Electronic Supplementary Information

Shape separation of colloidal gold nanoparticles through salt-triggered selective precipitation

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1. Experimentals

1.1 Chemicals.

Cetyltrimethylammonium bromide (CTAB) was purchased from Sigma and benzyldimethylhexadecylammonium chloride (BDAC) was purchased from TCI. $HAuCl_4 \cdot 4H_2O$, $AgNO_3$, $NaBH_4$, sodium citrate, L-ascorbic acid, KI and NaCl were all purchased from Shanghai Sinopharm Chemical Reagent Co. Ltd (China). Deionized water was used throughout the experiments. All the glassware was cleaned by aqua regia (HCl: HNO_3 in a 3:1 ratio by volume) and rinsed with water prior to the experiments.

1.2 Methods.

1.2.1 Synthesis of CTAB-capped gold seeds for growth of gold nanorods.

CTAB-capped gold seeds were prepared by adding 0.6 mL of ice-cold solution of 10 mM $NaBH_4$ to 10 mL of 0.25 mM $HAuCl_4$ prepared in 0.1 M CTAB solution, under vigorous stirring for two minutes. The yellow color changed immediately to brown, indicating the formation of gold seeds. These seeds were aged for 2 hours in order to allow the complete hydrolysis of unreacted $NaBH_4$.

1.2.2 Synthesis of citrate-stabilized gold seeds for growth of gold nanoplates

Citrate-stabilized gold seeds were synthesized by reducing 0.4 mL of 25 mM $HAuCl_4$ with 1 mL of ice-cold 0.1 M $NaBH_4$ with vigorously stirring. The reduction was done in the presence of 1 mL of 10 mM sodium citrate and 38.6 mL of water. Upon addition of the $NaBH_4$ solution, the solution turned a reddish orange color, indicating the generation of gold nanoparticles. The resulting solution was continually stirred for two minutes. The seed solution was allowed to stand for 2 hours to ensure the complete hydrolysis of unreacted $NaBH_4$.

1.2.3 Synthesis of crude gold nanorods solution

Our research focused on the gold nanorod system with an average aspect ratio > 5 and thus a binary surfactant mixture composed of BDAC and CTAB has to be employed. Briefly, the solutions were added in the following order: 100 mL of 0.1 M CTAB and 0.1 M BDAC mixtures solution, 1.0 mL of 10 mM silver nitrate solution, 2 mL of 25 mM aqueous $HAuCl_4$. To this was added 0.55 mL of 0.1 M L-ascorbic acid (AA) as reducing agent and the mixture was homogenized by stirring gently. Finally, 120 μL of CTAB-capped seed solution was added and

the whole solution was kept at 30 °C and left undisturbed overnight (12~14 h).

1.2.4 Synthesis of crude gold nanoplates solution

An initial crude gold nanoplates solution was prepared by a one-step seed-mediated, iodide ion- and CTAB-assisted approach with optimization. Typically, a 100 mL of growth solution containing 0.25 mM $HAuCl_4$ and 0.025 M CTAB was prepared. To this solution was added 55 μl of 0.1 M KI, 0.55 mL of 0.1 M AA and 0.55 mL of 0.1 M NaOH in turn and the resulting solution as growth solution was stirred gently. The orange color of the gold salt in the CTAB solution disappeared when AA was added, due to the reduction of Au^{3+} to Au^{+}. The growth of gold nanoplate was initiated by adding 0.1 mL of the citrate-stabilized seed solution to the growth solution. After the addition, the color of the growth solution changed from clear to light red, and then turned to violet red. The mixture solution was kept at 30 °C and left undisturbed for 6 h.

