

Supporting Information

Fluorescence turn-off-on for highly selective detection of serum L-cysteine based on AuNCs–AuNPs ensembles

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Experiment

Materials and chemicals

FeCl₂, FeCl₃, ZnSO₄, Al(NO₃)₃, CaCl₂, CrCl₃, KCl, MgSO₄, NaCl, (Ni)₂SO₄ and sodium citrate were obtained from Beijing Chemical Factory (Beijing, China). Other reagents were bought from Huixing Biotech Co., Ltd (Shanghai, China). All of the chemicals were of analytical grade.

Apparatus

The fluorescent spectra and intensity of all the samples were determined using an F-4500 fluorescence spectrometer (Hitachi, Japan). Ultraviolet-visible absorption spectra were measured with a TU-1900 UV-vis double-beam spectrometer (Purkinje General, China). Infrared spectra of L-Hyp@AuNCs were measured by Fourier transform infrared spectroscopy (FT-IR, TENSOR-27, Bruker technology Co., Ltd. Germany). Transmission electron microscope (TEM) images were observed with a transmission electron microscope (TECNAI G2 F20) (FEI, America) at a voltage of 200 kV. The particle size and zeta electric potential of L-Hyp@AuNCs, L-Hyp@AuNCs-AuNPs, L-Hyp@AuNCs-AuNPs/L-Cys and other compounds were monitored by dynamic light scattering (DLS, Malvern Instruments, the United Kingdom). X-ray photoelectron spectroscopy (XPS) was conducted with a VG Thermo Fisher Scientific (U. S. A.) X-ray photoelectron spectrometer (Model ESCALAB250-XL) for getting Au 4f spectrum of the resultant L-Hyp@AuNCs.

Synthesis of sodium citrate stabilized AuNPs

All of the glassware were thoroughly cleaned by using freshly prepared aqua regia (HCl:HNO₃ volume ratio=3:1), and rinsed thoroughly in water. The synthetic procedure of AuNPs was obtained by a simple method according to the reported method.^[1] Citrate-stabilized AuNPs (AuNPs) were synthesized by the reduction of HAuCl₄ with sodium citrate. Briefly, 10.0 mL of HAuCl₄ (1.0 M) was heated to reflux while stirring and then 1.0 mL of sodium citrate (38.8 mM) solution was added quickly. After the color change from pale yellow to deep red, the solution was refluxed for an additional 10.0 min and left to cool to room temperature. Then, the solution was stored at 4 °C for further use.

Selective sensing of L-Cys

Stock solutions of L-Cys, other L-amino acids and metal cation were prepared with water. Typically, 50.0 μL of L-Cys solutions at different concentrations, 50.0 μL Tris-HCl buffer (10.0 mM, pH 8.0), 100.0 μL of AuNPs solution and 200.0 μL of

L-Hyp@AuNCs were added into a microtube (1.0 mL). The resulting solutions were studied by fluorescence spectra with excitation at 345 nm (n=3). Similarly, 50.0 μ L of L-Cys solutions, 50.0 μ L of other coexisting compounds, 100.0 μ L of AuNPs solution and 200.0 μ L of L-Hyp@AuNCs were added into a microtube (1.0 mL). The resulting solutions were also measured by fluorescence spectra (n=3) .

References

- [1] W. F. Lan, Q. Q. Tan, J. Qiao, G. Y. Shen, L. Qi, D-proline capped gold nanoclusters for turn-on detection of serum raltitrexed, *Chin. Chem. Lett.*, 30 (2019) 1627-1630.

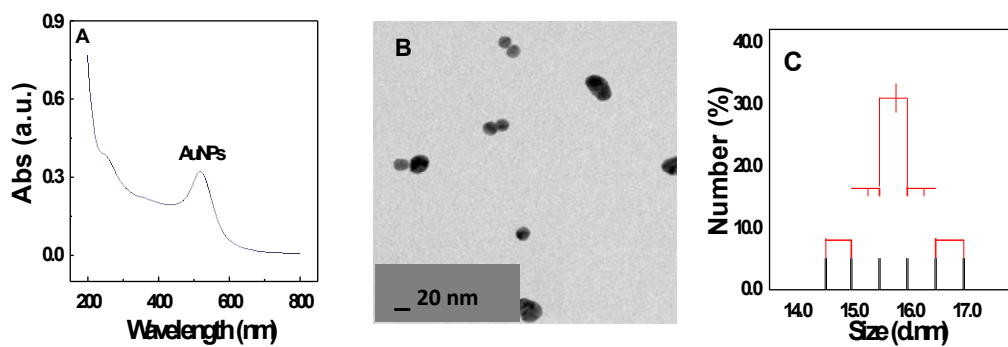


Fig. S1. UV-vis spectra (A), TEM (B) and DLS (C) of sodium citrate stabilized AuNPs.

