本科毕业论文

Facile synthesis of carbon-based fluorescent nanomaterials for sensitive detection of Fe^{3+}

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2022 年 06 月 1 日

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2022 年　5　月　22　日

Contents

Abstract

Carbon quantum dots (CQDs) are a new type of fluorescent nanomaterials, which not only have stable fluorescence properties and multi-functionality but also have a variety of raw materials and preparation methods, thus they can be widely used in cancer treatment, biosensing, catalysis and other fields. Fe is one of the most important elements in nature and one of the trace elements which is necessary for the human body. The metabolism and the necessary life activities are maintained by Fe. However, excessive iron can affect the human nervous system, heart, liver, etc., and even lead to iron poisoning. At present, due to human activities and industrial production, the iron content in the water environment in some places has already exceeded the standard, which means the real-time monitoring of iron is necessary. In this topic, we prepared Fe^{3+} sensor based on carbon quantum dots by one-step hydrothermal synthesis method with o-phenylenediamine and ethylene glycol as raw materials. The particle size of the obtained CQDs was uniform, about 5 nm, and the optimal excitation wavelength was 420 nm. In the absence of Fe^{3+}, CQDs can emit bright blue light. When the concentration of Fe^{3+} is gradually increased in the CQDs solution, fluorescence quenching will be caused by the complex reaction between Fe^{3+} and CQDs. Meanwhile, the fluorescence intensity and Fe^{3+} concentration has a good linear relationship. Through the fluorescence quenching analysis of CQDs by different metal ions, CQDs are specific to Fe^{3+}, which are basically unaffected by other common metal ions.

Keywords: Carbon quantum dots, hydrothermal, Fe^{3+}, fluorescence

摘　要

碳量子点是一种新型荧光纳米材料，不仅有着稳定的荧光性能和功能性，且其有多样化的原料和制备方式，所以能被广泛应用于癌症治疗，生物传感，催化等领域。Fe^{3+}是自然界最重要的元素之一，也是人体必需的微量元素之一，参与人体的新陈代谢和维持身体必须的生命活动。但过量的铁会影响人的神经系统，心脏，肝等，甚至会导致铁中毒。目前由于人类活动和工业生产，导致一些地方的水环境中的铁含量超标而影响周围生态，所以对于铁的实时监测十分重要。本课题我们以邻苯二胺和乙二醇为原料通过一步的水热合成法制备了基于碳量子点的 Fe^{3+} 传感器。所得的 CQDs 的粒径尺寸均一,约为 5 nm,最佳激发波长为 420 nm。没有铁离子存在时,CQDs 能够发出明亮的蓝光,当往 CQDs 中逐渐增加铁离子浓度时,铁离子与 CQDs 发生络合反应引起了荧光粹灭，CQDs 的荧光强度逐渐降低，且荧光强度与 Fe 浓度有良好的线性关系。并且通过不同金属离子对 CQDs 的荧光粹灭分析，CQDs 对 Fe^{3+} 有着特异性，且检测过程基本不受其他的常见的金属离子的影响。

关键词：碳量子点；溶剂热法；三价铁离子；荧光

1 Introduction

Heavy metals are important constituents of nature and are involved in the growth and metabolism of living organisms, and today they are widely used in modern technology such as aviation and medicine because of their special properties. However, due to human activities, many aquatic environments have been polluted by excessive levels of heavy metals, which can seriously affect the health of surrounding organisms. [1] Under the trends, the detection of heavy metals has become important research in the environmental industry.

