Supporting Information

Fabricating chiroptical starfruit-like Au nanoparticles via interface modulation of chiral thiols

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1. Experimental details

1.1 ***Materials***: Chlorauric acid ($HAuCl_4 \bullet 3H_2O$) and silver nitrate ($AgNO_3$) were purchased from Beijing Chemical Reagent Company. Sodium borohydride ($NaBH_4$) and L-ascorbic acid (AA) were purchased from Alfa Aesar. L-cysteine (L-Cys), D-cysteine (D-Cys), L-Homo-cysteine (Homo-CYS), N-acetyl-L-cysteine (L-NAC) and L-cysteine methyl ester (L-Cys-OMe) were purchased from Sigma. Cetyltrimethylammonium bromide (CTAB), L-glutathione (L-GSH) and L-oxidized glutathione (L-GSSG) were purchased from Amresco. Milli-Q Water (18 MΩ•cm) was used for the preparation of all solutions.

***1.2 Instruments*:** CD measurements were conducted on a JASCO J-1600 CD spectrometer and the bandwidth was set at 5 nm. Extinction spectra were obtained using a Cary 50 UV-vis-NIR spectrophotometer. SEM and TEM images were taken from a Zeiss JC-MerlinSEM with a voltage of 5 kV and Tecnai G2 20 S-TWIN TEM with an accelerating voltage of 200 kV, respectively. Dark field TEM images were taken from a JEOL 2100F AEM with an accelerating voltage of 200KV.

Spectra measurement: All extinction and CD spectra were obtained directly with solution samples, which were put into a 1cm × 1cm quartz cuvette for measurement.

1.3 Preparation of gold nanorods(AuNRs) core

AuNRs were synthesized using a seed-mediated growth procedure.

(1) Preparation of Au seed: CTAB-capped seeds were prepared by chemical reduction of $HAuCl_4$by $NaBH_4$ in the presence of CTAB: freshly prepared and ice-cold $NaBH_4$ (0.01 M, 10mL) was injected into a mixture of CTAB (0.1 M, 7.5 mL), $HAuCl_4$ (23 mM, 0.1mL) and deionized water (1.8 mL) under magnetic stirring for 3 min. The color of the solution turned from yellow to brown, indicating the formation of Au seeds. The seed solution was kept undisturbed at 30°C for 2-5 h before use.

(2) Preparation of AuNRs with LSPR maximum at ~730 nm (termed as Au730) and ~640 nm (termed as Au640).

Au730: The Au730 growth solution was made by mixing CTAB (0.1 M, 100 mL), $HAuCl_4$ (24 mM, 2 mL), $AgNO_3$ (0.1 M, 120 μL), and AA (0.1 M, 552 μL). The seed solution (120 μL) was added to the growth solution to initiate the growth of AuNRs. The well-mixed solution was kept undisturbed for 12 h, then AA (0.1 M, 552 μL) was added twice at 40 min intervals. The total reaction time was for 24 h.

Au 640: The Au 640 growth solution was made by mixing CTAB (0.1M, 100mL), $HAuCl_4$ (25mM, 2mL), $AgNO_3$ (0.1M, 50 μL) and AA (0.1M, 552 μL). The seed solution (120 μL) was added to the growth solution to initiate the growth of AuNRs. The well-mixed solution was kept undisturbed for 12 h, then AA (0.1 M, 552 μL) was added three times at 40 min intervals. The total reaction time was for 24 h.

After synthesis, the reacted growth solutions were centrifuged twice (9200 rpm, 10 min) and the obtained AuNR precipitates were redispersed in 2 mM CTAB solution.

1.4 Preparation of chiroptical starfruit-like gold nanoparticles (Au NPs)

The purified AuNRs werediluted with 10mM CTAB to an Au atom concentration of ~0.1mM. After adding 10 μL Cys (2 mM) into 1 mL AuNR suspension, the mixture was incubated at 30°C for 1h. Then, $AgNO_3$(10 mM, 2 μL), AA (100 mM, 1.6 μL) and $HAuCl_4$(25 mM, 4 μL) were added sequentially in above mixture solution. The Au overgrowth was initiated by putting reaction solution in a 70°C water bath. The overgrowth was stopped after 1 h by taking reaction tube from water bath.