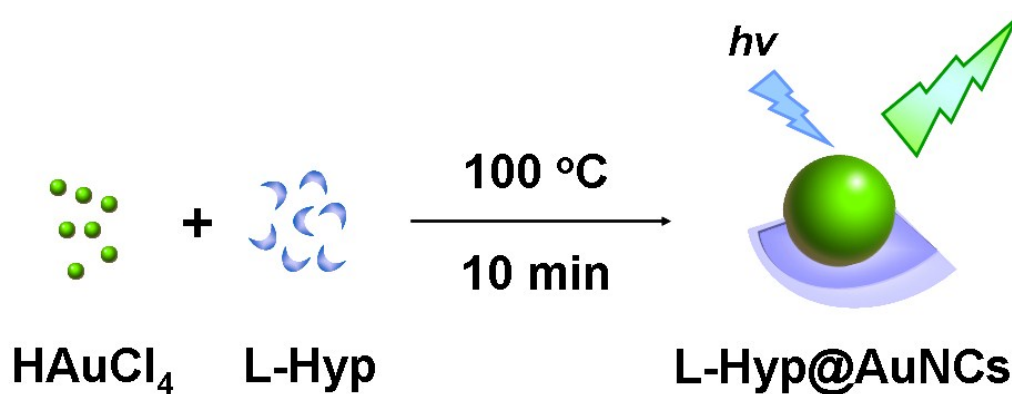


Fig. S2. Schematic illustration for the synthesis of fluorescent L-Hyp@AuNCs.

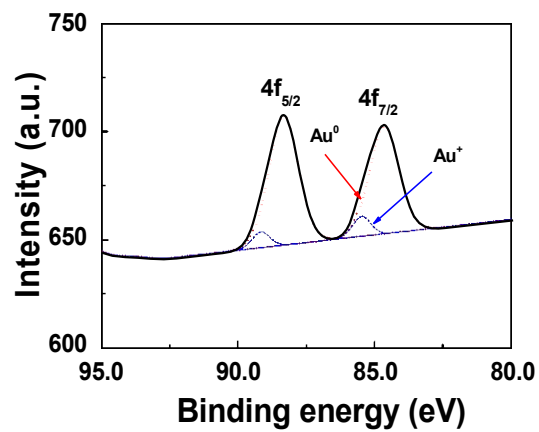


Fig. S3. XPS spectra of Au 4f orbitals of L-Hyp@AuNCs.

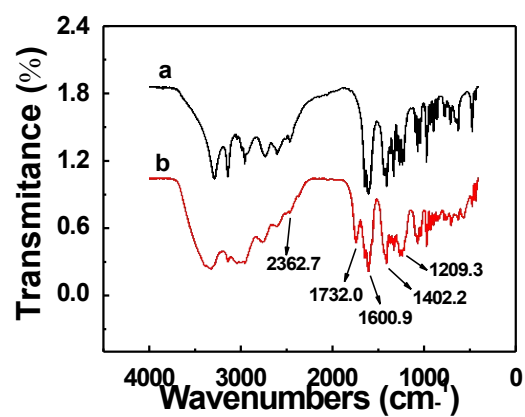


Fig. S4. FT-IR spectra of L-Hyp (a) and L-Hyp@AuNCs (b).

