

Article

A Multifunctional Magnetic Fluorescent Nanoprobe for Copper(II) Using ZnS-DL-Mercaptosuccinic Acid-Modified Fe₃O₄ Nanocomposites

Ping Xu ^{1,†}, Xin Chen ^{1,†}, Jie Chen ² , Shihua Yu ¹ , Xiaodan Zeng ² and Zhigang Liu ^{2,*}

¹ School of Chemical and Pharmaceutical Engineering, Jilin Institute of Chemical Technology, Jilin 132013, China; 13404490243@163.com (P.X.); xinxinchen22@163.com (X.C.); ysh@jlicet.edu.cn (S.Y.)

² Center of Characterization and Analysis, Jilin Institute of Chemical Technology, Jilin 132013, China; jiechendr@163.com (J.C.); jiangzxd@163.com (X.Z.)

* Correspondence: lzg@jlicet.edu.cn

† These authors contributed equally to this work.

Abstract: Cu²⁺ has increasingly become a great threat to the natural environment and human health due to its abundant content and wide application in various industries. DL-Mercaptosuccinic acid and ZnS-modified Fe₃O₄ nanocomposites were designed, synthesized, and applied in the determination of Cu²⁺. The prepared nanocomposites were characterized by scanning electron microscopy (SEM), transmission electron microscopes (TEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffractometer (XRD), X-ray photoelectron spectroscopy (XPS), vibrating sample magnetometer (VSM), and thermogravimetric analyzer (TG). The magnetic fluorescent nanoprobe exhibited highly selective and sensitive fluorescence-quenching characteristics with Cu²⁺ ions. The fluorescence detection linear range was 0–400 μM, with the detection limit being 0.489 μM. In addition, the magnetic fluorescent nanoprobe exhibited a high adsorption and removal rate for Cu²⁺. It had been successfully applied to detect Cu²⁺ in real water samples with a satisfactory recovery rate. The magnetic fluorescent nanoprobe could simultaneously realize the functions of enrichment, quantitative detection, and separation, reduce the pollution of copper ions and probes, and establish an environment-friendly detection method. Consequently, the magnetic fluorescent nanoprobe offered a new pathway for the removal and detection of not only Cu²⁺ but also other heavy metal ions in water.

Keywords: Fluorometric detection; magnetic separation; Fe₃O₄; copper(II); nanocomposites



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1. Introduction

Copper is an essential trace element and active component in the human body and plays an important role in signal pathways, multiple cell matrices, and other varieties of chemical, biological, and environmental systems [1–3]. It is an important catalytic cofactor for many metalloenzymes, including tyrosinase, ceruloplasmin, cytochrome, superoxide dismutase c-oxidase, and carbon monoxide dehydrogenases [4]. At the same time, low concentrations of copper absorption are necessary factors for the typical growth of active systems. Another biological importance of copper is that it is used randomly for agricultural, industrial, medicinal, and domestic purposes. Despite their importance, the wide use of Cu²⁺ in industry, which leads to excessive Cu²⁺ ions in the body, causes mild toxicity to the living organism, organ damage, and disruption of the body's metabolism. It can cause various detrimental effects, including Alzheimer's disease, asthma, pneumonitis, and central nervous system disorders, as well as Wilson's disease, lung cancer, and Parkinson's disease [5]. Therefore, the contamination of water bodies by copper ions (Cu²⁺) has become a significant component of environmental pollutants and an increasing threat to ecological systems and human health. The acceptable concentration of Cu²⁺ ions in portable water,

recommended by the World Health Organization (WHO), should be below 31.5 μM [6]. Therefore, research on the detection and determination of Cu^{2+} ions has attracted more and more attention. The development of a fast and convenient method for the identification of Cu^{2+} has become a particularly important demand.

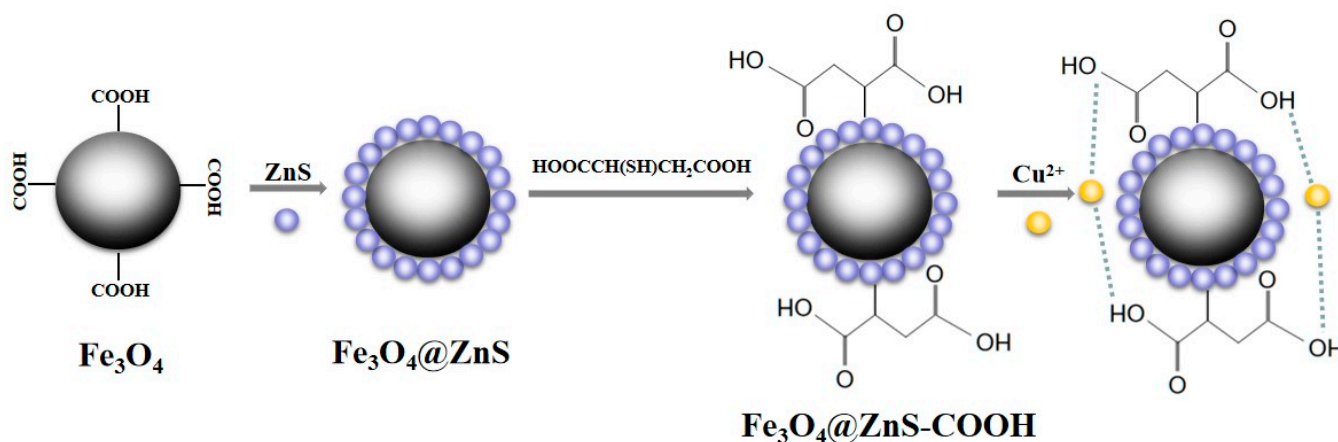
Though some traditional analytical methods with high sensitivity, such as graphite furnace atomic absorption spectrometry (GFAAS) [7], inductively coupled plasma emission spectroscopy (ICP-ES) [8], atomic absorption spectroscopy (AAS) [9], and chromatography, have been introduced to detect Cu^{2+} ions, they are time-consuming, have high repairing costs of tools, require expensive instruments and trained operators, and have complicated sample-making processes. These significant drawbacks make them not very convenient to use and apply.