1.5 Effect of concentrations of Cys

Different amounts (0-100μL) of L- or D- Cys (1mM) were added to 1mL Au NRs core suspension ([Au]=0.1mM, [CTAB]=10mM) andthe mixtures were incubated at 30°C for 1h.Then, growth solution, containing $AgNO_3$(10mM, 2μL), AA(0.1M, 1.6μL) and $HAuCl_4$(25mM, 4μL), was added. The reaction solution was quickly put into a 70°C water bath and reacted for 1h.

1.6 Effect of Cys incubation conditions

For the effect of Cys incubation conditions, 20μL 1mM L- Cys was used. For non-pre-incubation sample, L-Cys was added immediately before the addition of growth reagents. Two pre-incubation temperatures (30°C and 70°C) were chosen.

1.7 Monitoring overgrowth kinetics

To study the overgrowth kinetics, the amount of growth reagents was decreased to half of the amount mentioned above in order to slow down the growth speed. That is, $AgNO_3$(10mM, 1μL), AA(0.1M, 0.8μL) and $HAuCl_4$(25mM, 2μL) was added into 1mLAuNRs(dispersed in 10mM CTAB aqueous solution) suspension pre-incubated with 20μM L-Cys.

1.8 The effect of D-Cys pre-incubation in L-Cys-mediated Overgrowth

First, different amounts (0, 2, 5, 10, 20, and 40μL) of D-Cys (1mM) were added into 1mL Au730 ([Au]=0.1mM, [CTAB]=10mM) suspensions. The mixtures were incubated at 30°C for 1h. Afterthat, the mixtures were centrifuged.The precipitates were re-dispersed in 1mL water and then 20μL 1mM L-Cys was added, Without incubation, they were mixed with the growth reagents immediately to initiate Au depostion by putting in a 70°C water bath and reacted for 1h.

1.9 The effect of pre-adsorbed Cys in other thiol-mediated Overgrowth

For the manipulation of growth mode by Cys pre-adsorption, 2μL L-Cys of 1mM was first added to incubate with Au730 cores ([Au]=0.1mM, [CTAB]=10mM) at 30°C for 1h. Then, 20μL of different molecules(L-NAC, L-Homo-CYS, L-CYS-OMe, L-GSH and L-GSSG) of 1mM was added into the solution, respectively. After that, the growth reagents, $AgNO_3$(10mM, 1μL), AA(0.1M, 0.8μL) and $HAuCl_4$(25mM, 2μL) was added immediately to react at 70°C for 1h.

1.10 Effect of Au core concentration: the importance of anisotropy

To study the effect of anisotropy, 20μL L-Cys(1mM) was employed to incubate with 1mL gold cores at 30°C for 1h first.

For the anisotropy of the core, the AuNRs core was replaced with gold nanospheres(GNSs) core. The concentration of Au atoms was set at 0.1mM for GNSs. After pre-incubating with L-Cys, $AgNO_3$(10mM, 2μL), AA(0.1M, 1.6μL) and $HAuCl_4$(25mM, 4μL) was added to start growth at 70°C for 1h.

For the anisotropy of the overgrown shell, The concentration of Au730 is changed. The chosen rod concentrations are 0.01, 0.02, 0.04, 0.06, 0.08, and 0.1 nM, respectively. The corresponding concentrations of Au atoms are 0.01, 0.02, 0.04, 0.06, 0.08, and 0.1mM, respectively. 1 ml Au730of different concentrations was dispersed in 10mM CTAB and incubated with L-Cys first.Then, $AgNO_3$(10mM, 2μL),

AA(0.1M, 1.6μL) and $HAuCl_4$(25mM, 4μL) was added to start overgrowth at 70°C for 1h.