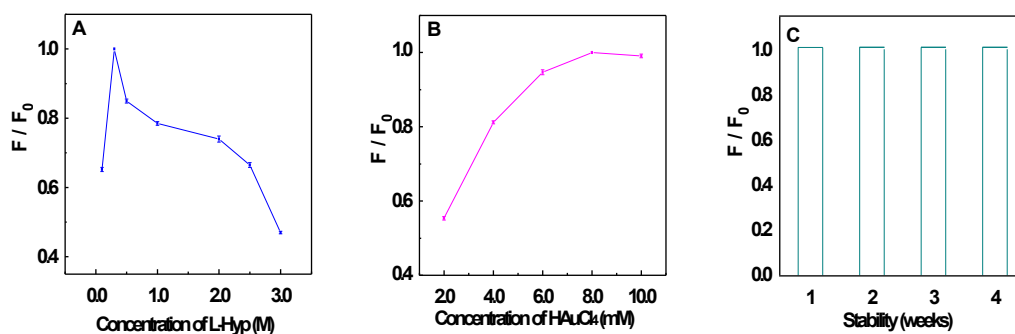


Fig. S5. Fluorescence intensity of the L-Hyp@AuNCs prepared with addition of L-Hyp (A) and HAuCl₄ (B); Stability of the as-prepared L-Hyp@AuNCs (C).

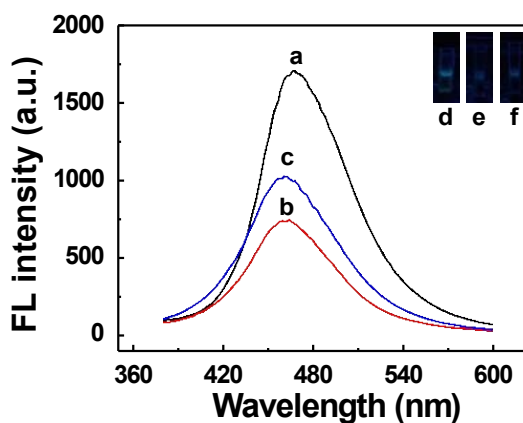


Fig. S6. The fluorescent spectra of L-Hyp@AuNCs (6.4 mM) (a); L-Hyp@AuNCs with addition of AuNPs (0.9 mM) (b); L-Hyp@AuNCs-AuNPs with addition of L-Cys (35.0 μM) (c). Inset: the photos of L-Hyp@AuNCs (d); L-Hyp@AuNCs-AuNPs (e); L-Hyp@AuNCs-AuNPs with addition of L-Cys (f) under UV light.

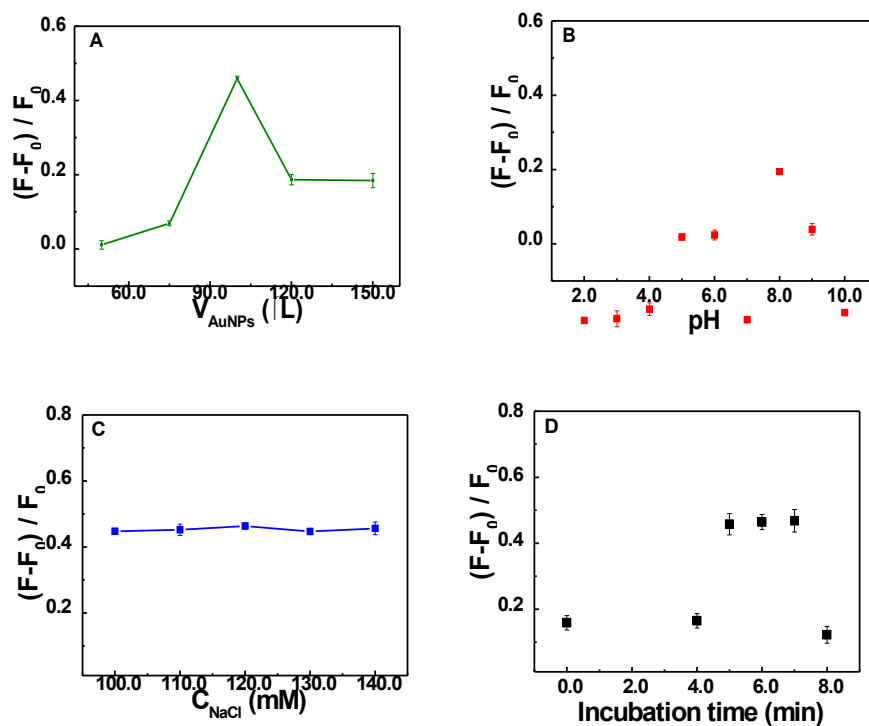


Fig. S7. Effect of AuNPs (A), buffer pH (B), ionic strength (C) and Incubation time (D) on the fluorescence intensity of the L-Hyp@AuNCs-AuNPs with addition of L-Cys.

