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Electronic Supplementary Information for

Chirality transfer of cysteine to the plasmonic resonance region through silver coating on gold nanobipyramids

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Experimental section

1. Materials and instruments.

Gold chloride trihydrate (HAuCl₄·3H₂O, >99%) was purchased from Sinopharm Chemical Reagent Co, Ltd (Shanghai, China). Cetyltrimethylammonium bromide (CTAB, >99%), cetyltrimethylammonium chloride (CTAC, 97%), sodium borohydride (NaBH₄, 99%), silver nitrate (AgNO₃, 99.8%), ascorbic acid (L-AA, >99%) were obtained from Aladdin. L-cysteine (L-Cys) and D-cysteine (D-Cys) were purchased from Sigma-Aldrich. All reagents were used as received. All solutions were prepared using ultrapure water (18.2 M Ω).

Absorption spectra were measured with an UV-3600 spectrophotometer (Shimadzu, Japan). SEM images were collected with a S-4800 field-emission SEM instrument (Hitachi, Japan) at 15 kV. CD spectra were recorded by a Jasco J-810 (Tokyo, Japan) spectropolarimeter in aqueous solution. A 400 μ L portion of each sample was infused into a 1 cm quartz cell and measured at the scan speed of 500 nm/min with a bandwidth of 10 nm. HAADF-STEM and elemental mapping were performed on an FEI Tecnai G2 F30 instrument (FEI, America). Ultrapure water obtained from a Millipore water purification system (18.2 M Ω •cm resistivity) was used in all experiments.

2. Synthesis of gold bipyramids (Au NBP).

Synthesis of Au NBP refers to previous literature reports¹ by seed-mediated two-step growth method. Firstly, initial gold seeds were prepared in a scintillation vial (50 mL) by fast reduction of HAuCl₄ (0.10 mL, 24 mM) with freshly prepared NaBH₄ (0.25 mL, 25 mM) in an aqueous CTAC solution (50 mM, 9.8 mL), in the presence of citric acid (1 M, 0.050 mL) under vigorous stirring at room temperature. The mixture turned from light yellow to brownish, indicating the formation of gold seeds. After 2 minutes, the vial was closed and the seed solution was heated in an oil bath at 80 °C for 90 minutes under gentle stirring, leading to a gradual color change from brown to red. Next, the thermally treated seed solution was removed from the bath and stored at room temperature. The final Au concentration in the seed solution was 0.25 mM. Then, a certain volume of gold seeds (adjusting the volume according to need) was added under vigorous stirring to an aqueous growth solution containing CTAB (100 mM, 100 mL), HAuCl₄ (10 mM, 5 mL), AgNO₃ (10 mM, 1 mL), HCl (1M, 2 mL) and AA (100 mM, 0.8 mL). The mixture was kept at 30 °C for 3 h. After resuspension with 10 mM CTAB in order to make Au NBP long-term stable, put it in a 4 °C refrigerator and save it for further use (due to the extremely high yield, no further purification is required).

3. Synthesis of Au NBP @Cys @Ag nanoparticles.

For the preparation of Au NBP @Cys @Ag NPs, First, Au NBP was centrifuged twice (12000 rpm, 15 min) and redispersed in ultrapure water to the Au atom concentration of about 0.05 mM. Then, 118 μ L CTAC (10 mM), 5 μ L HNO₃ (0.01 M) and L- or D-Cys solution (10 μ L, 1 mM) was added to 312 μ L of Au NBP dilution, followed by incubation at 30 °C for 60 min. Sequentially, AgNO₃ (10 mM, 45 μ L), AA (100 mM, 22.5 μ L) were added in above mixture solution. The Ag overgrowth was initiated by putting reaction solution in a 30 °C water bath and stopped after 1 h by taking reaction tube from water bath.

4. Cys acceleration effect on Au NBP@Ag.

To demonstrate the acceleration effect of Cys on Au NBP@Ag, 10 μL different concentration of L- or D-Cys were added to 435 μL Au NBP dilution (with 118 μL CTAC, 5 μL HNO₃) suspension and were incubated at 30 °C for 1h. Then, growth solution, containing AgNO₃(10 mM, 45 μL) and AA (0.1 M, 22.5 μL) was added.

5. Preparation of Au NBP @Ag NPs.

For the preparation of the Au NBP @Ag NPs, the same preparation method as that for above NPs was used except that no Cys solution was added and the reaction duration should be extended to 2 h at least.

