(Supporting Information)

Kinetic Control and Thermodynamic Selection in the Synthesis of Atomically Precise Gold Nanoclusters

Zhikun Wu,^{†‡} Mark A. MacDonald,[§] Jenny Chen,[†] Peng Zhang,[§] and Rongchao Jin[†]*

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Ave, Pittsburgh, Pennsylvania 15213 USA; Key Laboratory of Materials Physics, Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Chinese Academy of Sciences (CAS), Hefei 230031, Anhui, China; Department of Chemistry and Institute for Research in Materials, Dalhousie University, Halifax, Nova Scotia, B3H 4J3, Canada

1. Chemicals

Tetrachloroauric(III) acid (HAuCl₄·3H₂O, >99.99% metals basis, Aldrich), Tetraoctylammonium bromide (TOAB, \geq 99%, Fluka), Tetraoctylammonium chloride (TOAC, \geq 97%, Fluka), 2-Phenylethanethiol (PhCH₂CH₂SH, 99%, Acros Organics), Sodium borohydride (99.99% metals basis, Aldrich), Borane-*tert*-butylamine complex (powder, 97%, Aldrich), Silver trifluoro-acetate (99.99+%, Aldrich). Solvents: Toluene (HPLC grade, \geq 99.9%, Aldrich), Ethanol (absolute, 200 proof, Pharmco), Methylene chloride (HPLC grade, \geq 99.9%, Aldrich), Acetonitrile (HPLC grade, \geq 99.9%, Aldrich), Tetrahydrofuran (HPLC grade, \geq 99.9%, Aldrich). All chemicals were used as received. Nanopure® water (resistivity 18.2 M Ω ·cm) was purified with a Barnstead NANOpure DIwaterTM system.

All glassware was thoroughly cleaned with aqua regia (HCl: HNO₃=3:1, vol), rinsed with copious Nanopure water, and then dried in an oven prior to use.

2. Synthesis of Au₁₉(SCH₂CH₂Ph)₁₃ Nanoclusters

HAuCl₄·3H₂O (0.2245g, 0.57 mmol) was dissolved in ~0.5 ml EtOH, then tetraoctylammoniun bromide (TOAB, 0.3165g, 0.58mmol) and 14.3ml toluene were sequentially added to the gold salt solution. The resultant solution was cooled to 0 °C in an ice bath over a period of ~30 min under constant magnetic stirring. After that, magnetic stirring was reduced to a very low speed (~60 rpm), PhCH₂CH₂SH (0.42 mL, ~5 equivalents per mole of gold) was slowly added and the solution was kept under slow stirring at ~60 rpm. The solution color slowly changed from deep red to faint yellow, and eventually became clear over a ~6 h period. After that, 4.8 ml of toluene solution of borane-*tert*-butylamine complex (247.8 mg, 2.84 mmol) was slowly added to the solution in a dropwise fashion within a ~8 min period. After borane-*tert*butylamine complex addition, the reaction was allowed to further proceed for ~ 60 hours. The precipitate was washed thoroughly by EtOH, water, CH₂Cl₂, and dried for TGA analysis (identified to be Au(I)-SR, Figure S4). The solution was evaporated under a reduced pressure and washed thoroughly with EtOH, then recrystallized for several times.

It is worth noting that when the reducing agent was replaced to sodium borohydride (dissolved in water) while keeping other conditions the same, $Au_{25}(SR)_{18}$ clusters were indeed produced, indicating the important role of the reducing agent in the kinetically controlled synthesis of clusters.

A side-product of the Au₁₉ synthesis was identified to be Au(I)SR complexes. For comparison, we prepared Au(I)SR as follows. HAuCl₄·3H₂O (62.0 mg, 0.16 mmol) was dissolved in 4.4 mL THF in a tri-neck flask, and the resulting solution was cooled to 0 °C in an ice bath over a period of 30 min. PhCH₂CH₂SH (112 μ L, 5 equivalents per mole of gold) was slowly added to the flask; stirring was reduced to a very low speed (60 rpm). The yellow solution turned colorless overnight. The precipitate was collected, washed thoroughly with THF, water, EtOH and dried. TGA analysis was provided in Figure S4.

