Supporting information

Rhombic dodecahedral gold nanoparticles: chiral sensing probe for naked-eye recognition of histidine enantiomers

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Preparation of three kinds of gold nanoparticles with different shapes

All glasswares and magnetic stirrer bars were cleaned with aqua regia ($HCl : HNO_3 = 3 : 1$ v/v) and rinsed thoroughly with deionized (DI) water prior to use, and then oven-dried prior to use, to avoid unwanted nucleation during the synthesis, as well as aggregation of gold colloid solution.

The rhombic dodecahedral gold nanoparticles (RD-shaped GNPs) were synthesized using the seed-mediated method in aqueous cationic surfactant solutions. The seed-mediated method typically included two steps. First step is to prepare the gold seed solution. Briefly, a volume of 10 mL aqueous solution containing 2.5×10^{-4} M and $HAuCl_4$ and 0.10 M cetyltrimethylammonium chloride (CTAC) was prepared and stirred magnetically. Then, 0.45 mL freshly prepared ice-cold $NaBH_4$ (20 mM) was added. The resulting solution color immediately turned from yellow

to brown, indicating the formation of gold seed. The seed solution was aged for 2 h at 30 °C to decompose excess $NaBH_4$ by water before further application to gold nanorods synthesis.

The second step is the further growth of gold seed to form RD-shaped GNPs. Two vials were labeled A and B, respectively. 0.32 g CTAC surfactant was added into A and B vials, and then 9 mL deionized H_2O was added respectively (the concentration of CTAC in the final solution is 0.1 M). The vials were placed in a water bath set at 25 °C. Next, 380 μL of 10 mM $HAuCl_4$ solution, 50 μL of 1 mM KI and 220 μL of 40 mM ascorbic acid solution were introduced successively to form the growth solution. The color of growth solution changed from dark yellow to colorless, indicating the reduction of Au^{3+} to Au^{+} species. Finally, 25 μL of the seed solution was added to growth solution A with shaking until the solution color turned light pink (ca. 5 s). Then, 25 μL of solution A was added to the growth solution B with thorough mixing for 5−10 s. The solution was aged for 15 min and centrifuged at 9000 rpm for 10 min to collect the particles. After removing the top solution, 10 mL of deionized water was added to the precipitate, and the solution was centrifuged twice again using the same condition to remove excess CTAC. The final precipitates were collected and redispersed in 5 mL deionised water. The concentration of RD-shaped GNPs stock solution was estimated to be 3.2×10^{-10} M. The zeta potential of the obtained GNPs was measured to be

+24.2 mV, indicating that CTAC is capped on surface of nanoparticles.

The shape evolution of gold nanoparticle has been achieved by adjusting in the amount of $HAuCl_4$ Solution. The octahedra-shaped GNPs and rod-shaped GNPs were synthesized using the same method for RD-shaped GNPs, but changing the volume of 10 mM $HAuCl_4$ solution to 250 μL and 520 μL in both solution A and solution B.

The high angle annular dark filed scanning transmission electron microscopy (HAADF-STEM) image and the selected area electron diffraction (SAED) pattern of nanoparticles were performed under the acceleration voltage of 200 kV on a Thermo Fisher Titan cubed Themis G2 300 TEM equipped with a probe-forming Cs corrector.

Procedure of colorimetric chiral recognition

Firstly, to a one 1.5 mL-eppendorf tube were successively added 50 μL RD-shaped GNCs (0.5 nM), 50 μL BR buffer (pH 4.0), 150 μL L-His or D-His with the different concentrations. Secondly, the mixed solution was incubated at room temperature (ca. 25 °C) for 3 min. Lastly, the UV-vis-NIR spectra were measured. At the same time, the color of reaction solution was recorded with a 500-digital Cannon camera.

