Research Article

Carbon Quantum Dots-Based Fluorescent Hydrogel Hybrid Platform for Sensitive Detection of Iron Ions

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In this study, we prepared novel fluorescent carbon quantum dots/hydrogel nanocomposite material (CQDsHG) with good adsorption and stable fluorescence detection of Fe$^{3+}$. The materials were subsequently characterized according to their morphological features, chemical composition, adsorption, and optical properties. The carbon quantum dots (CQDs) were prepared using a microwave-assisted hydrothermal method in no more than 15 min, and the as-prepared CQDs exhibited excellent water solubility, as well as emitted strong bright blue fluorescence with an ultrahigh quantum yield of 93.60%. The CQDs were then loaded into a hydrogel (HG) using the sol-gel method to obtain a functional CQDsHG. The CQDsHG exhibited high adsorption amounts (31.94 mg/g) and a good quenching response for Fe$^{3+}$, thus, it could be used as a sensor to selectively detect Fe$^{3+}$ in the linear range of 0–150 μM with a detection limit of 0.24 μM. We observed minimal difference in the fluorescence lifetimes between the CQDsHG with and without a quencher (Fe$^{3+}$), with values of 5.816 ns and 5.824 ns, respectively, confirming that Fe$^{3+}$ was statically quenched on CQDsHG. The results indicated that the innovative combination of CQDs and HG can improve the synergistic performance of each component for the adsorption and quantitative detection of heavy metal ions in the aqueous environment.

1. Introduction

Iron (Fe$^{3+}$) is one of the most abundant and essential trace elements for humans and animals [1]. In humans, insufficient or excessive Fe$^{3+}$ levels can induce a variety of diseases including hemochromatosis, diabetes, liver damage, heart failure, anemia, and Parkinson’s disease [2, 3]. Therefore, Fe$^{3+}$ detection has attracted attention from researchers, and currently, a variety of well-established Fe$^{3+}$ detection methods have been reported, such as atomic absorption [4], inductively coupled plasma mass spectrometry (ICP-MS) [5] and electrochemical analysis [6]. However, most of these techniques require large instruments and complex procedures, which greatly limits their applications. In recent years, fluorescence analysis has attracted significant attention, as it offers advantages such as simple operation, high sensitivity, and a fast response time [7, 8].

Recently, there has been an increase in the use of carbon quantum dots (CQDs) as fluorescent probes for chemical sensing, including Hg$^{2+}$, Zn$^{2+}$, Pb$^{2+}$, and Fe$^{3+}$ [9–12], due to their unique optical properties, good biocompatibility, excellent water solubility, low cost, and low toxicity [13–15]. In addition, they can be used for a wide range of applications, including photocatalysis, bioimaging, and fluorescent textiles [15–19]. However, the main issue with carbon quantum dots-based sensors is that the fluorescent probes have to be mixed with aqueous solutions for subsequent fluorescence determination of the samples, which is not favorable for rapid in situ detection. Many CQDs applications can only be effectively implemented when they are embedded in solid matrices. Therefore, a quasi-solid platform that preserves the properties of CQDs in solution prevents fluorescence quenching due to self-aggregation of CQDs [20] and is used for CQDs dispersion and immobilization is necessary [21]. Among the various solid matrices, hydrogels are the preferred framework for CQDs, because they offer transparency, semi-wetting characteristics, simple processing, and a highly tunable 3D porous structure [22]. Furthermore, the high specific surface area allows the hydrogels to accommodate a variety of micro and nanoparticles.
This effectively prevents quantum dots clustering and greatly improves the fluorescence stability of the quantum dots. Several studies on the loading of CQDs into hydrogel networks have been reported [23–26], and CQDs/hydrogel composites have become important soft materials, with shared polymer and CQDs properties for use in interesting applications.

In this study, we fabricated a carbon quantum dots-based fluorescent hydrogel, which was used as a solid sensor for optical Fe$^{3+}$ detection. The CQDs, with an ultrahigh fluorescence quantum yield of 93.60%, were prepared using a microwave-assisted hydrothermal method with citric acid. Then, the synthesized CQDs were introduced into the hydrogel framework via physical crosslinking. We then investigated the properties, structures, adsorption models, and photoluminescence characteristics of the CQDsHG, and the sensing properties of the CQDsHG for Fe$^{3+}$ were explored. The results showed that the CQDsHG had potential applications as an effective bifunctional sensor with Fe$^{3+}$ detection and adsorption properties.

2. Materials and Methods

2.1. Materials. Citric acid monohydrate (CA), urea, aqueous ammonia (NH$_4$OH, 25%), glycine, and ethylenediamine (EDA) were provided by the Sinopharm Chemical Reagent Co. In addition, sodium dodecylbenzene sulfonate (SDBS), acrylic acid (AA), stearyl methacrylate (SMA), acrylamide (AM), potassium persulfate (KPS), CuSO$_4$, MgCl$_2$, FeCl$_3$, BaCl$_2$, CoCl$_2$, Pb(NO$_3$)$_2$, CaCl$_2$, CdCl$_2$, ZnCl$_2$, and HgCl$_2$ were provided by the Aladdin Industries. All reagents were analytical reagent grade and ultrapure water was used throughout the experimentation process.