In this situation, the selective and sensitive detection of Cu^{2+} has gradually become an important environmental chemistry research area. The fluorometric probes for recognizing Cu^{2+} ions have gained more and more attention in recent years; they have become a powerful sensing tool due to their easy operation, fast response time, high sensitivity, excellent selectivity, and technical simplicity with an obvious signal that can be seen with the naked eye and potential applications in biological and environmental systems [10,11]. Various small molecule fluorophores have been designed as probes to detect heavy metal ions based on fluorescence change; for example, single organic fluorophore molecules [12,13], fluorescent polymers [14], quantum dots [15], and covalent organic frameworks [2]. However, most of these fluorescent methodologies might be disturbed by changes in environmental conditions like the pH and other paramagnetic metal ions and cannot eliminate interference from other metal ions effectively, which greatly limits their potential applications. More importantly, these fluorescent probes cannot be separated from the detection system, which introduces further pollution to the environment. In this regard, developing versatile fluorescent probes to selectively detect and effectively remove heavy metal ions would be highly necessary.

As the Fe_3O_4 particles are especially reactive and their magnetic forces are reduced, the Fe_3O_4 particles are usually coated with a solid layer and thus build up a core-shell structure to prevent this reduction. Core-shell-nanostructure Fe_3O_4 nanoparticles ($\text{Fe}_3\text{O}_4\text{NPs}$) have been extensively studied and widely utilized in biosensors or adsorbents to remove dyes, heavy metals ions, and pharmaceuticals because of their facile preparation, superparamagnetic property, high facile magnetic recovery, high surface area, size regulation, high adsorption ability, biocompatibility, and easy preparation [16–18]. Thus far, more and more surface-coating Fe_3O_4 nanoparticles have been synthesized to improve the biocompatibility and multi-function. Zinc sulfide (ZnS) is one of the most commonly used as a solid coat due to its good thermal stability, high electric mobility, excellent transport properties, and the presence of polar surfaces [19,20]. Many new nanomaterials combined ZnS with various nanostructures and have been used in a wide range of applications because of their unique physical properties. At the same time, ZnS has been widely used in the design of fluorescence sensors because of its excellent thermal stability, adjustable fluorescence characteristics, high fluorescence quantum yield, as well as its non-toxic, stable chemical structure [21–23].

Considering that most fluorescent probes will bring secondary pollution to the environment when recognizing copper, we applied Fe_3O_4 as the core structure of the probe for the magnetic separation property and ZnS as the shell structure of the probe, and then a fluorescence probe with multiple functions of enrichment, separation, and detection was designed to solve the problem (Scheme 1). This magnetic fluorescent nanoprobe showed high sensitivity and selectivity to Cu^{2+} , and there was a good linear relationship in the concentration range from 0 to 400 μM , with the limit of detection (LOD) being 0.489 μM . This magnetic fluorescent nanoprobe was successfully used to detect Cu^{2+} in actual water samples with a satisfactory recovery rate. The magnetic fluorescent nanoprobe could enrich, detect, and separate the heavy metal ions at the same time and reduce secondary

pollution caused by the probe in an environmentally friendly way with high selectivity. It also provided a new way to detect and treat other heavy metal ions in water.



Scheme 1. Fabrication of $\text{Fe}_3\text{O}_4@\text{ZnS-COOH}$.

2. Materials and Methods

2.1. Materials

Ferric chloride (FeCl_3 , $\geq 99\%$), trihydrate sodium acetate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$, $\geq 99\%$), ethylene glycol (EG, $\geq 99\%$), zinc acetate ($\text{Zn}(\text{ac})_2$, 99%), sodium sulfide (Na_2S , 99%), polyethylene glycol 2000, and DL-Mercaptosuccinic acid were obtained from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China).

