Electronic Supplementary Information

Histidine-Triggered Turning-On of Gold/Copper Nanoclusters Fluorescence for Sensitive and Selective Detection of Histidine

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Contents

Supplementary information includes the experimental details including the materials and apparatus, the synthesis of Au/Cu NCs, characterization of His-induced fluorescence turn-on, and calibration curve and fluorimetric analysis of His in real samples. Figures are provided for the synthetic conditions of Au/Cu NCs, and the optimization of analysis conditions. Tables are provided for comparison of analytical performance for His and analysis of His in real samples.

1. Experimental section

Materials and reagents

Bovine serum albumin (BSA), copper sulfate pentahydrate ($CuSO_4$ $5H_2O$), and tetrachloroauric acid ($HAuCl_4$, 99.9%) were bought from Sigma–Aldrich (Shnaghai, China). Histidine (His), methionine (Met), asparagines (Asn), alanine (Ala), lysine (Lys), serine (Ser), leucine (Leu), glycine (Gly), phenylalanine (Phe), tryptophan (Trp), threonine (Thr), glutamate (Glu), arginine (Arg), trytophan (Try), valine (Val), and cysteine (Cys) as well as glutathione (GSH) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All of the other chemicals are of analytical grade, and all glasswares were cleaned by aqua regia and ultrapure water before use.

Apparatus

The fluorescence spectra were performed with F-7000 Fluorescence spectrophotometer (Hitachi, Japan). The absorbance spectra were conducted using U-2910 spectrophotometer (Hitach, Japan). The morphology of Au/Cu NCs was characterized with a transmission electron microscope (TEM) (Tecnai G2 F20 S-TWIN, FEI, USA) at 100 kV.

To prepare Au/Cu NCs

10 mM of $HAuCl_4$ solution (2.0 mL) was added into BSA aqueous solution (2.0 mL, 20 mg mL^{-1}) under vigorous stirring for 15 min. Then, $CuSO_4$ solution (0.80 mL, 9.0 mM) was dropwise syringed into above solution under vigorous stirring at 37 ℃. Afterwards, 1 M NaOH solution (0.20 mL) was introduced into above mixture and incubated at 37 ℃ for 8 h. Finally, the resultant solution was dialyzed against water for 24 h. The thus-yielded Au/Cu NCs was stored in darkness at 4 ^{o}C.

To characterize His-induced fluorescence turn-on

The His-induced fluorimetric turn-on efficiencies were recorded by an F-7000 Fluorescence spectrophotometer. Fluorimetric turn-on efficiency = $(F-F_0)/F_0 \times 100\%$, where F_0

and F are meant fluorimetric intensities of the Au/Cu NCs without and with His, respectively. The detection conditions for His were optimized, including concentrations of Au/Cu NCs, pH values, temperature and ionic strengths. The control experiments were performed by mixing Au/Cu NCs separately with His (500 nM) or different substates (each 10 μM) of amino acids (Met, Cys, Ala, Lys, Arg, Asp, Ser, Thr, Leu, Phe, Trp, Glu, Tyr, Gly, Val, and Asn) and GSH, their fluorescence intensities at 620 nm were measured for comparison.

Calibration curve and fluorimetric analysis of His in real samples.

Au/Cu NCs (100 μL, 2.0 mM) and His (100 μL, 500 nM) were mixed, fluorescence emission peaks at 620 nm were measured. The fluorescence turn-on efficiency was calculated. After that, the experimental procedure was the same as above, except to change the concentration of His.

The real sample was measured by standard addition method. Blood and urine samples, which were provided by the affiliated hospital of Qingdao University by collecting from healthy volunteers with informed consent. First, His standard solution was added to the sample solution, and then calculated recovery after measurement, in which experimental conditions are all optimized.

2. Supplementary figures:

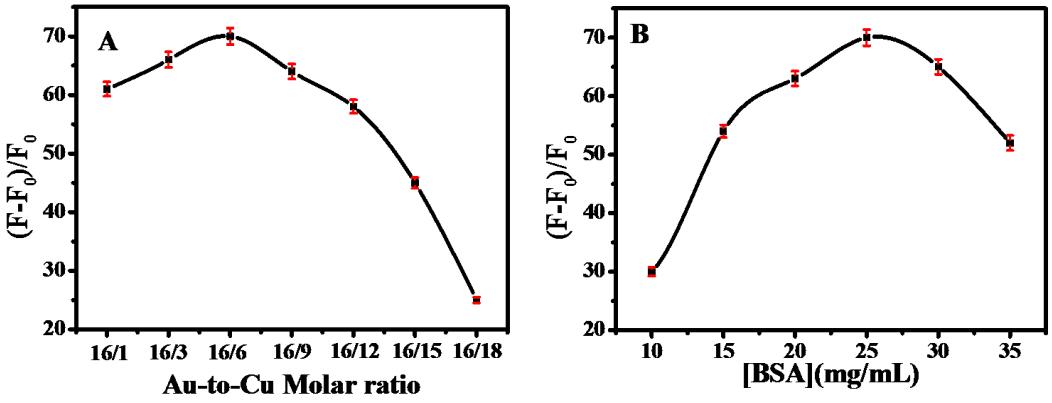

Fig S1. Effects of (A) Au-to-Cu molar ratio and (B) BSA dosage on the preparation of Au/Cu NCs on the fluorimetric turn-on efficiencies.

