Preparation of Carbon Quantum Dots from Traditional Chinese Medicine Residues and their Application in Metal Ion Detection

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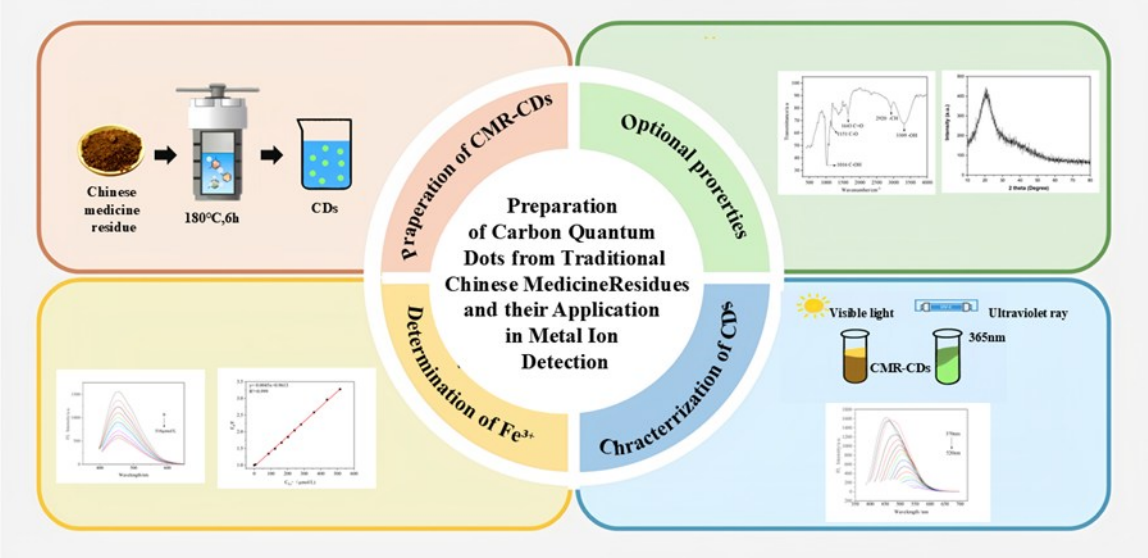
GRAPHICAL ABSTRACT



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The disposal of residues from traditional Chinese medicine results in resource waste and poses non-negligible environmental concerns. While the synthesis of carbon dots (CDs) from green raw materials has been widely studied, the use of Chinese medicine residues (CMR) which are rich in ligno-cellulosic components as a carbon source for CDs preparation remained largely unexplored. Notably, converting CMR into carbon dots (CMR-CDs) offered a dual benefit: it enhanced resource utilization and mitigated the environmental impact of these waste materials. In this study, CMR-CDs were synthesized *via* a simple, eco-friendly one-step hydrothermal method for metal ion detection. The CMR-CDs demonstrated highly selective fluorescence quenching toward Fe^{3+}, with a strong linear correlation (R^2 = 0.999) between fluorescence intensity and Fe^{3+} concentration (0 to 516 μmol/L). The detection limit was determined to be 6.0 μmol/L. These findings suggest that CMR-CDs hold significant potential for rapid and sensitive Fe^{3+} detection in future applications, while also highlighting the value of ligno-cellulosic waste in sustainable nanomaterial synthesis.

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Keywords: Chinese medicine residues; Carbon dots; Metal ion detection

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INTRODUCTION

Carbon dots (CDs), as a new type of nanomaterial with a size of less than 10 nanometers, have received great attention since they were first discovered by Scrivens in early 2004 (Xu *et al.* 2004). They integrate the advantages of traditional semiconductors (such as inorganic quantum dots) and small molecules (such as fluorophores), and they possess excellent photobleaching resistance, photostability, biocompatibility, and stable physicochemical properties (Luo *et al.* 2021; Kanwal *et al.* 2022). Compared with other nanomaterials (Liu *et al.* 2019), CDs have a wide range of potential application prospects in biomedical diagnosis and treatment (Chen *et al.* 2023; Govindarajan *et al.* 2024).