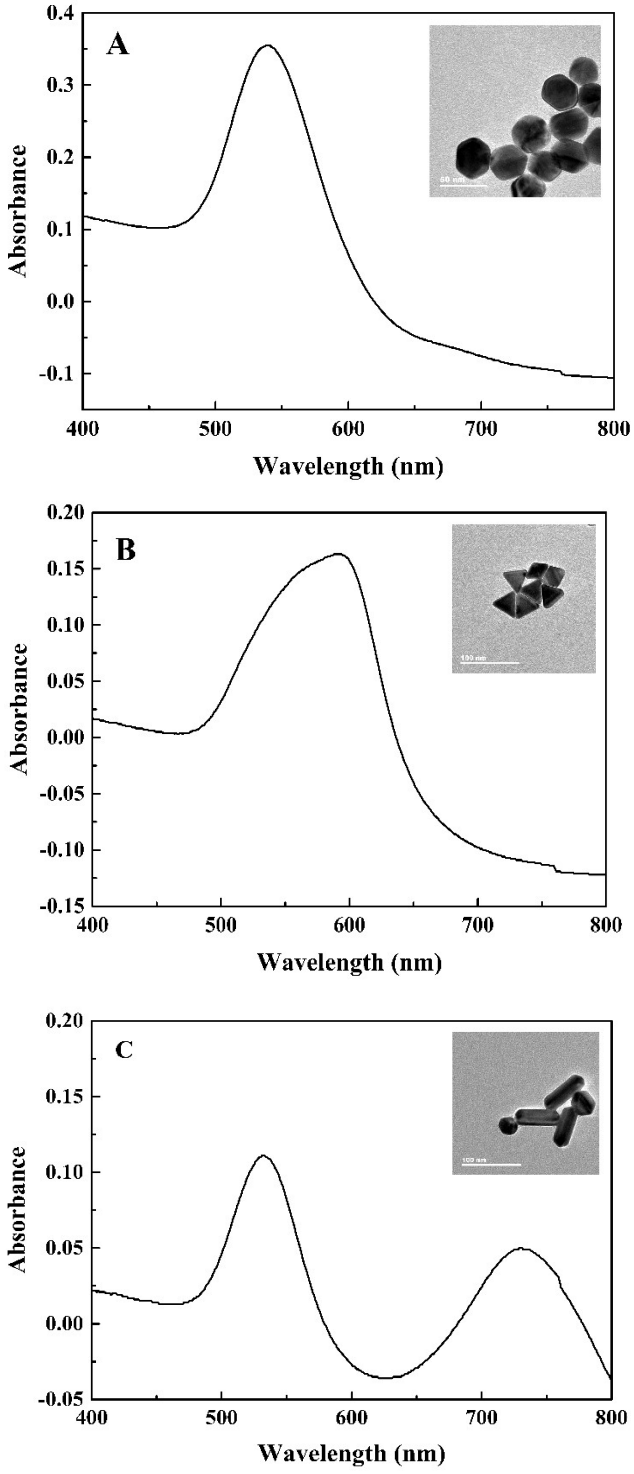

Figure S1. Absorption spectra of RD-shaped GNPs (A), octahedra-shaped GNPs (B) and rod-shaped GNPs (C). The inset shows the corresponding TEM images.