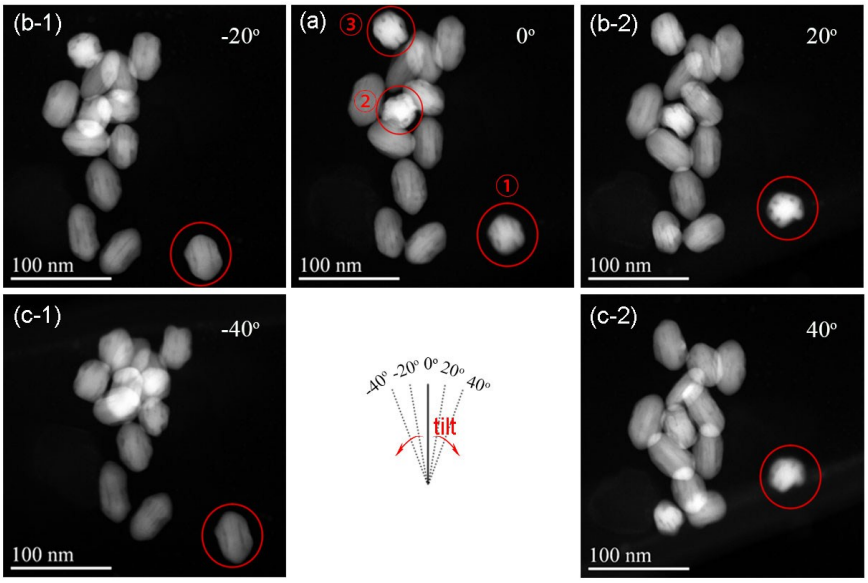

Figure S1 Dark field TEM images of Au NPs after overgrowth pre-incubated with 20μM Cys. From (a) to (c), TEM sample stage was tilted along x axis from 0° (**a**) to 20° (**b-1** and **b-2**), and then 40° (**c-1** and **c-2**). We can tell the convex on the Au NP surface from different tilt angles.

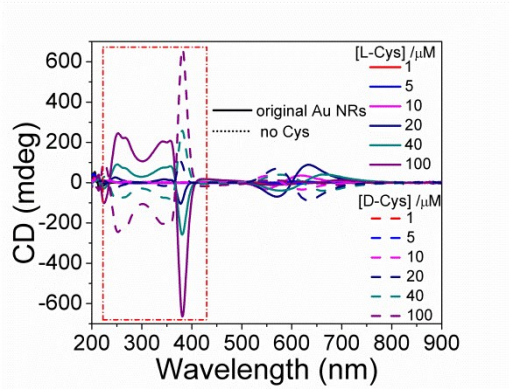

Figure S2 The CD spectra (including UV spectral range) of Au NPs mediated by different concentrations of Cys.

When [Cys] is higher than 20μM, a CD signal in UV spectral range occurs (see red dash-dot area). And the CD signal intensity increases with Cys amount. It indicates that the film containing complexes of Au ion and Cys molecules is chiral.

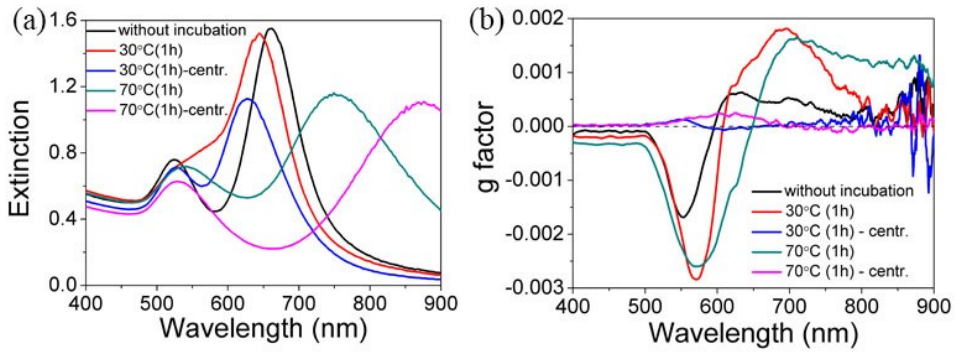

Figure S3 The extinction (a) and CD (b) spectra of resulted Au NPs with different pre-treatment conditions.

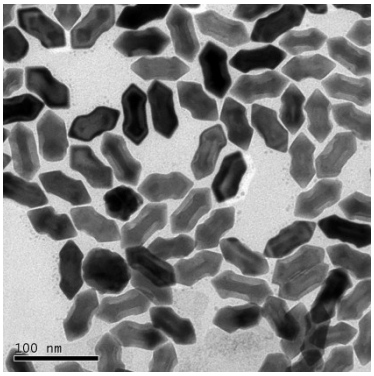

Figure S4 TEM image of Au730@Au NPs without Cys pre-incubation before overgrowth.