CDs synthesis methods are primarily categorized into two approaches: top-down and bottom-up methods. In top-down process, the macromolecule is destroyed or dispersed into small-sized CQDs by physical or chemical methods (Wang *et al.* 2019; Luo *et al.* 2021). In the bottom-up method, CDs are synthesized from small molecular precursors such as citric acid and glucose using various techniques, including microwave-assisted synthesis (Choi *et al.* 2017; Hu *et al.* 2021), thermal decomposition (Zhang, M. *et al.* 2020;

Zhang, W. *et al.* 2020), or hydrothermal treatment (Tomskaya *et al.* 2018). Hydrothermal synthesis is the most advantageous approach for CDs preparation because it is a simple, green, and environmentally friendly method (Liu *et al*. 2015; Xu *et al.* 2017).

Ligno-cellulosic material, comprising cellulose, hemicellulose, and lignin, has emerged as a sustainable and abundant carbon source for the synthesis of functional nanomaterials, including CDs (Gan *et al.* 2023). Its sustainability (Isikgor and Becer 2015), low cost, and environmental friendliness make it an ideal precursor for the green synthesis route of CDs. Thus, there is an urgent need to explore new carbon sources derived from lignocellulosic materials for the synthesis of CDs.

Previous studies have demonstrated that Chinese medicine residues (CMR) are mainly composed of lignocellulose and are rich in various nutritional components (Li *et al.* 2024). However, inappropriate disposal methods—such as incineration, stacking and landfilling—not only lead to significant resource waste but also contribute to environmental degradation (Meng *et al.* 2018; de Azevedo *et al.* 2019). Therefore, converting CMR into CDs offers a dual benefit: it provides an innovative carbon source for CDs synthesis while promoting the recycling of valuable resources and mitigating the environmental impact associated with these residues.

This study developed an approach utilizing CMR to synthesize green fluorescent CMR-derived carbon dots (CMR-CDs) through a one-step hydrothermal method. These CMR-CDs were successfully employed for metal ion detection, demonstrating their potential for practical applications in environmental monitoring and providing a sustainable solution for CMR utilization.

EXPERIMENTAL

Materials

CMR were provided by the pharmacy of a traditional Chinese medicine hospital in Shanxi province. The chemical reagents were purchased from Tianjin Comieo Chemical Reagent Co., Ltd. All reagents were used directly without further purification.

Preparation of the CMR-CDs

The CMR was dried in the constant temperature oven for 24 h, and then crushed in a pulverizer and passed through a 24-mesh sieve. Next, 1.5 g of CMR's powder and 60 mL of ultrapure water were added to a beaker. The mixed solution was stirred with a glass rod for 5 minutes, and then transferred to the high-pressure reaction kettle. The hydrothermal reaction was conducted at a constant temperature of 180 °C for 6 h. After cooling to room temperature, the untreated solution of CMR-CDs was filtered by a 0.22 μm filter paper to remove large impurities. A total of 25 mL of supernatant was transferred into a dialysis bag with cut-off of 1000Da; the purified CMR-CDs solution was obtained after 18 h. The solution was freeze-dried and stored.

Characterization Methods

The carbon structure of CMR-CDs was analyzed by X-ray diffractometer (Fringer Class, LANScientific, China). An infrared spectrometer (IRXross, Shimadzu, Japan) was employed to analyze the functional group and chemical composition of CMR-CDs. The fluorescence intensity of CMR-CDs was measured by a fluorescence spectrophotometer (F2710, Hitachi, Japan). The ultraviolet absorption spectrum of CMR-CDs was determined

using a UV spectrophotometer (TU-1901, Puxi, China).

Detection of Fluorescence Process

The mother liquors solution of Fe^{3+}, K^{+}, Na^{+}, Mg^{2+}, Ni^{+}, Cu^{2+}, Mn^{2+}, Co^{2+} and Al^{3+} were 0.05 mol/L, and 30 µL of the above solutions were pipetted for each experiment in the ion selectivity experiment. Mother liquors solution (570 µg/mL) was prepared by dissolving 2.85 mg of CMR powder in 5 mL ultrapure water, which was subsequently diluted to 57 µg/mL for the selectivity experiments of metal ions. Five minutes were waited after mixing Fe(III) ions with the CQDs before measuring fluorescence. The fluorescence intensity of the CMR-CDs solution without and with metal ions was recorded as F_0 and F, respectively. Finally, the ratio between (F_0-F) and F_0 was calculated.

The fluorescence intensity of CMR-CDs (1.6 mL, 2000 µg/mL) with different concentration of Fe^{3+} were investigated. The fluorescence intensity of the mixed solution of Fe^{3+} and CMR-CDs were recorded as F, and the fluorescence intensity of CMR-CDs solution without Fe^{3+} were recorded as F_0, finally the linear correlation coefficient (R^2) were calculated based on the value of F_0/F under different concentration of Fe^{3+}.