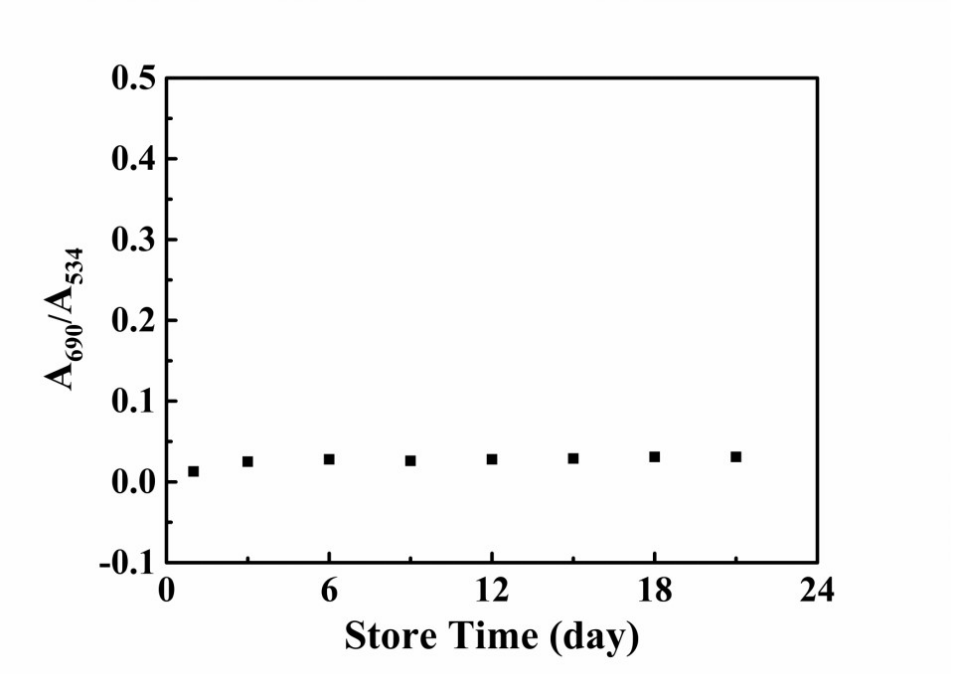

Figure S2. Store stability of the RD-shaped GNPs solution.

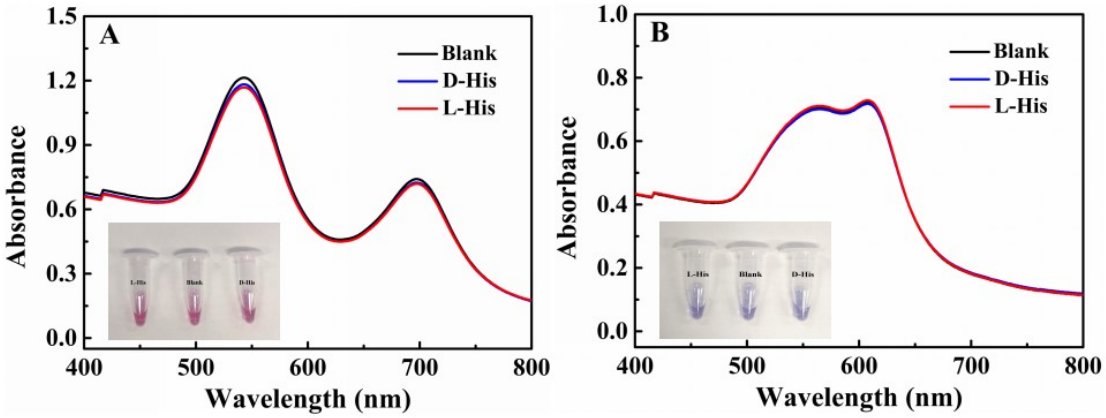

Figure S3. Absorption spectra of rod-shaped GNPs (A) and octahedra-shaped GNPs (B) in the presence of L-His or D-His. The inset shows the corresponding photographs.