2.2. Apparatus. The CQDs were prepared using a microwave-assisted-hydrothermal synthesizer (MD20H, Oprah Technology Group, Inc.). X-ray powder diffractograms were obtained using an X-ray diffractometer (D8-FOCUS, Bruker, Germany). Materials chemical compositions of the materials were measured using an X-ray photoelectron spectrometer (ESCALAB Xi+, Thermo Fisher Scientific, USA). The infrared spectra in KBr were obtained using a Fourier transform infrared spectrometer (FTIR BXII, Perkin-Elmer, USA). Raman spectra were recorded using a Raman spectrometer (LabRAM HR Evolution, HORIBA Scientific, France) with a 514 nm laser beam. The morphologies were observed by high-resolution transmission electron microscopy (JEM-2100F, JEOL Ltd., Japan). Fluorescence experiments were performed on a fluorescence spectrophotometer (FL-7000, Hitachi, Japan), and samples fluorescence lifetime measurements were obtained using steady-state transient fluorescence spectrometry (FL-7100, Hitachi, Japan). The UV/Vis spectrum was determined by a spectrophotometer (T6, Pu-Analysis General Co., Ltd., China and Cary series UV-Vis-NIR, Agilent Technologies, Inc.). Moreover, a flame atomic absorption spectrophotometer (FAAS, A-6300C, Shimadzu, Japan) and an inductively coupled plasma mass spectrometer (ICP-MS, 2030LF, Shimadzu, Japan) were used to detect the metal ions. Photographs were obtained with a quadruple UV analyzer (WFH-203C, Shanghai JingKe Industrial Co., Ltd., China). Lastly, compression tests were performed on HG and CQDsHG using a microcomputer-controlled electronic universal testing machine (104B-EX, Shenzhen Wan Xiao Testing Equipment Co., Ltd., China).

2.3. Design and Analysis of the Orthogonal Experiment. The orthogonal experiments were used to investigate the fluorescence quantum yield of the CQDs (details are presented in supplementary materials). The three-level four-factor orthogonal experiment was designed to investigate the effects of various reaction conditions, such as the citric acid dosage, reaction temperature, reaction time, and microwave power on the carbon quantum dots, and optimize the basic conditions (Tables S1–S3). Secondly, we designed the orthogonal experiments to determine the effects of nitrogen doping type and nitrogen doping amount on the fluorescence quantum yield (Tables S4–S6).

2.4. Synthesis of Carbon Quantum Dots (CQDs). In this study, the CQDs were synthesized using the microwave-assisted hydrothermal method. The citric acid (0.005 mol) was dissolved in water (10 mL) while stirring, followed by the addition of ethylenediamine (0.005 mol). The mixture was ultrasonicated for 3 min and then transferred to a 100 mL microwave digestion tank. The reaction was carried out at 700 W and 160°C for 15 min in a microwave-hydrothermal synthesizer, and the resulting CQDs solution was cooled to room temperature and filtered using a 0.22 μm filter membrane to remove any macromolecular impurities. Afterward, the solution was dialyzed for 9 h using a dialysis bag (MW500) and freeze-dried for 36 h to obtain the light-yellow N-doped CQDs.

2.5. Synthesis of the Fluorescent Hydrogel (CQDsHG). In this study, 2.30 g of SDBS and 12.80 g of AM were added to 60 mL (0.6 g/L) of CQDs solution. Then, 2.44 mL of AA and 1.15 g of SMA were added to the above solution, the mixture was stirred for 9 h using a dialysis bag (MW500) and freeze-dried for 36 h to obtain the light-yellow N-doped CQDs.

2.6. Determination of Fluorescence Quantum Yield. Fluorescence measurements were performed under the following conditions. The slit widths of the emission and excitation gap were 2.5 nm and 5 nm, respectively, the scan rate was 240 nm/min, and the photomultiplier tube voltage was 400 V. The fluorescence quantum yield (QY) of the CQDs
was examined based on the comparative method using quinin sulfate as the reference, which was calculated using Equation (1):

\[
\phi_x = \frac{\phi_{std} I_x A_{std} \eta^2}{I_{std} A_x \eta_{std}^2},
\]

where \( \phi \) is the fluorescence quantum yield, \( x \) represents the sample, std refers to the standard quinin sulfate (\( \phi_{std} = 0.54 \)), \( \eta \) is the solvent refractive index (1.33 for aqueous solution), \( A \) is the absorbance at the excitation wavelength (366 nm), and \( I \) is the integrated fluorescence intensity at the fluorescence emission spectrum. To minimize reabsorption effects, the optical absorbency values were below 0.1 at the excitation wavelength [10].

2.7. Pressure Performance Test. The CQDsHG was fabricated into a cylindrical specimen, and the diameter and original thickness of the specimen were measured with vernier calipers. The specimen was compressed at a uniform speed, with a load of 500 N and a speed of 50 mm/min, until the deformation reached 85%. The data were then saved to produce a graph.

2.8. Hydrogel Adsorption Experiments for Fe\(^{3+}\). The CQDsHG or HG samples were sliced into 0.9 cm thick discs with a diameter of 1 cm, and the mass of each disc was measured. The HG discs were placed in Fe\(^{3+}\) solutions, and Fe\(^{3+}\) concentrations in the solutions were analyzed before and after adsorption using ICP-MS. The adsorption amount was calculated according to Equation (2) [27]:

\[
q_t = \frac{(C_0 - C_t)V}{m},
\]

where \( q_t \) is the adsorption amount at adsorption time \( t \) (mg/g); \( V \) is the solution volume, (mL); \( C_0 \) and \( C_t \) are the concentrations of Fe\(^{3+}\) in the solution before and after adsorption by the hydrogel samples, (mg/L); and \( m \) denotes the weight of the original dry hydrogel used to test, (g).

