.; Whetten, R. L. *J. Phys. Chem. B* **1998**, *102*, 10643.
- (14) Wilcoxon, J. P.; Provencio, P. *J. Phys. Chem. B* **2003**, *107*, 12949.
- (15) (a) Negishi, Y.; Nobusada, K.; Tsukuda, T. *J. Am. Chem. Soc.* **2005**, *127*, 5261. (b) Negishi, Y.; Chaki, N. K.; Shichibu, Y.; Whetten, R. L.; Tsukuda, T. *J. Am. Chem. Soc.* **2007**, *129*, 11322. (c) Shichibu, Y.; Negishi, Y.; Tsunoyama, H.; Kanehara, M.; Teranishi, T.; Tsukuda, T. *Small* **2007**, *3*, 835.
- (16) Donkers, R. L.; Lee, D.; Murray, R. W. *Langmuir* **2004**, *20*, 1945.
- (17) Tracy, J. B.; Kalyuzhny, G.; Crowe, M. C.; Balasubramanian, R.; Choi, J.-P.; Murray, R. W. *J. Am. Chem. Soc.* **2007**, *129*, 6706.
- (18) Shichibu, Y.; Negishi, Y.; Tsukuda, T.; Teranishi, T. *J. Am. Chem. Soc.* **2005**, *127*, 13464.
- (19) Iwasa, T.; Nobusada, K. *J. Phys. Chem. C* **2007**, *111*, 45.
- (20) Odriozola, I.; Loinaz, I.; Pomposo, J. A.; Grande, H. J. *J. Mater. Chem.* **2007**, *17*, 4843.

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