Electronic Supplementary Information

Simple and Sensitive Fluorescence Sensing of Extreme Acidity Based on Inner Filter Effectof Ascorbic Acid to Fluorescent Au Nanoclusters

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Experimental section

Reagents

Bovine serum albumin (BSA) and L-ascorbic acid were bought from Sigma-Aldrich. HAuCl₄.3H₂O was purchased from Sinopharm Chemical Reagent Co., Ltd, (Shanghai, China). Histidine (His) and 1,1-mercaptoundcanoic acid (MUA) were purchased from Aladdin (Shanghai, China). Luria–Bertani (LB) medium, Agar, silver nitrate (AgNO₃), sodium borohydride (NaBH₄) and other chemicals were purchased from Chengdu Kelong Chemical Reagent Company (Chengdu, China). Na₂HPO₄-Citric Acid buffer solution was used for pH regulation. Ultrapure water (18.2 MΩ cm) was obtained from a water purification system (PCUJ-10, Chengdu Pure Technology Co., Ltd., Chengdu, China). All chemicals were of analytical grade and used directly without further purification.

Characterization

UV-vis absorption spectra were collected with a UV-1700 UV/Vis spectrophotometer (Shimadzu, Japan). The measurements of FL spectra were carried out on an F-7000 spectrofluorometer equipped with a plotter unit and a quartz cell (1 cm × 1 cm) (Hitachi, Japan). ¹H-NMR spectra were measured with an Avance II-600 MHz NMR spectrometer (Bruker Company, Switzerland) equipped with a 5 mm broad band observe probe. Fluorescence lifetime measurements were performed on a Fluorolog-3 spectrofluorometer (Horiba JobinYvon) with a spectra LED laser (280 nm, Horiba Scientific) as the excitation source and a picosecond photon detection module (PPD-850, Horiba Scientific) as the detector.`

Preparation of Au(Ag)NCs

All glassware was washed with Aqua Regia (HCl:HNO₃ volume ratio=3:1), and rinsed with ethanol and ultrapure water.

Alkanethiol-stabilized AuNCs¹ were synthesized through one-step fabrication. In brief, HAuCl₄ solution (0.3 mL, 10 mM) was added to His solution (5 mL, 40 mg/mL). After sufficient mixing, MUA (2 mL, 10 mM) was introduced, and then the mixture was incubation at room temperature for three days. The purified process is the same as BSA-AuNCs.

BSA modified AgNCs² were prepared by adding 5 mL of aqueous solution of AgNO₃ (0.01 M) to 5 mL of BSA solution (7.5×10^{-4} M) under vigorous stirring. After 2 min, 0.3 mL of NaOH (1 M) was added to the reaction mixture, and then NaBH₄ (0.01 M) was dropwised to the above solution until the color of the solution from colorless to reddish brown and keep the reaction for 5 min. The purified process is the same as BSA-AuNCs.

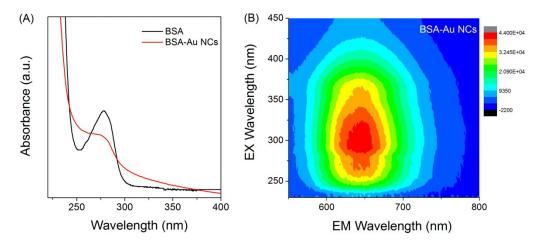


Fig. S1 Characterization of BSA-AuNCs: (A) UV-vis absorption; (B) 3D fluorescence spectra.

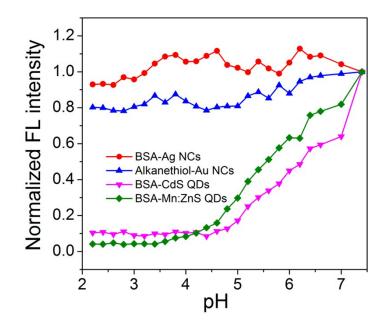


Fig.S2 The stability of fluorescent nanomaterials in acidic pH.

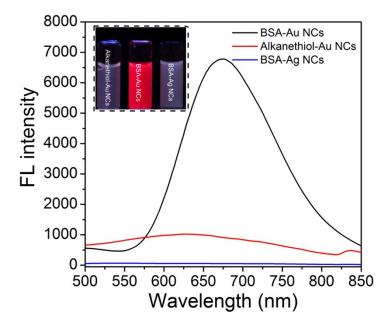


Fig.S3 FL emission spectra of metal clusters at the same concentration with exciting wavelength of 270 nm.