RESULTS AND DISCUSSION

Characterization of the CQDs Structural

The XRD pattern of the CDs (Fig. 1a) displays a strong peak at *ca.* 21 °, which reveals the amorphous carbon structure of the CDs. The functional groups of the CMR-CDs were presented in the infrared spectrum of CMR-CDs with the wavelength range of 4000 to 1000 cm^{-1}.

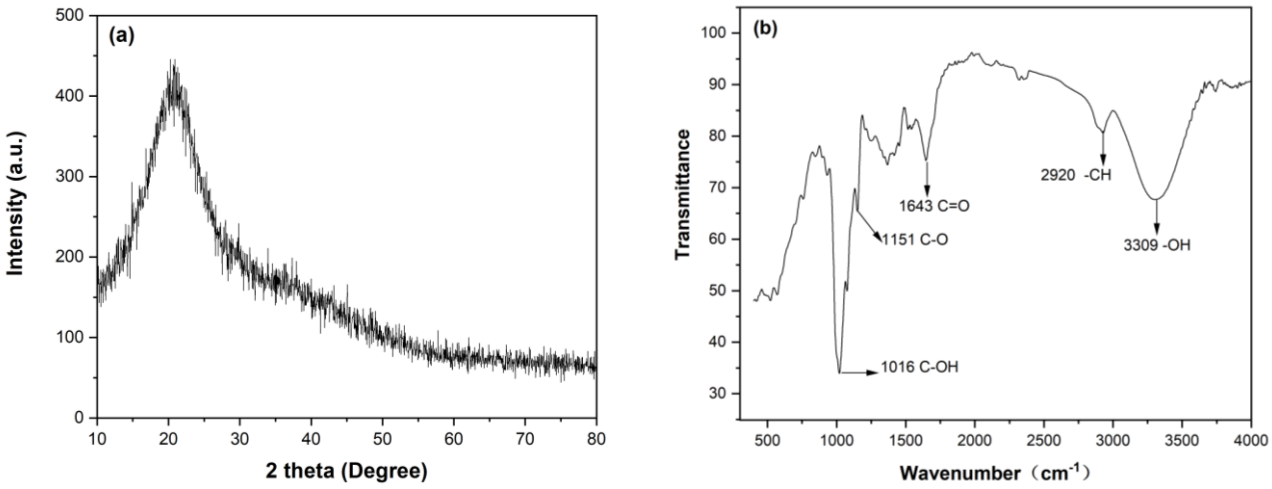

Fig. 1. (a) The XRD pattern of the CQDs and (b) Fourier transform infrared spectrum of CMR-CDs

As shown in Fig. 1b, the absorption peak at 1016 cm^{-1} corresponds to the stretching vibration of C-OH, and the peak at 1643 cm^{-1} is produced by stretching vibration of carbonyl. The absorption peak at 2920 cm^{-1} corresponds to the C-H stretching vibration, which may arise due to the methyl or methylene groups associated with aliphatic hydrocarbon (Yang *et al.* 2022). The broad absorption peak at 3309 cm^{-1} corresponds to the stretching vibration of -OH group (Dai *et al.* 2023). Therefore, CMR-CDs contain

water-soluble functional groups such as carboxyl, hydroxyl, and carbonyl on the surface. The presence of the carboxyl groups yields a negative ionic charge at the surface of the CMR-CDs, as well as a good water solubility.

Optical Properties of CQDs

As shown in Fig. 2a, there was an absorbance peak of CMR-CDs in the ultraviolet region at 273 nm, which is attributed to the π-π* energy transitions of the C=C bond with sp^2 hybridization (Xing *et al.* 2024; Yang *et al.* 2024). As shown in the inset photograph of Fig. 2a, the CMR-CDs solution was brownish yellow under sunlight and emitted bright green fluorescence under ultraviolet light (365 nm), which demonstrated that the CMR-CDs had the excellent capacity to absorb UV light of that wavelength.