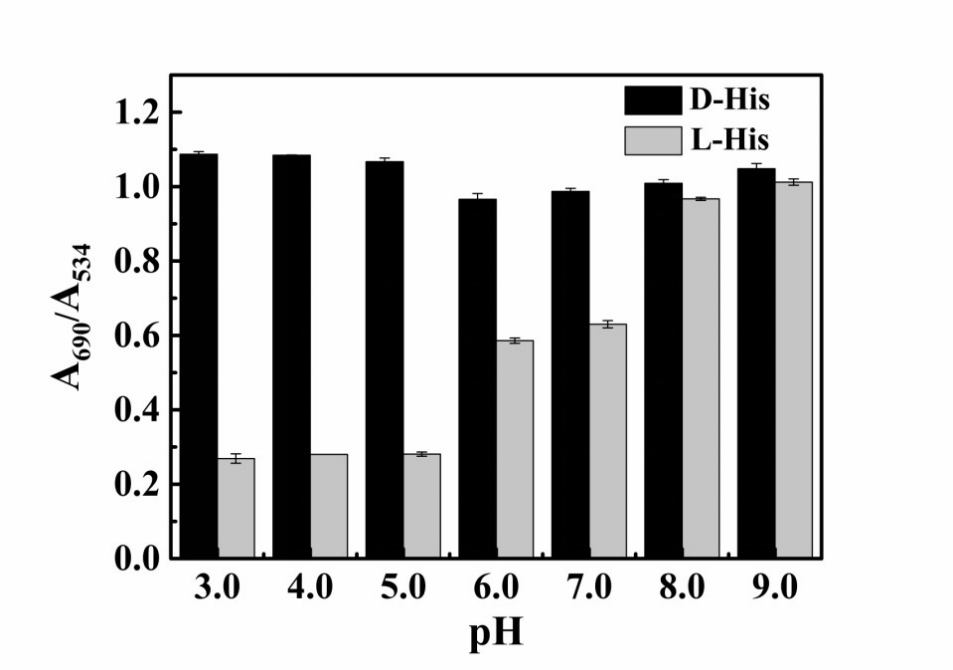

Figure S4. Effect of media pH on the chiral recognition of His. Experiment condition: 50 μL RD-shaped GNPs, 50 μL BR buffer, 100 μL L- or D-His (5 mM).

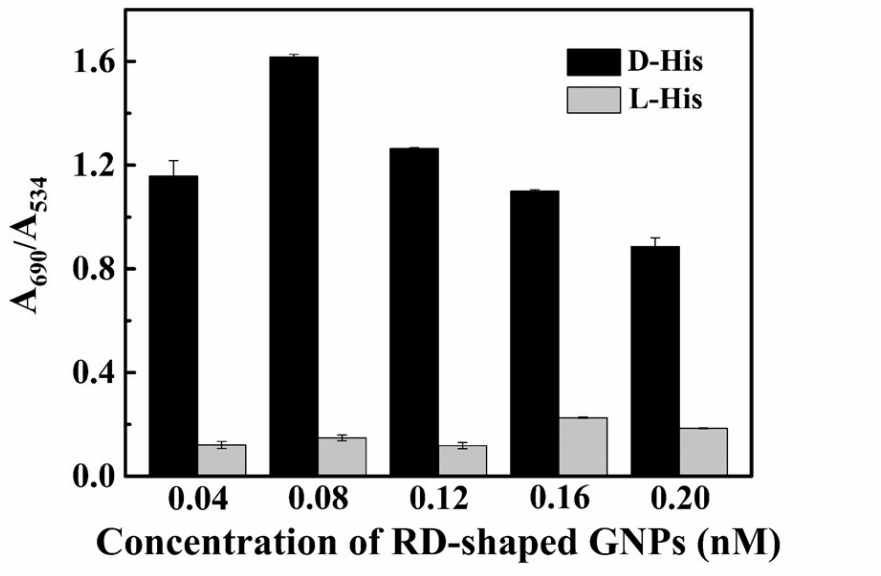

Figure S5. Effect of concentration of RD-shape GNPs on the chiral recognition of His (5 mM).

