Hydrothermal oxidation method to synthesize nitrogen containing carbon dots from compost humic acid as selective Fe(III) sensor

Yan Zhu¹, Ying Bao¹, Liping Wang⁴, Jingtao Bi¹, Yong Liu⁵ and Chuang Xie¹

¹ School of Chemical Engineering and Technology and State Key Laboratory of Chemical Engineering, Tianjin University, Tianjin, 300072, People’s Republic of China
² School of Environmental Science and Engineering, Tianjin University, Tianjin, 300072, People’s Republic of China

E-mail: yingbao@tju.edu.cn

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Abstract
Residual sludge which is generated as a by-product during wastewater treatment needs efficient and environmentally friendly disposal. In this work, nitrogen containing carbon dots (N-CDs) was synthesized via one-step hydrothermal oxidation of humic acid for the first time, which was alkalinely extracted from the compost of sludge. The successful doping of the functional groups (hydroxyl, carboxyl and amino) on the surface of N-CDs were characterized by x-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR). The optical properties of the synthetic N-CDs were obtained from Ultraviolet-visible spectroscopy and Photoluminescence spectra. The N-CDs had an average diameter at 1.88 nm and exhibited a well-defined spherical shape. The aqueous solution of N-CDs with excitation-dependent properties showed a strong blue emission with 8.8% quantum yield (QY) under an excitation wavelength of 340 nm, which indicate the synthesized N-CDs a promising sensing probes for iron ions in aquatic system. Moreover, the mechanism of the N-CDs sensing technique was investigated in detail, which can be explained by the fluorescence static quenching effect and a ground-state complex formed in this process. This research demonstrates an extremely sensitive method for detecting heavy metal Fe³⁺ at a lower 1.9 nM level by using N-CDs as fluorescent probes without a complicated procedure.

1. Introduction
A large amount of iron ion polluted wastewater is discharged into nature due to the widespread application and imperfect post-processing system in industrialized countries, leading to an increased accumulation of iron ion in the aquatic system [1, 2].

Although the iron element is essential for the human body, its excessive accumulation can cause damage [3]. Therefore, it’s an urgent task to probe and monitor the Fe³⁺ in the water system, such as rivers, ponds, streams and oceans. Various methods for measuring iron ion are developed, such as ion selective electrode, inductively coupled plasma mass spectrometry, atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry [4, 5]. These methods have some limitations of cumbersome sample preparation, time-consuming analysis, and expensive equipment. Moreover, due to the complex synthesis process of probes suitable for Fe³⁺ ion, relatively few organic molecular probes are used to detect Fe³⁺ ion. Among the emerging methods to probe Fe³⁺, fluorescence detection is a favourable one due to high sensitivity, selectivity and fast detection [6, 7].

Recently, fluorescent carbon dots (CDs) have attracted tremendous attention in the metal ions probing area due to their various advantages including excellent water-solubility, stable photoluminescence (PL), superior biocompatibility and eco-friendliness. It was reported that carbon dots are prepared from roasted chickpeas [8] and peels [9] for the detection of iron ions, but the limits of detection are only in the μM level. Although some
reported CDs show high sensitivity to $\text{Fe}^{3+}$ in nM concentration, they exhibit poor selectivity towards $\text{Fe}^{3+}$ coexisting with other metals such as $\text{Pb}^{2+}$ [10], $\text{Cu}^{2+}$ [11] and $\text{Fe}^{2+}$ [12], while there are always a variety of metal ions in industrial wastewater. Notably, there is no practical detector application. Therefore, it remains a challenge to develop high selectivity fluorescence probes for $\text{Fe}^{3+}$ detection. Doping strategy (nitrogen (N), phosphorus (P), sulfur (S) et al) was proposed to modulate the sensitivity and selectivity of CDs [13, 14], in other words, to synthesize carbon dots containing heteroatoms. Among the various elements, nitrogen can introduce surficial function group such as $-\text{N}–\text{H}$ and $-\text{C}–\text{N}$, which could efficiently modulated the inherent properties of CDs, including limited electronic property, surface and local chemical reactivity [15–17]. Furthermore, these functional groups on nitrogen containing carbon dots (N-CDs) have different affinities to various target metal ions, resulting in highly selective photoluminescence (PL) intensity quenching [18–20]. Although N-CDs is considered as a promising candidate for selective probing $\text{Fe}^{3+}$ ions, the hydrothermal reaction between carbon materials and nitrogen-containing precursors is time-consuming, uneconomical and not environmentally benign, inhibiting the further practical application of the N-CDs [11, 16]. Therefore, it is an urgent task to search for a cost-effective precursor containing both carbon and nitrogen, and to develop a large-scale quick method to synthesize highly photoluminescent N-CDs.

