

**Visual Test of Subparts per Billion-level Copper(II) by Fe₃O₄
Magnetic Nanoparticle-Based Solid Phase Extraction Coupled
with a Functionalized Gold Nanoparticle Probe**

Supplementary Information

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Experimental Section

Chemicals and Materials.

Cu(II) standard solutions were prepared by sequential diluting stock standard solution of 1000 µg/mL Cu(II) (GBW 08615, National Research Center for Certified Reference Materials, China) with water. Iron(II) sulfate, sodium hydroxide and potassium nitrate were obtained from Xilong Chemical Reagents Co. (Shantou, China). Ammonium pyrrolidinedithiocarbamate (PDC) was purchased from Alfa-Aesar, USA). L-cysteine was bought from Sigma (USA). Hydrogen tetrachloroaurate, sodium citrate, sodium chloride, citric acid and sodium phosphate dibasic were purchased from Sinopharm Chemical Reagent Co. (Beijing, China). All the chemicals were of analytical grade at least, and used as received without further purification.

Sample Collection and Preparation

To examine the applicability of the proposed method, Cu(II) concentrations in three real water samples including tap water, river water and effluent of wastewater treatment plant were tested. Tap water was collected in our laboratory after flowing for about 5 min. River water was collected from Songhua River (Heilongjiang, China). The effluent of treated wastewater was obtained from the Qinghe wastewater treatment plant (Beijing, China). Before extraction, the river water and the effluent were filtered through 0.25 µm micropore membranes.

Instruments

A permanent magnet with strength of 0.2 T was used for separation. An ultrasonic bath (KQ-300DE) used for mixing was from Kun Shan Ultrasonic Instruments Co., Ltd (Kunshan, China). The pH-meter (Orion 4 star, Thermo) was used for adjusting pH of extraction and chromogenic solvents. A multimode microplate spectrophotometer with a 96-well plate (Varioscan Flash, Thermo) was employed to record the absorbance. Both Fe₃O₄ NPs and Cys-AuNPs were characterized by TEM (H-7500, Hitachi, Japan) at 80 kV. The Zeta potential of Fe₃O₄ NPs was determined by Zetasizer Nano instrument (ZEN3600, Malvern). A vibrating sample magnetometer (VSM, LDJ9600) was used to describe magnetization curves of Fe₃O₄ NPs. Inductively

coupled plasma mass spectrometry (ICPMS, Agilent 7500ce) was applied to validate results got by the proposed method.

Preparation of Fe₃O₄NPs

Fe₃O₄ NPs were prepared by coprecipitation.¹ Briefly, in an oxygen-free environment, 10 mL of 2.0 M KNO₃ and 10 mL of 1.0 M NaOH were firstly added into 80 mL of FeSO₄ (0.7 g) solution, which quickly gave rise to a color change of the mixture to deep green. Then, the mixture was heated to 90°C and further incubated for 2 h, during which the solution color changed into black gradually which indicate the formation of Fe₃O₄ NPs. After that, the reactant solution was cooled to room temperature, and the prepared Fe₃O₄ NPs were separated by a permanent magnet from the reactant solution. The black collection was repeatedly washed with water until the upper solution appeared clear. Finally, Fe₃O₄ NPs were suspended into 80 mL water and stocked for use. The concentration of Fe₃O₄ NPs in this stock suspension was about 2.4 g/L. TEM (H-7500, Hitachi, Japan) analysis showed that particles sizes of Fe₃O₄ NPs were about 30 nm (Fig. S1A). Magnetic hysteresis curve (Fig. S1C) indicates that the prepared Fe₃O₄ NPs has strong magnetism and can easily separated form the bulk solution with common permanent magnets.

Preparation of Cys-AuNPs

AuNPs were synthesized by reduction of HAuCl₄ with sodium citrate.² In brief, 250 mL of 1 mM HAuCl₄ was heated to boiling for 30 min. Then, 25 mL of 38.8 mM trisodium citrate was added into the boiling solution quickly, during which the color of the mixture changed form light yellow to deep red. After that, the mixture was heated for another 30 min. Finally, the obtained AuNPs solution was cooled to room temperature under stirring. Cys-AuNPs were prepared as literature.³ Into 10 mL of the above obtained AuNP solution was added 200 μL L-cysteine (0.5 mM) under stirring, and the mixture was further stirred for 2 h at room temperature. TEM (H-7500, Hitachi, Japan) analysis showed that the average particles sizes of Cys-AuNPs were 15 nm (Fig. S1B). The concentration of Cys-AuNPs estimated form Beer's law was 15 nM.⁴