The adsorption kinetics experiments were carried out at different adsorption times (2.5, 5, 10, 20, 30, 60, 90, and 150 min), with a fixed initial concentration (100 mg/L). The quasi-first-order kinetics Equation (3) and quasi-second-order kinetics Equation (4) were fitted to the adsorption data, respectively [28]:

\[
\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t,
\]

\[
q_t = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t,
\]

Figure 1: Schematic showing (1) the preparation of the CQDs, (2) preparation of the CQDsHG, and (3) action mechanism of the CQDsHG as a sensor for Fe\(^{3+}\) detection.
\[ \frac{t}{q_t} = \frac{1}{k_1 q_{eq}} + \frac{1}{k_2 q_{eq}} t, \]  

where \( q_t \) and \( q_{eq} \) (mg/g) are the adsorption amounts at equilibrium and at time \( t \), respectively, and \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g/mg/min\(^{-1}\)) denote the equilibrium rate parameter of the quasi-first-order and quasi-second-order adsorption interactions.

The isothermal adsorption experiments were carried out at different initial concentrations (20, 40, 60, 80, and 100 mg/L). Then, the adsorption data were fitted using the Langmuir isothermal adsorption model (Equation (5)) and the Freundlich isothermal adsorption model (Equation (6)) [29, 30]:

\[ \frac{1}{q_{eq}} = \frac{1}{q_{max}} + \frac{1}{b q_{max} C_e}, \]  

\[ \ln q_e = \frac{1}{n} \ln C_e + \ln K_F, \]

where \( C_e \) (mg/L) is the equilibrium Fe\(^{3+}\) concentration, \( q_{max} \) (mg/g) denotes the theoretical maximum adsorption amount, \( b \) (L/mg) is the Langmuir adsorption constant, \( K_F \) (L/g) is the Freundlich constant that indicates the adsorption
amount, and n is the heterogeneity factor representing the adsorption intensity.

2.9. Real Sample Analysis. To evaluate the practicality of the CQDsHG for real sample analysis, Fe\(^{3+}\) concentrations in tap water and lake water were analyzed using the spiked recovery method with CQDsHG as a sensor. The lake water was sampled from the local Beichuan Lake, and all water samples were filtered through a 0.22 \(\mu\)m membrane before analysis.

3. Results and Discussion

3.1. Preparation Route of CQDsHG. The preparation route of the fluorescent hydrogel is shown in Figure 1. Citric acid and ethylenediamine were mixed to create N-doped CQDs with a uniform size using the microwave-assisted hydrothermal method in a remarkable 15 min. The quantum yield (QY) of the as-prepared CQDs reached 93.60%, which was higher than the reported results shown in Table S7. In order to find the mechanism for the ultrahigh quantum yield, we studied the synthetic condition of the CQDs by designing
orthogonal experiments, which gives the result as follows: EDA (0.005 mol) and citric acid (0.005 mol) at 160°C for 15 min at 700 W. The results show that N-doping is very important to improve quantum yield (QY). The highest QY of CQDs without N-doping was only 16.26%. After N-doping optimization, the QY of CQDs was improved a lot.

Then, the CQDsHG was successfully prepared using irregular free radical copolymerization, where the CQDs were used as the fluorescence source; AA and AM were the hydrophilic monomers; SMA was the hydrophobic monomers; SDBS was the surfactant, and KPS was the initiator. The CQDs could be dispersed and immobilized in the hydrogel through extensive hydrogen bonding to avoid leakage in water. Thus, the resulting CQDsHG exhibited synergistic performance of polymers and CQDs and emitted blue light under UV irradiation (365 nm) as shown in Figure 1. Follow-up studies showed that the CQDsHG could be used for quantitative detection of Fe^{3+} based on fluorescence quenching.

3.2. Characterization of the CQDs and CQDsHG. The obtained CQDs were almost spherical in morphology, with a particle size distribution mostly between 2 and 3 nm, and an average diameter of about 4.30 nm (Figure 2(a)). Furthermore, the HRTEM image showed a crystalline surface spacing of 0.35 nm (Figure 2(b)). As shown in Figure 2(c), the XRD pattern for the CQDs had a broad diffraction peak at 2θ = 25.1°, which corresponded to the (002) crystalline spacing of graphitic carbon, indicating that the synthesized CQDs had an amorphous structure. The calculated layer spacing d for the CQDs was 0.35 nm, which was consistent with the HRTEM result. The Raman spectrum of the CQDs (Figure S1) showed the characteristic G band (related to a crystalline sp^2 carbon network) at 1588 cm\(^{-1}\) and the D band (related to disordered graphite or glassy carbon) at 1348 cm\(^{-1}\), with an intensity ratio I_D/I_G of 1.00. The intensity ratio indicated defects of the CQDs with a partially disordered crystal structure, arising from the small sp^2 cluster size [31, 32]. In the UV/Vis spectra of the CQDs aqueous solution (Figure 2(d)), two typical absorption peaks at 238 nm and 346 nm were observed, corresponding to the π−π* transition of the aromatic sp^2-hybridized domains and n−π* transition of the sp^3-hybridized domains, respectively [23]. Upon excitation at 370 nm, the fluorescence spectra of the aqueous CQDs exhibited a strong blue emission at 450 nm, which confirmed that the CQDs had a larger Stokes shift [25].