In the past decades, the excess sludge in municipal wastewater treatment plants was mainly treated environmentally-unfriendly such as landfill, incineration [21]. Therefore, recycling sludge into high value-added products, such as humic acid, arising great attention [22, 23]. Composting is an ideal aerobic transformation process for biowaste stabilization [24]. Since the structures of humic acids contain conjugated double bonds and aromatic rings [25] and carbon dots were successfully hydrothermally synthesized from natural biomass which has similar structure with humic acid [26, 27]. Especially, humus contained carbon-based nanomaterials with low QY [28], graphene quantum dots was synthesized with fulvic acid via hydrothermal method without any additives [29], and N-CDs was prepared with fulvic acid, urea and citric acid by microwave-assisted pyrolysis [30]. It’s promising to utilize humic acid as a precursor containing nitrogen and carbon elements for hydrothermal oxidation to synthesize N-CDs with higher QY, realizing the resource utilization of sludge at the same time.

Here, the humic acid was first extracted from the compost of sludge and leaf for recycling solid waste. Then hydrothermal treatment of humic acid using hydrogen peroxide as an oxidant, blue fluorescent N-CDs was first synthesized within short time. A series of characterization methods including TEM, XPS, FT-IR and Raman analyses were used to evaluate the properties of the obtained N-CDs. The N element content in the obtained N-CDs was measured to be higher than the raw humic acid, illustrating the success of the synthetic method. The ultra-sensitivity and selectivity are found for $\text{Fe}^{3+}$, not for $\text{Li}^{+}$, $\text{Ag}^{+}$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{Ba}^{2+}$, $\text{Cu}^{2+}$, $\text{Sn}^{2+}$, $\text{Cu}^{2+}$, $\text{Al}^{3+}$, $\text{Cr}^{3+}$. Surprisingly, the prepared N-CDs showed sensitivity for $\text{Fe}^{3+}$ detection not only in aqueous solution but also in sensor strip based on paper. This research will provide a more convenient detection method of $\text{Fe}^{3+}$ in the treatment process of metal ions and significantly improve the high-value utilization of sludge.

2. Materials and methods

2.1. Chemicals

Humic acid, the source of nitrogen and carbon, was extracted from the humus which was obtained via composting defoliation and sludge from the sewage treatment plant in Jinnan District, Tianjin, China. The atomic percentage of nitrogen in humic acid is 1.05% as shown in table S1 is available online at stacks.iop.org/MRX/7/095008/mmedia. Hydrogen peroxide (30% wt) and ferric chloride hexahydrate were purchased from Chemart Chemical technology Co. Ltd (Tianjin, China). Dialysis bags (molecular weight cut off = 3.5 kDa) were obtained from Solarbio (USA). Standard stock solutions (5 mM) of metal ions ($\text{Li}^{+}$, $\text{Ag}^{+}$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{Ba}^{2+}$, $\text{Cu}^{2+}$, $\text{Sn}^{2+}$, $\text{Cu}^{2+}$, $\text{Al}^{3+}$, $\text{Fe}^{3+}$, $\text{Cr}^{3+}$) were prepared with Milli-Q water from the respective metal salts (LiCl, AgNO3, CaCl2, MgCl2·6H2O, BaCl2·2H2O, CuSO4·7H2O, SnCl2·2H2O, Cu(NO3)2, 3H2O, AlCl3, FeCl3·6H2O, Cr(NO3)3·9H2O). All chemicals were analytical grade and used directly. Water used for all experiments was provided by the Millipore water system (Milli-Q) with a resistivity of 17.9 MΩ cm.