Iron has been considered one of the most important elements in Heavy metals, which is involved in most of the life activities of almost all organisms, and proteins containing Fe^{3+} are an important subclass of the metalloproteins. [2] For humans, iron is required for nerve conduction, RNA and DNA synthesis, enzymes in the human body, cellular metabolism, etc. However, excess intake of iron in the body can lead to muscle damage due to oxidative stress and can even affect the nervous system, such as Alzheimer's disease and Parkinson's disease. [3-4] Besides, the quality of products will be affected by the inaccuracy of the detection of iron in the manufacturing industry. Therefore, the monitoring of the concentration of iron ions in different environments is essential, and the sensitive, easy and fast detection method becomes an additional important feature. [5-6]

Due to the environmental development mentioned above, the detection of Fe^{3+} has been a hot topic in recent years. Some traditional detection methods, such as atomic absorption spectroscopy, electrochemical, or different spectrophotometric methods, have achieved a high degree of accuracy. For instance, in 2018, Liu et al. used UV-Vis spectrophotometry to detect complexation reactions occurring between tannic acid compounds and Fe^{3+}, and in 2021 Zhang et al. prepared an off-on electrochemiluminescence sensor to achieve continuous detection of Fe^{3+}. [7-8] On the other hand, the operational difficulties, expensive equipment, and other objective factors lead to less application of those methods. Nowadays, it has been found that the quantum dots have better optical and electrical characteristics compared with other luminous materials, in the field of metal detection, fluorescence sensors have been widely studied due to their ease of operation, sensitivity, low price, and other advantages.

1.1 Carbon quantum dots (CQDs)

Quantum dots are a new type of semiconductor nanomaterial that can be excited to high-energy forms under UV irradiation and then emit excitation wavelengths to produce fluorescence, and the main components include a carbonaceous core and a surface passivation layer that has shown in **Fig. 1.1** Besides, different colors of fluorescence can be produced by changing the sizes of the quantum dots. [10] By comparing with organic fluorescent dyes, quantum dots have a wider absorption spectrum and narrower emission spectrum, which leads to a wider range of applications in detection. [11] Some of the fluorescent quantum dots with a wide range of applications are mainly semiconductor quantum dots, carbon quantum dots (CQDs), transition metal disulfide quantum dots, graphene quantum dots (GQDs), and black phosphorus quantum dots (BPQDs). The following is mainly focused on the explanation of the development background, preparation, and application of CQDs.

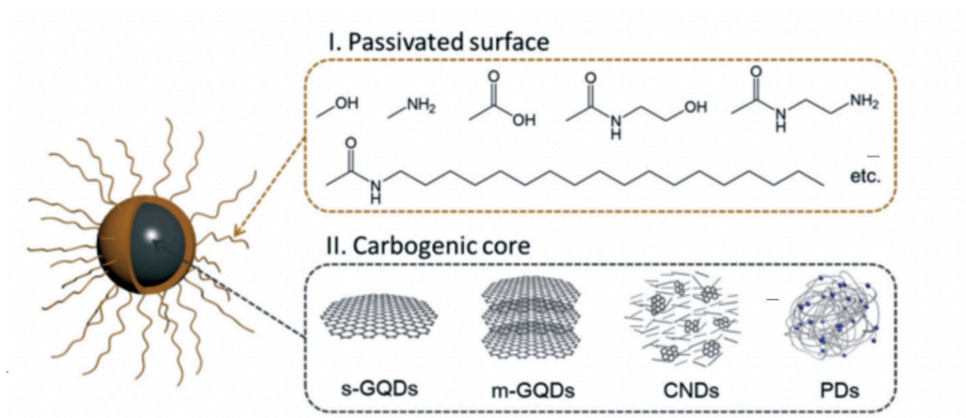

Fig. 1.1 The schematic diagram of GQDs (single layer), m-GQDs (multi-layer), CNDs (carbon nanodots), PDs (polymer dots). [9]

1.2 Fluorescence properties of CQDs

CQDs are carbon nanomaterials with excellent fluorescence properties and only 10 nm in size, which are widely used in chemical probes, targeted drug delivery, catalysis by their excellent photoelectric properties, electrical conductivity, solubility, and low toxicity. [12-13]

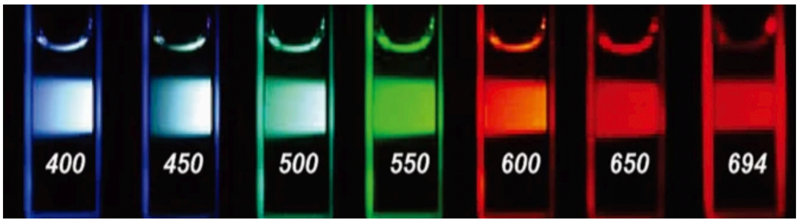

Fig. 1.2 Fluorescence of CQDs through band-pass filters of different wavelengths under the UV irradiation of 400 nm. [14]