2.2. Adsorbent Characterization

$\text{Fe}_3\text{O}_4@\text{ZnS}@\text{DL-Mercaptosuccinic acid}$ nanoparticles were analyzed by SEM (Quanta 200, FEI, Waltham, MA, USA) and TEM (JEM 2100, JEOL, Tokyo, Japan) to characterize their morphological structures. The FTIR (Thermo Scientific Nicolet IS50, Thermofisher, Waltham, MA, USA), XRD (D8FOCUS, Bruker, Berlin, Germany), and XPS (Krayos AXIS Ultra DLDX, Shimadzu, Kyoto, Japan) analyses were used to determine the crystal structures and chemical compositions of the $\text{Fe}_3\text{O}_4@\text{ZnS-COOH}$ nanoparticles. A VSM (7404 vibrating sample magnetometer, LakeShore, Carson, CA, USA) was used to acquire the magnetic characterization of the nanoparticles. TG (Discovery SDT650 synchronous TGA-DTA instrument, TA, New Castle, DE, USA) was used to determine the groups of DL-Mercaptosuccinic acid groups on the surface of the materials. A fluorescence spectrometer was used to measure the fluorescence intensity of $\text{Fe}_3\text{O}_4@\text{ZnS-COOH}$. AAS (ICP-OES: Thermo Fisher iCAP 7400, Thermofisher, Waltham, MA, USA) was used to measure the concentrations of Cu^{2+} in the adsorption solution.

2.3. Synthesis of Fe_3O_4 Nanoparticles

FeCl_3 (2.7 g) and $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ (7.2 g) were dispersed in EG (60 mL). Magnetic stirring (30 min) and sonication (30 min) were performed to promote dispersion. Then, the solution mixture was transferred to a 100 mL autoclave and heated at 200°C for 12 h. After the solution was left to cool to 25°C in the autoclave, the Fe_3O_4 NPs were obtained by magnetic separation, washed with distilled water and ethanol, and then oven-dried at 80°C for 6 h for further modification.

2.4. Synthesis of $\text{Fe}_3\text{O}_4@\text{ZnS}$ Nanoparticles

Fe_3O_4 and ZnS, with a certain weight ratio, were dissolved in deionized water, and then the two solutions were mixed. The reaction was continuously stirred at 80°C for 60 min and then ultrasonically treated at 50°C for 90 min. Subsequently, the resulting product was washed at least once by centrifugation at 1500 rpm for 12 min using deionized

water and ethanol. Finally, the collected black precipitate was dried at 60 °C for 12 h, and then the product was ground into fine powder to prepare the Fe₃O₄@ZnS magnetic fluorescent nanoparticles.

2.5. Synthesis of Fe₃O₄@ZnS-COOH Nanoparticles

A certain amount of Fe₃O₄@ZnS was taken to make it into an ethanol dispersion. A total of 5 mL of the Fe₃O₄@ZnS ethanol solution was placed into a round-bottom flask. Then, 5 mL of the DL-Mercaptosuccinic acid (75.074 mg, 0.1 mmol/L) ethanol solution was added. Then, the mixture was stirred in a water bath at 40 °C for 4 h in the dark. After the item was attracted by a magnetic force, it then underwent a thorough cleansing process with ultrapure water and ethanol. The prepared Fe₃O₄@ZnS-COOH microspheres were added to water to make a dispersion solution.

2.6. The Selective and Competitive Experiments

The interactions between Fe₃O₄@ZnS-COOH (0.2 mg/mL) and different metal ions (Cu²⁺, Co²⁺, Pb²⁺, Ni²⁺, Hg²⁺, Al³⁺, Cd²⁺, Zn²⁺, Fe²⁺, Fe³⁺, K⁺, Ca²⁺, and Na⁺) were investigated by designing selective experiments. In addition, the influence of different types of metal ions (Cu²⁺, Co²⁺, Pb²⁺, Ni²⁺, Hg²⁺, Al³⁺, Cd²⁺, Zn²⁺, Fe²⁺, Fe³⁺, K⁺, Ca²⁺, and Na⁺) on the interaction of Fe₃O₄@ZnS-COOH with Cu²⁺ was also explored. The concentrations of Cu²⁺ and different metal ions were 400 µM.

2.7. Adsorption Experiments

First, a Fe₃O₄@ZnS-COOH aqueous suspension was prepared using sonication with the pH regulated to 7.0. For the adsorption experiment, the Fe₃O₄@ZnS-COOH (0.2 mg/mL) suspension and different Cu²⁺ ion solutions were added to a conical flask and placed in a thermostatic shaker (200 rpm) for 12 h at room temperature. After the adsorption process was complete, the Fe₃O₄@ZnS-COOH was separated by an external magnet. The ion adsorption amount (Q, mg/g) was determined and calculated using the equation $Q = (C_0 - C) \times V/m$. Then, the remove rate (R, %) was calculated by the equation: $R = (C_0 - C)/C_0$, where m (g) defines the mass of Fe₃O₄@ZnS-COOH, C₀ (mg/L) is the initial concentration of Cu²⁺ ions in the solution, C (mg/L) is the final Cu²⁺ ion concentration in the solution, and V (L) is the volume of the solution.