6. Monitoring dynamic growth of Au NBP @Ag in the presence of Cys.

To study the dynamic growth, UV and CD spectrometer were used for monitoring the over progress. The amount of growth reagents containing AgNO₃ (10 mM, 45 μ L) and AA (0.1 M, 22.5 μ L) were added into 435 μ L Au NBP (with 118 μ L CTAC, 5 μ L HNO₃) suspension pre-incubated with different concentration L-Cys for 1 h.

7. Au NBP @ Ag with different Ag layer thickness (Ag₁ to Ag₈).

First, 118 μ L CTAC (10 mM), 5 μ L HNO₃ (0.01 M) and L- or D-Cys solution (10 μ L, 1 mM) was added to Au NBP solution (312 μ L dilution). Subsequently, the solution was incubated at 30 °C for 60 min. Then, keep the concentration ratio of AgNO₃ and AA identical (c_{AA}/c_{AgNO3} =5, making Ag⁺ react as completely as possible), for Ag₁ and Ag₂, we added AgNO₃ (1 mM) from 15.6 μ L to 31.2 μ L, subsequently the volume of AA solution (0.01 M) was a half of AgNO₃ for each sample. From Ag₃ to Ag₈, the amount of Ag⁺ (10 mM) added was corresponding to 6.24 μ L, 7.80 μ L, 15.60 μ L, 23.40 μ L, 31.20 μ L, 39 μ L, and the volume of the AA solution (0.1 M) was a half of AgNO₃ for each sample, too.

8. Au NBP @ L-Cys-centri. + D-Cys @Ag NPs and Au NBP @ D-Cys-centri. + L-Cys @Ag NPs.

For the preparation of Au NBP @ L-Cys-centri. + D-Cys @Ag NPs: First, 10 μ L of L-Cys (1 mM) were added into 435 μ L Au NBP (with 118 μ L CTAC, 5 μ L HNO₃) suspension and incubated at 30 °C for 1 h. After that, the mixtures were centrifuged (8000 rpm, 5 min). Then the precipitates were redispersed in same volume water and then 10 μ L D-Cys (1 mM) was added, they were mixed with the growth reagents immediately to initiate Ag deposition by putting in 30 °C water bath for 1h. The experimental operation steps of Au NBP@ D-Cys-centri. + L-Cys @Ag NPs was similar, except that L-Cys was replaced by D-Cys, and D-Cys was substituted to L-Cys.



Fig. S1 Extinction spectra of original Au NBPs.



Fig. S2. (A) High-resolution TEM image of Au NBP@Cys@Ag nanostructure, scale bar = 10 nm, the red dashed frame area was the Ag shell; (B) high-resolution TEM image of the Ag shell, scale bar = 5 nm, 0.23 nm corresponds to the separation of $\{111\}$ facets of Ag.



Fig. S3 CD spectra of L-Cys (A) and D-Cys (B) with different concentrations. The datas were smoothed by setting the points of window parameter to 5.



Fig. S4 CD spectra of Au NBP@L-Cys (A) and Au NBP@D-Cys (B) with different concentration of Cys, respectively.



Fig. S5 CD spectra of Au NBP@Cys@Ag and silver nanoparticles grown directly in the presence of cysteine.



Fig. S6 TEM (A) and CD spectra (B) of Au NBP@ L-Cys @Ag by reducing free Cys within Ag nanoshell, scale bar 20 nm.



Fig. S7 (A) Extinction spectra from a to d (Ag₁ to Ag₄); (B) Extinction spectra from e to h (Ag₅ to Ag₈); (C) and (D) Extinction spectra of dynamic growth of Au NBP@L-Cys@Ag from 1 to 35 min, $c_{L-Cys}=10 \mu M$, $c_{Ag+}=0.79$ mM.



Fig. S8 (A) Extinction and (B) plot of the length and width (equatorial zone) of Au NBP@Cys@Ag with increasing Ag⁺ added. (Ag₀ means original Au NBP; From Ag₁ to Ag₂, the amount of Ag⁺ (1 mM) added was 15.6 μ L to 31.2 μ L; From Ag₃ to Ag₈, the amount of Ag⁺ (10 mM) added was corresponding to 6.24 μ L, 7.80 μ L, 15.60 μ L, 23.40 μ L, 31.20 μ L, 39 μ L).



Fig. S9 TEM images of different Ag shell thickness on Au NBP @Cys, sacle bar =50 nm. (a-e, the amount of Ag⁺(10 mM) added was corresponding to 7.80 μ L, 14.04 μ L, 15.60 μ L, 31.20 μ L, 43.68 μ L)



Fig. S10 Extinction spectra of Au NBP @Ag in the absence of Cys (3 min interval).