1.3 Process status of CQDs

In 2004, Xu et al. discovered fluorescent carbon and short-tube carbon when separating the products. In their research, HNO_3 was applied to introduce the carboxyl group and NaOH was added to extract the precipitate when preparing single-walled carbon nanotubes by arc discharge method, and the hydrophilicity of the products was improved in this way. Meanwhile, the material with a fluorescent effect was found in the process of separation performed by gel electrophoresis, which is the first discovery of carbon quantum dots. [15]

Since the discovery of carbon quantum dots in 2004, the excellent luminescent properties and inexpensive preparation have been favored. In 2011, Liu et al. explored the synthesis of carbon quantum dots and found that under an argon atmosphere at 280 °C, white light quantum dots would be obtained by the decomposing of citric acid with the participation of the reaction solvent-lithium nitrate. If the surface coating is applied to the obtained quantum dots, the fluorescence yield will be greatly enhanced. In addition, fluorescent labeling materials with weak toxicity will be synthesized when the carbon quantum dots are functionalized in silane. [16]

As environmental protection has become a hot topic, people have started to explore more environmentally friendly methods for the synthesis of carbon ions. In 2014, the team of Xu investigated the green synthesis of carbon quantum dots by using apple juice as raw material and the hydrothermal method. Meanwhile, high specificity for the fluorescence quenching of Hg^{2+} of carbon quantum dots had been found. [17] In 2017, dairy waste is utilized by Pooja's team to synthesize carbon quantum dots that emit blue light, which can replace semiconductor quantum dots for real-time monitoring of selenite in water because of their extremely small environmental impact [18].

Recently, natural and degradable products have become a major hot topic, and carbon quantum dots generated from natural products have been widely studied consistently due to their excellent characteristics, so carbon quantum dots generated from natural products have received wide attention. In 2022, Nagaraj and Ramalingam's team synthesized CQDs by hydrothermal method based on Borassus flabellifer's endosperm. CQDs synthesized are successfully applied for the detection of Fe^{3+} in aqueous solution. [19] In the same year, Zhang et al. successfully synthesized CQDs with blue fluorescence and low biotoxicity using ginkgo nuclei, which could perform bioimaging in MCF7 cells and be successfully applied to the detection of nitrite in food toxins. [20]

1.4 The synthesis method of CQDs

Recently, carbon quantum dots have received extensive research and attention not only because of their excellent luminescence and detection capabilities but also because of their simple and convenient preparation methods and improved performance. At present, various methods for synthesizing carbon quantum dots have been developed. According to the different carbon sources of carbon quantum dots, they can be simply divided into "top-down" synthesis and "bottom-up" synthesis. [21] The "top-down" method is mainly to strip small-sized carbon quantum dots from large-sized carbon sources, such as arc discharge, laser ablation, electrochemistry, etc., which can decompose carbon-rich substances to obtain carbon nanotubes, carbon fibers, or other carbons quantum dots. "bottom-up" method mainly uses small carbon materials such as citric acid and glucose to synthesize carbon quantum dots by microwave synthesis method, hydrothermal method, etc. [22-24]

1.4.1 Laser ablation

Laser ablation can easily prepare high-purity nanoparticles without any surfactant or other chemical reagents. [25-27] Cui et al. synthesized CQDs using low-cost carbon cloth and a self-made dual-beam system, which not only synthesized fast, but also achieved a yield of up to 35.4%. Due to the electronic transition from the π* state to the surface state, the obtained CQDs are homogeneous with a stable and excitation-independent PL emission. [28]

1.4.2 Microware irradiation

Microwave is a fast and low-cost way to heat organic compounds. Using citric acid and 3,3'-diaminoaniline (DAB) as raw materials, Liao et al. obtained fluorescent carbon quantum dots by microwave heating. The CQDs obtained has good water solubility and can have different degrees of fluorescence quenching with Se as shown in **Fig. 1.3**, which can be used for the specific detection of Se. [29]