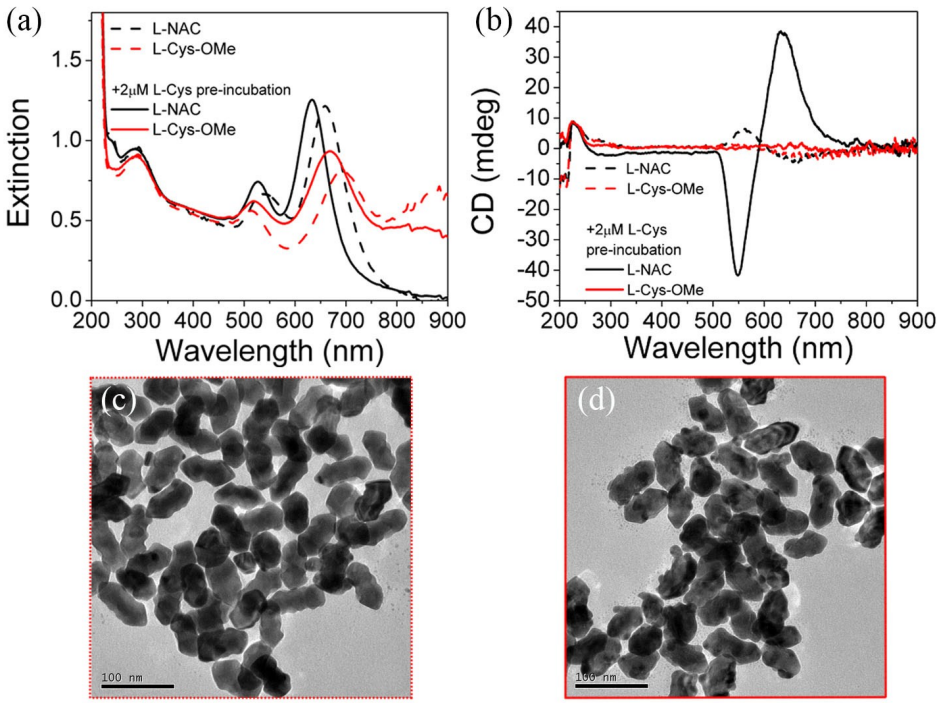

Figure S5 Extinction (a) and CD (b) spectra of Au NPs for L-NAC- (black) or L-Cys-OMe (red) - mediated growth with (solid lines) or without (dash lines) 2μM Cys pre-adsorption.And TEM images of the NPs via L-Cys –OMe mediated growth with (c)and without (d) Cys pre-incubation.