Fig. S11 CD spectra of Au NBP@Cys@Ag at different pH value of the solution. (A) at different acidic and alkaline solutions; (B) with the acid concentration was 10⁻² M, L inside brackets for Au NBP@L-Cys@Ag, and D inside brackets for Au NBP@D-Cys@Ag.



Fig. S12 Extinction spectra of Au NBP@Cys@Ag NPs by adjusting acid concentration to 0.01 M, reacted for 40 min (A) and 70 min (B), red line represented Au NBP@D-Cys@Ag, and the black line represented Au NBP@L-Cys@Ag, c_{Cys} = 10 μ M. c_{Ag+} =0.9 mM.

Table S1. Calculated g-factors for obtained Au NBP @ L/D-Cys @Ag core-shell nanocrystals by adjusting acid concentration to 0.01 M after reacting for 40 min.

CD peak	564 nm	498 nm	384 nm
$g_L(\times 10^{-3})$	-1.008	1.222	-0.323
$g_{D}(\times 10^{-3})$	1.258	-1.306	0.371

 $c_{\text{Cys}} = 10 \ \mu\text{M}, \ c_{\text{Ag+}} = 0.9 \ \text{mM}.$

Table S2. Calculated g-factors for obtained Au NBP @ L/D-Cys @Ag core-shell nanocrystals by adjusting acid concentration to 0.01 M after reacting for 70 min.

CD peak	508 nm	416 nm	352 nm
g _L (×10 ⁻³)	-0.457	0.451	-0.331
g _D (×10 ⁻³)	0.373	-0.300	0.238

 c_{Cys} = 10 μ M, $c_{\text{Ag+}}$ =0.9 mM.

Table S3 to Table S7. Calculated g-factors for obtained Au NBP @ L/D-Cys @ Ag with increasing Ag⁺ added.

Table S3. Calculated g-factors for obtained Au NBP @ L/D-Cys @ Ag shell nanocrystals.

CD peak	348 nm	378 nm	413 nm
$g_L(\times 10^{-3})$	0.069	0.167	-0.060
g _D (×10 ⁻³)	-0.065	-0.028	0.120

 $c_{\text{Cys}} = 10 \ \mu\text{M}, \ c_{\text{Ag}+} = 0.156 \ \text{mM}.$

Table S4. Calculated g-factors for obtained Au NBP @ L/D-Cys @ Ag shell nanocrystals.

CD peak	376 nm	416 nm
$g_L(\times 10^{-3})$	0.235	-0.070
$g_{D}(\times 10^{-3})$	-0.086	0.126

 $c_{\rm Cys}$ = 10 µM, $c_{\rm Ag^+}$ =0.187 mM.

Table S5. Calculated g-factors for obtained Au NBP @ L/D-Cys @ Ag shell nanocrystals.

CD peak	355 nm	377 nm	421 nm
$g_L(\times 10^{-3})$	-0.052	0.245	-0.075
$g_{\rm D}$ (×10 ⁻³)	0.072	-0.123	0.132

 c_{Cys} = 10 µM, $c_{\text{Ag+}}$ =0.218 mM.

Table S6. Calculated g-factors for obtained Au NBP @ L/D-Cys @ Ag shell nanocrystals.

CD peak	357 nm	378 nm	421 nm
g _L (×10 ⁻³)	-0.089	0.201	-0.063
g _D (×10 ⁻³)	0.126	-0.190	0.119

 c_{Cys} = 10 µM, $c_{\text{Ag}+}$ =0.312 mM.

Table S7. Calculated g-factors for obtained Au NBP @ L/D-Cys @ Ag shell nanocrystals.

CD peak	390 nm	418 nm
g _L (×10 ⁻³)	-0.164	0.260
g _D (×10 ⁻³)	0.289	-0.249

 $c_{\rm Cys}$ = 10 µM, $c_{\rm Ag^+}$ =0.780 mM.

Anisotropy factors (g-factors) represented the degree of asymmetry and the equation for calculating the gfactor in each data mode was given below²:

 $g = \Omega (mdeg)/(32980 \times A)$

where Ω (mdeg) and A were the CD signal intensity and the extinction of nanocrystal solution, respectively.

References

- 1. A. Sanchez-Iglesias, N. Winckelmans, T. Altantzis, S. Bals, M. Grzelczak and L. Liz-Marzan, *J. Am. Chem. Soc.*, 2017, **139**, 107-110.
- 2. Y. Zhao, L. G. Xu, W. Ma, L. B. Wang, H. Kuang, C. L. Xu and N. A. Kotov, *Nano.Lett.*, 2014, 14, 3908-3913.