Detection of Fe³⁺ and Hg²⁺ ions by using High Fluorescent Carbon Dots Doped With S and N as Fluorescence Probes

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Abstract

In this paper, carbon quantum dots (S-N-CDs) containing sulfur and nitrogen were synthesized using citric acid and thiourea. The average particle size of N-S-CDs is 8nm. The N-S-CDs surface contains various of functional groups, which has good water solubility. The fluorescence quantum yield of N-S-CDs is as high as 36.8%. N-S-CDs emits strong blue fluorescence in aqueous solution and has good photostability in neutral and alkaline NaCl solution. N-S-CDs has unique selectivity and high sensitivity to Fe^{3+} and Hg^{2+} ions, and the lowest detection limits are 1.4 μM and 0.16 μM , respectively. Under the interference of other metal ions, Fe^{3+} and Hg^{2+} ions can still effectively and stably quench the fluorescence of N-S-CDs. In addition, in the detection of actual samples, N-S-CDs can effectively detect Fe^{3+} and Hg^{2+} ions in tap water and lake water.

1. Introduction

Water is the source of life, people's domestic water is polluted by heavy metal ions with the development of industry. It has caused serious harm to human health, which has become a major problem worldwide. As a toxic metal, mercury ion Hg^{2+} has the characteristics of persistence, easy migration and biotoxicity [1, 2], and is easily bioaccumulated in human body through the food chain [3]. For normal organisms, excessive absorption of Hg^{2+} ions can cause damage to the central nervous system, kidneys and intestines, and in severe cases can lead to death [4]. Fe^{3+} is essential in most organisms. Although its content is small in the human body, it plays an important role, not only promoting the synthesis of hemoglobin and various enzymes [5], but also participating in oxygen uptake and transport, cell metabolism, enzyme catalysis and other processes [6]. Lack or excess of Fe^{3+} may lead to a variety of disorders and diseases [7]. Therefore, the determination of Hg^{2+} and Fe^{3+} is very important. At present, traditional metal ion detection methods include atomic absorption method [8], electrochemical assays [9], electrodialysis method, etc [10]. Although the above methods are popular and reliable, the relevant professional, expensive equipment and skilled operators are needed. The fluorescent probe be used for detection of metal ions in biological and environmental samples by using the optical quenching of metal ion pairs, which can avoid complex pretreatment process, do not need to use complex instruments, and has the advantages of simple operation and high sensitivity. However, the probes constructed by traditional metal materials have some problems, such as poor solubility, high cytotoxicity, poor photostability, which hinder the application in the actual environment. Fortunately, as the next generation of detection agent, carbon quantum dots (CDs) can effectively solve the above shortcomings.

As a new type of fluorescent probe. Carbon quantum dots can be used to detect various metal ions because of their photoluminescence and high selectivity for metal ions [11–15]. Besides, the CDs has following advantages, low toxicity, good chemical stability [16], environment-friendly and light-resistant bleaching [17], which makes it attract wide attention by researchers. There are a variety of raw materials [18] and synthesis methods for preparing CDs, such as arc discharge [19], laser ablation [20], plasma treatment [21], electrochemical oxidation [22], hydrothermal oxidation [23] or acid oxidation [24],

microwave radiation [25] and so on. However, the quantum yield of the synthesis method of single carbon source is low, making it difficult to apply on a large scale. Increasing research proves that the surface passivation and functionalization of CDs can both increase the FLQY of CDs and the number of surface functional groups [26]. When S and N elements are doped into the carbon point, the FLQY and properties are significantly improved. Therefore, it is necessary to investigate the CDs doping with S and N elements to improve the performance and the FLQY.

In this paper, sulfur and nitrogen co-doped carbon quantum dots were synthesized using citric acid and thiourea as raw materials. The morphology and surface functional group of the carbon point were observed by TEM, FTIR and XPS. The fluorescence stability of the synthesized carbon point was analyzed by fluorescence spectrum. Besides, the selectivity and sensitivity to metal ions of the N-S-CDs were tested. Also, the N-S-CDs was applied to the determination of Hg^{2+} and Fe^{3+} ions in tap water and lake water

2. Experimental

2.1. Materials and instruments

Citric acid, thiourea, dichloromethane, cyclohexane, dimethylformamide (DMF), anhydrous ethanol, NaCl, NaOH, HCl, H_2SO_4 (98%) were obtained from Tianjing Yongda Company. BaCl_2 , CaCl_2 , CuSO_4 , MgCl_2 , FeCl_3 , $(\text{CH}_3\text{COO})_2\text{Zn}$, MnCl_2 , $\text{Cd}(\text{NO}_3)_2$, $\text{Cr}(\text{NO}_3)_3$, FeCl_2 , $\text{Pb}(\text{NO}_3)_2$ and $\text{Hg}(\text{NO}_3)_2$ were purchased from Alfa Aesar brands. All the solvents and chemicals were analytically pure and can be used without further treatment. Ultra-pure water was used for all experimental water.

