Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Chiroptical Study of Bimetal-cysteine Hybrid Composite: Interaction between Cysteine and Au/Ag Alloyed Nanotubes

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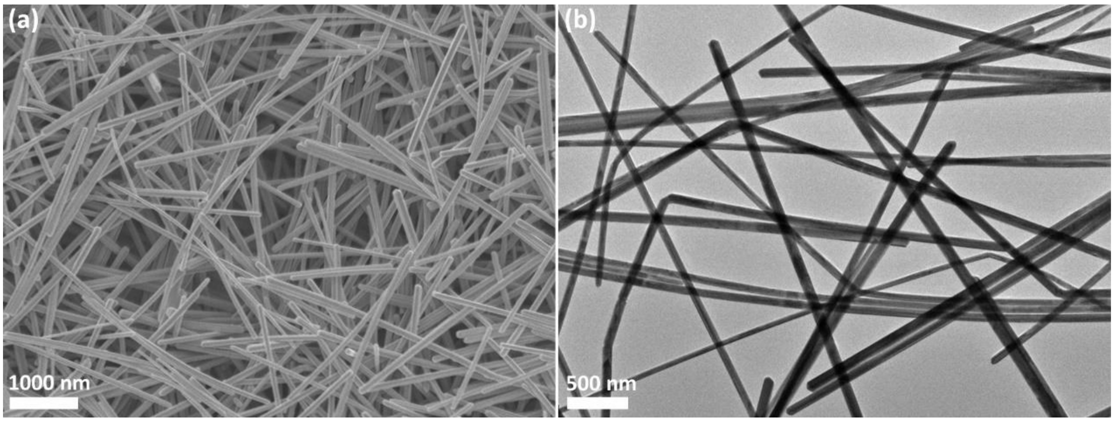

Fig. S1. The SEM image (a) and TEM image (b) of original Ag nanorods.

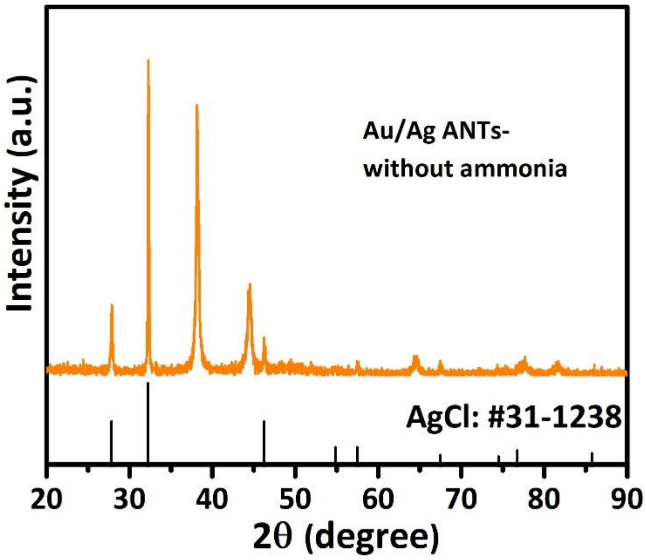

Fig. S2. The wide-angle X-ray diffraction (XRD) spectra of Au/Ag ANTs before treated with ammonia.

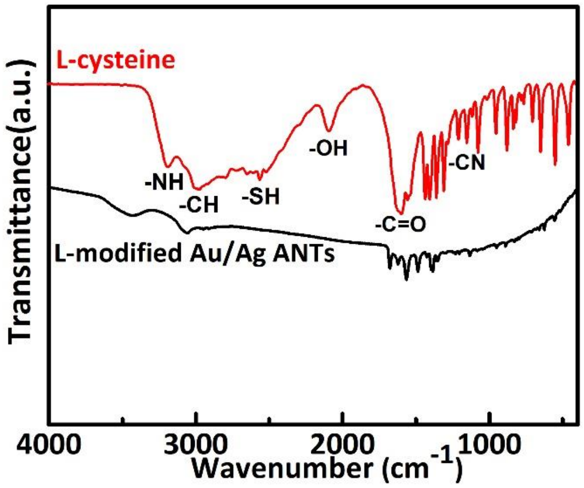

Fig. S3. The FTIR spectra of L-cysteine and L-modified Au/Ag ANTs.

