Pollution caused by copper is one of the key factors of environmental contamination. As one of the heavy metals, copper is hard to decompose in nature; the biological enrichment of which may lead to severe damage to health. Cu$^{2+}$ detection, thus, possesses a bright application prospect both in environment protection and in human health. In this paper, a dual-functional fluorescence-magnetic composite nanoplatform has been designed to sensitively detect, meanwhile, capture, and remove Cu$^{2+}$ in the solution of water and ethanol (1:1, v/v). The core-shell structure nanoparticle synthesized by using Fe$_3$O$_4$ as core and SiO$_2$ as shell is covalently bonded with rhodamine derivatives on the silica layer to construct the nanoplatform. The emission is increased upon the addition of Cu$^{2+}$, showing fluorescence turn on effect for the detection, and the limit of detection is as low as 1.68 nM. Meanwhile, Cu$^{2+}$ ions are captured by the coordination with rhodamine derivatives and can be removed with the help of magnetic field.

1. Introduction

With the increasing development of social productivity, copper pollution as a representative of heavy metal contamination is getting worse. Copper dust, which is made by the weathering of the rocks, mining, metallurgy, and machine process, will result in pollution of air, water, and soil [1–3]. Meanwhile, copper is hard to decompose in nature, and the resulting enrichment through food chain may lead to severe damage to health [4, 5]. As an essential trace element, copper ions, if in improper dose [6], are likely to cause human poisoning, and illness involves the nervous system, digestive system, cardiovascular system, endocrine system, and so on, among which are known to the majority including Alzheimer’s disease, hepatic cirrhosis, leucoderma, and skeleton deformity [7–10]. Therefore, the development of new methods for the detection and removal of copper ions in the environment has attracted a lot of research interests in the past decades.

There are many techniques at present to detect Cu$^{2+}$, such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS) [11–13]. But difficulties still exist in trace analysis, due to the limited sensitivity and detection limits (LOD) of machine. In addition, expensive test cost, large amounts of time in sample preparation, and inconvenience for on-site analysis are the stumbling blocks to Cu$^{2+}$ detection, both in life and environment. As an effective approach, the fluorescence method has advantages of technical simplicity, high sensitivity, fast response time, and nondestructive imaging [14–16]. In terms of fluorescence determination, the key procedure is to design and synthesize fluorescent probes to detect metal ions or biomolecules by monitoring luminescence quenching [17–20] or enhancement phenomenon [21–23] upon the interaction with testing samples. Lots of fluorescent probes have been developed for detection of Cu$^{2+}$ ions with high sensitivity and selectivity [24–26].
Among these reports, rhodamine compounds have shown significant advantages over some traditional fluorophores due to their attractive feature such as high photostability, wide wavelength range, and high fluorescence quantum yield and thus become an extensive research topic in the field of chemistry and biology [27–30]. However, fluorescent probes with single structure often suffer from some drawbacks, such as low detect efficiencies, separation difficulties, and secondary pollution to environment. Nanoplatform which combined the inorganic-organic composite together fills the gap by its prominent advantages in complementation and cooperatives in multifunction. As for inorganic composite, magnetic nanoparticles provide us an environmental friendly way of separation and recycle [31–33]. There are different ways in ion detection and removal based on the functionalized magnetic nanoplatform. One of the common ways is adsorption. For instance, Cu$^{2+}$ ions are absorbed by hydroxyl groups from β-cyclodextrin and silane [34]. Another method of ion capture is coordination; for example, 8-hydroxyquinoline-2-carboxylic acid is adopted as chelator to coordinate with copper ions [35].

As one of the famous fluorescent probes, rhodamine derivatives have advantages on high absorbance, improved fluorescence quantum yield, and better photostability. Super-paramagnetic nanomaterial is suitable for magnetic separation and fast enrichment. In this work, we have designed a core-shell-structured nanoplatform, in which Fe$_3$O$_4$ is core, SiO$_2$ is shell, and rhodamine derivatives are loaded on the layer of SiO$_2$. The synthesized hybrid can realize the fluorescence turn on effect for the Cu$^{2+}$ detection and Cu$^{2+}$ removal with the help of external magnetic field.