The molded images of the carbon dots were recorded by the FEI Talos200S transmission electron microscope(TEM) under the 200kV acceleration voltage. FTIR were recorded on the Nicolet 670 FTIR spectrometer. The fluorescence spectroscopy and absorption spectra of the sample were acquired from Hitachi F-2700 spectrophotometer and Tu-1810 UV-Vis spectrophotometer. The X-ray photoelectron spectroscopy(XPS) analysis by K-AlphaPlus electronic energy spectrometer. The carbon dot was synthesized in the WGL-45B electrothermal blast drying tank.

2.2. Synthesis of N-S-CDs

0.25g citric acid and 0.25g thiourea were added into 20ml ultra-pure water and ultrasound was used to fully dissolve for 30min. Then, the fully dissolved solution was heated at 180 °C for 8 h in a polytetrafluoroethylene hydrothermal reactor. After that, the CDs solution was centrifuged at 10000 rpm for 20 min. Next, the clarified solution was filtered with 0.22 μm filter membrane, and then dialyzed twice in a dialysis bag with a molecular weight cut-off of 1000. Finally, the liquid from the second dialysis was stored at 4 °C.

2.3. Stability test of N-S-CDs

The aqueous solution of N-S-CDs was added to various solvents (ultra-pure water, anhydrous ethanol, dichloromethane, cyclohexane and dimethylformamide solution). After reaching the equilibrium, the fluorescence intensity under the excitation of 350nm ultraviolet light was measured.

Secondly, the fluorescence intensity of N-S-CDs in different PH values were measured. The solution of carbon quantum dots with the same concentration was poured into the solution with different PH values, which configured with HCl and NaOH.

Thirdly, the same concentration of carbon quantum dots solution was poured into different concentrations of NaCl solution. The fluorescence intensity was measured in this way to test the stability of CDs in salt solutions.

2.4. Hg^{2+} and Fe^{3+} sensing

All metal ion experiments were prepared under the same conditions. Measuring the selectivity of N-S-CDs to metal ions, 100 $\mu\text{mol/L}$ concentration of 1 mL of various metal cation solutions (Fe^{2+} , Ca^{2+} , Mg^{2+} , Fe^{3+} , Ni^{2+} , Pb^{2+} , CO^{2+} , Zn^{2+} , Cu^{2+} , Cd^{2+} , Cr^{3+} , Hg^{2+}) was combined with 1 mL of diluted N-S-CDS solution. The mixed solution was fully fused and stood for 20min. Then, the fluorescence intensity of emission wavelength of each solution was measured by fluorescence spectrophotometer to compare the selectivity of carbon quantum dots to metal ions.

Different concentrations of Fe^{3+} solutions (0,5,10,30,60,90,100,120,180,210,270,330,400,500,600 μM) were added to the diluted N-S-CDs solution. Their fluorescence emission intensities at 350nm excitation wavelengths were compared.

Different concentrations of Hg^{2+} solution (0,5,10,30,60,90,100,120 μM) were blended with 1 mL diluted N-S-CDs solution. The fluorescence intensity of each solution under 350nm excitation light was measured.

2.5. Quantum yield measurements

To measure the quantum yield of N-S-CDs, Quinine sulfate (QY 54% at 350 nm excitation) solution was chosen as a reference. The QY of CDs was calculated via the following formula[27]:

$$\phi_s = \phi_{st} (A_{st}/I_{st}) (I_s/A_s) (\eta_s/\eta_{st})^2$$

Where “ ϕ ” is relative QY, “A” is optical density. “I” stands for the integrated emission intensity, “ η ” is the refractive index of the solvent. After calculation, the QY of N-S-CDs is 36.8%.

3. Results

3.1. Characterization of N-S-CDs

The microstructure of the N-S-CDs is observed by TEM. The N-S-CDs exhibits ball shapes with uniform particle size, well-dispersed without serious agglomeration (Fig. 1a). The diameter of the N-S-CDs is in a

range of 5-9nm and the main size is distributed around 8nm, as is shown in Fig. 1b.