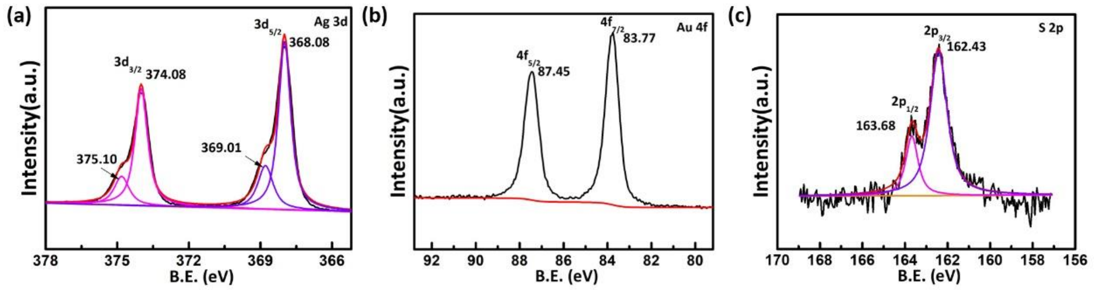

Fig. S4. The XPS spectra of L-modified Au/Ag ANTs: (a) Ag element; (b) Au element; (c) S element.

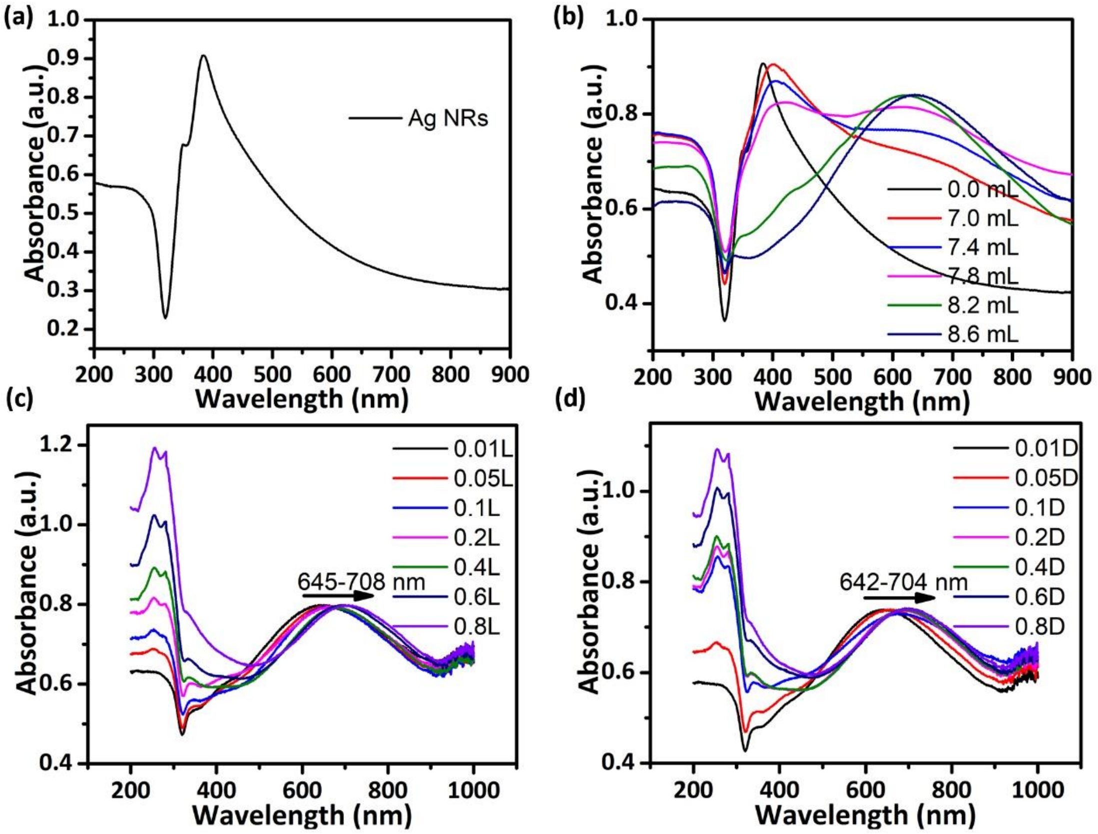

Fig. S5. The UV-vis spectra of (a) Ag NRs; (b) products after reacting with different amounts of $HAuCl_4$; (c) L-modified Au/Ag ANTs produced from different L-cysteine concentrations. The 0.01-0.8L denotes 0.01-0.8 mM L-cysteine involved in the reaction. (d) D-modified Au/Ag ANTs produced from different D-cysteine concentrations. The 0.01-0.8D denotes 0.01-0.8 mM D-cysteine involved in the system.