3. Results and Discussion

3.1. Characterization of Fe₃O₄, Fe₃O₄@ZnS, and Fe₃O₄@ZnS@DL-Mercaptosuccinic

The morphologies of Fe₃O₄, Fe₃O₄@ZnS, and Fe₃O₄@ZnS@DL-Mercaptosuccinic acid were analyzed by SEM (first line) and TEM (second line). As shown in Figure 1a–c, with the number of layers increased, all materials were still spherical. The commercial Fe₃O₄, with a diameter distribution from 150 to 250 nm, reveals that Fe₃O₄ MNPs have a regular and uniform distribution. The particle diameter of the three samples increased, accompanied by more rougher surfaces and more irregular fine particles. In addition, a TEM image (Figure 1c second line) of Fe₃O₄@ZnS-COOH, with a diameter distribution from 200 to 300 nm, was achieved. It can be concluded that the introduction of ZnS and DL-Mercaptosuccinic acid improved the crystal growth process of Fe₃O₄, leading to the changes in morphologies observed in materials.

FTIR spectroscopy was applied to identify the functional groups of these nanoparticles, and the results are illustrated in Figure 1d. It can be seen in Figure 1d that the FTIR spectra of the bare ZnS showed characteristic peaks at 640 and 716 cm^{−1}. The spectra of the Fe₃O₄@ZnS-COOH composites were highly similar to ZnS at these two peaks. The typical peaks around 584 cm^{−1}, referring to the Fe-O bond vibration, could also be found in Fe₃O₄ and Fe₃O₄@ZnS-COOH. Finally, the peaks at around 1550 cm^{−1} were attributed to the stretching vibration of the C=O bonds that may originate from the residual Fe₃O₄ on the surface of the particles [24]. As can be seen from the comparison of Fe₃O₄@ZnS-COOH and DL-Mercaptosuccinic acid, two typical peaks at about 1728 cm^{−1} and about

2930 cm^{-1} could be found. The peaks at about 1728 cm^{-1} and 2930 cm^{-1} were assigned to the vibration of the -COOH and C-H bonds, which are supposed to stem from the residue of DL-Mercaptosuccinic acid. The results proved that the magnetic nanoparticles $\text{Fe}_3\text{O}_4\text{@ZnS@DL-Mercaptosuccinic acid}$ had been successfully synthesized.