The surface functional groups of N-S-CDs is conducted by FT-IR spectrum and the result is shown in Fig. 2. The peak of N-S-CDs in the range of 3220–3360 cm^{-1} should be the characteristic peak of the stretching vibration overlapping O-H band and N-H band. The presence of these functional groups provides excellent water solubility to the carbon points. The strong absorption peak of 1636 cm^{-1} is the stretching vibration peak of C = O, indicating the existence of carbonyl group. The peak value at 1394 cm^{-1} belongs to C-N stretching vibration. The broad vibration bands at 1340 and 1064 cm^{-1} generated from the bending vibrations of C-N and C = S, respectively. These results indicated that the surface of N-S-CDs was rich in amino, hydroxyl, carbonyl and other functional groups, which also indicated the existence of N and S in N-S-CDs.

In order to have a more comprehensive understanding of N-S-CDs. The surface elements and functional groups of N-S-CDs were analyzed by XPS. The full scan spectrum of XPS showed that the surface of N-S-CDs mainly contained C, O, N and S, and the contents were 50.63%, 31.125%, 11.88% and 6.36%, respectively. The XPS shows three peaks at 531.58, 401.07 and 284.82eV, which correspond to O1s, N1s and C1s (Fig. 3a). The peaks at 227.08eV and 163.21eV are due to S_{2s} and S_{2p}. So, the N and S elements are successfully doped in carbon dots. The N-H, C-N-C and N-H are attributed to N1s (Fig. 3c). The XPS spectrum of C1s shows three peaks, they are accordingly due to C = C, C-OH, and C = O groups (Fig. 3b). Three peaks can be seen in the XPS spectrum of S_{2p}, which are related to sulfoxide, C = S and -SH, respectively (Fig. 3d).

3.2. The optical properties of N-S-CDs

Using UV-vis spectrum, it is found that N-S-CDs has two absorption peaks at 232 nm and 330 nm (Fig. 4). The weak absorption peak at 232nm may be due to the absorption of the $\pi \rightarrow \pi^*$ transition of C = C, and the wider one at 340nm should be formed by the $n \rightarrow \pi^*$ transition of C = O [28, 29]. This also confirms the existence of C = C and C = O in N-S-CDs.

The fluorescence properties of S-N-CDs were further studied by fluorescence spectrum. It is found that the maximum excitation wavelength is 350nm, and the maximum emission wavelength is 440nm (Fig. 5a). The picture shows that the color of CDs solution is light yellow. It emits strong blue fluorescence under ultraviolet light. When increasing the excitation wavelength (300nm-390nm), the emission peak of N-S-CDs shows red shift, and its intensity increases at first and then decreases (Fig. 5b). The results show that the carbon quantum dots have significant wavelength dependence, which can be attributed to emissive traps and the electronic conjugate structure of S-N-CDs. The reason may be attributed to the size effect of S-N-CDs with different light-emitting sites on the surface or carbon quantum dots with different particle sizes.

As a fluorescent detector, it is necessary to measure the stability of N-S-CDs in different solvent environments. Therefore, the fluorescence intensity of N-S-CDs in various solvents was measured. The

fluorescence intensity of N-S-CDs in different solvents is different (Fig. 6c). N-S-CDs are easily soluble in polar solvents such as water, methanol and dimethylformamide, but their solubility in non-polar solvents such as dichloromethane and cyclohexane become very small. This is due to the protonation of the solvent. Due to the effect, hydrogen bonds are easily formed between the unbonded n electrons of the hydrophilic group of carbon quantum dots and the polar solution to enhance fluorescence emission.

Mixing N-S-CDs with NaCl solutions, it was found that the fluorescence of N-S-CDs did not change significantly with the concentration of NaCl solution increasing from 0 to 3 mol/L (Fig. 6b). It indicates that its fluorescence emission was not affected by the ionic strength of the medium.

The influence of the PH value on the fluorescence performance was further investigated. Figure 6a, the fluorescence intensity of N-S-CDs in neutral and alkaline solutions is stronger than in acidic solutions and has a good stability with the change of PH.

From the analysis above, N-S-CDs can be used as a reliable fluorescence detector for neutral and alkaline aqueous solution with high ion concentration.

