

硝酸辅助合成水溶性绿光碳点及其在pH测量与Fe³⁺检测中的应用

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摘要: 以柠檬酸、甲酰胺与浓硝酸为原料合成了绿色荧光碳点(CDs), 对其物相、形貌及荧光性能进行了表征, 并研究了其在离子检测及荧光标记方面的应用。结果表明: 所合成的 CDs 呈现良好的水溶性; 当以 360~460 nm 波长的光激发时, 该 CDs 发出明亮的绿色荧光, 并且发射峰的位置不随激发光波长而改变, 其量子产率高达 44.2%; 同时, 该绿光 CDs 对 pH 敏感, 体系 pH 值在 4.5~8.5 范围内时, 其归一化荧光强度与 pH 间有较好的线性关系; 此外, 该绿光 CDs 对 Fe³⁺ 有较好的选择性响应, 在 0~1 000 $\mu\text{mol}\cdot\text{L}^{-1}$ 范围内, 体系的荧光淬灭效率(I_0/I)与 Fe³⁺ 浓度有良好的线性关系, 检出限为 9.8 $\mu\text{mol}\cdot\text{L}^{-1}$ 。

关键词: 绿光碳点; 水溶性; 荧光材料; 铁离子检测; pH 响应

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Nitric Acid Assisted Synthesis of Water-Soluble Green Fluorescent Carbon Dots for pH Measurement and Fe³⁺ Ions Detection

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Abstract: A green fluorescent carbon dots (CDs) was synthesized from citric acid, formamide and concentrated nitric acid. The phase compositions, morphologies and fluorescence properties were characterized. The applications of the as-prepared CDs in ion detection and fluorescence imaging were studied as well. The results show that the as-synthesized CDs presented a good water-solubility and emitted bright green fluorescence with an excitation-independent photoluminescence (PL) behavior when the excitation wavelength ranged from 360 to 460 nm. The quantum yield was as high as 44.2%. Meanwhile, the green fluorescent CDs was pH sensitive and the normalized fluorescence intensity was linearly proportional to the pH values of solutions in a range of 4.5~8.5. Furthermore, the CDs also exhibited excellent selective response to Fe³⁺ with a good linear relationship between the fluorescence quenching efficiency (I_0/I) and the Fe³⁺ concentration in a range of 0~1 000 $\mu\text{mol}\cdot\text{L}^{-1}$, and the detection limit was calculated to be 9.8 $\mu\text{mol}\cdot\text{L}^{-1}$.

Keywords: green fluorescent carbon dots; water-soluble; fluorescent imaging material; iron ion detection; pH response

In the past decade, the fluorescent carbon dots (CDs), as a kind of new fluorescent material, has dem-

onstrated its bright application prospects in cell imaging^[1], photocatalysis^[2], photoelectric devices^[3], biosen-

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sors^[4] and other fields due to its unique luminescence characteristics, stable optical properties^[5] and other advantages. Compared with traditional semiconductor quantum dots, fluorescent carbon dots exhibit better biocompatibility since they are free of toxic heavy metals. However, most of the reported fluorescent carbon dots emit blue light, which are similar to the blue fluorescence emitting from the fluorescent substances in the organism after excitation, resulting in a relatively low signal-to-noise of the living body fluorescence imaging^[6]. Meanwhile, the short-wavelength excitation light will be harmful to living cells and biological systems^[7]. Obviously, these shortcomings seriously hinder their further application in the biological field. Therefore, synthesizing long-wave emission fluorescent carbon dots has gradually become a new research hotspot. Recently, some red or green fluorescent carbon dots have been reported with the efforts of the researchers. Gao et al.^[8] synthesized carbon dots that emitted red fluorescence in DMSO. Ding et al.^[9] obtained different long-wave emission fluorescent carbon dots by separating via silica column chromatography. Lu et al.^[10] acquired an orange-red fluorescent polymer carbon dots in alcohol with a quantum yield (QY) of 30.64%, in which dopamine and *o*-phenyldiamine were used as the carbon source. Xu et al.^[11] reported a green fluorescent CDs (QY=2.46%) prepared by hydrothermal method using aniline and urea as raw materials. Miao et al.^[12] synthesized fluorescence carbon dots from citric acid and urea, which could emit green fluorescence in ethanol. However, the reported long-wave emission CDs usually suffer from several drawbacks such as poor water-solubility, low quantum yield, expensive raw materials, complex synthesis processes and single function. Consequently, it is still a challenge to develop cheaper and simpler processes to synthesize long-wave emission fluorescent carbon dots that can serve multiple purposes with good water-solubility and high quantum yield.