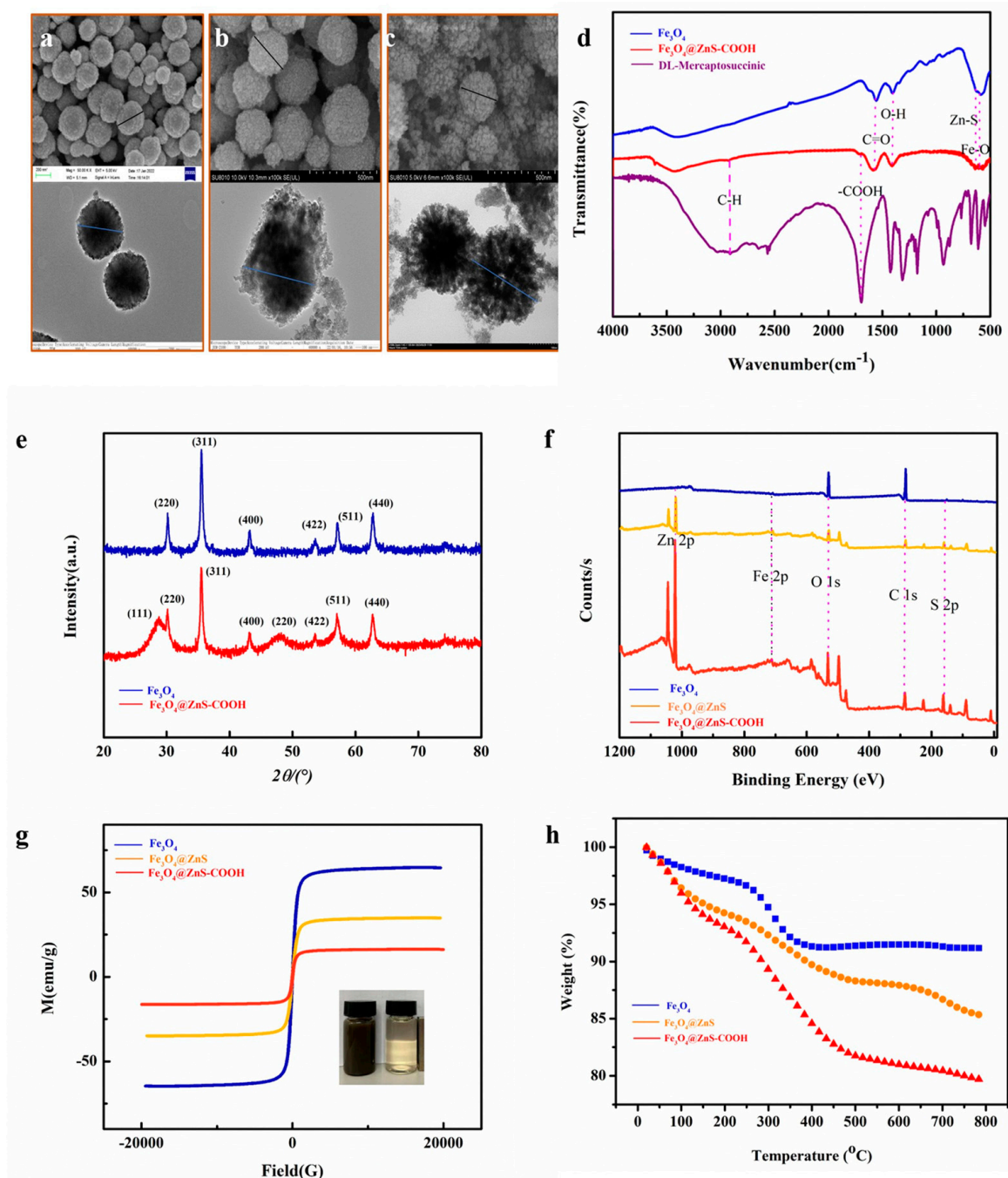


Figure 1. (a) SEM and TEM images of Fe_3O_4 ; (b) SEM and TEM images of $\text{Fe}_3\text{O}_4\text{@ZnS}$; (c) SEM and TEM images of $\text{Fe}_3\text{O}_4\text{@ZnS@DL-Mercaptosuccinic}$; (d) FTIR spectra of Fe_3O_4 , $\text{Fe}_3\text{O}_4\text{@ZnS}$, and $\text{Fe}_3\text{O}_4\text{@ZnS@DL-Mercaptosuccinic}$; (e) XRD patterns of Fe_3O_4 and $\text{Fe}_3\text{O}_4\text{@ZnS}$; (f) XPS spectra of Fe_3O_4 , $\text{Fe}_3\text{O}_4\text{@ZnS}$, and $\text{Fe}_3\text{O}_4\text{@ZnS@DL-Mercaptosuccinic}$; (g) hysteresis loops of Fe_3O_4 , $\text{Fe}_3\text{O}_4\text{@ZnS}$, and $\text{Fe}_3\text{O}_4\text{@ZnS@DL-Mercaptosuccinic}$; (h) thermogravimetric analysis curves of Fe_3O_4 , $\text{Fe}_3\text{O}_4\text{@ZnS}$, and $\text{Fe}_3\text{O}_4\text{@ZnS@DL-Mercaptosuccinic}$.

To determine the crystal structure of the synthesized material, XRD analysis was used to characterize Fe_3O_4 and $\text{Fe}_3\text{O}_4\text{@ZnS}$. The results are illustrated in Figure 1e. The results

showed that the peaks at about 30.1° , 35.6° , 43.1° , 53.7° , 57.1° , and 62.8° were found in all diffraction patterns, which could be attributed to the (220), (311), (400), (422), (511) and (440) planes of Fe_3O_4 , respectively. The peaks at about 28.9° , 47.7° , and 57.0° were attributed to the characteristic peaks of (111), (220), and (311) of ZnS [25]. The peaks of the $\text{Fe}_3\text{O}_4@\text{ZnS}$ (in Figure 1e) could be seen with the slightly decreased intensity of typical peaks, and the positions of the peaks were unchanged. The results suggested that the coating of the ZnS and DL-Mercaptosuccinic acid layers did not disrupt the crystalline structure of Fe_3O_4 .

Figure 1f shows the XPS full spectrum of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{ZnS}$, and $\text{Fe}_3\text{O}_4@\text{ZnS}@$ DL-Mercaptosuccinic acid nanoparticles, indicating the presence of five elements (Fe, O, Zn, S, and C). The XPS spectrum of the Fe 2p characteristic peak was at 709.8 eV. The XPS spectrum of O1s, with a peak at 529.6 eV, is attributed to the O and Fe-O bonds. The binding energy peaks at 1019.2 eV are attributed to the spin-orbital splitting of Zn^{2+} [26]. The binding energy peaks at 159.2 eV correspond to S 2p_{3/2} and S 2p_{1/2}, indicating S^{2-} in the samples. The peaks at the binding energies of 282.7 eV come from the carbon and carboxyl functional groups of DL-Mercaptosuccinic acid.

The response of the materials to an external applied magnetic field is decided by saturation magnetization, which significantly affects the efficiency of magnetic separation in aqueous solution. Therefore, these three types of magnetic nanoparticles were analyzed by VSM, and the results are shown in Figure 1g. With the externally applied magnetic field changing from -20 kOe to 20 kOe, the saturation magnetization of the samples decreased from 64.5 ± 0.1 emu/g to 34.7 ± 0.1 emu/g and 16.3 ± 0.1 emu/g, along with the core-shell structure thickening gradually. They all showed typical hysteresis loops and superparamagnetic properties. Though the enlarged particle diameter hampered the magnetic performance of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{ZnS}@$ DL-Mercaptosuccinic still possessed excellent magnetism, making this magnetic nanomaterial a promising detection and separation tool.

