## **Supporting Information**

**Chemicals.** BSPP, tetrachloroauric acid (HAuCl<sub>4</sub>), sodium citrate, L-cysteine (L-Cys), D-cysteine (D-Cys), DL-cysteine (DL-Cys), L-glycine (L-Gly), L-alanine (L-Ala), L-tyrosine (L-Tyr), L-threonine (L-Thr), D-threonine (D-Thr), L-glutamic (L-Glu) and D-glutamic (D-Glu) were supplied by Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. Unless specifically indicated, all other chemicals were purchased from Shanghai Chemical Reagents Company (Shanghai, China). Ultrapure water was purified using a Millipore Milli-Q purification system (18.2 M $\Omega$ /cm, Millipore, Molsheim, France). All glassware was thoroughly cleaned with freshly prepared aqua regia and then washed with ultrapure water prior to use.

**Measurements.** UV-visible (UV/vis) spectra were acquired with a UNICO 2100 PC UV/vis spectrophotometer. CD spectra were recorded on a J-710 spectropolarimeter (Jasco, Japan). UV/vis and CD spectra were analyzed with the Origin Lab software. Spectra were collected over the range of 200-800 nm. A cuvette with a path length of 1.0 cm was utilized. Dynamic light scattering (DLS) was performed with a Zetasizer Nano ZS system (Malvern). JEOL JEM-2100 operating at an acceleration voltage of 200 kV was utilized for transmission electron microscopy (TEM) images. Prior to TEM examination, 7.2  $\mu$ L of each sample was dried on a carbon film of TEM copper grids. All solutions were filtered using 0.45 or 0.22  $\mu$ m filters.

**Synthesis.** The synthesis of citrate-capped gold nanoparticles (Au NPs) 25 nm in diameter followed the procedures described previously using sodium citrate reduction<sup>1</sup>. HAuCl<sub>4</sub> (49.2 mL, 0.01%) was heated to boiling and an aqueous solution

of trisodium citrate (0.8 mL, 1wt%, freshly prepared) was quickly added under vigorous stirring and reflux. After several minutes, the color of the solution changed from blue to bright red. After boiling for 15 min, the solution was cooled to room temperature and stored at 4°C. The concentration of Au atoms in Au NPs was determined by UV/vis spectroscopy (25 nm Au NP equivalent to 2 nM).



Figure S1. CD spectral of NPs dimers assembled by L-Cys (A), DL-Cys (B) and D-Cys (C).



**Figure S2.** Representative TEM images for plasmonic chiral sensing platform in the range of 0-100 nM L-Cys.



**Figure S3.** UV/Vis spectra of plasmonic chiral sensing platform assembled by L-Cys (A) and D-Cys (B).



Figure S4. Dynamic light scattering spectra of Au NPs (A), dimer assembled by L-Cys (B), DL-Cys (C) and D-Cys (D).



**Figure S5.** The specificity of plasmonic chiral sensing platform. The concentration of Cys analogues is 100 nM, respecitively.



Figure S6. CD spectral of Cys samples with various enantiomeric compositions (L/D = 0.100, 20:80, 40:60, 50:50, 60:40, 80:20, 100:0).



**Figure S7.** CD responses (A) and Plots of  $CD_{525nm}$  vs. concentrations (B) for the "unknown" sample in plasmonic chiral systems. (C) Slope of unknown sample (blue dash dot) in the Figure *vs*. L-Cys compositions.

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## Reference

 Xu, L. G.; Zhu, Y. Y.; Ma, W.; Chen, W.; Liu, L. Q.; Kuang, H.; Wang, L. B.; Xu, C. L. J Phys Chem C 2011, 115, 3243-3249.