1.2.5 Separation procedures

For a typical separation procedure of gold nanorods, a 20 mL of the crude gold nanorod solution was firstly centrifuged at 16500 g/min for 20 min to get rid of the extra CTAB and BDAC molecules. This was done because that CTABr or BDAC, while in high concentration (0.1 M), is very easy to subject to crystallization at ambient temperature. After centrifugation, the precipitates contained gold nanorods and by-products were dispersed by water to reach a volume of 20 mL again. The total concentration of the residual CTAB and BDAC in solution is ~ 5 mM. To this solution was added by a 20 mL of 1.72 M NaCl aqueous solution. The mixture solution was then kept for 4 h at ambient temperature without disturbance. Most of gold nanorods deposited on the bottom of the beaker during the incubation period, and were easily collected by remove of the supernatant using a pipette. The gold nanorods precipitate was re-dispersed to form colloidal dispersion by ultrasonication for further characterization.

For a typical separation procedure of gold nanoplates, a 20 mL of 0.24 M NaCl aqueous solution was added to a 20 mL of crude gold nanoplates solution. After this, the mixture solution was incubated for 4 h. Most of gold nanoplates deposited on the bottom of the beaker during the incubation period. These gold nanoplates were re-dispersed to form colloidal solution by ultrasonication for further characterization.

The kinetic absorption spectra recording were also done. For the case of nanorod system, different sets of experiments were performed wherein the concentration of solution was varied.

Typically, a 2-mL aliquot of gold nanorods mixture was placed in separate test tubes, then, a 2-mL aliquot of varied concentrations of NaCl solution (0.86 M, 1.72 M, 3.44 M and 5.16 M) was added to these tubes respectively. Time-varied UV-vis-NIR spectra were obtained on a UNICO 2802S spectrophotometer in a wavelength range of 300 to 1100 nm using a 2 mm path length quartz cuvette. For the case of nanoplate system, the procedures were similar with above mentioned description of nanorod system, except that the concentration of NaCl solution was changed.

1.2.6 Instrumentation.

The morphologies of the gold NPs were characterized by a Carl Zeiss Ultra Plus Field Emission Scanning Electron Microscope with an accelerating voltage of 20.0 kV. The UV-vis-NIR absorption spectra of the gold NPs solutions were recorded by a UNICO 2802S spectrophotometer in a wavelength range of 300 to 1100 nm. Solution-based ξ-potential analyses were completed on a Delsa 440sx zeta potential Analyzer.

2. Additional SEM images and absorption spectra.

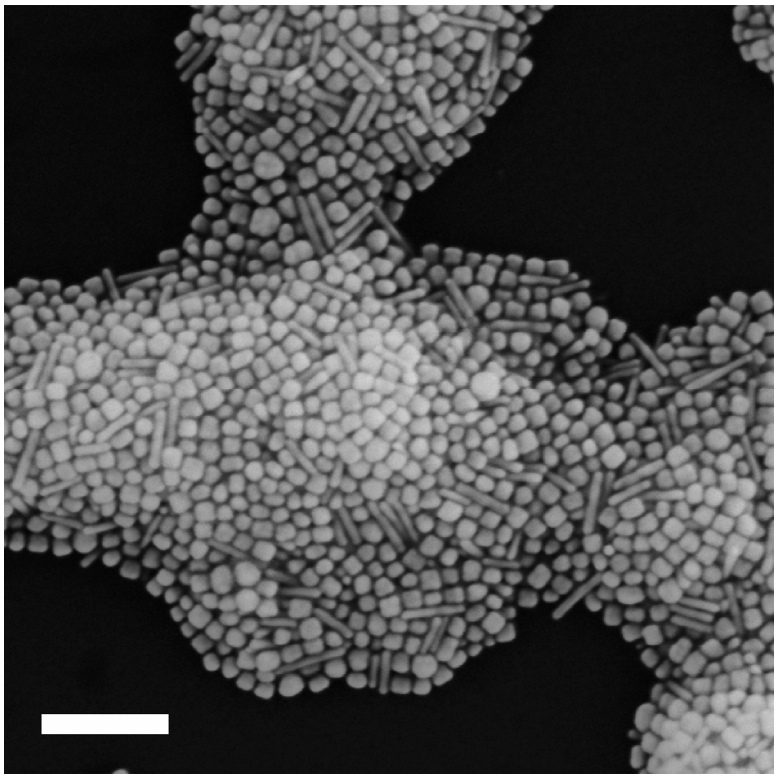

Fig. S1. SEM image of gold NPs in supernatant after the separation of gold nanorods. Scale bar is 100 nm.