### 2. Experimental Section

#### 2.1. Materials

1-Octadecene (ODE, technical grade, 90%), oleic acid (OA, technical grade, 90%), IGEPAL CO-520, and tetraethyl orthosilicate (TEOS, GC, ≥99%) were purchased from Sigma-Aldrich Co. Ltd. (China). Sodium oleate (CP), n-Hexane (AR, 97%), ammonia solution (AR), and salicylaldehyde were obtained from Shanghai Aladdin Chemistry Co. Ltd. (Shanghai, China). Hydrazine hydrate (85%), rhodamine B, and (3-isocyanatopropyl)triethoxysilane (GR, 95%) were purchased from J&K Technology Co. Ltd. Toluene (AR), iron (III) chloride hexahydrate (AR), and anhydrous ethanol (99.7%, AR) were obtained from Sinopharm Chemical Reagent Co., China. All the agents above were used without further purification. Aqueous solution of different ions, such as Cu$^{2+}$, K$^+$, Ba$^{2+}$, Co$^{2+}$, Ca$^{2+}$, Na$^+$, Mn$^{2+}$, Mg$^{2+}$, Ni$^{2+}$, and Hg$^+$, was prepared, respectively, from its chloride salts. Water used during the experiments was deionized water.

#### 2.2. Preparation of Fe$_3$O$_4@$SiO$_2$. Fe$_3$O$_4$ was synthesized through pyrolysis method according to the previous report [36] with some modification. 40 mmol of FeCl$_3$·6H$_2$O and 40 mmol of sodium oleate were dispersed into 80 mL of ethanol. Then, the resulted solution was mixed with 60 mL of deionized water and 140 mL of n-hexane and kept in 70°C for 4 h. After that, 30 mL of deionized water was then added to wash the product. At last, the oil phase was gathered and dried overnight. Next, 36 g of the resulting iron oleate complex was dissolved in 20 mmol of OA and 200 g of ODE; the mixture was reacted at 320°C for 30 min under Ar. After cooling at room temperature, the solid product was
collected and washed with 20 mL of n-hexane for 3 times. Finally, the nanocrystals were dispersed in n-hexane (30 mg/mL) for storage.

Reversed-phase microemulsion method was used in forming silica layer outside of the Fe$_3$O$_4$. 250 μL of Fe$_3$O$_4$ dispersion was diluted with 10 mL of n-hexane. 50 μL of CO-520 was added while vigorously stirring, then kept at the same condition continuously for 30 min. Next, 2 μL of TEOS was added slowly. Afterwards, 10 μL of ammonia solution was added and the mixture was stirred continuously for 20 h. The resulting products were washed using ethanol as precipitant via centrifugal separation for 3 times. At last, Fe$_3$O$_4$@SiO$_2$ was obtained and dispersed in 5 mL of ethanol at 4°C.

2.3. Preparation of Fe$_3$O$_4$@SiO$_2$@P. The rhodamine derivative (P for short) was synthesized according to our previous article [37]. 60 mg of Fe$_3$O$_4$@SiO$_2$ nanoparticles was redispersed in 20 mL of toluene, and then the solution was heated to 80°C. 20 μL of (3-isocyanatopropyl)triethoxysilane was added by drops, and the temperature was kept at 110°C for 12 h. After that, P (120 mg) distributed in 1 mL of toluene was injected into the reactant rapidly and then, kept at 110°C for another 12 h. After cooling down to room temperature, Fe$_3$O$_4$@SiO$_2$@P was collected via centrifugation and washed with alcohol for three times. Finally, Fe$_3$O$_4$@SiO$_2$@P was dispersed in 5 mL of ethanol and sealed for storage at 4°C for further use.

2.4. Characterization. The morphology features of nanoparticles were observed by transmission electron microscope (TEM, JEM-200CX) at 200 kV. Vibrating sample magnetometer (VSM, 7407; lakeshore) was used for evaluating the magnetic properties of the samples.