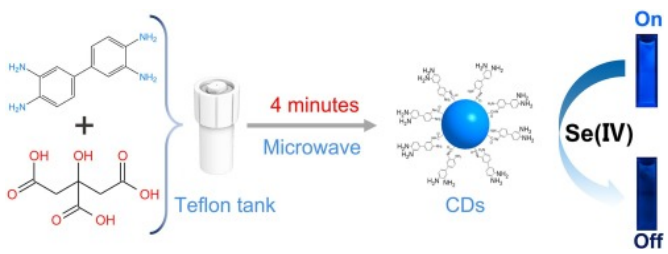

Fig. 1.3 Process Mechanism of Microwave Preparation of Fluorescent CQDs. [29]

1.4.3 Hydrothermal method

Hydrothermal synthesis is a widely used method for synthesizing carbon quantum dots, which is non-toxic and has a little environmental impact, making it widely used. [30] Guo's team used citric acid and diethylphenylmethylamine as raw materials to prepare nitrogen-doped CQDs by a hydrothermal method with a yield of 84.79%, which was successfully applied to the detection of Ellagic acid. [32] At present, the hydrothermal method has been applied to the green synthesis of various carbon quantum dots. Paul et al. used jackfruit peel and tamarind peel as carbon sources to obtain blue luminescent carbon dots with anticancer activity by hydrothermal method. The team successfully developed a green and non-toxic way to prepare carbon quantum dots, and the obtained results can be applied to medicine. [33]

1.5 The conclusion of this study

Herein, a fluorescent carbon quantum dot was successfully prepared by a one-step hydrothermal reaction with the raw material of o-phenylenediamine and ethylene glycol. At the same time, the blue fluorescence can be emitted by the CQDs obtained under UV light, which can be utilized for the detection of Fe^{3+} with high specificity. Consequently, some of the shortcomings of other synthesis methods are successfully solved by this one-step hydrothermal synthesis, such as the cumbersome process of chemical ablation steps, low yield of laser ablation, etc. Besides, the obtained CQDs react very quickly in the detection process of metal ion pairs, improving the efficiency of the detection process.

2 Experimental

2.1 Chemicals

The organic drugs used in this experiment were o-phenylenediamine (o-PD), ethylene glycol, anhydrous ethanol. Fe^{3+} obtained from the corresponding metal salts. Among them, the ferric chloride hexahydrate used was purchased from Sinopharm Chemical Co, o-PD, ethylene glycol and anhydrous ethanol received from Aladdin Biological Technology Co. (Shanghai, China).

Throughout the study, the specifications of the reagents used were analytically pure and ultra-pure water of 18.25 MΩ·cm was used (UPR-II-40L, Sichuan, China).

2.2 Instruments

Table 1: Characterization test instruments

Name	Model	Production company
UV-Vis Spectrophotometer	2800S	Shanghai ShunyuHengping Scientific Instrument Co.
Fourier infrared spectrometer	Nexus670	Thermo Nicolet Co. (Amarica)
X-Ray Diffractometer	D8ADVANCE03030502	Bruker Co. (Germany)
Laser particle size	Zetasizer Nano ZS90	Malvern Panalytical, (Britain)

2.3 Preparation of the CQDs

In this experiment, carbon quantum dots were synthesized by the hydrothermal method which can be used as detection reagents for Fe^{3+}. First, 0.3 g of o-PD was weighed and dissolved with 1 ml of ethylene glycol in 19 ml of anhydrous ethanol (the glass apparatus used for the experiment were soaked with hydrochloric acid and then washed), The mixture was then transferred to the 50 ml Teflon liner of the autoclave, which was subsequently carefully sealed. After the preparation, the reaction was heated in a drying oven at 220℃ for 8 hours.

At the end of the reaction, the reactor needs to be cooled sufficiently to room temperature and then taken out to obtain a dark brown solution containing CQDs. After the basic preparation was completed, the obtained product was purified by dialysis and then dried by freezing, and finally, the prepared product was stored in the fridge at 4℃.