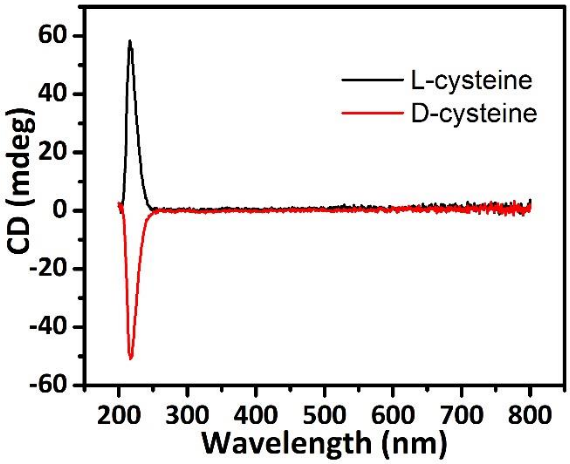

Fig. S6. The CD spectra of 1 mM L/D-cysteine.

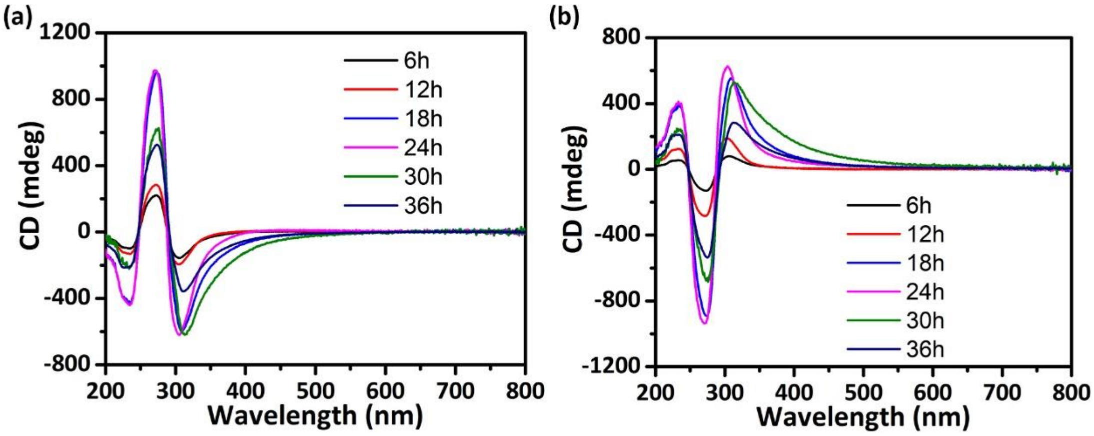

Fig. S7. The CD spectra of (a) L-modified Au/Ag CANTs and (b) D-modified Au/Ag CANTs at different reaction time.

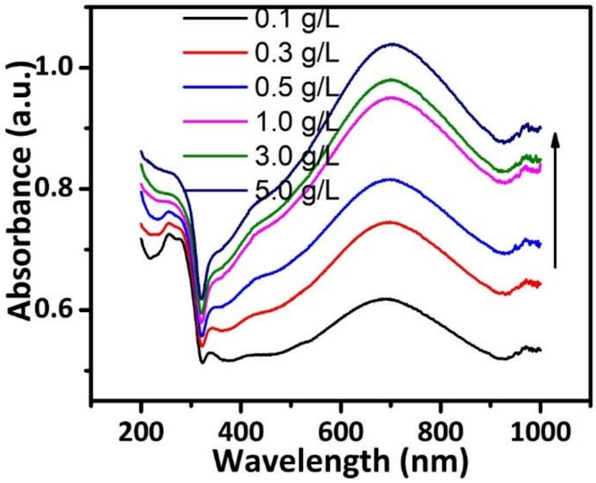

Fig. S8. The UV-vis spectra of L-modified Au/Ag ANTs with different PEI concentrations.