2.2. Synthesis of N-CDs

Humic acid (0.075 g), H2O2 (1.5 ml) and Milli-Q water (5.0 ml) were treated hydrothermally in a Teflon-lined autoclave at 100 °C for 2 h. After cooling down naturally, the mixture was sonicated for 15 min and centrifuged at 15,000 rpm for 15 min. The supernatant was subjected to dialysis for 24 h at room temperature, change water twice after four hours, eight hours, and the dialysis product was freeze-dried to obtain brown N-CDs for characterization and use.
2.3. Characterizations of N-CDs
Transmission electron microscope (TEM, JEM-2100F) was used to observe the morphology of the products. The surface functional properties of N-CDs was investigated by x-ray photoelectron spectroscopy (XPS; ESCALAB 250Xi) and Raman spectroscopy. Raman spectra (Renishaw, λ_ex = 532 nm) and FT-IR spectra (Bruker Alpha, 4 cm⁻¹ resolution) were carried to examine the structure. Zeta potentials were obtained to measure the stability of the N-CDs (Zetasizer Nano Series, Malvern). An Edinburgh Instruments FLS1000 spectrophotometer was employed for the corrected steady-state fluorescence emission spectra and histograms of the instrument response functions (using a LUDOX scatter). Concentration of iron ions in lake water was measured by ICP-MS (Agilent 7700X).

2.3.1. Calculation of quantum yield (QY)
The quantum yield of N-CDs was calculated by comparing the PL intensities and integrated absorption of N-CDs samples with quinine sulfate (Qs, QY = 0.54 at 360 nm). To minimize the re-absorption effect, the absorbance of the N-CDs solution was kept below 0.10. Quinine sulfate was dissolved in 0.1 M H₂SO₄, while N-CDs were dissolved in Mill-Q water. The QY was calculated by the following equation:

\[ \Phi_{N-CDs} = \Phi_{Qs} \times \left[ \frac{I_{N-CDs}}{I_{Qs}} \right] \times \left[ \frac{A_{Qs}}{A_{NS}} \right] \times \left[ \frac{\eta_{N-CDs}}{\eta_{QS}} \right] \times 100\% \]  

where, Φ, I correspond to integrated absorbance values and PL intensity of the Qs and N-CDs, respectively, the refractive index η is the same for Qs and N-CDs which is 1.33.

2.4. Detection of iron ions
The detection of metal ions was carried out in aqueous solution at room temperature. A standard stock solution of 5 mM Fe³⁺ was prepared by dissolving FeCl₃·6H₂O in water and then diluted with Milli-Q water to obtain a series Fe³⁺ solution with different concentrations. 50 mg of N-CDs was dispersed into 50 ml of Milli-Q water and then passed through a 0.22 μm water filtration membrane to obtain N-CDs solution. The N-CDs aqueous solution was mixed with Fe³⁺ aqueous solution with the concentration varying from 0 to 0.005 M at a volume ratio of 2:1, and the fluorescent intensity was recorded from 360 to 650 nm with excitation wavelength at 340 nm. The same procedure was performed for the detection of other metal ions at a concentration of 5 mM including Li⁺, Ag⁺, Ca²⁺, Mg²⁺, Ba²⁺, Co²⁺, Sn²⁺, Cu²⁺, Al³⁺, Cr³⁺. Finally, to evaluate the selectivity of N-CDs for iron ion, 0.5 ml of standard stock metal ions solutions with or without Fe³⁺ were added into N-CDs solution. All the fluorescent intensities were recorded after equilibration.

2.5. Detection of iron ions in lake water
The real water samples from the Youth Lake of Tianjin University, Tianjin, China was centrifuged to remove a large number of solid particles, and then supernatant was filtered small impurities with a 0.22 μm water-based filter membrane. The treated sample was sealed and stored without adding other reagents, which was directly used to measure the Fe³⁺ concentration in the water sample.

3. Results and discussion
3.1. Synthesis and characterizations of N-CDs
Humic acid (HA), which is extracted from compost following the alkaline method specified by the National Humic Acid Association (IHSS), is abundant in carbon and carboxyl groups, as shown in scheme 1. After hydrothermal treatment accompanied by hydrogen peroxide, humic acid was oxidized and pyrolyzed to form a series of small molecule products [31], Finally, nano-scaled N-CDs with uniform molecular weight distribution was obtained after dialysis.