2.4 Detection of Fe^{3+}

Under normal circumstances, 15 ml of the final product is taken and placed into 3 ml of ultrapure water to dilute and mixed thoroughly to obtain a solution containing CQDs. The absorption spectrum is measured by a UV-Vis absorption spectrometer, and it is found that the fluorescence is the strongest when the excitation wavelength is 420 nm. Different concentrations of Fe^{3+} were added to the obtained solution and oscillated sufficiently, and the excitation wavelength of 420 nm was selected to irradiate it to measure the change of its fluorescence intensity. The selectivity of the sensor is to replace Fe^{3+} with other metal ions such as Co^{2+}, Ca^{2+}, Al^{3+}, and other steps are repeated with the process mentioned above.

3 Results and Discussion

3.1 Preparation and characterization of CQDs

Stable CQDs were successfully synthesized using o-phenylenediamine and ethylene glycol by hydrothermal method. Firstly, CQDs are characterized by transmission electron microscopy (TEM), and clear and uniformly distributed particle images are obtained, as shown in **Fig. 3.1(a).** It is shown that the synthesized CQDs are circular and have good dispersion, and most of the CQDs are about 4.5 nm in diameter as the information shown in **Fig. 3.1(b)** and roughly the same thickness. When the obtained carbon quantum dots are characterized by XRD, as shown in **Fig. 3.2.(a)**, there is a broad diffraction peak at about 22.5, which is consistent with the (002) crystal plane of carbon, indicating the amorphous character of carbon. [21] Besides, it shows that under the conditions of high temperature and high pressure, the obtained product CQDs have been fully carbonized. [22]

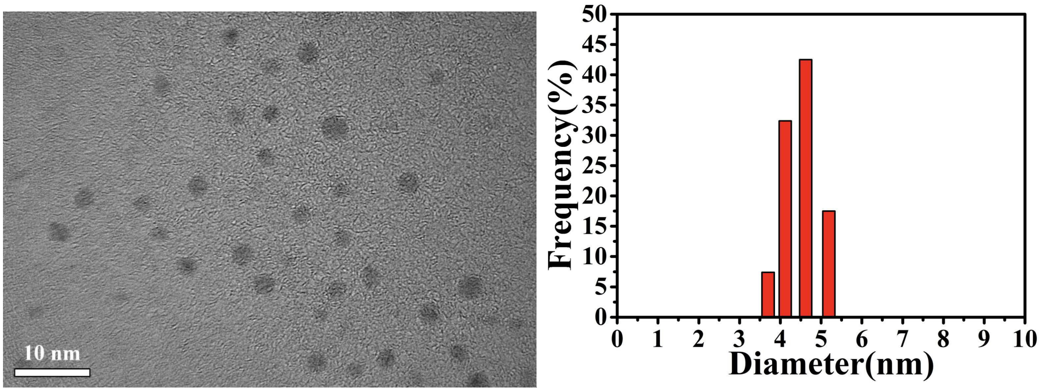

Fig.3.1 TEM image of CQDs (a), the particle size distribution map (b).

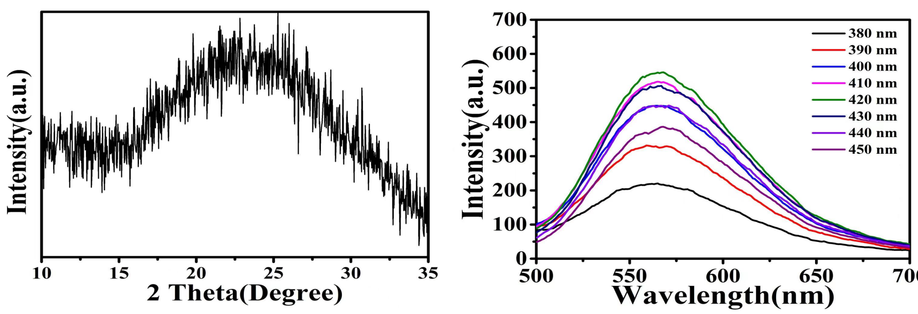

Fig.3.2 XRD pattern of CQDs (a), emission spectra of CQDs excited at different excitation wavelengths(b).