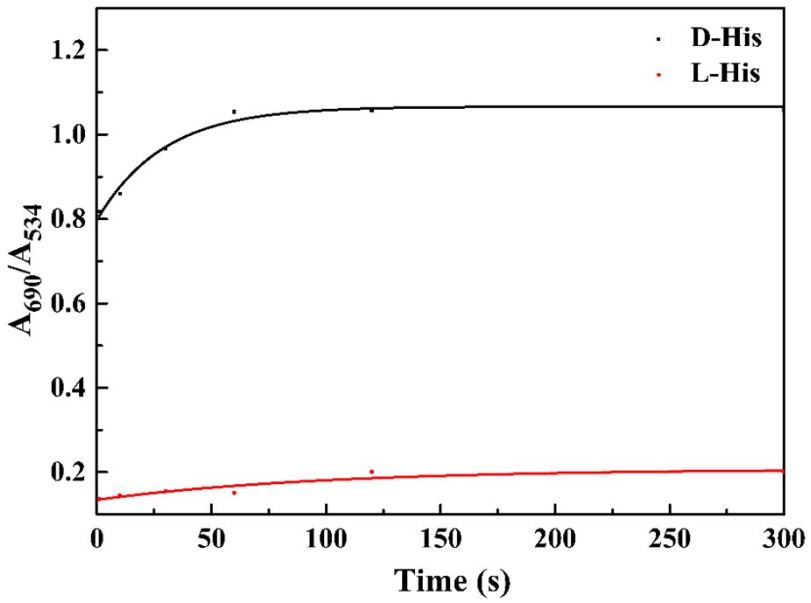

Figure S6. Effect of interaction time on A_{690}/A_{534} of RD-shaped GNPs upon the addition of L- or D-His. Experiment condition: 50 μL RD-shaped GNPs, 50 μL BR buffer (pH 4.0), 100 μL L- or D-His (5 mM).

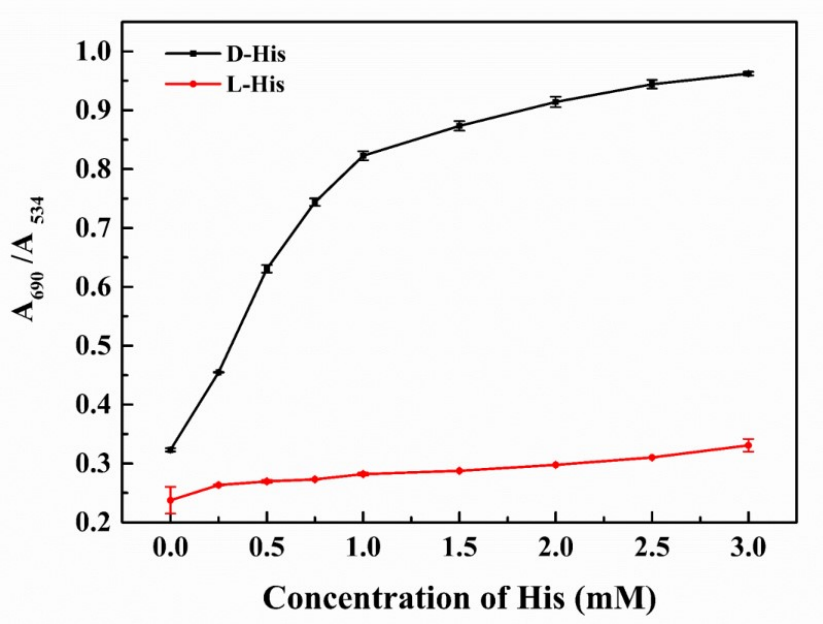

Figure S7. Plots of A_{690}/A_{534} of RD-shaped GNPs upon the addition of L- or D-His. Experiment condition: 50 μL RD-shaped GNPs, 50 μL BR buffer (pH 4.0), 100 μL L- or D-His.

Table S1. Determination of enantiomeric excess of D-His in synthetic

samples using the HPLC and this method.

