Supporting Information for

Facile, Large Scale Synthesis of Dodecanethiol Stabilized Au_{38} Clusters

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Experimental Details

1. Chemicals

Glutathione (G-SH, 98%, Acros Organics), Tetrachloroauric(III) acid ($HAuCl_4 \cdot 3H_2O$, 99.99%, Aldrich), Sodium borohydride ($NaBH_4$, 99.99%, Aldrich), 1-Dodcanethiol (C_{12}-SH, 98%, Acros Organics), Acetone (HPLC grade, 99,9%, Sigma-Aldrich), Toluene (HPLC grade, 99.9%, Sigma-Aldrich), Ethanol (HPLC grade, Sigma-Aldrich) were used as received.

2. Synthesis of Au_{38} clusters

2.1. Synthesis of Au:SG clusters.

The Au:SG clusters were synthesized by a literature method.[1-5] Typically, 0.3 mmol $HAuCl_4 \cdot 3H_2O$ was first dissolved in 20 ml methanol and 1.2 mmol GSH was dissolved in 10 ml water. The two solutions were then mixed to form a cloudy suspension, which was known to be Au(I)-SG polymers.[1] The mixture solution was cooled to 0 ^oC in an ice bath. $NaBH_4$ (3 mmol, dissolved in 6ml cool nanopure water) was rapidly added to the suspension under vigorous stirring. Upon addition of $NaBH_4$, the solution color immediately changes to black, indicating the formation of Au:SG clusters (in a mixture). The solution was allowed to react for another hour. The resulting precipitation was collected by centrifugation and washed several time with methanol.

2.2. Ligand exchange with 1-dodcanethiol to produce Au_{38} clusters.

The Au:SG clusters were dissolved in 4 ml H_2O. Then, 6 ml acetone and 8 ml dodcanethiol (C_{12}-SH) were added; the C_{12}-SH phase forms the upper layer and the aqueous solution of Au:SG clusters forms the bottom layer. The solution was heated to 80^oC and allowed to react for several hours under vigorous stirring. After 3 hrs, the Au clusters were found to

completely transfer to the organic phase. During the phase transfer process, gold cluster core etching and secondary growth occurs. The isolated dodcanethiol phase was washed thoroughly with excess ethanol and then with acetone to remove excess dodecanethiol and by-products. The major fraction containing Au_{38} clusters was extracted with toluene from the crude product. The purity of Au_{38} clusters were further improved by extraction with a mixed toluene/acetone (1:5 v:v) solvent. Typically, 50-100mg pure $Au_{38}(SR)_{24}$ clusters were obtained when 1g $HAuCl_4 \cdot 3H_2O$ was used as precursor.

3. Characterization

UV-vis spectra of Au_{38} clusters in toluene were recorded on Hewlett- Packard (HP) 8453 diode array spectrophotometer and Varian Cary 5000 UV-vis-NIR spectrophotometer at room temperature. The purity of Au_{38} clusters was analyzed by size exclusion chromatography (SEC, PLgel column, particle size: 3 μm, pore diameter: 100Å) with HP Agilent 1100 HPLC system. A diode array detector *in situ* measures the UV-vis spectra (190 to 950 nm) of the eluate. The mobile phase was CH_2Cl_2 at a flow rate of 0.5 mL/min. Thermal gravimetric analysis (TGA) (~ 2 mg sample used) was conducted under a N_2 atmosphere (flow rate ~50 mL/min) on a TG/DAT6300 analyzer (Seiko Instruments, Inc); the heating rate was 10 ^oC/min. NMR spectra of gold cluster solution (~10 mg/ml in CD_3Cl) were acquired on a Bruker Avance^{TM} 300 MHz spectrometer. Laser desorption ionization (LDI) mass spectrometry was performed on a PerSeptive Biosystem Voyager DE super-STR time-of-flight (TOF) mass spectrometer. Electrospray ionization mass spectra were obtained using a Waters Q-TOF mass spectrometer equipped with Z-spray source. The source temperature was kept at 70 C. The sample was directly infused at 5 μL/min. The spray voltage was kept at 2.20 kV and the cone voltage at 60V. The sample was dissolved in toluene (1mg/ml) and diluted 1:2 in dry methanol (50 mM CsOAc).

References

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Supporting Figures

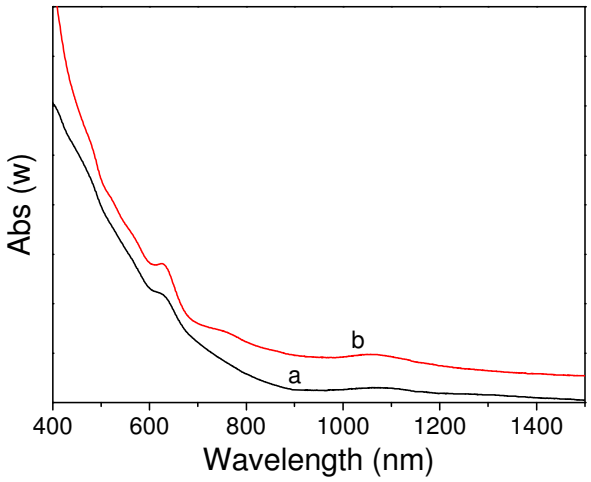

Figure S1. Spectrum (a): The UV-vis spectrum of fraction extracted with toluene from the crude product. Spectrum b: The UV-vis spectrum of purified Au_{38} cluster (through further extraction with a mixed toluene/acetone (1:5 v:v) solvent).

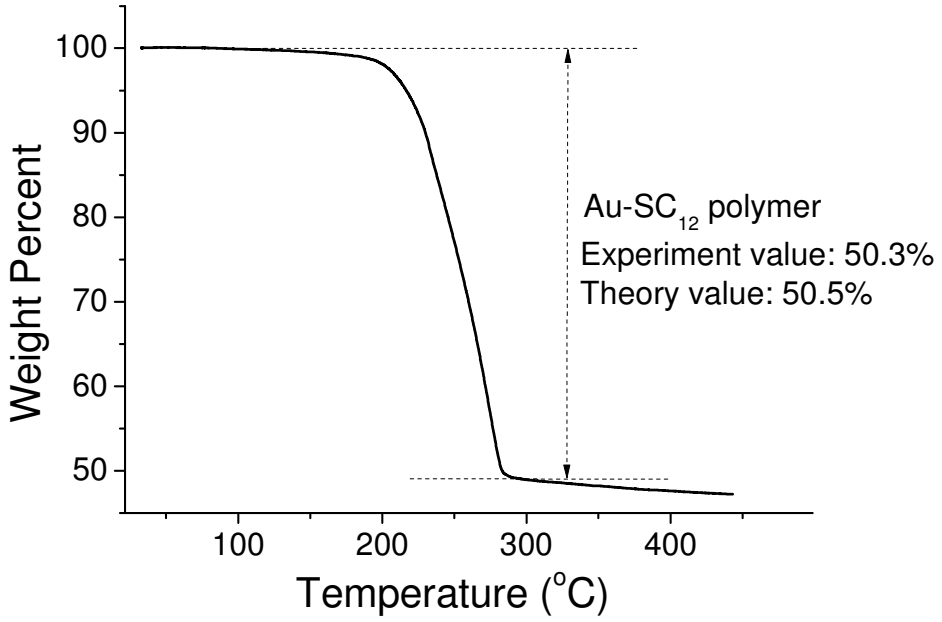

Figure S2. TGA of Au(I)-SC_{12} residual (~3 mg sample was used, N_2 flow: 50 mL/min)