3.3. Selectivity and interference study

Investigate the sensing performance of N-S-CDs, its selectivity to metal cations is an important parameter. Adding 1.0 mL different metal ions solution such as Ca^{2+} , Mg^{2+} , Fe^{3+} , Ni^{2+} , Pb^{2+} , Co^{2+} , Zn^{2+} , Cu^{2+} , Cd^{2+} , Cr^{3+} , Hg^{2+} ions ($100 \mu\text{mol} \cdot \text{L}^{-1}$) into N-S-CDs solution. Figure 7 shows the relative fluorescence intensity (F/F_0) changes when different metal ions are added. F is the fluorescence emission intensity of different metal ions, and F_0 is the fluorescence intensity of N-S-CDs. It is observed from the spectrum that Hg^{2+} and Fe^{3+} have obvious fluorescence quenching phenomenon for N-S-CDs, while Fe^{2+} has slight quenching phenomenon. The fluorescence quenching of other metal ions can be negligible. In addition, Hg^{2+} and Fe^{3+} have almost no influence on the quenching of N-S-CDs under the interference of other metal ions (Fig. 8).

S

Figure 8 (a) Fluorescence intensity of N-S-CDs after the coexistence of other metal ions and Fe^{3+} . (b) Fluorescence intensity of N-S-CDs after the coexistence of other metal ions and Hg^{2+} .

Most of the fluorescence emission of CDs may be caused by the recombination of radiation produced during exciton trapping due to surface defects. These excitons can be quenched by non-radiative electron transfer between CDs and metal ions [30]. The surface of N-S-CDs is rich in functional groups, which can introduce a large number of defects as excitation energy traps. These surface functional groups can form complexes with Hg^{2+} and Fe^{3+} , resulting in electron transfer and fluorescence quenching [31]. Compared with other metal ions, oxygen-containing functional groups have a strong affinity with Fe^{3+} , and the rapid electron transfer between them leads to fluorescence quenching. There are a lot of -OH and -COOH on the

surface of N-S-CDs, which can combine with Fe^{3+} to promote fluorescence quenching[33]. Besides, the addition of sulfur can promote the transfer of electrons between N-S-CDs and metal ions. Hg^{2+} can be easily bind to C-S in N-S-CDs, thus facilitating the detection of Hg^{2+} [32]. Another possibility of quenching is that the absorption of the adsorbed complex overlaps partly or completely of the excitation and/or emission spectra of N-S-CDs [34]. Then, we tested the UV-Vis of Hg^{2+} and Fe^{3+} ions. Figure 9, the absorption spectrum of Fe^{3+} partially overlaps with the excitation or emission spectra of N-S-CDs. The absorption spectra of Hg^{2+} did not overlap. Therefore, the influence of internal filtration effect (IFE) is excluded.

3.4. Detection of Hg^{2+} and Fe^{3+} ions

The effect of different concentrations of Fe^{3+} on the fluorescence of N-S-CDs was studied(Fig. 10a). With the increase of Fe^{3+} ions concentration from $1.0\mu\text{M}$ to $600\mu\text{M}$, the PL intensity of N-S-CDs gradually decreases. When the Fe^{3+} ions concentration reaches $180\mu\text{M}$, the quenching degree reaches 80%. The Fig. 10b shows that there exhibits well linear relationship between the concentration of Fe^{3+} ions and the fluorescence intensity of N-S-CDs from $40\mu\text{M}$ to $130\mu\text{M}$. The linear equation is expressed as:

$$F_0/F = 0.02132[\text{Fe}^{3+}] + 0.34945, (R^2 = 0.995).$$

F_0 is the fluorescence intensity of N-S-CDs, and F is the Fluorescence intensity after adding Fe^{3+} . Under the same experimental conditions, according to the formula $3S_d/k$ (21 groups of parallel measurements), the LOD of Fe^{3+} ions is $1.4\mu\text{M}$.

After that, the fluorescence intensity of N-S-CDs was detected with the increase of Hg^{2+} concentration. (Fig. 10c). The PL of N-S-CDs decreases gradually, and shows a good linear relationship from $40\mu\text{M}$ to $80\mu\text{M}$ (Fig. 10d). The linear equation is expressed as:

$$F_0/F = 0.18611[\text{Hg}^{2+}] - 6.27114, (R^2 = 0.994).$$

The LOD of Hg^{2+} is $0.16\mu\text{M}$.

3.5. Measurement of Hg^{2+} and Fe^{3+} in real samples

Test the effect of N-S-CDs in tap water and lake water. First of all, the tap water and lake water were filtered using $0.22\mu\text{m}$ syringe filter. Then carry on the recovery experiment. As shown in Table 1, the results are consistent with the concentration of added metal ions. The quantitative recovery of Fe^{3+} ions is between 97.16% and 103.62%, and the quantitative recovery of Hg^{2+} ions is between 93.58% and 101.22%. The above results indicate that N-S-CDs has potential applicability in the determination of Hg^{2+} and Fe^{3+} ions in the tap water and lake water.