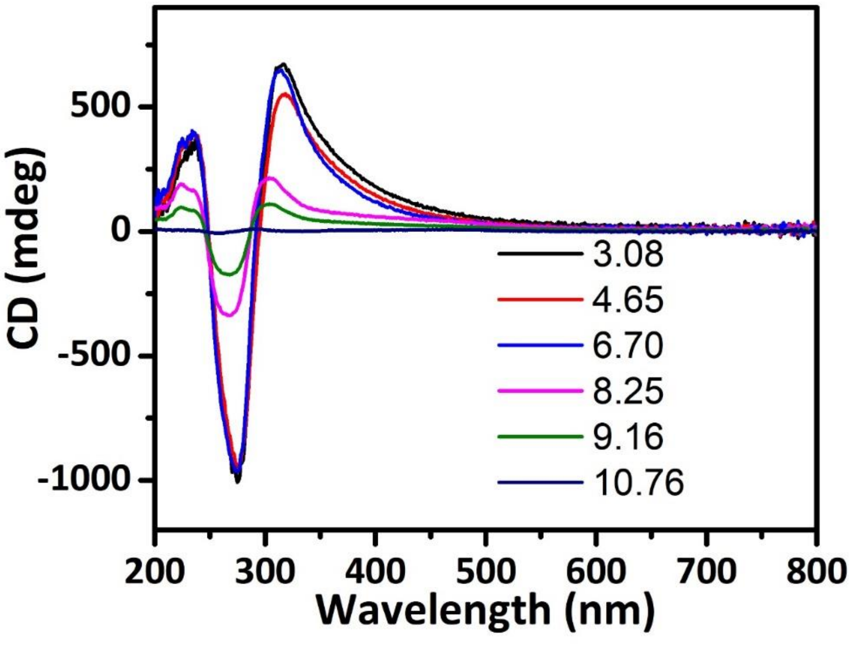

Fig. S9. The CD spectra of D-modified Au/Ag ANTs at different pH values.

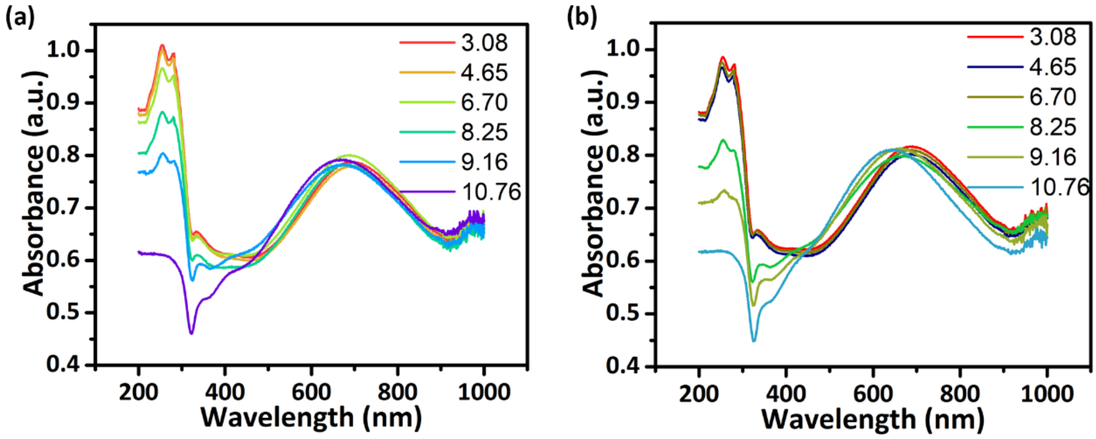

Fig. S10. The UV-vis spectra of (a) L-cysteine and (a) D-cysteine modified Au/Ag ANTs at different pH values.