Figure 1: The TEM images of (a) Fe$_3$O$_4$, (b) Fe$_3$O$_4$@SiO$_2$, and (c) Fe$_3$O$_4$@SiO$_2$@P. (d) Magnetic hysteresis loop of Fe$_3$O$_4$@SiO$_2$ (black line) and Fe$_3$O$_4$@SiO$_2$@P (red line).
magnetic properties at room temperature. Fourier transform infrared (FTIR, AVATAR370, Nicolet) spectroscopy was to analyze functional groups from synthesized materials. Structure analysis of organic molecules was performed by Fourier superconducting nuclear magnetic resonance spectrometer (AVANCE 500 MHz, BRUKER), using tetramethylsilane (TMS) as an internal standard. To detect the actual ion concentrations, inductively coupled plasma atomic emission spectroscopy (ICP-AES, HORIBA JOBIN YVONSAS) was employed. Fluorescent properties were determined by a LS-55 spectrophotometer. The excitation wavelength was 520 nm, and the emissions were collected from 470 to 750 nm. All the measurements mentioned above were conducted at room temperature.

2.5. Cu$^{2+}$ Response and Removal. A stock solution of Fe$_3$O$_4$@SiO$_2$@P (10 mg/mL) was prepared in the solution of water and ethanol (1:1, v/v). Stock solutions of the metal ions (0.1 M) were prepared in deionized water. Titration experiments were performed by adding Cu$^{2+}$ solution incrementally to a solution of Fe$_3$O$_4$@SiO$_2$@P (2.5 mL). For the selectivity experiments, the test samples were prepared by adding appropriate amounts (100 equiv.) of metal ion solution to 2.5 mL of a solution of Fe$_3$O$_4$@SiO$_2$@P. In competition experiments, Cu$^{2+}$ was added to the solutions containing Fe$_3$O$_4$@SiO$_2$@P and other metal ions of interest. In Cu$^{2+}$ removal experiments (three parallels), Cu$^{2+}$ (1 mL, 0.1 M) was added in Fe$_3$O$_4$@SiO$_2$@P (2.5 mL) and dispersed evenly. Under magnet treatment, the resulted supernate was
Figure 4: (a) Photos of Fe₃O₄@SiO₂@P with (C–F) or without (A, B) Cu²⁺ under daylight (A, C, E) or UV-visible light (B, D, F) by using magnet (E, F) or no magnet (A–D); (b) photos of Fe₃O₄@SiO₂@P after the addition with various metal ions, respectively; (c) ion competition experiment of Fe₃O₄@SiO₂@P in the presence of 2.5 μM Cu²⁺, upon the background of various metal ions (2.5 μM).
collected, respectively, after 5 min and 10 min. All solutions were stirred for 3 min at room temperature and then used for the spectroscopic test.

3. Results and Discussions

3.1. Morphology and Structure Characterization. As illustrated in Scheme 1, Fe₃O₄ nanoparticle was designed as the core, and its intrinsic magnetism was the critical factor for separation and removal of Cu²⁺ with external magnetic field. As Figure 1(a) showed, Fe₃O₄ was uniform and monodisperse and the measured diameter was 9.88 ± 0.79 nm. By utilizing reversed-phase microemulsion method, solid silica was coated on the surface of Fe₃O₄ via hydrolysis-condensation reaction of TEOS. The obtained Fe₃O₄@SiO₂ possessed regular morphology with the average diameter of 21.63 ± 1.57 nm, and the average thickness of silica layer was about 5 nm measured from the TEM images (Figure 1(b)). The magnetic nanoplatform Fe₃O₄@SiO₂@P was finally achieved by the nucleophilic addition reaction between the amino group of (3-isocyanatopropyl)triethoxysilane and the hydroxyl group of P. Some aggregation appeared after loading of P (Figure 1(c)); this is mainly because of the hydrophobic property of the organic probe molecule P. The saturated magnetization of Fe₃O₄@SiO₂ was 43.4 emu/g, as shown in Figure 1(d). After combining with organic probe molecules, the saturated magnetization of the hybrid probe was decreased to 22.6 emu/g. It is suggested that the outer nonmagnetic composite leads to the decrease of maximum saturation magnetizations.