Sample	HPLC (%)	This method (%)	Relative error (%)
Sample 1	100.00	100.76±0.26	0.76
Sample 2	72.19	74.01±0.19	2.52
Sample 3	50.69	48.26±0.12	-4.79
Sample 4	24.11	24.52±0.14	1.70
Sample 5	-0.32	-0.33±0.13	3.13
Sample 6	-26.01	-25.48±0.10	-2.04
Sample 7	-49.22	-49.89±0.15	1.18
Sample 8	-74.14	-74.98±0.10	1.13
Sample 9	-100.00	-99.90±0.08	-0.10

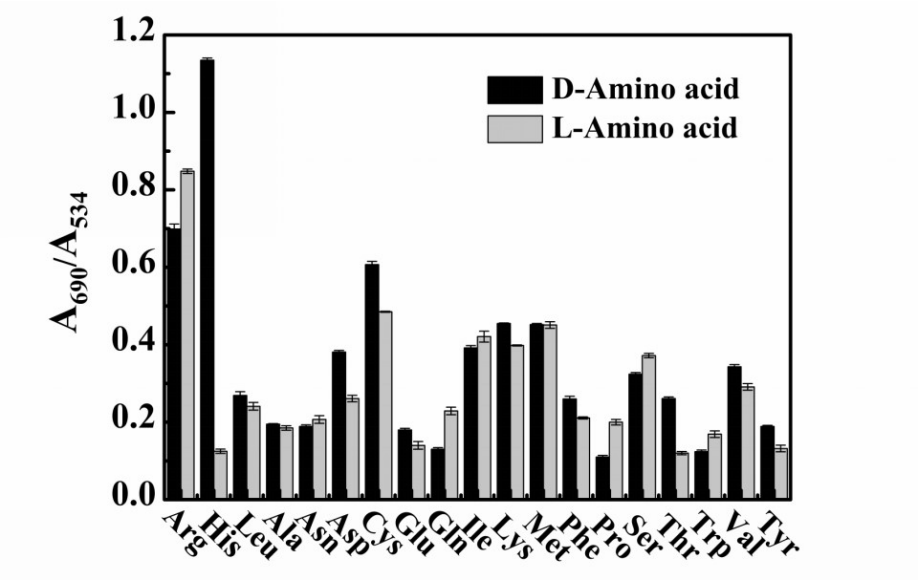

Figure S8. Plots of A_{690}/A_{534} of the RD-shaped GNPs upon the addition of different α-amino acid enantiomers. Experiment condition: 50 μL RD-shaped GNPs, 50 μL BR buffer (pH 4.0), 100 μL α-amino acid enantiomers (5 mM).

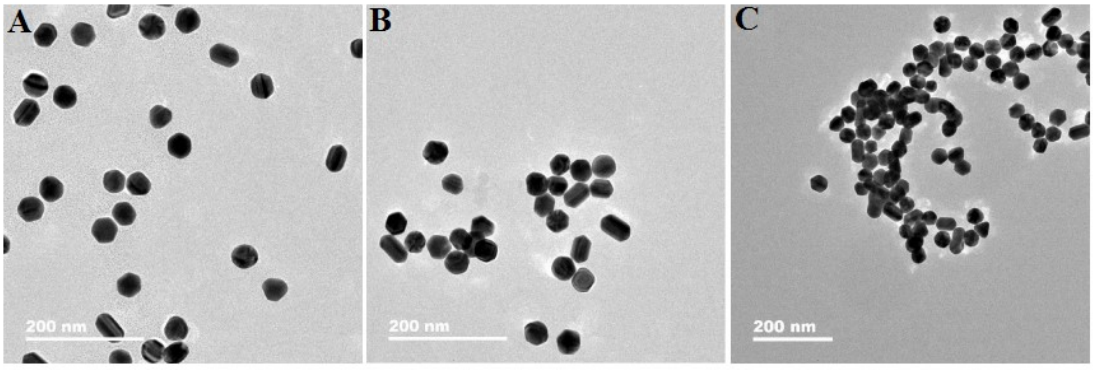

Figure S9. TEM images of RD-shaped GNPs (A), RD-shaped GNPs + L-His (B), and RD-shaped GNPs + D-His (C).