CDs luminescence is dependent on the excitation wavelength (Xing *et al.* 2024). As shown in Fig. 2b, the excitation wavelength of CMR-CDs increased from 370 nm to 520 nm with the increase of 10 nm, while the emission wavelength shifted from 454 nm to 522 nm. The fluorescence intensity gradually decreased when the excitation wavelength increased, and the optimal excitation wavelength was 370 nm. These results were consistent with previous reports. The dependence of excitation wavelength may be due to particle size and surface defects (LeCroy *et al.* 2017; Nguyen *et al.* 2020).

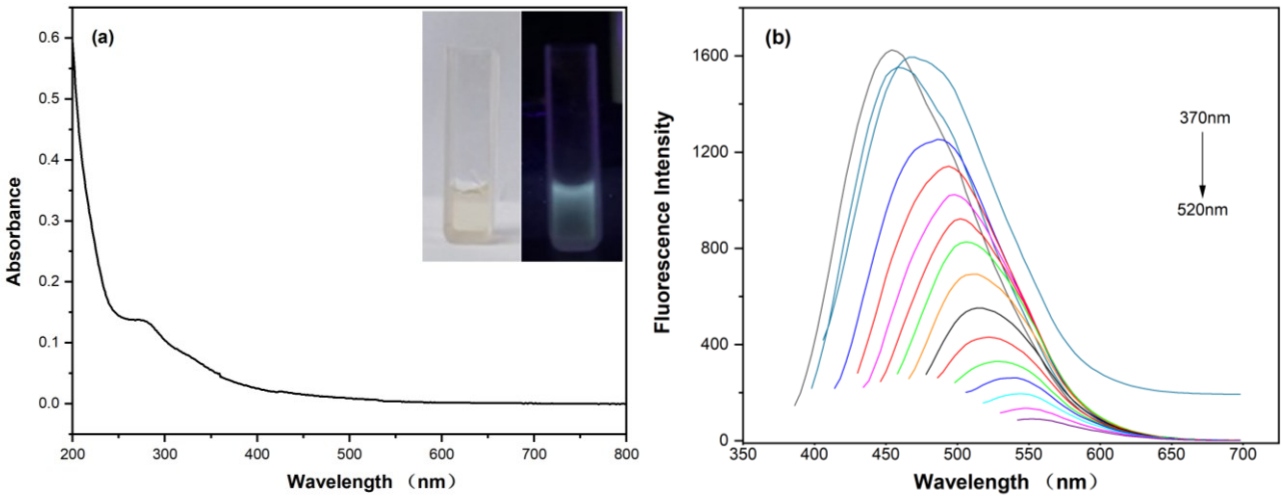

Fig. 2. (a) UV-visible absorption spectra of CMR-CDs. Inset photographs of CMR-CDs solutions under sunlight (left) and ultraviolet light (right) and (b) Emission spectra of CMR-CDs at different excitation wavelength

Application of CMR-CDs in Metal Ion Detection

The selectivity was investigated by adding Fe^{3+} and other metal ions, including K^+, Na^+, Ba^{2+}, Ni^+, Mg^{2+}, Mg^{2+} and Co^{2+} ions. As shown in Fig. 3, the quenching ratio (F_0-F)/F_0 for CMR-CDs in Fe^{3+} solution was nearly 96%, while the quenching ratio of CMR-CDs in other metal ions was below 10%, which indicated that the CMR-CDs had higher selectivity for Fe^{3+}.

As shown in the Fig. 4a, the fluorescence intensity of the CQDs decreased as the Fe^{3+} concentration increased. A linear relationship was observed for the Fe^{3+} concentration in the range 0 to 516 μmol/L (Fig. 4b), with the corresponding calibration curves F_0/F=0.0045[Fe^{3+}] + 0.9613 (R^2=0.999). Previous studies demonstrated that the detection

limit of the ion can be calculated as the ratio of three times of the standard deviation of blank experiment to the slope of the calibration curve (Yang *et al.* 2022). In this study, the detection limit of Fe^{3+} ion was 6.0 μmol/L, which indicated that CMR-CDs can quantitatively analyze Fe^{3+} and had potential application value in environmental detection.