XPS was used to determine the functional groups and elemental composition on the CQDs surfaces. In the wide-scan XPS spectrum of the CQDs (Figure 3(a)), three major peaks at 284.6, 399.9, and 532.4 eV were observed, which were attributed to C1s, N1s, and O1s, respectively. The contents of carbon, nitrogen, and oxygen were calculated to be 57.48%, 11.82%, and 30.70%. Furthermore, the high-resolution XPS spectra of C1s (Figure 3(b)) had four constituents of carbon bonds, corresponding to C-C at 284.8 eV, C-N at 285.7 eV, C-O at 286.8 eV, and C=O at 288.1 eV, respectively [33]. As shown in Figure 3(c), the N1 spectra could be curve fitted with three peak components at 399.4, 400.3, and 400.8 eV, which were attributed to the electron binding energies of C-N-C, C-N, and N-H [34]. In the O1 spectra (Figure 3(d)), the two peaks at 532.2 and 534.7 eV were attributed to the electron binding energies of C=O and C-OH [33, 35]. Thus, the XPS results confirmed that the synthesized CQDs contained a large number of hydrophilic groups, which enhanced the hydrogen-bonding interaction between carbon dots and hydrogels.

FTIR spectrum of the CQDs, HG, and CQDsHG are shown in Figure 4(a), showing characteristic bands of -OH, C=O, C=C, and N-H at 3443 cm\(^{-1}\), 1710 cm\(^{-1}\), 1560 cm\(^{-1}\), and 3209 cm\(^{-1}\), respectively [36–38]. The FTIR and XPS results supported that the synthesized CQDs contained a large number of hydrophilic groups, which enhanced the hydrogen-bonding interaction between carbon dots and hydrogels.

The effect of CQDs addition on the mechanical strength of the hydrogel was examined by a pressure test and the results were shown in Figure 4(b). The hydrogel was
Figure 5: (a) The equilibrium adsorption amount of the CQDsHG and HG for Fe$^{3+}$, (b) quasi-first-order and (c) quasi-second order kinetics plots for the adsorption of the Fe$^{3+}$ on CQDsHG and HG, (d) effect of initial concentrate of Fe$^{3+}$ on adsorption, (e) linear plots of Langmuir, and (f) Freundlich isotherms for Fe$^{3+}$ adsorption by the CQDsHG and HG.

Table 1: Kinetic parameters of quasi-first-order and quasi-second-order models for Fe$^{3+}$ adsorption on hydrogels.

| Adsorbents | q_e, exp (mg/g) | Quasi-first-order | Quasi-second-order |
|------------|----------------|------------------|--------------------|
| CQDsHG     | 31.94          | 18.2642          | 0.0378             | 0.9606             | 34.2465          | 0.0009             | 0.9945             |
| HG         | 15.74          | 7.6895           | 0.0320             | 0.7947             | 16.6667          | 0.0040             | 0.9797             |
compressed by applying pressure using an electronic universal compressor. Approximately 180 kPa and 120 kPa of pressure were required to compress the CQDsHG and HG from 1 to 0.5 cm (50% deformation), respectively. When the pressure was removed, both hydrogels recovered completely, indicating that the CQDsHG and HG exhibited good elasticity. With increasing pressure, the HG produced irreparable cracks at 85% deformation, but the CQDsHG did not. This indicated that the addition of CQDs improved the mechanical strength of the CQDsHG to a certain extent [25].

3.3. Fe^{3+} Ion Adsorption Experiments. Figure 5(a) shows the Fe^{3+} adsorption amounts of the HG and CQDsHG. Compared to the HG (15.74 mg/g), CQDsHG had a higher adsorption amount for Fe^{3+} (31.94 mg/g), indicating that the addition of CQDs had an effect on the adsorption

Figure 6: (a) Fluorescence spectra of the CQDsHG, (b) excitation wavelength-dependent fluorescent emission spectra of the CQDsHG, (c) fluorescent emission spectra of the CQDsHG and HG (insets are the photographs of CQDsHG and HG under day light and UV light), (d) influence of CQDsHG thickness on fluorescence intensity, (e) storage stability of the CQDsHG, and (f) photos of CQDsHG under UV light (365 nm).
amount of the hydrogel [39]. This was because CQDs addition increased the crosslinking point of the polymer, allowing more functional groups to chelate and absorb Fe$^{3+}$. Therefore, the hydrogel can provide mechanical and chemical stability to CQDs. Conversely, the introduction of CQDs also improved the structure and performance of the hydrogel to some extent. To better understand the adsorption mechanism of the hydrogel, quasi-first-order kinetics Equation (3) and quasi-second-order kinetics Equation (4) were fitted to the adsorption data, respectively. The fitting results are shown in Figures 5(b) and 5(c), and the calculated parameters are given in Table 1. The results showed that Fe$^{3+}$ adsorption on the CQDsHG could be modeled using the quasi-second-order kinetic model, and that the adsorption control mechanism of CQDsHG for Fe$^{3+}$ was chemical adsorption.

In the solutions with different Fe$^{3+}$ concentrations, the CQDsHG showed a higher adsorption amount than the HG. The adsorption data were then fitted using the Langmuir isothermal adsorption model (Equation (5)) and the Freundlich isothermal adsorption model (Equation (6)), respectively. According to the determination coefficients (Figures 5(e) and 5(f)), the Freundlich adsorption isotherm model was more suitable for the Fe$^{3+}$ adsorption isotherm of CQDsHG, indicating that the adsorption of Fe$^{3+}$ by CQDsHG was limited by multilayer coverage.

3.4. Fluorescent Measurements of the CQDsHG. Figure 6(a) displays the optimal excitation and emission trait of the CQDsHG, under 370 nm excitation, where the strongest emission peak appeared at 450 nm. We observed that the emission of the CQDsHG was dependent on the excitation wavelength, which shifted toward the long-wavelength direction with increasing excitation wavelength.
This phenomenon is common in fluorescent carbon materials, which is due to the surface state affecting the energy bandgap of CQDs [40, 41].

