

Supporting Information

Thioanisole Induced Size-Selective Fragmentation of Gold Nanoparticles

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This supporting material contains supplementary data on materials and apparatus, the synthesis procedure of gold nanoparticles (AuNPs) and their mean diameter calculations along with standard deviation values and data for control experiment with 1-hexanethiol.

Contents:

- Section I** Materials and Apparatus;
- Section II** Synthetic Procedure of AuNPs;
- Section III** Calculations of the Mean Diameters and Standard Deviation Values of AuNPs;
- Section IV** Data for control experiment with 1-hexanethiol;

Section I

Materials and Apparatus

HAuCl₄·3H₂O was purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received. Thioanisole, sodium citrate, 1-hexanethiol and other chemical reagents used for synthesis were of analytical grade, obtained from commercial suppliers and used without further purification unless otherwise noted. The gold nanoparticles solution was prepared by using Milli-Q water (Millipore Milli-Q System: Millipore, USA, 18 MΩ.cm). Absorption spectra of the solutions were recorded by using an Ocean Optics 2000+ UV-Vis spectrophotometer. Raman spectra were recorded using a portable Raman spectrometer (BWS415, B&W Tek Inc., USA) with an excitation wavelength of 785 nm, a resolution of 5 cm⁻¹, and a beam diameter of 10 μm. The samples for recording the SERS spectra were prepared by mixing 30 μL (1 mM) of thioanisole in AuNPs (2 mL) of different colloid solutions in a glass cell. In this study, we used excitation wavelength of 785 nm which is most commonly used for compact low cost instruments with laser power operated at 80 mW with an acquisition time of 30 s. The size and shape of the gold colloids were investigated with a JEOL JEM 2100 TEM instrument operated at an accelerating voltage of 200 kV (JEOL 2100, JEOL Ltd., Japan). The TEM samples were prepared by drop casting the solutions on carbon-coated copper grids and then dried at room temperature.

Section II

Synthesis of Gold Nanoparticles

The gold nanoparticles (*ca.* 20.1 nm, 42.9 nm, 63.9 nm) were synthesized by modified citrate reduction method.¹ All the glass wares were dipped overnight in aqua regia (HCl:HNO₃ in a ratio of 3:1) and washed with plenty of water followed by sonication in milliQ water for at least 5 min. The AuNPs of size *ca.* 20 nm were synthesized by already reported method.² 50 mL of the aqueous solution of HAuCl₄ (0.01% wt %) was heated to boil under vigorous stirring. Then, 260 μL of aqueous sodium citrate (1 % wt %)³ was added at once in the boiling solution for 63.9 nm and 350 μL was added for 42.9 nm size, which resulted in a rapid color change from light yellow to black and then reddish purple within few min. It was kept boiling for further 10 min to ensure complete reduction of HAuCl₄. The solution was cooled to room temperature and characterized by UV-Vis spectroscopy and HR-TEM.

As it is difficult to synthesize spherical AuNPs of large size by one-step reduction process, therefore, small diameter colloids (~ 20 nm) prepared by citrate-reduction method were used as seeds in a second reduction step to synthesize 80.4 nm and 92.3 nm diameter Au colloids^{4, 5} which seemed to be more effective in obtaining nearly spherical nanoparticles. In the seeded growth mechanism, the Au (III) is reduced at room temperature on the surface of small nanoparticles by citrate or hydroxylamine as the reducing agent.⁶ In a clean beaker, 2 mL of seed solution (20 nm) and 0.2 mL of hydroxylamine

hydrochloride was added in 30 mL water, followed by drop wise addition of 0.1% of HAuCl_4 at room temperature along with vigorous stirring until the required size was achieved, which was also monitored visually by color change and later on confirmed by UV-Vis and HR-TEM.

Section III

Mean Diameter and Standard Deviation Values of Gold Nanoparticles

We have estimated the mean diameter and standard deviation values by considering at least 50 NPs for each sample and the NPs were randomly selected from the HR-TEM images. The standard deviation values for each sample of AuNPs before and after addition of thioanisole are given in Table S1.

Table S1: Mean diameter and standard deviation values of AuNPs before and after addition of thioanisole.

Gold Nanoparticles before addition of thioanisole		Gold Nanoparticles after addition of thioanisole	
Mean diameter (nm)	Standard deviation (nm)	Mean diameter (nm)	Standard deviation (nm)
20.1	2.33	20.3	2.36
42.9	6.0	42.5	5.8
63.9	15.7	*63.1, 3.4	*15.2, 2.6
80.4	18.2	5.5	2.2
92.3	21.5	4.9	2.0

*Due to partial fragmentation, there mainly exist two distinct sizes. The larger ones are only aggregates whereas the smaller ones are fragments. It should be noticed that aggregated particles form a common grain boundary and are not well separated from each other.