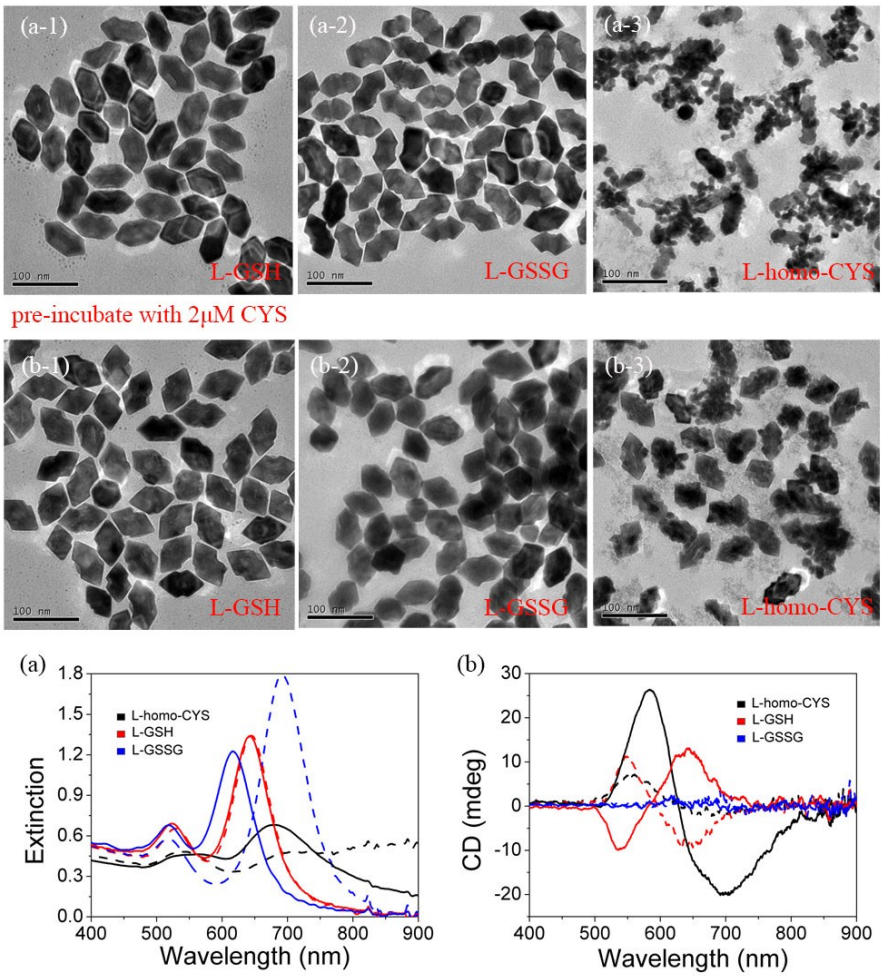

Figure S6 TEM images of the resulted NPs grown in the media of 20μM L-GSH (**a-1**), L-GSSG (**a-2**), L-homo-Cys (**a-3**) and NPs pre-incubated with 2μM L-Cys before overgrowth in these 20μM different thiols: (**b-1**) L-GSH, (**b-2**) L-GSSG, (**b-3**) L-homo-Cys. The extinctionspectra (**a**), CD spectra(**b**) of the resulted NPs with(**solid lines**) and without(**dash lines**) pre-incubation of 2 μM L-Cys before overgrowth in the media of 20μM different thiols.

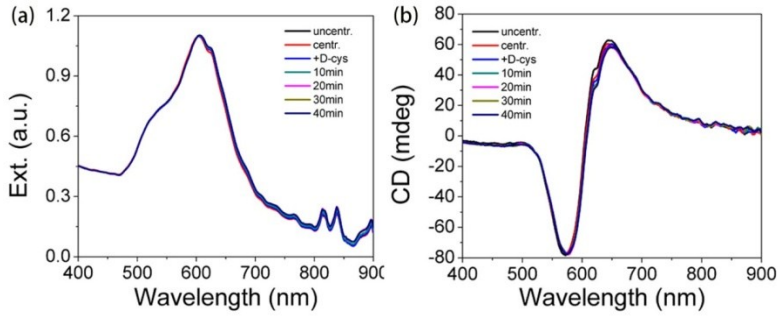

Figure S7 Effect of adding D-Cys (100 μM) on extinction spectra (a) and CD spectra of Au NR@Au nanoparticles obtained via L-Cys-mediated overgrowth. [L-Cys]= 20 μM.

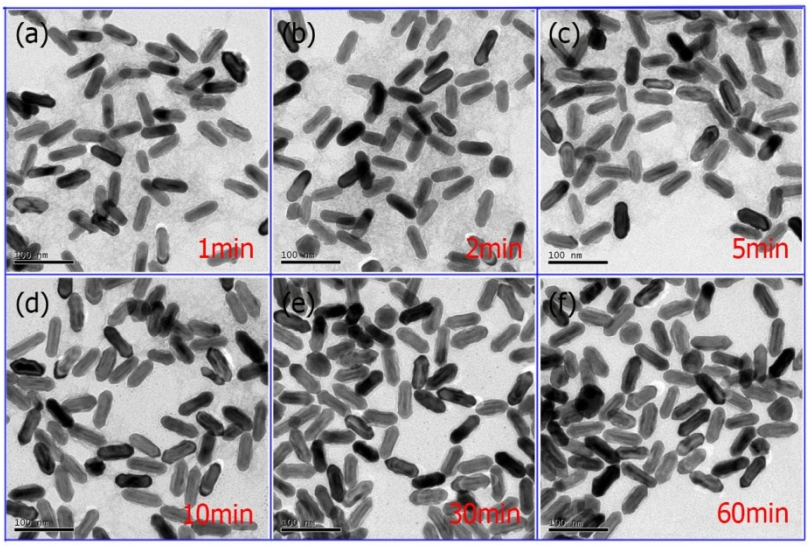

Figure S8 TEM images of Au730@Au NPs after different overgrowth times.

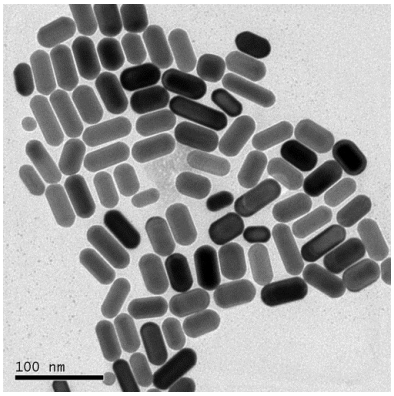

Figure S9 TEM image of Au640 cores.