The photographs of the HG and CQDsHG under day light and ultraviolet light (Figure 6(c)) showed that the HG had no obvious fluorescence emission under 370 nm excitation, while the CQDs exhibited fluorescent behavior even if they were crosslinked into the polymer. The highest fluorescence intensity was obtained when the CQDsHG thickness was 9 mm (Figure 6(d)). The CQDsHG was stored in a sealed dark environment at 4°C.

Table 2: Comparison of the probes for the detection of Fe³⁺ ions.

| No. | Probe                                      | QY (%) | Linear range | Detection limit | Adsorption amount (mg/g) | Ref  |
|-----|--------------------------------------------|--------|--------------|-----------------|--------------------------|------|
| 1   | CQDs from pear juice                       | 18.00  | 0–50μM       | 2.28μM          | ——                       | [11] |
| 2   | Chitosan hydrogel                           | ——     | ——           | 0.12nM          | ——                       | [43] |
| 3   | PNIPAAm-CQD hydrogel                        | ——     | 1μM–1mM      | 0.27μM          | 208.25                   | [25] |
| 4   | Smart hydrogel with CQDs                    | 28.00  | 10–100μM     | 0.06μM          | ——                       | [23] |
| 5   | Acrylamide hydrogel                         | ——     | 0–50μM       | 1.10μM          | ——                       | [44] |
| 6   | Graphene oxide derived from Quercus ilex fruits | 3.03  | 0.1–1μM     | 34.50nM         | ——                       | [45] |
| 7   | A pyrene fluorescent probe                  | ——     | 0–200μg/L    | 9.00μg/L        | ——                       | [12] |
| 8   | Pyridinyl conjugate of UiO-66-NH₂ as chemosensor | ——     | ——           | 0.19μM          | ——                       | [46] |
| 9   | Bimetallic Ln-MOFs                          | ——     | ——           | 4.47μM          | ——                       | [47] |
| 10  | Hydrophilic P(Am-CD-AMPS) microgel          | ——     | 0–5mM        | 3.20μM          | 102.13                    | [48] |
| 11  | High luminescent Eu³⁺ doped nanoparticle    | ——     | 10μM–90μM    | 63.20nM         | ——                       | [49] |
| 12  | CQDsHG                                     | 93.60  | 0–150μM      | 0.24μM          | 31.94                     | This work |

Table 3: Determination of Fe³⁺ in real samples.

| Sample                | Spiked amount(μM) | CQDsHG Found(μM) | Recovery (%) | FAAS Found(μM) | Recovery (%) |
|-----------------------|-------------------|------------------|--------------|----------------|--------------|
| Tap water             | 0                 | 7.36             | ——           | 6.50           | ——           |
|                       | 5                 | 12.63            | 105.40       | 11.56          | 101.20       |
|                       | 50                | 61.78            | 108.84       | 60.38          | 107.76       |
|                       | 0                 | 5.46             | ——           | 4.13           | ——           |
| Beichuan River water  | 5                 | 10.69            | 104.60       | 9.22           | 101.80       |
|                       | 50                | 59.19            | 107.46       | 58.87          | 109.48       |
and fluorescence measurements were obtained at one-week intervals, and the results are shown in Figures 6(e) and 6(f). After five weeks, no chalking or cracking of the CQDsHG was observed, and the change of fluorescence intensity was less than 6%, indicating that the CQDsHG has storage stability.

3.5. Fluorescence Detection of Fe³⁺. To evaluate the detection performance of the CQDsHG for metal ions, fluorescence quenching experiments were performed in the presence of interfering ions, specifically Ca²⁺, Mg²⁺, Co²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Pb²⁺, Ba²⁺, and Hg²⁺, at 1 mM. Compared to the CQDsHG, the Fe³⁺ contents in tap water and river waters were analyzed using the spiked recovery method with the addition of Fe³⁺ ranged from 0 to 150 μM, the curve of F₀/F fitted well to the Stern-Volmer relationship. KSV was 388.56 L/mol, and kq was calculated to be 6.6 × 10¹⁰ L/(mol·s) much larger than 2 × 10¹⁰ L/(mol·s), implying a static quenching [50].

In order to explore the quenching mechanism, the average fluorescence lifetime of the CQDsHG without (τ₀) and with (τ₁) the addition of Fe³⁺ was also examined (Figure S3), and the results were τ₀ = 5.816 ns and τ₁ = 5.824 ns. Apparently, the addition of the quencher (Fe³⁺) did not significantly shorten the fluorescence lifetime of the CQDsHG, which proved that the existence of the static quenching process [15, 51].

In addition, the UV/Vis absorption spectrum of the CQDsHG was also investigated to further confirm the fluorescence quenching mechanism. As shown in Figure S4, the absorption peak of the CQDsHG at 329 nm disappeared. This phenomenon may be due to the combination of Fe³⁺ and functional groups (amino, hydroxyl, and carboxyl groups) on the surface of the CQDsHG. The difference further proves the mechanism of static quenching [37, 51].

4. Conclusions

In this study, a fluorescent hydrogel nanocomposite with Fe³⁺ adsorption and sensing capability was fabricated based on CQDs. The easily prepared hydrogel nanocomposite improved the synergistic performance of the CQDs and HG. The CQDs were dispersed and immobilized in the hydrogel through extensive hydrogen bonding, which avoided leakage in water. The hydrogel nanocomposite was stable and exhibited a higher adsorption property and mechanical strength than the HG. Furthermore, the fluorescence intensity of the CQDsHG at an excitation wavelength of 370 nm was significantly quenched when Fe³⁺ was added to the CQDsHG, and it could be used to quantitatively detect Fe³⁺ in the range of 0-150 μM, with the detection limit of 0.24 μM. Thus, the satisfactory detection results in real samples demonstrated that the CQDsHG could be used as a bifunctional platform to qualitatively detect and remove trace metal ions.