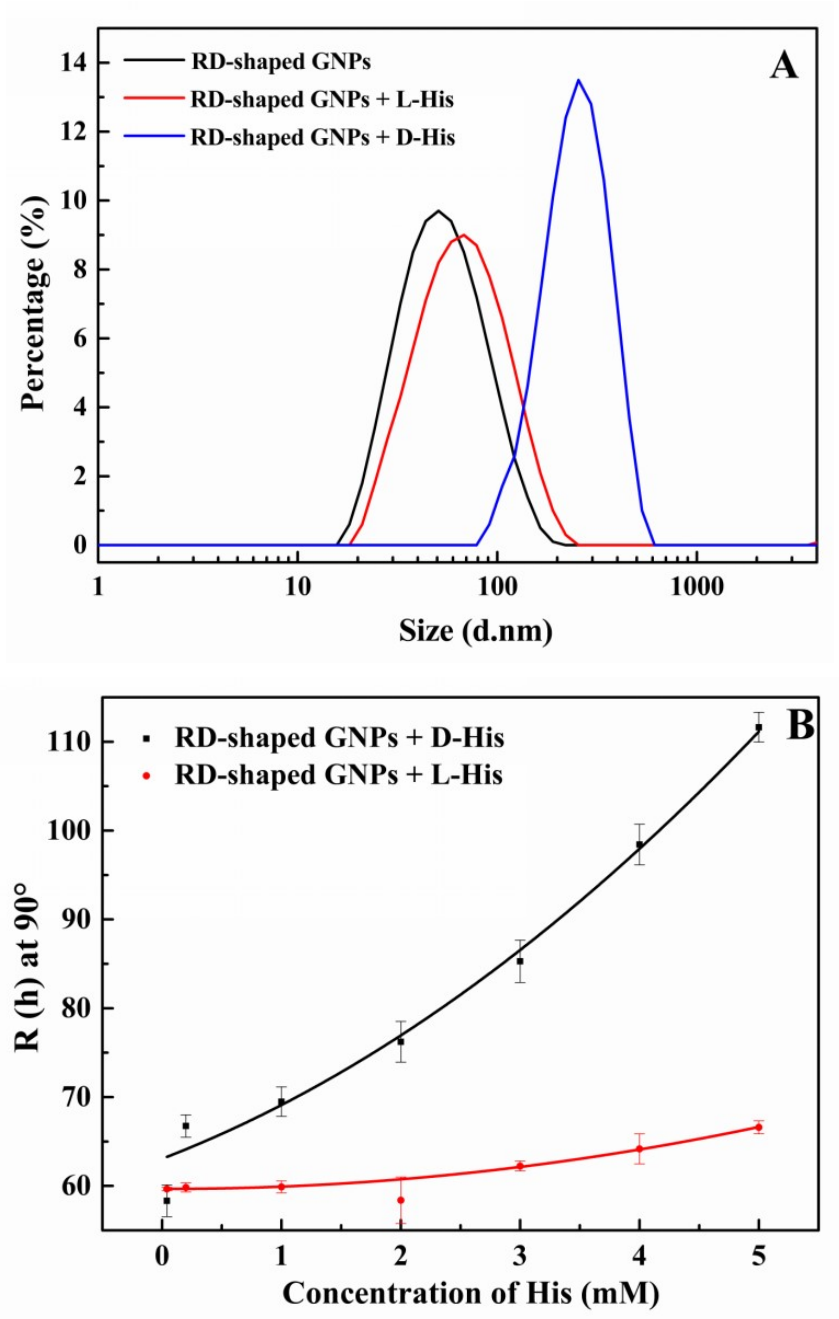

Figure S10. (A) Dynamic light scattering (DLS) curves of RD-shaped GNPs, RD-shaped GNPs+D-His, and RD-shaped GNPs+L-His. (B) DLS curves of RD-shaped GNPs solution upon addition of L-His or D-His at different concentrations. Experiment condition: 50 μL RD-shaped GNPs, 50 μL BR buffer (pH 4.0), 100 μL L- or D-His.