The size and morphology of the as-prepared N-CDs were characterized by the high-resolution TEM (HRTEM). As shown in figure 1(a), the N-CDs are well separated and quasi-spherical with a size distribution from 1.5 to 2.5 nm. The distances between the lattice fringes are further studied to be 0.218 nm (figure 1(b)) and 0.355 nm (figure 1(c)), corresponding to the (010) in-plane lattice spacing and inter-layer distance of graphite [32, 33]. Furthermore, Raman analysis of N-CDs (figure 1(d)) revealed the existence of D and G bands at ~1390 cm⁻¹ and ~1600 cm⁻¹, respectively, confirming the synthesized N-CDs contain sp² and sp³ hybridized carbon atoms and their architectures belonging to the carbon nanostructure family. Notably, the observed higher intensity of the G band than the D band verified the high quality of the synthesized products [6].
XPS measurements investigated the chemical compositions and chemical bonding environment of the N-CDs. The three peaks at 287.2, 401.5 and 534.4 eV in XPS spectrum (figure 2(a)) can be attributed to C 1s, N 1s and O 1s spectra respectively [34], suggesting that the synthesized N-CDs contains C, O and N elements with atom ratio of C:O:N = 67.56: 27.61: 4.82, compared with HA contains lower oxygen atom content of 21.66% (table S1). The C 1s XPS spectrum (figure 2(b)) exhibit three different peaks at 284.7, 285.7, and 288.7 eV corresponding to the carbon species in –sp²C–sp²C, C=O and C–N bonds, respectively. The two peaks at 533.6
and 532.1 eV in the O 1s spectrum (figure 2(c)) are assigned to O=\(\text{C}\)--OH and C–O groups. These peaks clearly confirm that the surface of synthesized N-CDs has abundant carboxyl and hydroxyl groups. In addition, the peak at 399.9 eV in the N 1s spectrum (figure 2(d)) is related to N in a graphite-like structure (N-C)\(_3\) and pyridinic-like N, while the peak at 401.8 eV is related to the N–H bond [33], confirming the existence of –NH\(_2\) surficial function group. The relative contents of pyridine N and N-H were calculated to be 79.3% and 20.7%, respectively, suggesting that the N element exists not only on the skeleton structure but also on the surface group.

Furthermore, FT-IR was performed to characterize the structure of N-CDs. The peaks at 1406 and 2937 cm\(^{-1}\) in the FT-IR spectrum (figure 3(a)) suggest vibrations of C=C bonds and the presence of C–H stretching [35]. The emerging peaks at 1707 and 1657 cm\(^{-1}\) are associated with C=O in carbonyl moieties [36], the stretching vibrations at 1177 and 1040 cm\(^{-1}\) were attributed to phenolic C–OH and C–OH of tertiary alcohol respectively, further certifying that oxygen-containing functional groups, especially –OH and –COOH are majorly present in the N-CDs. In addition, the wide band of the N–H stretching vibration can be detected at 3236 cm\(^{-1}\) [37], which verified the existence of –NH\(_2\) group.

To verify the surface functional groups of the synthesized N-CDs, zeta potential measurement was performed. The zeta potential was found to be \(-22.5 \text{ mV}\) without adjusting the pH of its aqueous solution. The value of zeta potential illustrates the presence of the negatively charged functional surface group and the stability of the system [38].

Above all, the traditional TEM, XPS, FT-IR and zeta potential analyses provided sufficient information on the diverse properties of N-CDs, such as size distribution, C, O, N element contents, surface group etc. Particularly, the surface of the prepared N-CDs was conformed to have nitrogen-containing groups and plentiful oxygen-containing functional groups, which not only improves its solubility in water but also adjusts its fluorescence performance, being conducive to its subsequent application.
3.2. Fluorescence detection of N-CDs