Iron ion (Fe³⁺) is one of the essential trace elements in the human body. It is an essential component of heme groups and iron-sulfur protein. It plays a crucial role in many physiological activities, including en-

zyme catalysis, oxygen transportation, oxygen metabolism, transcriptional regulation and other processes^[13]. Studies have demonstrated that the deficiency or excess of iron ions in the human body can lead to various physical problems such as anemia, heart failure and tissue damage^[14]. Therefore, it is very important to detect Fe³⁺ selectively and accurately in the environments and organisms. So far, the methods for detecting Fe³⁺ mainly include spectrophotometry^[15], inductively coupled plasma-mass spectrometry^[16], atomic absorption spectrometry^[17] and electrochemistry^[18]. These detection methods show high precision and accuracy. However, they usually require complicated operation process, cumbersome sample processing and expensive equipment, which make them difficult to suit for rapid detection. Fluorescence spectrometry can be designed to detect metal ions due to their high sensitivity, convenience and fast response. Nevertheless, the reported fluorescent probes, such as the organic chromophore, the fluorescent conjugated polymer and the traditional semiconductor quantum dots, are generally toxic, water insoluble and poor biocompatibility, which may limit their applications in biological detection. Accordingly, it is very important and necessary to develop a low-cost, biocompatible, low-toxic, water-soluble fluorescent probe for Fe³⁺ detection.

In this work, a good water-solubility green fluorescence-emitting carbon dots was synthesized using cheap citric acid, formamide and concentrated nitric acid as raw materials. The fluorescence performance of as-prepared CDs was examined, and its possible applications in anti-counterfeiting technique, the pH probe and Fe³⁺ detection were investigated.

1 Experimental

1.1 Experimental materials

Citric acid, HCONH₂, CH₃COCH₃, HNO₃, KBr, Fe(NO₃)₃, NiCl₂ and Cu(NO₃)₂ were purchased from Xilong chemical industry Co., Ltd.; SnCl₂, NaOH, MgCl₂, AgNO₃, CrCl₃, HgCl₂, Pb(NO₃)₂, Cd(NO₃)₂ and BaCl₂ were obtained from Sinopharm Chemical Reagent Co., Ltd. The reagents used were all AR grade. The ultrapure water used in the experiment was from

HHitech Medium-S800UVF with a resistivity of 18.2 M Ω ·cm.

1.2 Synthesis of CDs

The preparation of the CDs precursor was similar to the related literature^[8]. Firstly, 1.53 g of citric acid was dissolved in 25 mL formamide thoroughly to form a clear solution. Afterward, the as-prepared solution was transferred to 50 mL Teflon-lined stainless-steel autoclave and heated at 160 °C for 6 h in an oven. After cooling down to room temperature, the as-prepared solution was centrifuged at the speed of 16 000 r·min⁻¹ for 5 min. The precipitate was washed with acetone until the supernatant being colorless and dried in an oven at 60 °C for 12 h to obtain the CDs precursor.

Then, 0.04 g of CDs precursor reacted with 0.5 mL of concentrated nitric acid for 1 min at room temperature. After that, ultrapure water was added into the mixture to prepare 50 mL solution. Subsequently, the mixed solution was centrifuged at the speed of 16 000 r·min⁻¹ for 5 min. The supernatant (the green fluorescent CDs solution) was retained and stored at 4 °C for further research.

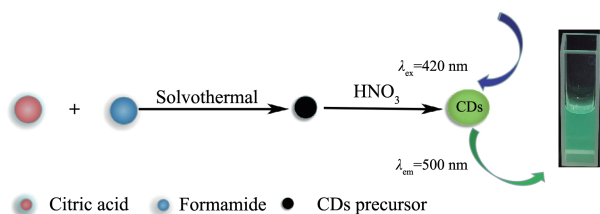


Fig.1 Schematic diagram of synthesis of green fluorescent CDs

1.3 Characterization of CDs

After lyophilizing the CDs with BIOCOOL Pilot 2-4LD vacuum freeze dryer, its phase composition was characterized by the Bruker D8 Advance X-ray diffractometer operated at 40 kV and 40 mA with a graphite monochromatized Cu K α_1 radiation ($\lambda=0.154\ 06\ \text{nm}$). The sample was tested at a scan rate of 6 (°)·min⁻¹ with the scanning 2 θ angles from 10° to 70°. The morphology, size and dispersibility of the sample were observed by FEI Tecnai F20 field emission high resolution-transmission electron microscope (HRTEM) at an accelerating voltage of 200 kV. The functional groups of the samples were measured by Fourier transform infra-

red spectroscopy (FT-IR, IRPrestige-21) using the KBr pellet technique with a scan range of 4 000~400 cm⁻¹.