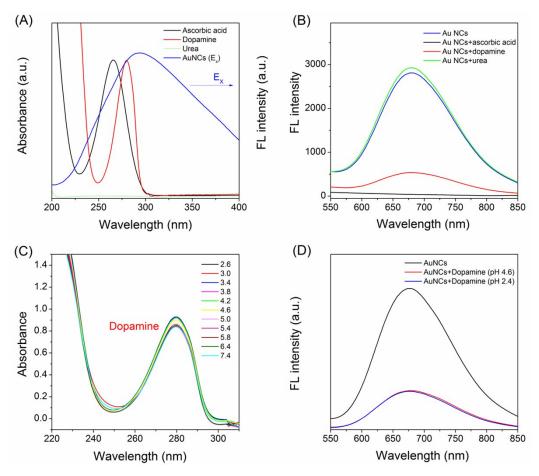


Fig. S4 The effect of redox potential molecules : (A) UV-Vis spectra of different redox potential molecules at pH 4.6; (B) fluorescence quenching of the Au NCs (10 μ M) by different redox potential molecules (1 mM) at pH 4.6; (C) absorption spectra of dopamine at different pH buffer; and (D) the modulation of the fluorescence responses of AuNCs by 1 mM dopamineat pH 2.4 and 4.6, respectively.

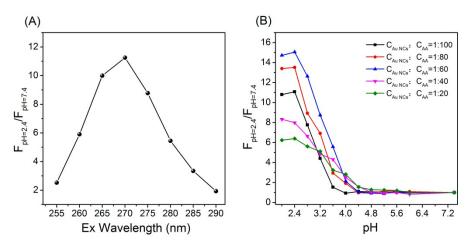


Fig. S5. Optimization of the IFE conditions: (A) excitation wavelength; and (B) proportion of absorberand fluorophore.

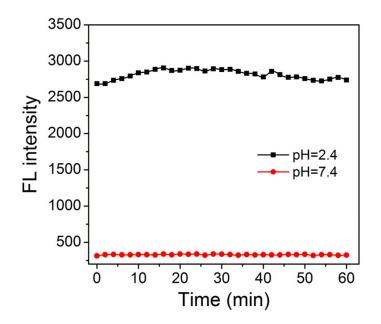


Fig. S6. The photostability of the probe at pH 7.4 and 2.4 (λ_{ex} = 270 nm, λ_{em} = 670 nm).

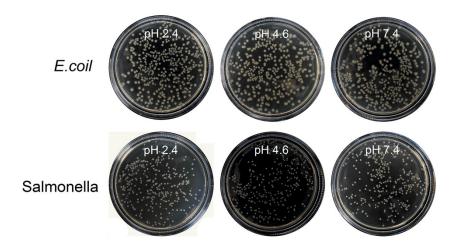


Fig. S7 Photographs of colonies of E. coli and Salmonella incubated on agar plates at acidic pH.

Table S1. Comparison with other methodologies

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Probe	Step of	Detection range	Ref
	synthesis	(pH)	
Organic dye 1	3	1.8-3.4,11.6-13.3	3
Organic dye 2	5	0.5-2.5	4
Organic dye 3	3	1.5-3.6	5
Fluorescent protein 1	3	1.7-4.1	6
Fluorescent protein 2	4	2-7	7
AuNCs+AA	1	2.4-4.6	This method

References

- 1. P. Bian, J. Zhou, Y. Liu and Z. Ma, *Nanoscale*, 2013, 5, 6161-6166.
- 2. S. Ghosh, U. Anand and S. Mukherjee, *Anal. Chem.*, 2014, 86, 3188-3194.
- 3. M. H. Su, Y. Liu, H. M. Ma, Q. L. Ma, Z. H. Wang, J. L. Yang and M. X. Wang, *Chem. Commun.*, 2001, 11, 960-961.
- 4. Y. Q. Tan, J. C. Yu, J. K. Gao, Y. J. Cui, Z. Y. Wang, Y. Yang and G. D. Qian, *RSC Adv.*, 2013, 3, 4872-4875.
- 5. L. Fan, S. Q. Gao, Z. B. Li, W. F. Niu, W. J. Zhang, S. M. Shuang and C. Dong, *Sens. Actuator B-Chem.*, 2015, 221, 1069-1076.
- 6. M. Y. Yang, Y. Q. Song, M. Zhang, S. X. Lin, Z. Y. Hao, Y. Liang, D. M. Zhang and P. R. Chen, *Angew. Chem.-Int. Edit.*, 2012, 51, 7674-7679.
- 7. M. Y. Yang, A. S. Jalloh, W. Wei, J. Zhao, P. Wu and P. R. Chen, *Nat. Commun.*, 2014, 5, 10.