The UV–Vis absorption, excitation and emission spectra of N-CDs are shown in figure 3(b). Similar to most of the carbon dots, the UV–Vis absorption spectra of the obtained N-CDs has a broad absorption with a weak shoulder at approximately 300 nm in the visible range, which originates from n–π* transition of C=O bonds and agrees well with the reported CDs [39]. Under the excitation wavelength of 340 nm, the emission spectrum shows a sharp peak at 438 nm, showing a stokes shift of 98 nm, indicating the strong anti-interference ability of N-CDs in fluorescence detection [33]. With the excitation wavelength increasing from 330 to 400 nm, the emission peak showed slightly redshift from 432 nm to 463 nm in figure 3(c). This phenomenon indicates that the surface defects resulted in the excitation-dependent properties [40]. The excitation-dependent properties provided multicolour fluorescence under different excitation wavelengths, which implies potential applications of N-CDs [41]. Moreover, the PL quantum yield (QY) for the as-prepared N-CDs is calculated to be 8.8%, and table 1 shows a comparison in quantum yield with the reported values suggesting that the synthesized N-CDs has a relatively higher quantum yield among these carbon dots and could efficiently be used potentially for sensor [39]. This property might originated from a series of energy levels in surface states under the influence of various kinds of functional groups like C=O, C–NH2, and C–OH, as illustrated in the FT-IR spectrum (figure 3(a)) [42, 43].

As a superior performed fluorescence sensor, the stability of N-CDs needs to be tested, which is critical for the application. Fluorescence intensity slightly decreased under continuous 60 min excitation (340 nm) with the xenon lamp illuminating (300 W), illustrating anti-light bleaching properties of the N-CDs (figure S1). Besides, as shown in figure 3(d), the N-CDs were stored at room temperature with stability for over three months, showing a faint decrease of fluorescence intensity, which guarantees the application as a fluorescence sensor.

Figure 3. (a) FT-IR absorbance before and after binding with Fe3+ (inset: change in zeta potential); (b) UV–Vis absorption, emission and excitation spectrum of N-CDs in aqueous solutions (1.0 mg ml−1), λex = 340 nm and λem = 438 nm; (c) PL excitation wavelength dependent emission behavior; (d) The stability of N-CDs stored in room temperature after 3 months. Inset: photographs of the aqueous solutions of N-CDs after 3 months (A) and freshly prepared (B) under 365 nm UV light.
To obtain a better fluorescence effect, the optimization of solution pH value was also investigated. Under the neutral condition (pH ~ 7), the emission intensity of N-CDs was twice that in acidic (pH ~ 2) and alkaline (pH ~ 12) solutions (figure S2). The deprotonation of carboxyl groups of N-CDs in alkaline solution increases the electrostatic repulsions between particles, overcoming the trend of aggregation through layer–layer stacking, so the N-CDs exist in a stable non-aggregated state [45]. Therefore, it is worth noting that the fluorescence also exists under acidic and alkaline conditions, which is beneficial to its application in practical environment.

### 3.3. Selective and sensitivity of Fe$^{3+}$

The changes of fluorescence had been studied with the existence of metal ions at 5 mM to evaluate the selectivity of fluorescence quenching by various metal ions, including Li$^+$, Ag$^+$, Mg$^{2+}$, Ba$^{2+}$, Co$^{2+}$, Ca$^{2+}$, Sn$^{2+}$, Al$^{3+}$, Fe$^{3+}$ and Cr$^{3+}$. As shown in figure 4(a), only Fe$^{3+}$ can lead to significant fluorescence quenching, revealing the superior selectivity toward Fe$^{3+}$ compared with other tested metal ions. The quenching mechanism of Fe$^{3+}$ on N-CDs could be ascribed to the stronger affinity between Fe$^{3+}$ and hydroxyl groups of N-CDs than other metal ions due to the lower solubility product constant of iron complex [42].

In order to investigate the dependence of fluorescence intensity on the ions concentration, different concentrations of Fe$^{3+}$ solutions were mixed with N-CDs solution. Figure 4(b) displays that the fluorescence intensity gradually decreased with the increase in concentration of Fe$^{3+}$. When the concentration of Fe$^{3+}$ changes from 0 to 1 μM and from 10 to 250 μM, there are two linear relationships. The linear correlations can be fitted to the linear regression equation $(F_0-F)/F_0 = 0.00582C + 0.2023$ and $(F_0-F)/F_0 = 0.0007C + 0.303$, with $R^2 = 0.980$ and $R^2 = 0.973$, respectively, where $C$ implied the concentration of Fe$^{3+}$ (figure 4(d)). The linear relationships could be used as a working curve for the detection of iron ion concentration. Furthermore, the detection limitation (DL) was calculated to be 1.9 nM based on signal-to-noise ratio $3\sigma/K$ ($\sigma$ is the intensity standard deviation of the blank samples for ten times scans, $K$ is the slope of the regression equation), illustrating the extreme sensitivity. To evaluate the performance of N-CDs as a fluorescence probe, a comparison of the method with the published work related to fluorescence detection of Fe$^{3+}$ based on CDs was listed in table 2, showing the prepared N-CDs can detect iron ion at a lowest concentration.