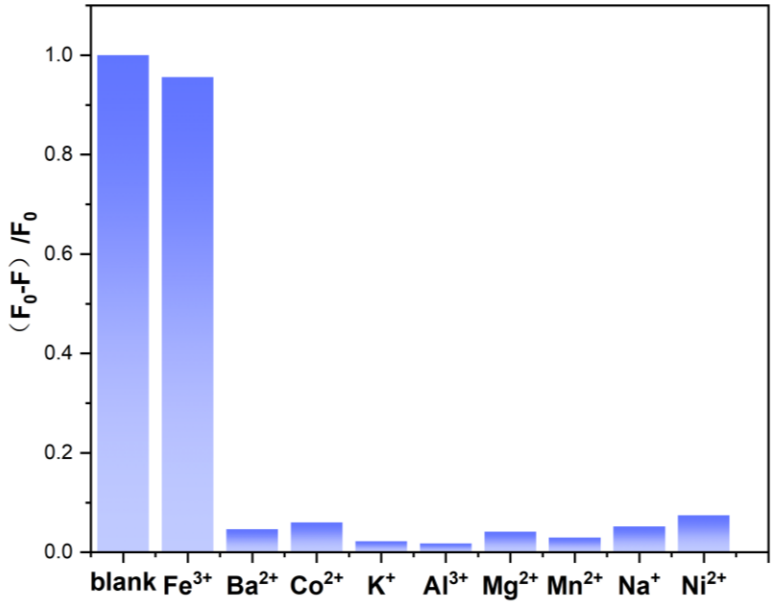

Fig. 3. Selectivity of CMR-CDs to Fe^{3+} ions

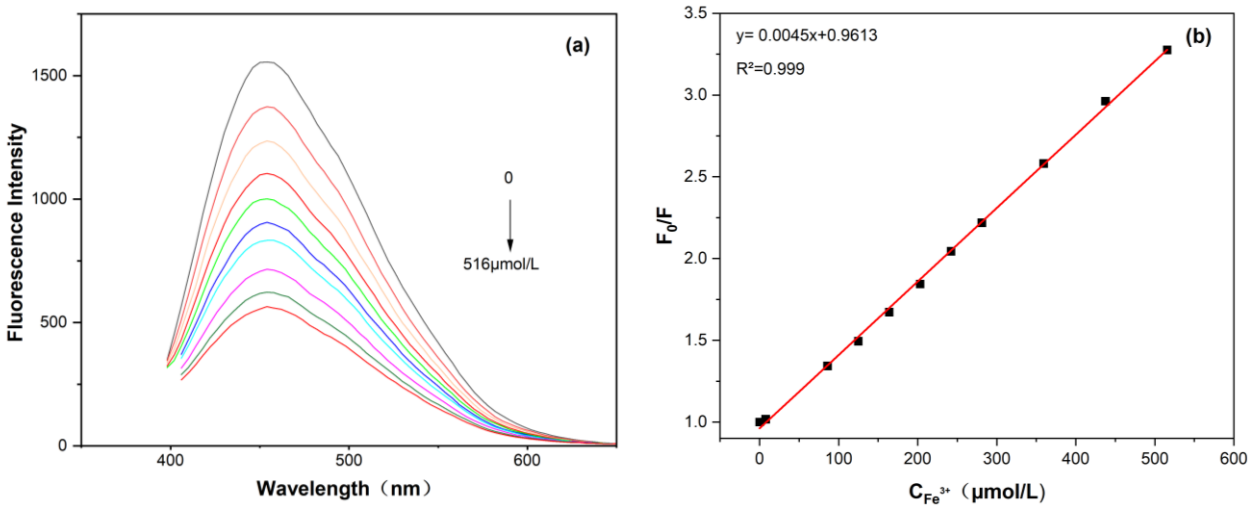

Fig. 4. (a) Fluorescence spectra of CMR-CDs in response to different Fe^{3+} concentrations and (b) Linear relationship between F_0/F and Fe^{3+} in the range of 0 to 516 μmol/L

CONCLUSIONS

1. A simple, green, and promising route for the synthesis of carbon dots (CDs) with one-step hydrothermal process was established using Chinese traditional medicine residues (CMR) as a carbon source. The prepared CMR-CDs with good water solubility, and abundant water-soluble functional groups on the surface. This study highlights the

potential application value of CMR, which is rich in lignocellulose, in the synthesis of CDs, indicating its potential to become a sustainable raw material.

2. The CMR-CDs emitted green fluorescence under the UV-Visible light. The CMR-CDs equipped the excitation wavelength-dependence property. The optimal excitation and emission wavelength were 370 nm and 454 nm.
3. CMR-CDs exhibited excellent selective fluorescence quenching response to Fe^{3+}. The low detection limit and the broad detection range of the Fe^{3+}, which are promising for wide applications in environmental monitoring.

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