To rule out the presence of Cl⁻ or Br⁻ ions in the cluster composition, we performed precipitation tests with silver trifluoroacetate. First, we performed tests by adding 1µL of 0.045M tetraoctylammoniun bromide (or chloride) solution (THF as solvent) to 60 µL of 1.5 mM silver trifluoroacetate solution, vortexed for 30 sec., centrifuged at 6000 rpm for 2 min. White precipitates were observed by naked eyes, demonstrating the viability of observing AgX (X=Br, Cl) precipitates by visual check at this halide concentration. Increasing the amount of the phase-transfer agent or silver salt (for example, increase to 2-fold), operate in the otherwise same conditions, more precipitates can be found. These experiments show that small amounts of halide ions can be visually detected (the detection limit is at least $< 0.1 \ \mu$ M). Then, to test possible Cl⁻ or Br⁻ present in the nanocluster as a counter ion, we performed the following test. 1.4 mg of nanoclusters (~0.25 µmol) was dissolved in 60 µL of 7.5 mM silver trifluoroacetate solution; the mixture was votexed for 30 sec., centrifuged (6000 rpm) for 2 min., but no white precipitate was found. Further, the mixture was centrifuged at 14000 rpm for 8 min., still no precipitates were found. Increasing the amount of nanocluster and silver salt to 4-fold and operating in the similar manner, we still didn't find any precipitates. Those experiments demonstrated clearly that the cluster doesn't contain chloride or bromide, consistent with XPS analysis.

3. Characterization

UV-Vis absorption spectra of Au nanoclusters in CH₂Cl₂ were recorded using a Hewlett-Packard (HP) 8453 diode array spectrophotometer. The purity of the as-prepared Au clusters was analyzed by size exclusion chromatography (SEC) on an HP Agilent 1100 system using a PLgel column (particle size: 3 µm, pore diameter: 100 Å). A diode array detector (DAD) in situ monitors the optical absorption spectrum (190-950 nm range) of the eluted solution. The purity of the clusters can be verified by comparing the UV-vis spectra at different times of the peak (e.g. peak point, left and right points at half height of the peak). Thermogravimetric analysis (TGA) was carried out using a TG/DTA6300 (Seiko Instruments, Inc.) thermogravimetric analyzer. Typically, ~2 mg of solid nanoclusters was used. Other experimental conditions are as follows: heating rate 5°C/min, N₂ flow rate 50 mL/min. ¹H NMR spectra of Au nanoclusters were collected with a Bruker Avance 300 MHz spectrometer. Chloroform-d was used as solvent. Electrospray ionization mass spectra were acquired using a Waters O-TOF mass spectrometer equipped with Z-spray source. The sample was dissolved in toluene (~1 mg/ml) and diluted 1:2 in dry methanol (50 mM CsOAc). The sample was directly infused at 5 µL/min. The source temperature was kept at 70 °C. The spray voltage was kept at 2.20 kV and the cone voltage at 60V.

XPS experiments were conducted at the Spherical Grating Monochromator (SGM) beamline of the Canadian Light Source (CLS). All samples were prepared by depositing a thin layer of nanoclusters onto a Si(111) wafer. Samples were then loaded into the SGM vacuum chamber, operated at a base pressure or 7.5×10^{-10} torr and a temperature of 85 K. All spectra were collected with a photon energy of 800 eV. To determine the Au/S ratio in Au₁₉(SR)₁₃, a sample of Au₂₅(SR)₁₈ was used to calibrate the atomic sensitivity factors from the Au 4f and S 2p signal whereby:

$$\frac{N_{Au}}{N_S} = \frac{I_{Au}S_S}{I_SS_{Au}}$$

where *N* represents the number of a particular nuclei in a sample, *I* represents the detected peak area for the Au 4f or the S 2p regions, and *S* represents the atomic sensitivity factor for each nuclei. For the Au 4f and S 2p regions of Au₂₅(SR)₁₈ an S_S/S_{Au} ratio was found to be ~0.14, which was used to determine the Au:S value of the product reported in this work (i.e. 1.43 ± 0.04). The reported Au:S value represents the average and variance of the experimental Au:S ratios collected from three different spots on the Si wafer.

4. Supporting Figures



Figure S1. A) NMR spectrum of as-prepared nanoclusters; B) NMR spectrum of free phenyethylthiol. Solvent: CDCl₃.



Figure S2. Thermogravimetric analysis (TGA) of the nanocluster (atmosphere: $N_2 \sim 50$ mL/min, 10 °C/min).



Figure S3. (A) UV-vis spectrum of the Au_n clusters extracted from the crude product of Au₁₉. For comparison, the spectra of Au₂₅(SC₂H₄Ph)₁₈ clusters are also shown. (B) LDI mass spectrum of the extracted clusters. The results show that the small amount of byproduct (Au_n) is Au₂₅.



Figure S4. Comparison of TGA curves of the precipitates from the Au_{25} reaction mixture, from the Au_{19} reaction mixture, as well as the Au(I)-SC₂H₄Ph aggregates. These results confirm that the precipitate from the Au_{19} reaction mixture is Au(I)-SR.



Figure S5. Comparison of the UV-vis absorption spectra of $Au_{19}(SR)_{13}$, $Au_{25}(SR)_{18}$ and $Au_{38}(SR)_{24}$, where, R=C₂H₄Ph.