Considering the sustainability of the quenching effect, the recovery of fluorescence intensity was investigated by adding EDTA in N-CDs/Fe$^{3+}$ solution. After the introduction of Na$_2$EDTA, the fluorescence intensity of N-CDs/Fe$^{3+}$ solution was hardly changed (figure 4(c)). This phenomenon suggests that Na$_2$EDTA cannot destroy the strong interaction between Fe$^{3+}$ and N-CDs [46], which suggesting that even if iron ion is not in the free state, N-CDs can be used as a robust detection of iron ion.

To check whether the N-CDs could effectively detect Fe$^{3+}$ in the presence of other metal ions, the fluorescence of the N-CDs was measured with all metal ions including and excluding Fe$^{3+}$ (5 mM) (figure S3). The results illustrate that there is extensive fluorescence intensity quenching of the N-CDs in the presence of all metal ions while no visible change is observed without Fe$^{3+}$, providing the promise for N-CDs to detect iron ion in the sample of complex metal ions.

On the other hand, the practical feasibility of N-CDs for probing Fe$^{3+}$ in the actual sample of water has also experimented. The fluorescence intensity of N-CDs decreased with the addition of lake water, and when the lake water was added from 0 to 300 ml, the $F_0-F/F_0$ of N-CDs show a good linear correlation with the volume of the Youth Lake (figure 5(a)). The volume ratio of N-CDs to the volume of the tested sample was 2: 1 in the standard linear regression curve in figure 4(d), so when adding 250 μl of the sample into 500 μl N-CDs solution, the average $(F_0-F)/F_0$ value obtained from the equation in figure 5(b) after repeating the experiment three times. Then according to $(F_0-F)/F_0 = 0.0007C + 0.303$, the C was calculated to be 20.4 mM, which is the concentration of Fe$^{3+}$ in the lake water. In order to investigate the accuracy of the method, lake water sample was measured by ICP-MS to obtain an Fe$^{3+}$ content of 19.5 mM, indicating good consistency was obtained in the

### Table 1. Contrasts of the quantum yield of the N-CDs with those of other CDs obtained from natural precursors.

| Materials                                      | QY (%) |
|------------------------------------------------|--------|
| Elliott soil from International Humic Substances Society [28] | 0.67   |
| Low-quality coal-derived humic acid [44]       | 2.28   |
| Bee Pollens [45]                               | 6.1    |
| Pipe tobacco [25]                              | 3.2    |
| Apple juice [20]                               | 4.27   |
| Humic acid (this work)                         | 8.8    |
lake water sample by this N-CDs with that obtained by ICP-MS. It can be concluded that the N-CDs is sensitive, rapid and straightforward for the determination of trace Fe$^{3+}$ in actual water samples from this result.

### 3.4. Possible sensing mechanism

Fluorescence quenching usually originates from static or dynamic quenching in which the fluorescent molecule binds with the quencher [47]. Dynamic quenching can be explained as: through the mechanism of energy transfer or charge transfer, the N-CDs in excited state returns to the ground state by colliding with the quencher [48]. On the contrary, static quenching occurs when the ground state N-CDs combine with the quencher to form a non-fluorescent ground-state complex [12]. The type of quenching can be judged by detecting the fluorescence lifetime and the formation of the complex. To better understand the quenching mechanism, the Stern–Volmer relationship was utilized to describe the kinetics of static and dynamic quenching processes [1, 6]:

![Figure 4](image)

**Figure 4.** (a) Selective quenching effect of various metal ions on N-CDs; (b) PL emission spectra of N-CDs mixed with Fe$^{3+}$, excitation wavelength at 340 nm, Fe$^{3+}$ concentrations from 1 to 600 μM; (c) Effect of EDTA on the fluorescence intensity of N-CDs/Fe$^{3+}$ complex under different concentrations of Fe$^{3+}$; (d) The linear plot of ($F_0$–$F$)/$F_0$ versus the concentration of Fe$^{3+}$.