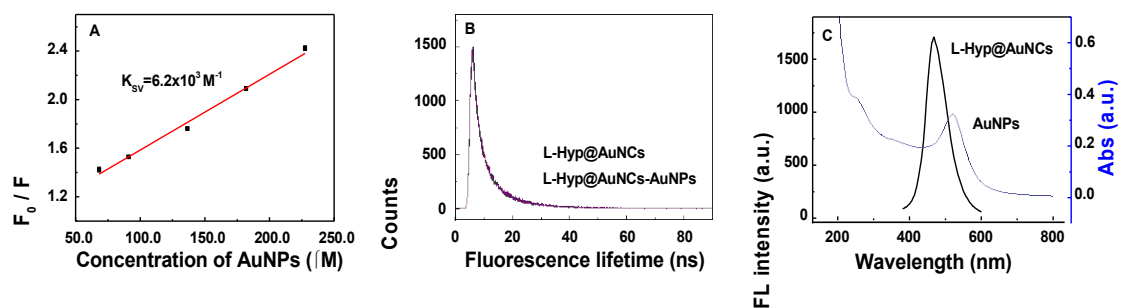


Fig. S8. (A) Stern-Volmer plot of L-Hyp@AuNCs fluorescence quenching in absence (F_0) and presence of AuNPs (F); (B) Fluorescence lifetime (τ_0) of L-Hyp@AuNCs in the absence and presence of AuNPs; (C) UV-vis absorption spectra of aqueous AuNPs and the fluorescence emission spectrum of L-Hyp@AuNCs.

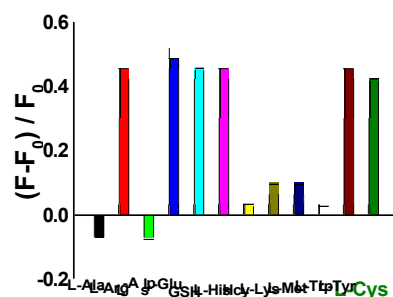


Fig. S9. Effect of different L-amino acids on the fluorescence intensity, using single L-Hyp@AuNCs as the fluorescent sensing probe.

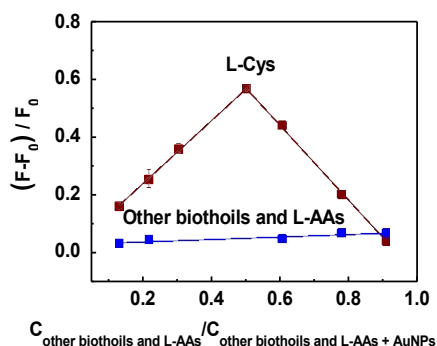


Fig. S10. Job's plot for L-Hyp@AuNCs-AuNPs with L-Cys or other biothoils and L-amino acids (L-AAs). The total concentration of mixture was kept at 0.23 mM.

Table S1 Comparison of different AuNCs probes for detection of L-Cys

AuNCs	Synthesis conditions	Wavelength (nm)		Linear range (μM)	Samples	Ref.
		λ_{EX}	λ_{EM}			
BSA@AuNCs-KI ₃	100 °C 8 min	480	640	0.0057-5.0	L-Cys and Hcy in human serum	J. Nebu, et al. <i>Anal Bioanal Chem</i> 2019, 411, 997
BSA@AuNCs-NBD	37 °C 12 h	480	540	8.3-100.0	L-Cys and Hcy in HeLa cells	H. Yu, et al. <i>New J Chem</i> 2017, 41, 4416
GSH@Au/AgNCs	80 °C 6 h	360	412/616	0.05-10.0	L-Cys and Hcy in human urine/ serum	M. W. Liu, et al. <i>Microchim Acta</i> 2018, 185,147
GSH@AuNCs	70 °C 24 h	360	575	0.4-120.0	L-Cys and Hcy in HeLa cells	Q. Lai, et al. <i>Microchim Acta</i> 2019, 186, 327
L-Hyp@AuNCs-AuNPs	100 °C 10 min	345	465	1.5-35.0	L-Cys in human serum	This work