Fourier transform infrared spectroscopy (FTIR) of Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂@P was carried out in order to testify the successful loading of P. As Figure 2 showed, FTIR of Fe₃O₄@SiO₂ exhibited two characteristic bands of silica layer. Peak at 1094 cm⁻¹ was attributed to Si-O-Si symmetric stretching vibrations, and peak at 562 cm⁻¹ was assigned to Si-O symmetric stretching vibrations. The spectrum of Fe₃O₄@SiO₂@P showed C=C symmetric stretching vibrations at 1616 cm⁻¹, 1514 cm⁻¹, and 1461 cm⁻¹, which belonged to benzene ring. Also, C=O stretching vibration at 1616 cm⁻¹ was appeared; thus, it could be concluded that covalent bonding existed between P and silica.

3.1.1. Sensing and Capture of Cu²⁺. The ion-responsive mechanism was achieved due to the well-known equilibrium between the nonfluorescent spirolactam and the fluorescent ring-opened amide of rhodamine. The emission spectrum of Fe₃O₄@SiO₂@P upon various concentrations of Cu²⁺ is shown in Figure 3(a). Under the excitation at 520 nm, the emission bands centered at 552 nm appear and the intensities increase evidently with the Cu²⁺ concentration increased. This indicates that the ring-open process of the rhodamine B unit in P happened. A linear correlation between the emission intensity and concentration of Cu²⁺ in the range of 0–25 nM can be observed (Figure 3(b)). The limit of detection (LOD) was calculated as low as 1.68 nM by the following formula LOD = 3Sₛ₀/S (where Sₛ₀ is the standard deviation of the blank measurements, S is the slope of the calibration curve, and 3 is the factor at the 99% confidence level), suggesting the high sensitivity of the nanoplatform for detecting Cu²⁺.

Benefits from the intrinsic structure of P and the magnetic properties of Fe₃O₄, the nanoplatform can realize the fluorescent detection of Cu²⁺ with naked eyes and removal of Cu²⁺ with the help of magnetic field. As shown in Figure 4(a), before the addition of Cu²⁺, the hybrid nanoplatform was light brown color and nonfluorescent. When Cu²⁺ was added, the hydrazide group and O-acyl hydroxylamines bonded with Cu²⁺, and thus led to the opening of the spirolactam ring in P molecule. The resulting conjugate π-bond facilitates the enhancement of fluorescence intensity at 550 nm. Also, photoinduced electron transfer (PET) was blocked; thus, the solution of fluorescence probe turned into pink color [38–40]. The Cu²⁺ removal effect of the nanoplatform was shown in Figure 4(a) (E, F). We can see that, after a few seconds, the nanoplatform together with Cu²⁺ gathered to the side of cuvette under magnetic field treatment. The removal efficiency of Cu²⁺ was 75% calculated from ICP-AES results. Furthermore, the selective experiments were done to demonstrate the nanoplatform which can detect Cu²⁺ exclusively over other metal ions. As shown in Figure 4(b), there was nearly no color change upon the introduction of other metal ions, including K⁺, Ba²⁺, Co²⁺, Ca²⁺, Na⁺, Mn²⁺, Mg²⁺, Ni²⁺, and Hg²⁺. Additionally, competition experiments were further carried out by adding Cu²⁺ to the solutions containing both nanoplatform and the metal ions of interest. As shown in Figure 4(c), these coexistent ions had negligible interference on Cu²⁺ sensing; even the competitive ions were present at high concentrations.

4. Conclusions

In brief, a dual-functional hybrid nanoplatform Fe₃O₄@SiO₂@P had been successfully prepared. In this nanoplatform, the Fe₃O₄ as the core endowes it with magnetism; SiO₂ as one thin layer bridges the inorganic-organic composites together; rhodamine derivative P is designed for fluorescent sensing of Cu²⁺. Benefits from the intrinsic structure of P and the magnetic properties of Fe₃O₄, the nanoplatform can realize the fluorescent detection of Cu²⁺ with naked eyes and removal of Cu²⁺ with the help of magnetic field. This nanoplatform was featured on simple operation, uniform particle size, structural stability, and excellent magnetic responsibility and thus can be used for the cell imaging of Cu²⁺ or removal of Cu²⁺ from the environmental pollution.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.


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