Supporting information

Chemical Controlled Reversible Gold Nanoparticles Dissolution and Regeneration at Room-Temperature

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Experimental Details

Materials and Methods

All chemical include Chloroauric acid (HAuCl₄) (99.9%), 1-naphthalenethiol (99%), 2-naphthalenethiol (99%), phenylthiol (97%), 1-hexanthiol (95%), 1-dodecanethiol (98%), oleylamine (tech.), and toluene (anhydrous, 99.8%) were purchased from Aldrich and Sigma and used as received.

Synthesis of the oleylamine capped gold nanoparticles. In a typical synthesis, 50 mg of HAuCl₄ was dissolved in 5 ml of oleylamine and 5 ml anhydrous toluene. The reaction mixture was then ultra-sonicated for 15 min to achieve a homogeneous orange solution that was next transferred to a reaction flask equipped with a nitrogen gas inlet and condenser. Under nitrogen environment, the reaction temperature was increased to 80°C and maintained for 3 hr. During this time, a gradual color change from orange to colorless to pink, and finally to red was observed. Particle purification was accomplished by repeated centrifugation of the solution: the reaction mixture was first diluted with hexane in a 50/50 volume ratio, followed by addition of ethanol to precipitate the particles. The precipitates were centrifuged for 10 min and the centrifuge pellet was re-dispersed into hexane. This process was repeated three times and re-dissolved in hexane. TEM analysis was used to measure the particles sizes, which show an average diameter of 10 ± 0.9 nm. The uniform sizes of resultant AuNPs was also confirmed by dynamic light scattering (DLS), which showed a similarly narrow particle-size distribution.
Dissolution of the gold nanoparticles or bulky gold by aromatic thiols. The oleylamine-capped gold nanoparticles solution was adjust to a concentration of OD_{520} = 2.2 and used for all of the following experiments except specially noted. To test the dissolution in a low concentration of aromatic thiols, 3 µl of 1-naphthalenthiol was added to 4 ml of oleylamine capped gold nanoparticles solution in a vial and shake quickly to mix the thiols and gold nanoparticles. The solution color change was monitored using UV-vis spectrophotometer and small amount sample was taken out at different time for TEM and MS measurement.

Au nanostructures engineering

Regeneration of gold nanoparticles by using H_{2}O_{2} treatment. To the solution of the formed Au(NaphSH)_{2} (1.5 ml) added 20 µl of the 30% H_{2}O_{2} solution with a rapid shaking and let stand on a lab bench. After several min, obvious red color were observed, indicating the formation of regenerated gold nanoparticles.

Air-oxygen oxidation studies. The formed Au(NaphSH)_{2} solution from dissolution of oleylamine capped Au nanoparticles were sealed in a vial and the solution was incubated at room temperature for 1 week. Solution color was found to change from colorless to red, indicates the regeneration of Au nanoparticles. The formed Au nanoparticles were characterized by UV-vis spectra, TEM, and HRTEM analysis. To confirm the formation of single crystalline Au nanoparticles, individual Au nanoparticles were not only characterized by HRTEM image, but also analyzed by using FFT pattern, which show the single crystalline pattern.

Single crystalline Au nano-sheets regeneration. The formed Au(NaphSH)_{2} solution formed from dissolution of oleylamine capped Au nanoparticles was dropped onto a TEM grid, and then let it evaporation slowly in a close chamber that saturated with hexane vapor. After the sample was dry, the whole TEM grid was rinsed into hexane to dissolved any organic residue, the then dried in air before TEM measurement.

Au nanofibers generation. To the formed Au(NaphSH)_{2} solution added 10 fold of the free 1-NaphSH and the solution was incubated at room temperature for 30 min. 2 ul of the solution
was dropped onto a TEM grids and dried in air. The dried TEM sample was then rinsed in hexane to remove any organic soluble residue and dried in air again.

**Au nanocluster generation.** The formed Au(NaphSH)₂ solution formed from dissolution of oleylamine capped Au nanoparticles was refluxed at 70 °C for 1 week till the solution color change from colorless to brown. The formed Au nanoclusters solution was characterized by fluorescence spectroscopy which shows yellow emission and their morphologies were characterized by TEM analysis.

**Control experiments.** In order to establish the relationship between the role of aromatic units and the 2D assembly of Au atoms, control experiments were performed. Pure 1-naphthalenthiol solution was cast on the carbon coated TEM grids or on the highly ordered pyrolytic graphite (HOPG), large crystalline sheet structures of 1-NaphSH were observed under TEM view. Unfortunately, these organic assemblies are unstable under TEM electronic beam, no electron pattern and HRTEM image can be obtained. The control experiment suggests that the packing of aromatic unites served as important archetype in the formation of 2D structured single crystalline gold nano-sheets.

**TEM and MS spectra measurement.** TEM samples were prepared by dropping 2 µl of the Au solution onto carbon coated copper grids and allowing it to dry in air for 2-3 min, and then washed with hexane. TEM images HRTEM images were performed with JEOL 2100 TEM microscope, operated at 200 kV. Mass spectra were characterized with a MALDI mass spectrometer. One or two drop of the sample solution was deposited on a steel sample plate and allowed to dry in air, then analyzed with a Bruker Daltonics “FLEX” MALDI-TOF MS, and ionization with nitrogen laser (337 nm).
**Figure S1.** (left) TEM images of the formed 3-D ordered assembly of Au nanoparticles induced by addition of NaphSH (sample was collected 10 min after addition of NaphSH). (right) TEM images of the dissolved Au nanoparticles aggregates after 2 hour incubation in solution of NaphSH at room temperature.

**Figure S2.** Full tof-MS spectra (span from 100 to 15,000 Da) of gold nanoparticles in 5 mM NaphSH after 12 hour incubation at room temperature.
Figure S3. Regeneration of Au nanoparticles from mono-Au cluster by air oxygen. (a) UV-vis spectra of the regeneration of gold nanoparticles by air oxygen at room temperature. Inset shows photos of solution color changes under room light. (b) TEM images of the air-oxygen re-generated Au nanoparticles. (c) Single crystalline HRTEM image of individual Au nanoparticles. Inset shows the corresponding FFT patterns.
**Figure S4.** $^1$H-NMR spectra of regenerated gold nanoparticles in CDCl$_3$. 