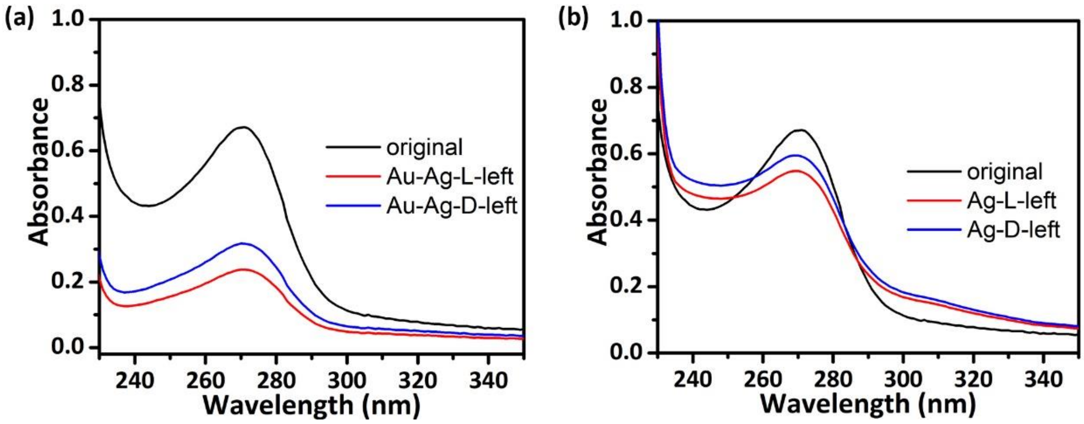

Fig. S11. The UV-vis spectra of TTCA obtained from the TCDI treated supernatant of 1 mM cysteine-modified (a) Au/Ag ANTs and (b) Ag NRs. The “original” represents the products from the individual 1 mM cysteine, which was measuring the spectrum by diluting 20 times due to the detection limit restriction of this cyclization reaction detected method for cysteine.

The calculation of anisotropic factors of cysteine-modified Au/Ag ANTs and Ag NRs

Anisotropic factor *g* is defined as follows:

g$=\frac{\Delta\varepsilon}{\varepsilon}$, where $\Delta\varepsilon=\varepsilon_L-\varepsilon_R$ and $\varepsilon=\varepsilon_L+\varepsilon_R$, ε_L and ε_R are the molar extinction coefficients for left circularly polarized (LCP) and right circularly polarized (RCP) light, respectively. According to the Lambert-Beer Law: $A=\varepsilon\times c\times l$, where A is the sum absorbance of left and right circularly polarized light, *c* (mol L^{-1}) is the concentration of the sample, and *l* (cm) represent the length of the cell. So, ΔA, the difference between absorbance of LCP and RCP light can be described as: $\Delta A=\Delta\varepsilon\times c\times l$, where θ is the molar ellipticity and $\theta=\Delta\mathrm{A}(\ln 10/4)(180/\pi)=33\times\Delta A$.

Therefore, g factor can be obtained by: $\mathrm{g}=\frac{\theta}{33\times A}$

Table S1. Anisotropy Factor (g factor) of cysteine-modified Au/Ag ANTs and cysteine-modified Ag NRs.

	Positive CD peak		Negative CD peak	
	λ/nm	*g*	*λ/nm*	*g*
cysteine-modified Au/Ag ANTs	271	0.029	271	-0.028
cysteine-modified Ag NRs	277	0.016	277	-0.015

The calculation of the amount of cysteine molecules absorbed in the complex of cysteine-modified Au/Ag ANTs and Ag NRs.

1. Theoretical basis. We selected a method based on a cyclization reaction reported in the literature.[1] After cysteine is treated with TCDI, the stable cyclic derivative 2-thioxothiazolidine-4-carboxylic acid (TTCA) has an intense UV absorption at 272 nm, in which the intensity of this peak is proportional to the amount of cysteine. Therefore, the unreacted cysteine concentration in the hybrid system can be determined. Evidently, the amount of hybrid cysteine molecules in the complex is equal to the amount of cysteine molecules initially minus that remaining in the system.

2. Measurement experiment. Typically, the 12 mL supernatant was obtained from 1 mM cysteine-modified Au/Ag ANTs. After adding phosphate to adjust its pH to 8.2, the solution was treated with 2 mL TCDI in acetonitrile (0.15 mM) stirring at room temperature for 2 h. When the process was complete, the UV-vis spectrum was directly measured. For the standard cysteine analysis, we calculated that the final cysteine concentration in the system of 1 mM cysteine-modified Au/Ag ANTs was 0.833 mM. The corresponding UV-vis spectra were shown in Fig. S11. The amount of hybrid cysteine molecules can be calculated as follows:

$$\boldsymbol{N_{Cys}} = \frac{\boldsymbol{C_{Cys}}}{\boldsymbol{C_{nanostructure}}}$$