Fig.3.2. (b) shows the emission spectra of CQDs excited by different excitation wavelengths from 380 to 450 nm, when the excitation light is 420 nm, the CQDs exhibit common excitation-dependent photoluminescence (PL) behavior. [31]

3.2 Fluorescence sensing of Fe^{3+}

The obtained CQDs can be applied as a qualified fluorescence sensing of the efficient detection for Fe^{3+}. As the information demonstrated in **Fig. 3.3(a-b)**, the second fluorescence peak of CQDs was changed after the addition of Fe^{3+}, which means that new substances are formed after adding Fe^{3+}. Based on previous studies, fluorescence quenching is caused by the complex formed by Fe^{3+} and carbon quantum dots. [34] Accordingly, Fe^{3+} can change the fluorescence intensity of CQDs, so it can be successfully used for detection.

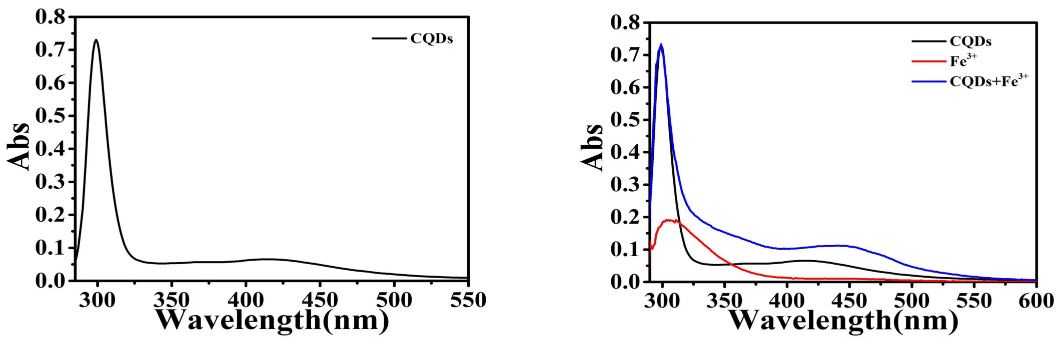

Fig.3.3. UV-Vis absorption spectrum of CQDs solution(a), UV-Vis absorption spectrum of solution after adding Fe^{3+}(b).

3.3 Analyze performance

In the in-depth analysis of the Fe^{3+} sensor based on CQDs, different concentrations of Fe^{3+} were added to the final product, and it can be seen from the **Fig. 3.4(a)** that with the increase of Fe^{3+} concentration, the fluorescence intensity at the excitation wavelength of 565 nm gradually decreased. The standard curve was drawn according to the change of fluorescence intensity at 565 nm as shown in the **Fig. 3.4(b)** between 1μM and 100 μM, the change ratio of Fe^{3+} concentration and fluorescence intensity showed a good linear law with a linear correlation coefficient of 0.9953, which showed that the method has the advantages of high sensitivity and easy operation. Thus, the CQDs based senser can be used for the detection of Fe^{3+} in various environments.

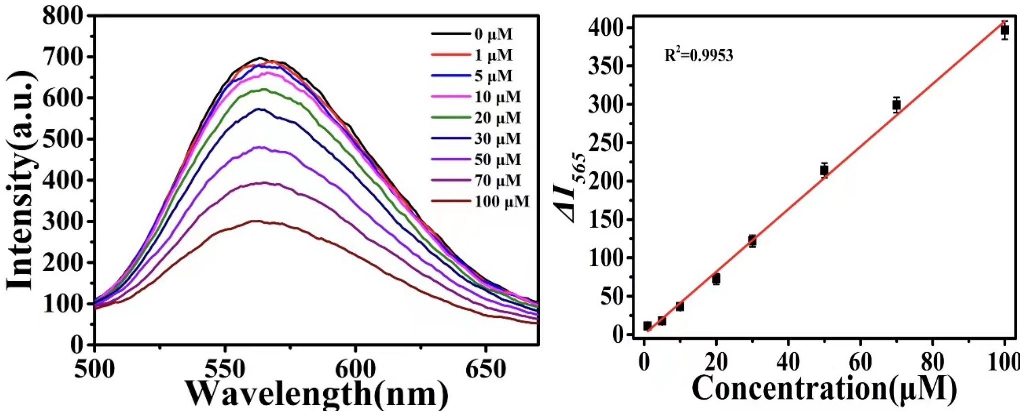

Fig.3.4. Changes in fluorescence spectra of CQDs are prepared by adding different Fe^{3+} concentrations (a). The linear curve of the change value and the corresponding Fe^{3+} concentration (b).