### Table 2. Detection limit of CDs for Fe$^{3+}$ in other research and this work.

| Method                        | materials                                      | Linear range  | DL   | References |
|-------------------------------|------------------------------------------------|---------------|------|------------|
| Solid state method            | Citric acid and 1,10-phenanthroline             | 0–50 μM       | 35 nM| [12]       |
| Hydrothermal synthesis        | Glucose and boric acid                          | 0–16 μM       | 242 nM| [35]       |
| Facile electrochemical        | Graphite rods                                   | 0–0.7 μM      | 4.2 nM| [14]       |
| Microwave-assisted pyrolysis method | Fulvic acid, urea, and citric acid               | 0–100 μM      | 0.102 μM| [30]       |
| Hydrothermal synthesis        | Humic acid                                     | 0–1 μM        | 1.9 nM| This work  |

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Where \( F_0 \) and \( F \) are the fluorescence intensities before and after the addition of the quencher, respectively. \([Q]\) implies the quencher concentration in solution, and \( K_{SV} \) is quenching constant.

To explain the possible mechanism, the Stern–Volmer analysis of the fluorescence quenching experiment is shown in figure 5(c), the calculated quenching equation is \( F_0/F = 1.1881 + 0.0027[Q] \) in nM Fe\(^{3+}\) range with a \( R^2 \) value of 0.9918, showing an excellent linear Stern–Volmer relationship in N-CDs for Fe\(^{3+}\) detection.

According to the principle of fluorescence quenching described above, the inferred quenching mechanism might be a static or dynamic quenching model. To further confirm the quenching type, fluorescence lifetime and FT-IR spectra of N-CDs before and after the addition of iron ion were tested.

Fluorescence decay traces of N-CDs were recorded at excitation 340 nm by the single-photon timing method. According to the results (table S2), the average fluorescence lifetime of N-CDs is measured to be 7.301 ns, and the N-CDs aqueous solution with the presence of Fe\(^{3+}\) is 7.160 ns, showing little change. In addition, the formation of the complex was confirmed by the decrease in zeta potential from \(-22.5\) to \(-13.3\) mV (inset of figure 3(a)). On the other hand, ions binding effect was investigated through FT-IR spectra of N-CDs before and after metal ions quenching (figure 3(a)). The submerge vibration peaks at 1177 cm\(^{-1}\) in the FT-IR spectrum confirms the probable binding of Fe\(^{3+}\) with the hydroxyls on N-CDs. To sum up, this quenching process completely conforms to the static quenching mechanism.

3.5. Application of Fe\(^{3+}\) sensor

Supposing that N-CDs can be made into a simple iron ion detection application, especially without complicated device, which is both economical and convenient. The low-cost and easy-to-handle cellulose filter paper was tested here as a sensor strip. The N-CDs bounded paper-based strips were immersed in different concentrations of Fe\(^{3+}\) solutions for 5 min, and then placed under a 365 nm UV lamp illumination. As shown in figure 5(d), this sensor is hypersensitive to the iron ion under fluorescence emission and luminosity of the images decrease with
the Fe$^{3+}$ solutions varying from 100 nM to 30 uM. This method provides an efficient and convenient way to test the Fe$^{3+}$ in target sample qualitatively.

4. Conclusion

In this study, a low-cost and plain method was adopted to recycle solid waste effectively and economically. N-CDs modified with functional groups could be prepared by a moderate hydrothermal method to achieve resource utilization of sludge. N-CDs with 8.8% quantum yield showed a stable blue fluorescence when exposed to UV filter. High-resolution imaging and spectral analysis confirmed the successful synthesis of nanomaterial. Furthermore, N-CDs was investigated as the selective and sensitive fluorogenic sensor for detecting iron ion concentration with the low detection limit at 1.9 nM, and further paper implementation was tested with visible fluorescence quenching results from 250 nM to 50 μM concentration range. The quenching mechanism was determined as the static quenching. This method is considered as a promising candidate for iron ion sensing in real water samples with quick procedure.

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Conflicts of interests

There are no conflicts to declare.

ORCID iDs

Ying Bao @ https://orcid.org/0000-0002-4461-8035
Yong Liu @ https://orcid.org/0000-0002-6551-1608

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