Data Availability

The data used to support the findings of this study are included within the article, and any further information is available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.
Acknowledgments

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Supplementary Materials

The following are available online at http://www.com/xxx/s1. Table S1: the factors and levels of the orthogonal experiment (basic conditions); Table S2: the orthogonal experiment scheme (basic conditions); Table S3: the numerical of orthogonal tests (basic conditions); Table S4: the factors and levels of the orthogonal experiment (doping conditions); Table S5: the orthogonal experiments scheme (doping conditions); Table S6: the numerical of orthogonal tests (synthetic conditions); Table S7: comparison of nitrogen doping amount and fluorescence quantum yield under various methods for the preparation of carbon quantum dots; Figure S1: Raman spectra of the CQDs; Figure S2: the calibration curves and linear equation for fluorescence quenching ratio and concentration of Fe³⁺; Figure S3: Fluorescence decay traces of the CQDsHG with and without the addition of Fe³⁺ (1 mM); Figure S4: UV–Vis absorption spectra of the CQDsHG (black), Fe³⁺ (blue), and CQDs+Fe³⁺ system (red), respectively. (Supplementary Materials)

References

[1] L. L. Dunn, Y. S. Rahmanto, and D. R. Richardson, “Iron uptake and metabolism in the new millennium,” Trends Cell Biology, vol. 17, no. 2, pp. 93–100, 2007.
[2] D. Zhao, X. H. Liu, Y. Zhao et al., “Luminescent Cd(II)–organic frameworks with chelating NH2 sites for selective detection of Fe(III) and antibiotics,” Journal of Materials Chemistry A, vol. 5, no. 30, pp. 15797–15807, 2017.
[3] X. H. Zhou, L. Li, H. H. Li, A. Li, T. Yang, and W. Huang, “A flexible Eu(III)-based metal-organic framework: turn-off luminescent sensor for the detection of Fe(III) and picric acid,” Dalton Transactions, vol. 42, no. 34, pp. 12403–12409, 2013.
[4] G. A. Antunes, H. S. dos Santos, Y. P. da Silva, M. M. Silva, C. M. S. Piatnicki, and D. Samios, “Determination of iron, copper, zinc, aluminum, and chromium in biodiesel by flame atomic absorption spectrometry using a microemulsion preparation method,” Energy & Fuels, vol. 31, no. 3, pp. 2944–2950, 2017.
[5] D. V. Biller and K. W. Bruland, “Analysis of Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in seawater using the Nobias-chelate PA1 resin and magnetic sector inductively coupled plasma mass spectrometry (ICP-MS),” Marine Chemistry, vol. 130, pp. 12–20, 2012.
[6] Y. Zhu, D. Pan, X. Hu, H. Han, M. Lin, and C. Wang, “An electrochemical sensor based on reduced graphene oxide/gold nanoparticles modified electrode for determination of iron in coastal waters,” Sensors and Actuators B: Chemical, vol. 243, no. 5, pp. 1–7, 2017.
[7] Z. Nan, C. Hao, X. Zhang, H. Liu, and R. Sun, “Carbon quantum dots (CQDs) modified ZnO/CdS nanoparticles based fluorescence sensor for highly selective and sensitive detection of Fe(III),” Spectrochimica Acta part A-Molecular and Biomolecular Spectroscopy, vol. 228, article 117717, 2020.
[8] X. Zhang, J. Lu, X. Zhou, C. Guo, and C. Wang, “Rapid microwave synthesis of N-doped carbon nanodots with high fluorescence brightness for cell imaging and sensitive detection of iron(III),” Optical Materials, vol. 64, pp. 1–8, 2017.
[9] H. B. Ahmed and H. E. Emam, “Environmentally exploitable biocide/fluorescent metal marker carbon quantum dots,” RSC Advances, vol. 10, no. 70, pp. 42916–42929, 2020.
[10] S. Jing, Y. Zhao, R. Sun, L. Zhong, and X. Peng, “Facile and high-yield synthesis of carbon quantum dots from biomass-derived carbons at mild condition,” ACS Sustainable Chemistry & Engineering, vol. 7, no. 8, pp. 7833–7843, 2019.
[11] G. S. Das, J. P. Shim, A. Bhatnagar, K. M. Tripathi, and T. Kim, “Biomass-derived carbon quantum dots for visible-light-induced photocatalysis and label-free detection of Fe(III) and ascorbic acid,” Scientific Reports, vol. 9, no. 1, article 15084, 2019.
[12] G. Wang, X. Liu, S. Cai et al., “A pyrene fluorescent probe for rapid detection of ferric ions,” Journal of Fluorescence, vol. 31, no. 3, pp. 713–718, 2021.
[13] Y. Meng, Y. Jiao, Y. Zhang et al., “Multi-sensing function integrated nitrogen-doped fluorescent carbon dots as the platform toward multi-mode detection and bioimaging,” Talanta, vol. 210, article 120653, 2020.
[14] Y. Xie, D. Cheng, X. Liu, and A. Han, “Green hydrothermal synthesis of N-doped carbon dots from biomass highland barley for the detection of Hg²⁺,” Sensors, vol. 19, no. 14, article 3169, 2019.
[15] D. Xu, N. Fu, Y. Xie et al., “Easy formation of nitrogen-doped carbon dots towards Hg²⁺ fluorescent measurement and multicolor intracellular imaging,” Materials Chemistry and Physics, vol. 266, article 124547, 2021.
[16] R. M. Abdelhameed, M. El-Shahat, and H. E. Emam, “Employable metal (Ag & Pd)@MIL-125-NH2@cellulose acetate film for visible-light driven photocatalysis for reduction of nitroaromatics,” Carboxylate Polymers, vol. 247, article 116695, 2020.
[17] H. B. Ahmed, K. M. Abualnaja, R. Y. Ghareeb, A. A. Ibrahim, N. R. Abdelsalam, and H. E. Emam, “Technical textiles modified with immobilized carbon dots synthesized with infrared assistance,” Journal of Colloid and Interface Science, vol. 604, no. 2, pp. 15–29, 2021.
[18] H. E. Emam, H. B. Ahmed, E. Gomaa, M. H. Helal, and R. M. Abdelhameed, “Recyclable photocatalyst composites based on Ag3VO4 and Ag2WO4 @MOF@cotton for effective discoloration of dye in visible light,” Cellulose, vol. 27, no. 12, pp. 7139–7155, 2020.
[19] H. E. Emam, M. El-Shahat, M. S. Hasanin, and H. B. Ahmed, “Potential military cotton textiles composed of carbon quantum dots clustered from 4–(2,4-dichlorophenyl)–6–oxo–2–thioxohexahydropyrimidine–5–carbonitrile,” Cellulose, vol. 28, no. 15, pp. 9991–10011, 2021.
[20] S. Mohammadi, S. Mohammadi, and A. Salimi, “A 3D hydrogel based on chitosan and carbon dots for sensitive fluorescence detection of microRNA-21 in breast cancer cells,” Talanta, vol. 224, no. 27, article 121895, 2021.
[21] J. R. Bhamore, T. J. Park, and S. K. Kailasa, “Glutathione-capped Syzygium cumini carbon dot-amalgamated agarose hydrogel film for naked-eye detection of heavy metal ions,” Journal of Analytical Science and Technology, vol. 11, no. 1, pp. 1–9, 2020.
[22] W. Su, R. Wang, C. Qian, X. Li, Q. Tong, and T. Jiao, “Research progress review of preparation and applications of fluorescent hydrogels,” *Journal of Chemistry*, vol. 2020, Article ID 8246429, 17 pages, 2020.