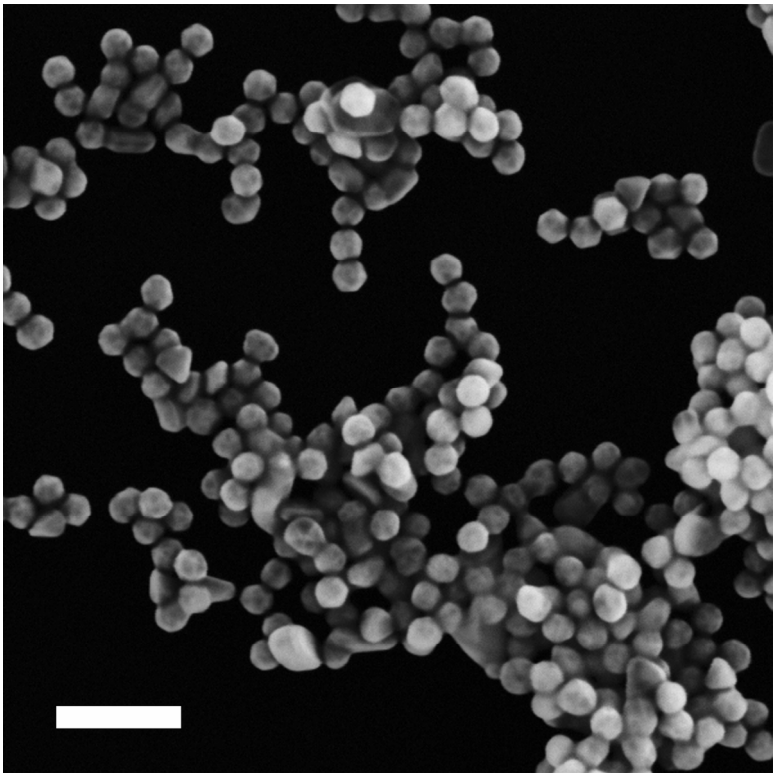

Fig. S2. SEM image of gold NPs in supernatant after the separation of gold nanoplates. Scale bar is 100 nm

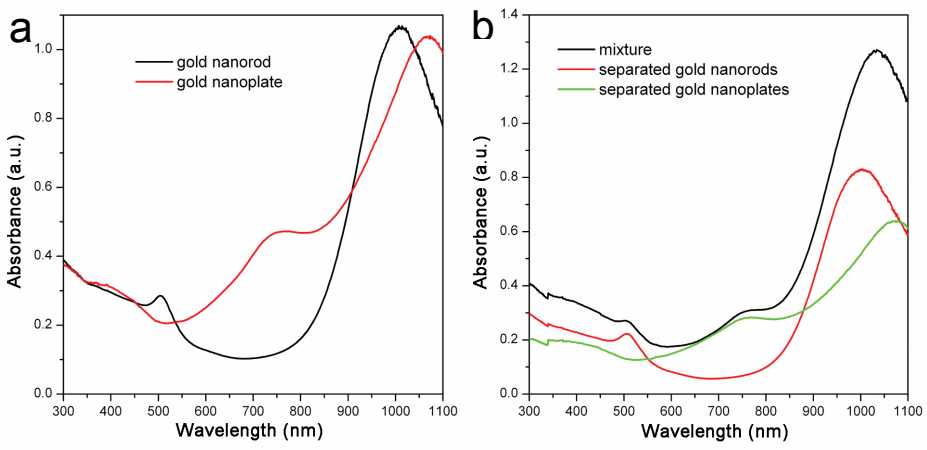

Fig. S3. Absorption spectra of (a) purified gold nanorods solution and purified gold nanoplates solution before mixing; (b) equivolume (10 mL : 10 mL) mixture solution of nanorods and nanoplates (black curve), supernatant after the treatment under 0.43 M NaCl solution (red curve) and re-dispersed solution of the precipitates (green curve).