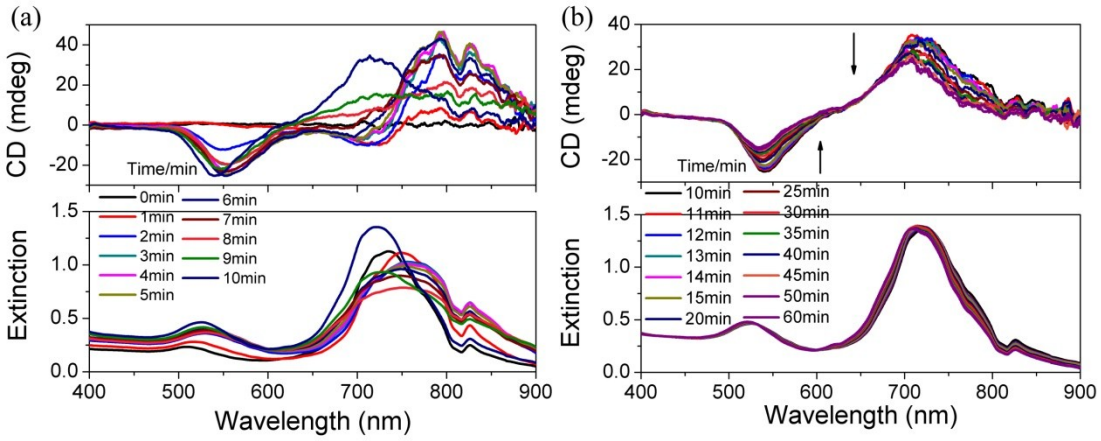

Figure S10 Evolutions of CD (**upper part**) and extinction spectra (**lower part**) of Au NPs using Au730 cores during the overgrowth. Left **(a)**: 0-10min. Right **(b)**: 10-60min.

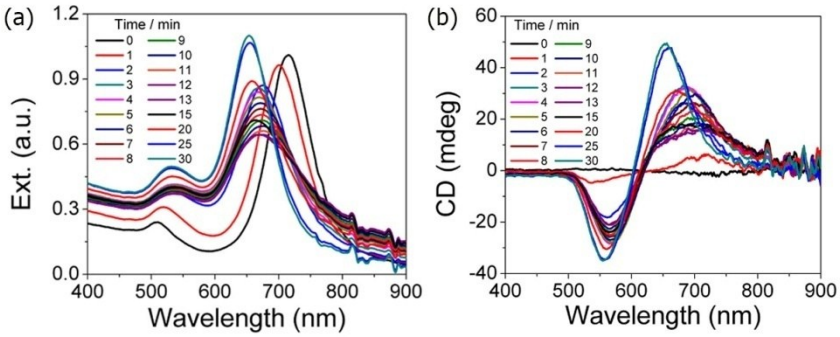

Figure S11 The evolutions of extinction (**left**) and CD spectra (**right**) of Au NPs using Au730 as cores during overgrowth at 50°C.

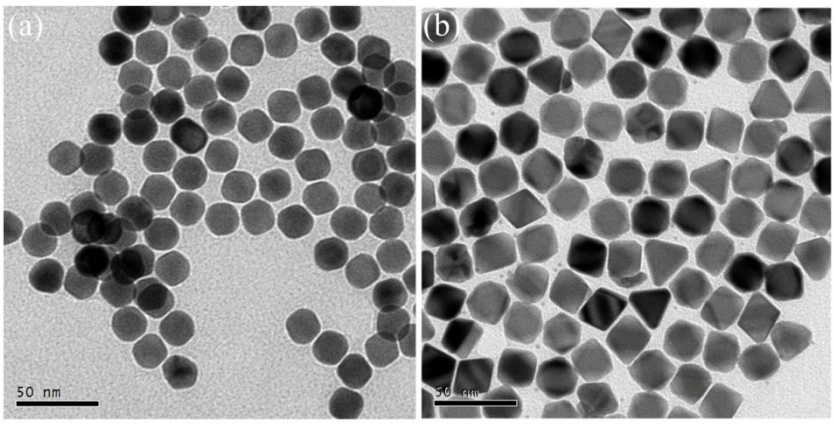

Figure S12 The typical TEM image of GNSs incubated with 20 μM Cys before **(a)** and after **(b)** overgrowth.