[23] C. Cheng, M. Xing, and Q. Wu, “Green synthesis of fluorescent carbon dots/hydrogel nanocomposite with stable Fe\(^{3+}\) sensing capability,” *Journal of Alloys and Compounds*, vol. 790, pp. 221–227, 2019.

[24] N. Gogoi, M. Barooah, G. Majumdar, and D. Chowdhury, “Carbon dots rooted agarose hydrogel hybrid platform for optical detection and separation of heavy metal ions,” *ACS Applied Materials Interfaces*, vol. 7, no. 5, pp. 3058–3067, 2015.

[25] D. Zhang, X. Tian, H. Li, Y. Zhao, and L. Chen, “Novel fluorescent hydrogel for the adsorption and detection of Fe (III),” *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 608, article 125563, 2021.

[26] M. Zhou, J. Guo, and C. Yang, “Ratiometric fluorescence sensor for Fe\(^{3+}\) ions detection based on quantum dot-doped hydrogel optical fiber,” *Sensors and Actuators B: Chemical*, vol. 264, pp. 52–58, 2018.

[27] X. Zheng, D. Wu, T. Su, S. Bao, C. Liao, and Q. Wang, “Magnetic nanocomposite hydrogel prepared by ZnO-initiated photopolymerization for La (III) adsorption,” *ACS Applied Materials Interfaces*, vol. 6, no. 22, pp. 19840–19849, 2014.

[28] Y. Zhan, X. Luo, S. Nie, Y. Huang, X. Tu, and S. Luo, “Selective separation of Cu(II) from aqueous solution with a novel Cu(II) surface magnetic ion-imprinted polymer,” *Industrial & Engineering Chemistry Research*, vol. 50, no. 10, pp. 6355–6361, 2011.

[29] B. Qiu, C. Xu, D. Sun et al., “Polyaniline coated ethyl cellulose with improved hexavalent chromium removal,” *ACS Sustainable Chemistry & Engineering*, vol. 2, no. 8, pp. 2070–2080, 2014.

[30] W. Xu, W. Zhang, Y. Li, and W. Li, “Synthesis of acrylic-lignosulfonate resin for crystal violet removal from aqueous solution,” *Korean Journal of Chemical Engineering*, vol. 33, no. 9, pp. 2659–2667, 2016.

[31] M. Zhang, L. Bai, W. Shang et al., “Facile synthesis of water-soluble, highly fluorescent graphene quantum dots as a robust biological label for stem cells,” *Journal of Materials Chemistry*, vol. 22, no. 15, pp. 7461–7467, 2012.

[32] L. Wang, W. Li, L. Yin et al., “Full-color fluorescent carbon quantum dots,” *Science Advances*, vol. 6, no. 40, article eabb6772, 2020.

[33] R. Liu, Y. Zhang, Y. Piao, and L. Y. Meng, “Development of nitrogen-doped carbon quantum dots as fluorescent probes for highly selective and sensitive detection of the heavy-ion Fe\(^{3+}\),” *Carbon Letters*, vol. 31, no. 4, pp. 821–829, 2021.