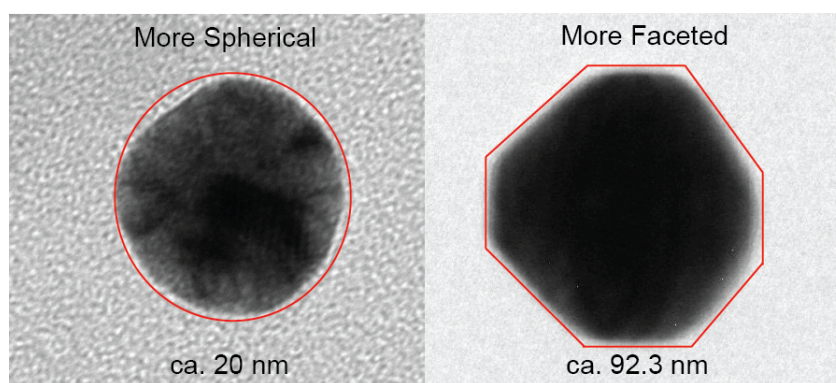


Fig. S1 HR-TEM images of AuNPs of different sizes showing a comparison of the spherical and faceted shape, depending upon the size.

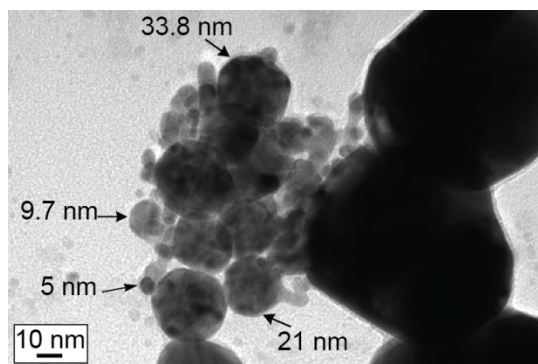


Fig. S2 TEM micrograph of 92.3 nm AuNPs taken 3 h later after the addition of thioanisole, showing the intermediate stage of the fragmented particles where large and small particles could be found, mean diameter d and standard deviation s values are given here ($d= 33.8, s= 3.93, d= 21, s= 1.41, d= 10, s= 0.67, d= 5, s= 1.22$).

Section IV

Experimental Data for Control Experiment with 1-hexanethiol

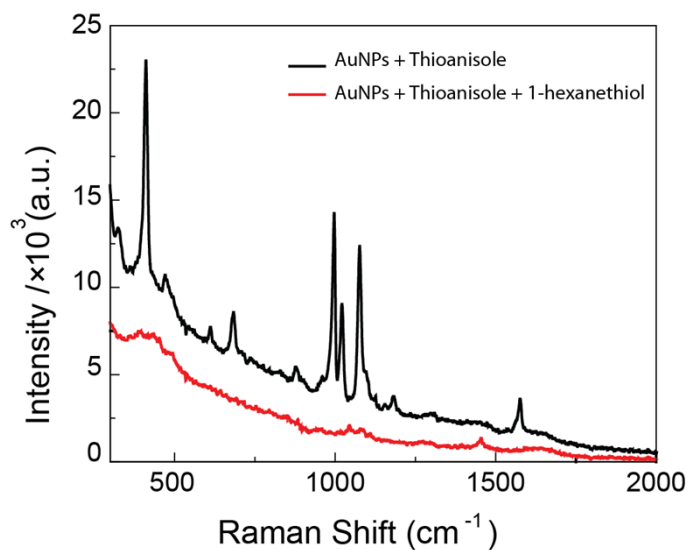


Fig. S3 SERS spectra of AuNPs adsorbed by thioanisole and quenched 4 h later, after adding 1-hexanethiol.

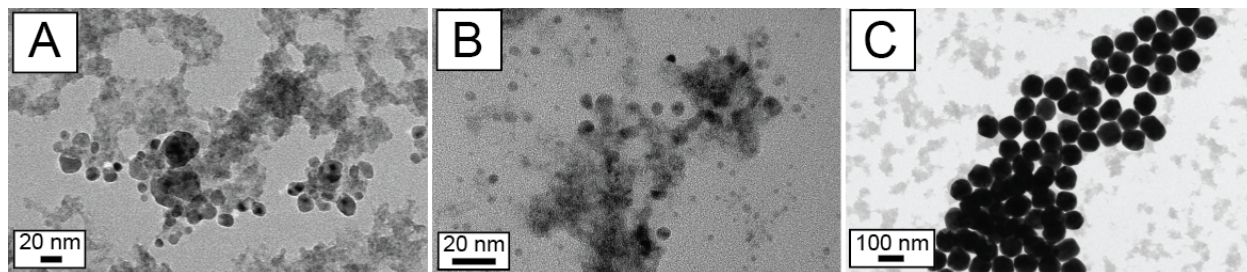


Fig. S4 HR-TEM micrographs of 92.3 nm AuNPs (A) 4 h later after the addition of 1-hexanethiol in AuNPs solution containing thioanisole, (B) 28 h later, after addition of thioanisole, (C) AuNPs solution containing only 1-hexanethiol after 24 h.

References

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