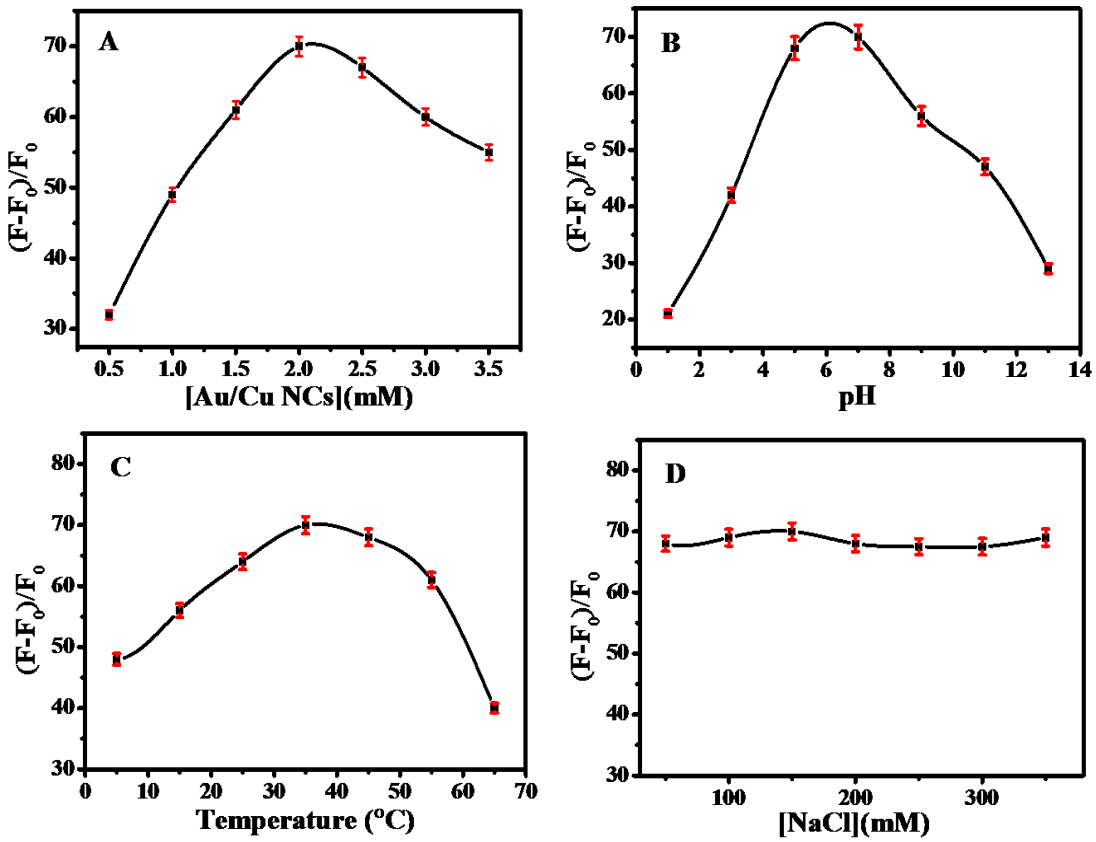

Fig S2. Effects of (A) Au/Cu NCs dosage, (B) buffer pH, (C) Temperature, and (D) ionic strength (in NaCl concentration) on the fluorimetric turn-on efficiencies of Au/Cu NCs-His. Au/Cu NCs, 2.0 mM; His, 500 nM.

3. Supplementary Tables:

Table S1. Comparison of analytical performance for His by different methods

Materials	Analysis methods	Linear range (nM)	LODs (nM)	Reference
Imidazole-functionalized silicon QDs	Colorimetry	10–1000	10	1
SAA-AgNPs	Colorimetry	500–3500	57	2
MWCNTs	Electroanalysis	200–10000	5.8	3
Cu MOFs	Electroanalysis	100– 200000	25	4
Nitrogen-doped carbon nanoparticle	Fluorimetry	500–60000	150	5
ZnS QDs	Fluorimetry	1250–30000	740	6
Pyrene–naphthalene conjugate	Fluorimetry	10–10000	10	7
Vitamin B6 derivative	Fluorimetry	0-3000	300	8
Au/Cu NCs	Fluorimetry	3.0 –10000	0.9	This work

Table S2 Analysis of His in real samples

Sample	Spiked (μM)	Detected (μM)	RSD (%, n=5)	Recovery (%)
Urine	0	0.58 ±0.018	3.07	—
	2	2.53 ±0.066	2.60	97.5
	4	4.65 ±0.096	2.06	101.75
Human serum	0	0.98 ±0.031	3.19	—
	2	3.19 ±0.093	2.93	110.5
	4	5.19 ±0.098	2.28	105.25

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