[34] S. Zhang, X. Liu, H. Xu et al., “Nitrogen-doped carbon quantum dots from polyethylenimine for optical dual mode determination of Cu\(^{2+}\) and L-cysteine and its logic gate operation,” *ACS Applied Materials & Interfaces*, vol. 12, no. 42, pp. 47245–47255, 2020.

[35] M. Li, X. Li, M. Xu et al., “A ratiometric fluorescent hydrogel of controlled thickness prepared continuously using microtomy for the detection and removal of Hg(II),” *Chemical Engineering Journal*, vol. 426, article 131296, 2021.

[36] S. Chen, M. X. Liu, Y. L. Yu, and J. H. Wang, “Room-temperature synthesis of fluorescent carbon-based nanoparticles and their application in multidimensional sensing,” *Sensors and Actuators B: Chemical*, vol. 288, no. 3, pp. 749–756, 2019.

[37] J. Hou, J. Yan, Q. Zhao, Y. Li, H. Ding, and L. Ding, “A novel one-pot route for large-scale preparation of highly photoluminescent carbon quantum dots powders,” *Nanoscale*, vol. 5, no. 20, pp. 9558–9561, 2013.

[38] Y. Li, Y. Liu, X. Shang, D. Chao, L. Zhou, and H. Zhang, “Highly sensitive and selective detection of Fe\(^{3+}\) by utilizing carbon quantum dots as fluorescent probes,” *Chemical Physics Letters*, vol. 705, pp. 1–6, 2018.

[39] C. Hu, R. An, L. Han, X. Wang, Y. Shi, and R. Ran, “Preparation of high strength double physically cross-linked hydrogels by immersion method–how to avoid uneven soaking,” *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 559, pp. 74–82, 2018.

[40] Q. Luo, H. Yuan, M. Zhang et al., “A 3D porous fluorescent hydrogel based on amino-modified carbon dots with excellent sorption and sensing abilities for environmentally hazardous Cr(VI),” *Journal of Hazardous Materials*, vol. 401, article 123432, 2021.

[41] S. Zhu, Q. Meng, L. Wang et al., “Highly photoluminescent carbon dots for multicolor patterning, sensors, and bioimaging,” *Angewandte Chemie*, vol. 125, no. 14, pp. 4045–4049, 2013.

[42] K. He, X. Zhan, L. Liu, X. Ruan, and Y. Wu, “Ratiometric fluorescent paper-based sensor based on CdTe quantum dots and graphite carbon nitride hybrid for visual and rapid determination of Cu\(^{2+}\) in drinks,” *Photochemistry and Photobiology*, vol. 96, no. 5, pp. 1154–1160, 2020.

[43] S. Maity, N. Parshi, C. Prodhan, K. Chaudhuri, and J. Ganguly, “Characterization of a fluorescent hydrogel synthesized using chitosan, polyvinyl alcohol and 9-anthraldehyde for the selective detection and discrimination of trace Fe\(^{3+}\) and Fe\(^{2+}\) in water for live-cell imaging,” *Carbohydr Polymers*, vol. 193, pp. 119–128, 2018.

[44] X. Liu, Z. Chen, R. Gao, C. Kan, and J. Xu, “Portable quantitative detection of Fe\(^{3+}\) by integrating a smartphone with colorimetric responses of a rhodamine-functionalized polyacrylamide hydrogel chemosensor,” *Sensors and Actuators B: Chemical*, vol. 340, p. 1299958, 2021.

[45] C. Tewari, B. SanthiBhushan, A. Srivastava, and N. G. Sahoo, “Metal doped graphene oxide derived from Quercus ilex fruits for selective and visual detection of iron(III) in water: experiment and theory,” *Sustainable Chemistry and Pharmacy*, vol. 21, no. 6, article 100436, 2021.

[46] A. Helal, M. E. Arafat, and M. M. Rahman, “Pyridinyl conjugate of UiO-66-NH\(_2\) as chemosensor for the sequential detection of iron and pyrophosphate ion in aqueous media,” *Chemosensors*, vol. 8, no. 4, article 122, 2020.

[47] P. Jia, Z. Wang, Y. Zhang et al., “Selective sensing of Fe\(^{3+}\) ions in aqueous solution by a biodegradable platform based lanthanide metal organic framework,” *Spectrochimica Acta part A: Molecular and Biomolecular Spectroscopy*, vol. 230, article 118084, 2020.

[48] D. Zhang, H. Li, J. Li et al., “Hydrophilic P(AM-CD-AMPS) microgel for visual detection and removal metal ions in aqueous solution,” *Applied Surface Science*, vol. 512, article 145668, 2020.

[49] A. Dwivedi, M. Srivastava, A. Srivastava, and S. K. Srivastava, “Synthesis of high luminescent Eu\(^{3+}\) doped nanoparticle and its application as highly sensitive and selective detection of Fe\(^{3+}\) in real water and human blood serum,” *Spectrochimica Acta part A: Molecular and Biomolecular Spectroscopy*, vol. 260, article 119942, 2021.
[50] F. Wang, X. Fu, X. Chai, Q. Han, H. Wang, and Q. Hao, “Highly selective fluorometric detection of para-nitrophenol from its isomers by nitrogen-doped graphene quantum dots,” *Microchemical Journal*, vol. 168, no. 40, article 106389, 2021.

[51] X. Zhao, S. Liao, L. Wang, Q. Liu, and X. Chen, “Facile green and one-pot synthesis of purple perilla derived carbon quantum dot as a fluorescent sensor for silver ion,” *Talanta*, vol. 201, pp. 1–8, 2019.