These three types of magnetic nanoparticles were estimated by TGA, and the results are shown in Figure 1h. The initial weight loss at 20 – 140 °C was ascribed to the evaporation of water molecules in the polymer matrix. The second weight loss that occurred between 120 and 800 °C was about 14%, which could be attributed to polymer chain degradation. From Fe_3O_4 to $\text{Fe}_3\text{O}_4@\text{ZnS}@$ DL-Mercaptosuccinic, the total weight loss was about 8.0%, 14.0%, and 21%, respectively.

In combination with the above experimental results, it is proved that the magnetic fluorescence nanoparticle $\text{Fe}_3\text{O}_4@\text{ZnS}@$ DL-Mercaptosuccinic ($\text{Fe}_3\text{O}_4@\text{ZnS}-\text{COOH}$) had been successfully synthesized.

3.2. Spectroscopic Characteristics of the Magnetic Fluorescence Nanoprobe

The spectroscopic characteristics of the magnetic fluorescence nanoprobe with Cu^{2+} were investigated first (Figure 2). When excited at 370 nm, the maximal strong fluorescence emission peak of the magnetic fluorescence nanoprobe at 425 nm could be observed. When Cu^{2+} is added, the fluorescence intensity is greatly quenched. The result indicated that the probe could be used as a fluorescent probe to detect Cu^{2+} .

Based on the result that the Cu^{2+} ion can react with this magnetic fluorescence nanoprobe and quench its fluorescence intensity, the fluorescence intensity before and after adding different concentrations of Cu^{2+} was measured and calculated as a function of the Cu^{2+} concentration. In Figure 3, the fluorescence intensity value shows an excellent linear relationship with the Cu^{2+} concentration in 0 – 400 μM ($R^2 = 0.9906$), and the LOD was calculated to be 0.489 μM . The LOD value was much lower than the current metal concentration limits in drinking water (~ 20 $\mu\text{mol/L}$), which is regulated by the U.S. Environmental Protection Agency [14]. As summarized in Table 1, based on the detection range and LOD, the modified magnetic fluorescence nanoprobe exhibits a wide detection range and excellent LOD.

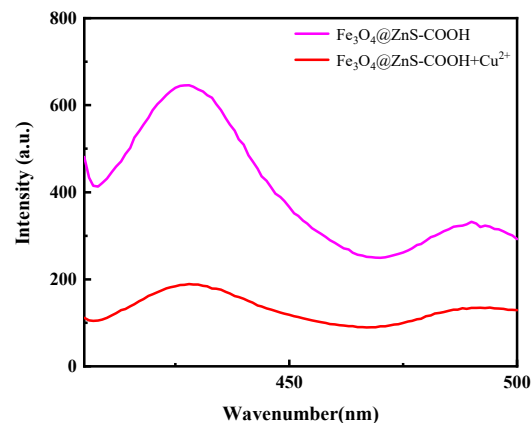


Figure 2. The fluorescence spectra of the magnetic fluorescent nanoprobe (0.2 mg/mL) before and after the addition of Cu^{2+} (400 μM).

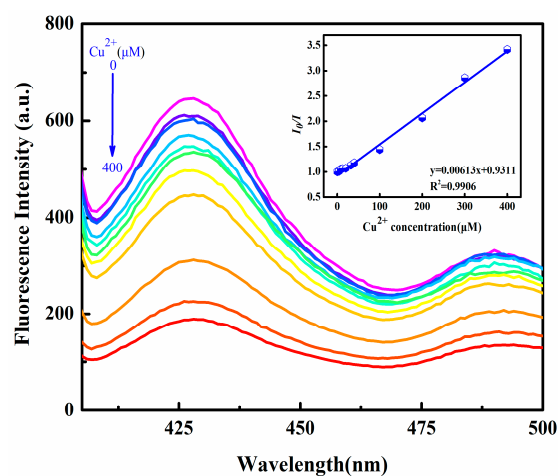


Figure 3. Cu^{2+} detection limit tests with concentration of Cu^{2+} varying from 0 to 400 μM .

Table 1. The work of other articles was compared with the detection of Cu^{2+} in this work.

Probe	Liner Range	LOD	References
CSFH	0–14 μM	0.25 μM	[27]
SQDs	20–200 μM	6.78 μM	[28]
D-GT	0–20 μM	0.69 μM	[29]
CeO ₂ nanoparticles	20–80 μM	9.8 μM	[30]
Carbon dots	0–100 μM	0.106 μM	[31]
$\text{Fe}_3\text{O}_4@\text{ZnS-COOH}$	0–400 μM	0.489 μM	this work

3.3. Specificity and Anti-Interference Capability of the Magnetic Fluorescent Nanoprobe

A new type of magnetic fluorescent nanoprobe was developed, which recognizes Cu^{2+} through the fluorescence quench of the probe. The response effect of the magnetic fluorescent nanoprobe among a variety of metal ions (Cu^{2+} , Co^{2+} , Pb^{2+} , Ni^{2+} , Hg^{2+} , Al^{3+} , Cd^{2+} , Zn^{2+} , Fe^{2+} , Fe^{3+} , K^+ , Ca^{2+} , and Na^+) were measured using a fluorescence spectrophotometer, respectively (Figure 4a). With the addition of metal ions, other metal ions except Cu^{2+} weakly quenched the fluorescent intensity of the magnetic fluorescent nanoprobe. When added with Cu^{2+} , the fluorescent intensity of the magnetic fluorescent nanoprobe decreased significantly. Consequently, the recognition of Cu^{2+} by the magnetic fluorescent nanoprobe can be fulfilled quickly and effectively. It is a competitive fluorescent nanoprobe for the sensitive and selective determination of Cu^{2+} .

