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Efficient Synthesis of Au₉₉(SR)₄₂ Nanoclusters

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Experimental Section

Chemicals.

Tetrachloroauric(III) acid (HAuCl₄·3H₂O, 99.99% metal basis, Aldrich), tetraoctylammonium bromide (TOAB, 98%, Fluka), sodium borohydride (99.99% metals basis, Aldrich), thiophenol (99%, Sigma–Aldrich), *n*-hexanethiol (99%, Sigma–Aldrich), tetrahydrofuran (THF, HPLC grade, 99.9%, Aldrich), toluene (HPLC grade, 99.9%, Aldrich), methanol (absolute, 200 proof, Pharmco), methylene chloride (HPLC grade, 99.9%, Sigma–Aldrich), acetone (HPLC grade, 99.9%, Sigma–Aldrich). All chemicals were used as received. Nanopure water (resistivity 18.2 MΩ·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.

Synthesis of the polydispersed $Au_n(SC_6H_{13})_m$ nanoclusters.

All steps were run under an air atmosphere. salts of gold (HAuCl₄·3H₂O, 60 mg) was added in a threeneck round-bottom flask (100 mL) with TOABr (96 mg) in THF solution (15 mL). The solution was stirred for 15 min, and *n*-hexanethiol (53 μ L) was added to the flask; the solution was allowed to stir for 15 min (800 rpm), with a slow color change to a pale yellow or colorless (Au(III) was reduced to Au(I)). Then, NaBH₄ (70 mg) was dissolved in cold water (5 mL) and added to the flask quickly. The color of the solution rapidly became black, indicating the formation of Au nanoclusters. The reaction mixture was stirred for additional 2 h. The crude product was obtained after removing THF solvent. And then the product was washed with methanol for 3 times. The polydispersed Au_n(SC₆H₁₃)_m nanoclusters were obtained after the extraction of the crude product with acetone.

Synthesis of the monodispersed $Au_{99}(SPh)_{42}$ nanoclusters.

The above obtained polydispersed $Au_n(SC_6H_{13})_m$ nanoclusters was added in a one-neck round-bottom flask (10 mL), 0.6 mL thiophenol was added and the solution was heated to 80 °C and maintained at this temperature for overnight. During the long time etching process, the initial polydisperse $Au_n(SC_6H_{13})_m$ nanoclusters were finally converted to monodisperse $Au_{99}(SR)_{42}$ nanoclusters. The organic phase was thoroughly washed with methanol to remove excess thiophenol. Then, the $Au_{99}(SR)_{42}$ nanoclusters were simply extracted with dichloromethane. The yield of the $Au_{99}(SPh)_{42}$ nanoclusters was ~15% based on the gold salt.

Characterization of Gold Nanoclusters.

The UV-Vis spectra of the Au nanoclusters (dissolved in CH_2Cl_2) were acquired on a Hewlett-Packard (HP) Agilent 8453 diode array spectrophotometer at room temperature. The purity of the as-prepared Au₉₉(SPh)₄₂ nanoclusters 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 (300-950 nm range) of the eluted solution. The purity of the cluster can be verified by comparing the UV-vis spectra at different times of the peak (e.g., peak point, left and right points at bottom of the peak). Matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) and LDI-MS was performed with a PerSeptive Biosystems Voyager DE super-STR time-of-flight (TOF) mass spectrometer. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenyldidene]malononitrile (DCTB) was used as the matrix in MALDI-MS analysis. Typically, 1 mg matrix and 0.1 mL analyte stock solution were mixed in 100 µL CH₂Cl₂. 10 µL solution was applied to the steel plate and then air-dried prior to MALDI-MS analysis. Thermal gravimetric analysis (TGA) (~2 mg sample used) was conducted in a N₂ atmosphere (flow rate ~50 mL/min) on a TG/DAT 6300 analyzer (Seiko Instruments, Inc); the heating rate was 10 °C/min. Powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using Cu K α radiation.