Table.1 Recovery tests for determination of Hg^{2+} and Fe^{3+} in tap water and lake water($n = 3$).

		Type	Spiked(μM)	Found(μM)	Recovery(%)	RSD(% $n = 3$)
1	Fe^{3+}	tap water	45.0	44.23	98.28	1.65
			50.0	50.91	101.82	1.83
			55.0	53.44	97.16	1.32
2		lake water	45.0	46.63	103.62	2.15
			50.0	1.27	102.54	2.67
			55.0	55.82	101.49	2.89
3	Hg^{2+}	tap water	45.0	42.11	93.58	1.02
			50.0	48.64	97.28	1.89
			55.0	53.64	97.53	1.69
4		lake water	45.0	44.32	100.72	2.23
			50.0	50.61	101.22	1.94
			55.0	54.92	99.85	2.11

4. Conclusion

In this paper, citric acid and thiourea were used as precursors to synthesize N-S-CDs with high fluorescence quantum yield (36.8%). The average particle size of carbon quantum dots was 8nm and the dispersion was good. The surface contained a variety of functional groups and had good hydrophilicity. The fluorescence of N-S-CDs is stable in high ion concentration, neutral and alkaline aqueous solution. The carbon dots can selectively detect Fe^{3+} and Hg^{2+} ions with high sensitivity and the LOD is 1.4 μM and 0.16 μM , respectively. Through the actual sample detection, N-S-CDs can effectively detect Fe^{3+} and Hg^{2+} ions in tap water and lake water, which has a good application prospect as a fluorescence detector.

Declarations

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contributions

H L: Resource, Writing-review and Editing. H X: Methodology, Investigation, Writing. H L: Software, Data curation. All authors read and approved the final manuscript.

Consent to participate and Consent for publication

All authors agree to participate and agree to publish.

Availability of data and material/ Data availability

All data generated or analysed during this study are included in this published article.

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Figures

Figure 1

(a) TEM images of N-S-CDs. (b) Particle size distribution histogram of the N-S-CDs.

Figure 2

The FTIR spectra of N-S-CDs

Figure 3

(a) XPS spectra of N-S-CDs. (b) High-resolution XPS data of C1s .(c) High-resolution XPS data of N1s .(d) High-resolution XPS data of S2p.

Figure 4

UV-vis spectrum and photos of cds in the sun and under ultraviolet lights.

Figure 5

(a) EX and EM spectra of N-S-CDs.(b) Fluorescence spectra with increasing excitation wavelength(280-400nm).

Figure 6

(a) The curve of fluorescence intensity at different PH values.(b) The curve of fluorescence intensity of N-S-CDs under different ion concentration.(c) Histogram of fluorescence intensity of carbon points in different solvents.

Figure 7

Fluorescence intensity of N-S-CDs after adding different metal ions.

Figure 8

Figure 8 displays two plots, (a) and (b), showing the fluorescence intensity of N-S-CDs after the coexistence of other metal ions and Fe³⁺. Plot (a) shows the fluorescence intensity of N-S-CDs after the coexistence of other metal ions and Fe³⁺. Plot (b) shows the fluorescence intensity of N-S-CDs after the coexistence of other metal ions and Hg²⁺.

Figure 9

Figure 9 displays two plots, (a) and (b), showing the fluorescence intensity of N-S-CDs after the coexistence of other metal ions and Fe³⁺. Plot (a) shows the fluorescence intensity of N-S-CDs after the coexistence of other metal ions and Fe³⁺. Plot (b) shows the fluorescence intensity of N-S-CDs after the coexistence of other metal ions and Hg²⁺.

Figure 10

Figure 10 shows the effect of Fe^{3+} and Hg^{2+} on the fluorescence intensity of CDs. Panel (a) shows the fluorescence spectra of CDs in the presence of Fe^{3+} at various concentrations (0 to 600 μM). Panel (b) shows the linear equation for detecting Fe^{3+} based on the fluorescence intensity ratio F_0/F . Panel (c) shows the fluorescence spectra of CDs in the presence of Hg^{2+} at various concentrations (0 to 120 μM). Panel (d) shows the linear equation for detecting Hg^{2+} based on the fluorescence intensity ratio F_0/F .