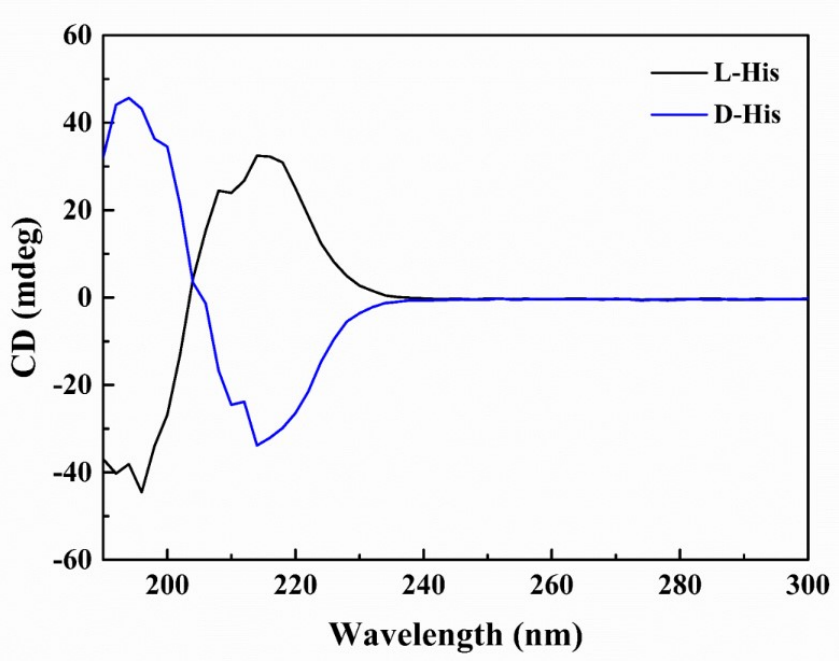

Figure S11. CD spectra of L-His and D-His.

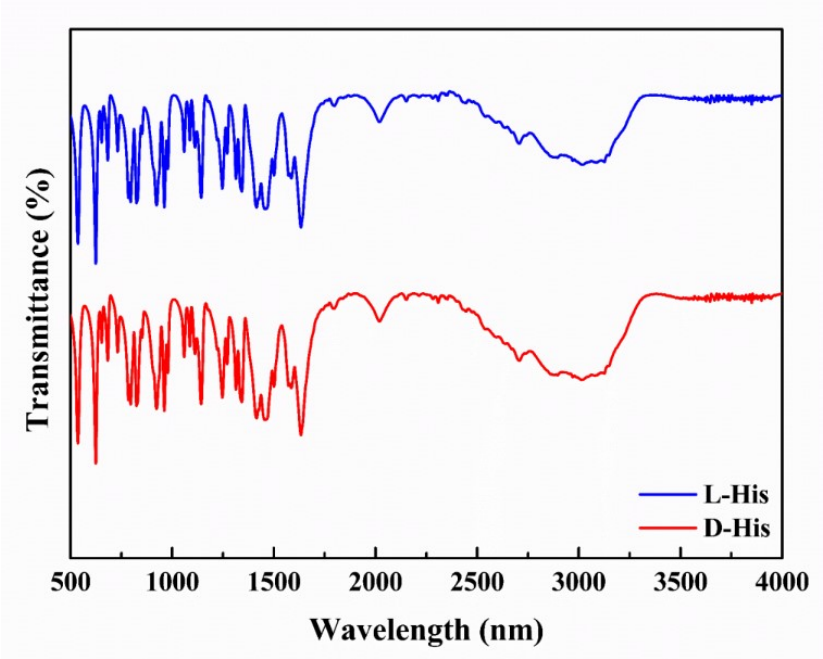

Figure S12. FT-IR spectrum of L- or D-His.