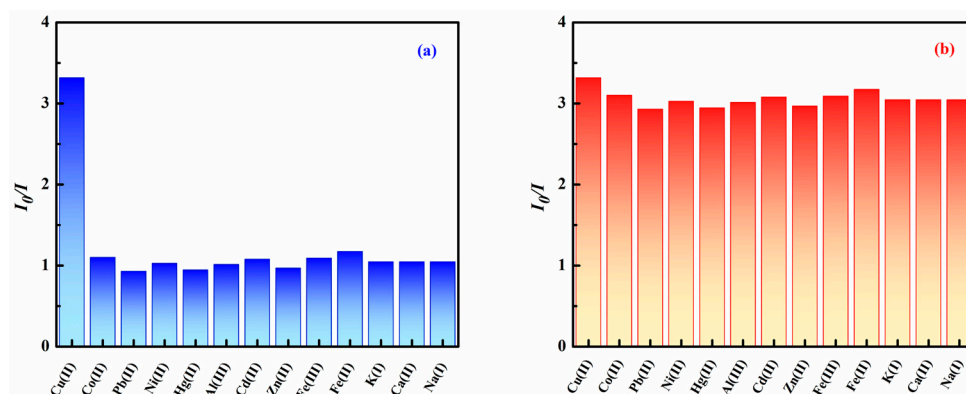


Figure 4. The fluorescence selectivity response of magnetic fluorescent nanoprobe with different surveys: (a) individual metal ions (400 μ M for each ion); (b) Cu²⁺ blend with other metal ions (400 μ M).

Considering that when the magnetic fluorescent nanoprobe was used to detect Cu²⁺ in water, it may be interfered with by other metal ions; thus, the interference experiment needs to be evaluated. The common metal ions (Cu²⁺, Co²⁺, Pb²⁺, Ni²⁺, Hg²⁺, Al³⁺, Cd²⁺, Zn²⁺, Fe²⁺, Fe³⁺, K⁺, Ca²⁺, and Na⁺) in water were selected for the test as follows: the interfering ions (400 μ M) and Cu²⁺ (400 μ M) were added to the solution of magnetic fluorescent nanoprobe solution (0.2 mg/mL), and the fluorescence spectra were tested. The obtained results are shown in Figure 4b. The results showed that these metal ions did not introduce too much interference to the detection and did not affect the selectivity of the probe. These results demonstrated the high selectivity of the magnetic fluorescent nanoprobe to Cu²⁺ against metal ions. It possesses many potential applications in detecting Cu²⁺, both in the biological and physiological fields.

3.4. Adsorption Capacity and Removal Rate Study

The adsorption capacity is one of the most important properties of nanomaterials, so adsorption tests were performed in a centrifuge tube (10 mL) to provide the adsorption amount of the magnetic fluorescent nanoprobe. As the results listed in Table 2 show, the magnetic fluorescent nanoprobe showed excellent adsorption capacity (310.239 mg/g) and a high removal rate (97.64%).

Table 2. Comparison of copper adsorption by different nanomaterials.

Nanomaterials	Q (mg/g)	References
Lignosulfonate adsorbent	450.3	[32]
CS/CMGG composite hydrogel	151.51	[33]
Ni-MOF-CMC	216.95	[34]
3D GO-MT aerogels	33.91	[35]
Cu ²⁺ ion-imprinted polymers (RH-CIIP)	87.8	[36]
Fe ₃ O ₄ @ZnS-COOH	310.239	This work

3.5. The Practicability of Magnetic Fluorescent Nanoprobe on the Detection of Cu²⁺

To validate the applicability of the magnetic fluorescent nanoprobe for determining Cu²⁺, three actual water samples (tap water, bottled water, and electrolysis wastewater) were analyzed. River water samples were obtained from a local Songhua river (Jilin), and the tap water samples were collected from Jilin Water Group Co., Ltd. (Jilin, China). All the water samples needed to be filtered with a 0.45 μ m water-phase microporous membrane and were analyzed at least three times. In these actual samples, the Cu²⁺ could be detected directly, and the results are summarized in Table 3. The recoveries for real Cu²⁺ detection are in the range of 83.00%–108.00% with relative standard deviation (RSD) values below