M-SPE of Cu(II) by Fe₃O₄NPs

Into 200 mL Cu(II) standard or sample solution (pH 8.0) was added NaCl (1%, w/v) and Fe₃O₄NPs (12.5 mg/L). After shaking at 200 rpm for 10 min, the Fe₃O₄NPs capturing Cu(II) were magnetically separated and transferred into a 10 mL centrifugal tube, and the upper water phase was discarded.

Colorimetric Test of Cu(II) with Cys-AuNPs

Into the centrifugal tube with the separated Fe₃O₄NPs was added 120 µL of 0.2 M tris-H₃BO₃ buffer solution (pH 8.5) and 80 µL of Cys-AuNP stock solution (15 nM), and mixed ultrasonically for 8 min to enhance interaction. Then, the mixture was separated by a magnet for 3 min, and the Cu(II) concentration can be determined by visual test the reduction of the reddish color of the upper solution.

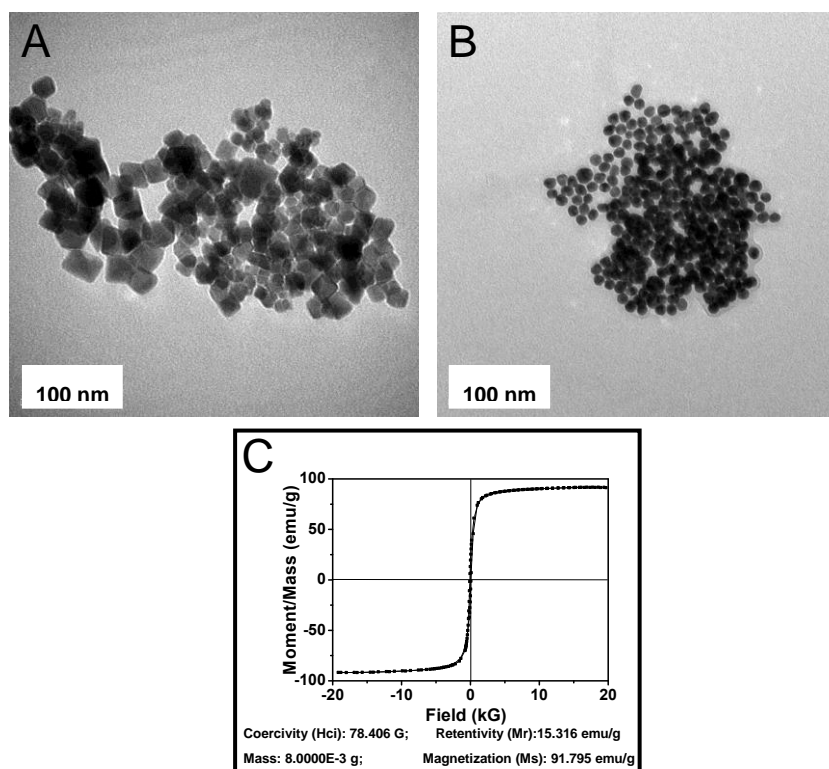


Fig. S1 Characterization of the synthesized nanomaterials. (A), TEM image of Fe₃O₄NPs; (B), TEM image of Cys-AuNPs; (C), magnetic hysteresis curve of Fe₃O₄NPs.

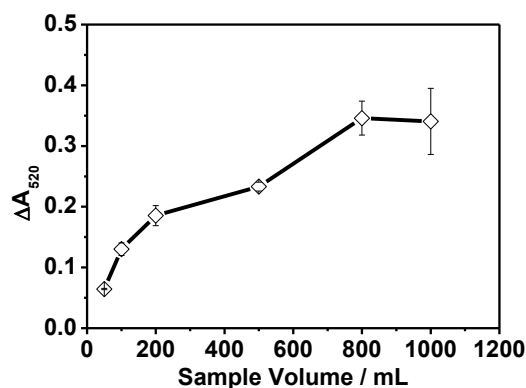


Fig. S2 Effect of sample volume on the extraction efficiency of Cu(II) represented by ΔA_{520} .