In our system, the NRs are larger in scale (~80 nm in diameter; ~20 μm in length) and every NR is considered as a cylinder. The atomic volume of the noble metal with a face-centered cubic structure is 0.017 nm^3. The mass of Ag element in 0.4 mL Ag NRs was 0.39 mg based on the ICP analysis. The concentration of the nanotubes in the system can be calculated as follows:

$$\boldsymbol{C_{nanotube} = C_{Ag\ nanowire} = \frac{m_{Ag}/M_{Ag}}{\left(\pi\left(\frac{D}{2}\right)^2 L/v_{Ag}\right)\times V_{system}}}$$

$$\boldsymbol{= \frac{0.39\times10^{-3}g/107.86g\ mol^{-1}}{\left(3.14\times\left(\frac{80\ nm}{2}\right)^2\times20\times10^3nm/0.017nm^3\right)\times12\times10^{-3}L}}$$

$$\boldsymbol{= 5.096\times10^{-14}mol\ L^{-1} = 5.096\times10^{-11}mM}$$

Table S2. The amount of adsorbed cysteine on the nanostructures surface.

	Au/Ag ANTs		Ag NRs	
	Au/Ag-L	Au/Ag-D	Ag-L	Ag-D
C$_{left}$	15 μM	20 μM	35 μM	38 μM
N$_{Cys}$	1.605×10^{10}	1.595×10^{10}	1.565×10^{10}	1.560×10^{10}

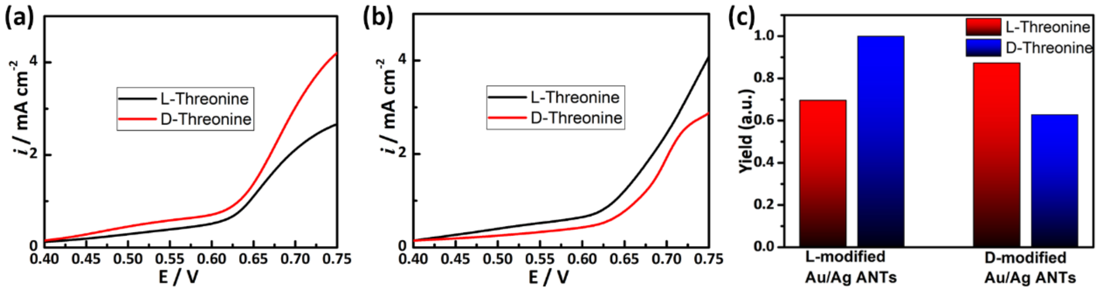

Fig. S12. The voltammograms of L/D-threonine enantiomers on the (a) L-modified Au/Ag ANTs (b) D-modified Au/Ag ANTs functionalized electrodes, (c) the reaction yields of the threonine enantiomers on the cysteine-modified Au/Ag ANTs electrodes. And the reaction yield Y has been normalized with the largest value designed as 1.

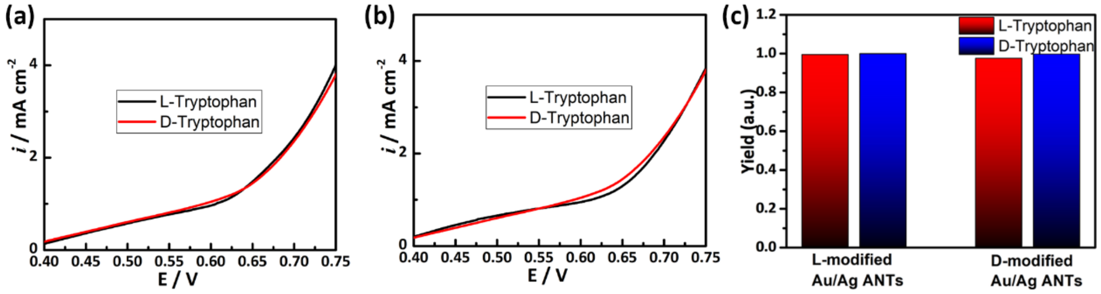

Fig. S13. The voltammograms of L/D-tryptophan enantiomers on the (a) L-modified Au/Ag ANTs (b) D-modified Au/Ag ANTs functionalized electrodes, (c) the reaction yields of the tryptophan enantiomers on the cysteine-modified Au/Ag ANTs electrodes. And the reaction yield Y has been normalized with the largest value designed as 1.

REFERENCES

1. V. Amarnath, K. Amarnath, Specific determination of cysteine and penicillamine through cyclization to 2-thioxothiazolidine-4-carboxylic acids, *Talanta* **2002,** *56*, 745-751.