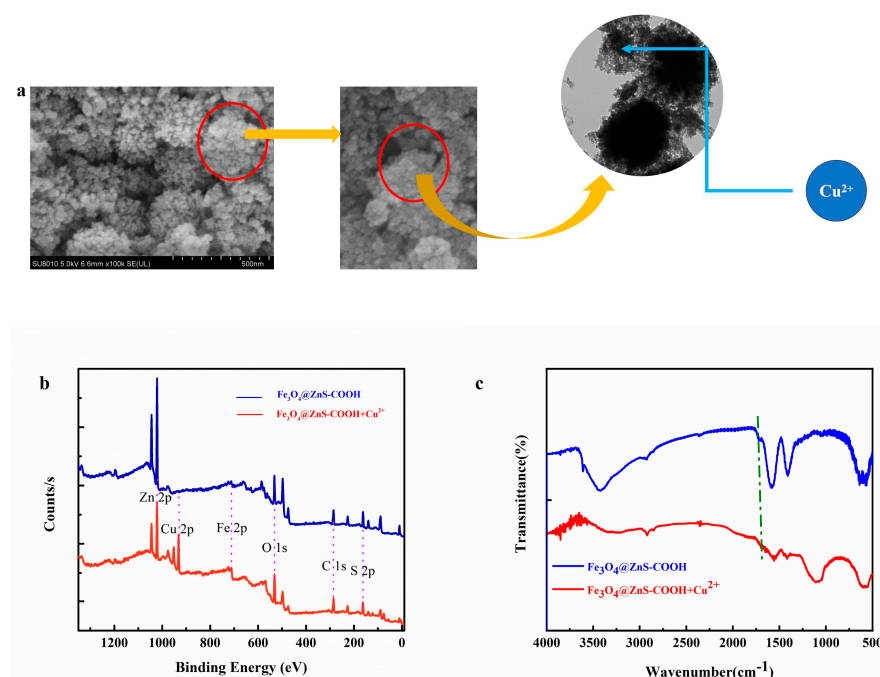
4.53%. The results confirm the good performance of the magnetic fluorescent nanoprobe for real sample detection.

Table 3. The performance of the magnetic fluorescent nanoprobe in real samples.

Sample	Added (μM)	Measured (μM)	Recovery (%)	RSD (%)
Tap water	1	0.93	93.00	2.00
	5.0	4.92	98.40	2.52
	10.0	10.50	105.00	3.21
Bottled water	1	1.08	108.00	2.93
	5.0	5.13	102.60	3.26
	10.0	10.45	104.50	2.85
Electrolysis wastewater	1	0.83	83.00	4.53
	5.0	4.20	84.00	3.93
	10.0	8.75	87.50	4.62

3.6. Detection Mechanism

The Cu^{2+} -binding mechanism was schematically illustrated in Scheme 2. The analyses of the functional groups and morphological features were examined using SEM, FTIR, and XPS spectra to confirm how Cu^{2+} ions were detected by the magnetic fluorescent nanoprobe.



Scheme 2. (a–c) Illustration of plausible Cu^{2+} -binding mechanism with the magnetic fluorescent nanoprobe.

After interacting with Cu^{2+} , metal particle deposition was found on the surface of the magnetic fluorescent nanoprobe, suggesting that Cu^{2+} ions have adhered successfully to the surface of the magnetic fluorescent nanoprobe (Scheme 2a). We analyzed the changes in the XPS spectra of the magnetic fluorescent nanoprobe before and after adding Cu^{2+} to further prove the detection mechanism of the magnetic fluorescent nanoprobe (Scheme 2b). The XPS full-scanning spectra of the magnetic fluorescent nanoprobe and the magnetic fluorescent nanoprobe after the detection of Cu^{2+} exhibited a new peak (932.6 eV), which was assigned to Cu 2p [37], confirming that Cu^{2+} had been adsorbed on the surface of the magnetic fluorescent nanoprobe. Finally, as can be seen in Scheme 2c, the position of

-COOH-containing groups in the $\text{Fe}_3\text{O}_4@\text{ZnS-COOH}$ is blue-shifted from 1728 cm^{-1} to 1683 cm^{-1} following Cu^{2+} adsorption. The reason for the change in the infrared absorption peak of the carboxyl group may be that the oxygen atoms in the carboxyl group cooperate with Cu^{2+} to form a synergistic complex. The oxygen atom of the carboxyl group is negatively charged, indicating that the -COOH group can adsorb Cu^{2+} through an electrostatic interaction. It is speculated that the oxygen atom of the -COOH group provides electrons to Cu^{2+} , resulting in a charge transfer, thus resulting in changes in the infrared spectrum [34].

4. Conclusions

In general, DL-Mercaptosuccinic acid-modified $\text{Fe}_3\text{O}_4@\text{ZnS}$ was prepared by the solvothermal method and was designed as a multi-functional magnetic fluorescent nanoprobe for the sensitive and selective detection of Cu^{2+} . The results of SEM, TEM, FRIT, XRD, and XPS proved that the magnetic fluorescent nanoprobe had been successfully synthesized. The fluorescence assay showed outstanding detection performance, with a wide linear range (0–400 μM), high linearity ($R^2 = 0.9906$), and low LOD (0.489 μM). The probe has been successfully applied to the determination of Cu^{2+} in real water samples and has realized three functions: enrichment, detection, and separation. Herein, this magnetic fluorescent nanoprobe developed a three-in-one functional detection system, aiming at providing an environmentally friendly probe by modifying the recognized probe for other heavy metal ions.

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