Sample: 1.0 $\mu\text{g/L}$ Cu(II) in tris-HCl buffer solution (pH=8.0), 2.5 μM PDC and 12.5 mg/L Fe_3O_4 NPs; extraction time and shaking rate: 30 min at 250 rpm; separation: 3 min by a common permanent magnet; chromogenic reagent: 7.5 nM Cys-AuNPs; desorption: ultrasonic (10 min).

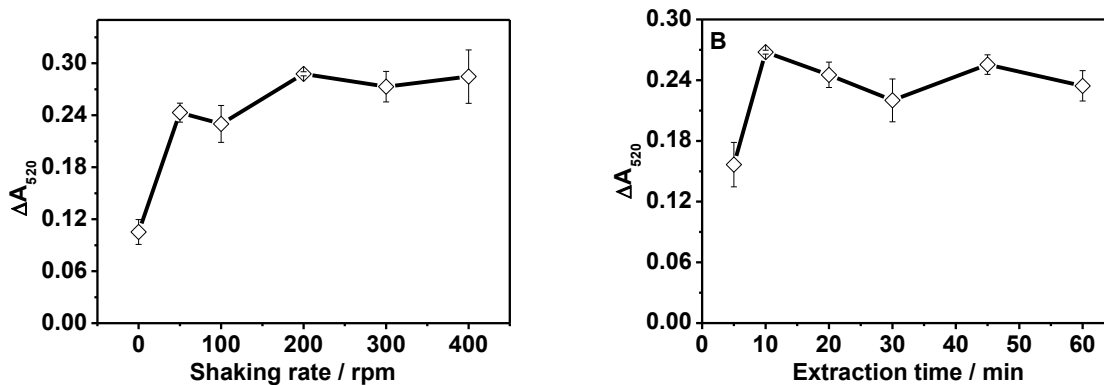


Fig. S3 Effects of shaking rate (A) and time (B) on the extraction efficiency of Cu(II) represented by ΔA_{520} .

Sample: 200 mL of 1.0 $\mu\text{g/L}$ Cu(II) in tris-HCl buffer solution (pH=8.0), 2.5 μM PDC and 12.5 mg/L Fe_3O_4 NPs; separation: 3 min by a common permanent magnet; chromogenic reagent: 7.5 nM Cys-AuNPs; desorption: ultrasonic (10 min).

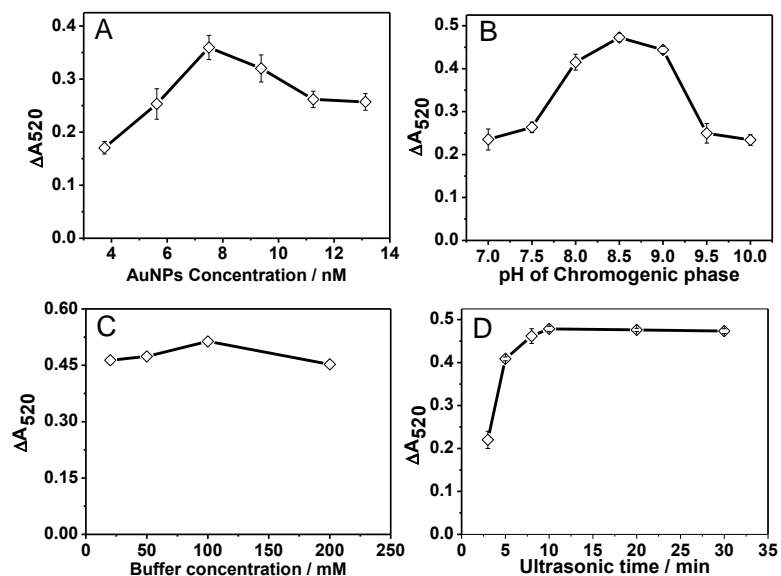


Fig. S4 Optimization of chromogenic reaction conditions including Cys-AuNPs concentration (A), pH of Cys-AuNPs solution (B), buffer concentration (C), and desorption time (D). Sample: 200 mL reagent water spiked with 1.0 $\mu\text{g/L}$ Cu(II) in tris-HCl buffer solution (pH=8.0), 2.5 μM PDC, 12.5 mg/L Fe_3O_4 NPs and 1% NaCl (w/v); extraction time and shaking rate: 30 min at 200 rpm; separation: 3 min by a common permanent magnet.

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