3.4 Selectivity of CQDs with different metal ions

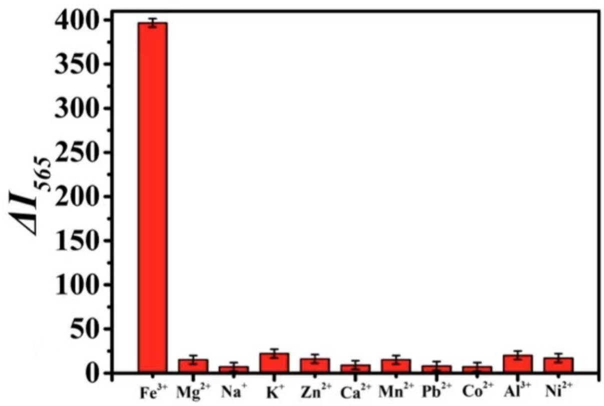

Fig.3.5. Fluorescence selectivity of the CQDs in the presence of various metal ions.

In order to explore the specificity of the obtained CQDs, and the ability of different metal ions to interfere with the system of the obtained CQDs, the final product was subjected to a selectivity assay, and the results are shown in **Fig.3.5**. In the case of the selectivity of CQDs, such as Mg^{2+}, Al^{3+}, Mn^{2+}, Na^{+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, the fluorescent spectrum hardly changes, which proves that these metal ions cannot undergo fluorescence quenching with the obtained CQDs, so significant interference won't be caused by them for the detection of Fe^{3+}. These results suggest that the generated CQDs are highly specific and sensitive to Fe^{3+} ions and can be used as fluorescent sensor probes for the selective detection of Fe^{3+} ions.

4 Conclusion

In conclusion, we prepared an efficient, satisfying, and convenient Fe^{3+} sensor based on CQDs via the solvothermal reaction of o-phenylenediamine and ethylene glycol. The prepared CQDs have stable fluorescence, and the change of fluorescence quenching intensity under different Fe^{3+} concentrations has a stable linear relationship with Fe^{3+} ions, so it can be applied to the detection of Fe^{3+} ions in real situations. Besides, due to the specificity of CQDs sensors, it can be applied to more fields. However, there are still many challenges in the research of carbon quantum dots. (1) Although carbon quantum dots are prepared in various ways, their production is still limited, which is hard to be commercialized. (2) The luminescence of carbon quantum dots is affected by the particle size, but the method to control the particle size of carbon quantum dots should be extensively studied.

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致 谢

读书不觉春已深，一寸光阴一寸金。

一转眼大学时光已到末尾，整个论文的准备过程更像是结束大学步入社会的一场课程，在写论文与准备实验的过程中，让我对四年的所学习的知识进行了系统的复习与整理，并对不同的分析产物的进行了深入分析，了解了其所具备的应用价值及商业价值。在这一研究学习中，更多的培养了我了解与掌握一种新知识的能力，并能够在将来的工作中得以应用。这一切所有的成果，都要感谢杨升宏老师的指引和王科师兄一路的耐心指导与指正，他们是我在大一时第一次进入实验室的指路人，他们教会我的不只是化学知识与实验技巧，更多的是学习与生活中所要具备的思维方式，他们让我领会到了大学教书育人的宗旨。从文献的阅读，各部分内容的撰写到最后格式的修改，都离不开老师与同学们的帮助，所以论文的顺利完成离不开所有人的帮助。

在此对大学期间遇见所有的老师和同学致以崇高的敬意与祝福。