The fluorescence spectra of the samples were tested with Shimadzu RF-5301 fluorescence spectrometer. The fluorescence lifetime of the sample was measured using a FLS-980 fluorescence spectrophotometer with 359 nm as the excitation wavelength. The QY of CDs was measured according to the method described in the literature^[19]. The rhodamine 6G was chosen as the standard substance. The UV absorption values of CDs solution and rhodamine 6G (dissolved in absolute ethanol) were measured by UV-1600PC ultraviolet spectrophotometer (the UV absorption value was ensured to be below 0.1^[20]). The UV absorption values and the fluorescence emission curve of the CDs solution and the rhodamine 6G solution were measured with excitation at 420 nm. The calculated peak area and the measured UV absorption value were substituted into the following formula:

$$\Phi_x = \Phi_s (A_s/A_x)(F_x/F_s)(\eta_x^2/\eta_s^2) \quad (1)$$

Where Φ is the QY ($\Phi_s=95\%$), A is the ultraviolet absorption value, F is the integral area of the fluorescence emission curve, η is the refractive index of the solvent, s is the standard substance, and x is the sample to be tested.

1.4 Effect of pH values on the fluorescence of the CDs

To investigate the effect of pH value of the solution on the fluorescence intensity of the green fluorescent CDs, experiments were carried out in PBS with diluted HCl or NaOH to adjust the pH values from 1 to 10. The solutions for testing were prepared by mixing the CDs original solution and the above PBS solution with a designated pH value by a volume ratio of 1:49, and then trace amounts of 1 mol·L⁻¹ HCl or 1 mol·L⁻¹ NaOH was used to fine-tune the pH value of the as-prepared mixture. The changes in fluorescence intensity of CDs were measured using 420 nm as the excitation wavelength.

1.5 CDs for Fe³⁺ detection

To investigate whether the green fluorescence of the as-prepared CDs can be quenched by Fe³⁺ ions, the CDs original solution was diluted by ultrapure water

with a volume ratio of 1:49 and then 1 mol·L⁻¹ Fe³⁺ was dropped into the diluted CDs solution to form a solution with a Fe³⁺ concentration of 20 mmol·L⁻¹. The fluorescence intensities of diluted CDs solution before and after adding Fe³⁺ were first estimated by visual inspection and precisely tested with Shimadzu RF-5301 fluorescence spectrometer.

And then, the selectivity and specificity of the as-prepared CDs in Fe³⁺ ions detection was evaluated as follows: 1 mol·L⁻¹ of Mⁿ⁺ solution (Mⁿ⁺=Fe³⁺, Ba²⁺, Ag⁺, Cd²⁺, Cr³⁺, Hg²⁺, Mg²⁺, Ni²⁺, Pb²⁺, Sn²⁺, Zn²⁺) was added into the diluted CDs solution (1:50 dilution of CDs original solution by ultrapure water) to form a solution with a Mⁿ⁺ concentration of 20 mmol·L⁻¹. The fluorescence intensities of the above solutions were measured under the same test conditions.

To examine the sensitivity of the as-prepared CDs in Fe³⁺ ions detection, 100 μL of different concentrations of Fe³⁺ solutions was added into 4.9 mL of CDs diluted solution (dilution ratio being 1:50) to prepare solutions with Fe³⁺ concentration of 0~20 mmol·L⁻¹, their emission fluorescence spectra were measured under the same test parameter.

2 Results and discussion

2.1 Analysis of phase, morphology and functional groups of CDs

Fig. 2a is the X-ray diffraction (XRD) pattern of the as-prepared CDs. The broad diffraction peak centered at $2\theta=26^\circ$ can be attributed to amorphous carbon. And the d value (0.34 nm) is similar to the graphite lattice space, indicating a graphite structure being in the CDs^[21-23].

It can be observed from the TEM and HRTEM images of the CDs sample (Fig. 2b and c) that the CDs particles were well dispersed quasi-spherical nanoparticles. The particle diameter was 1.64~5.91 nm, and the average particle diameter was (3.40±1.03) nm. The measured lattice spacing was about 0.24 nm, which was close to the lattice spacing of graphene (1120)^[24]. In addition, as shown in Fig. 2c, most particles were amorphous particles without any obvious lattice fringes, which is consistent with the XRD pattern results.

Fig. 2d is the comparison of infrared spectra of CDs precursors and CDs samples. There were broad absorption peaks at 3 000~3 500 cm⁻¹ and weak absorption peaks at 2 809, 2 989 and 2 820 cm⁻¹ in

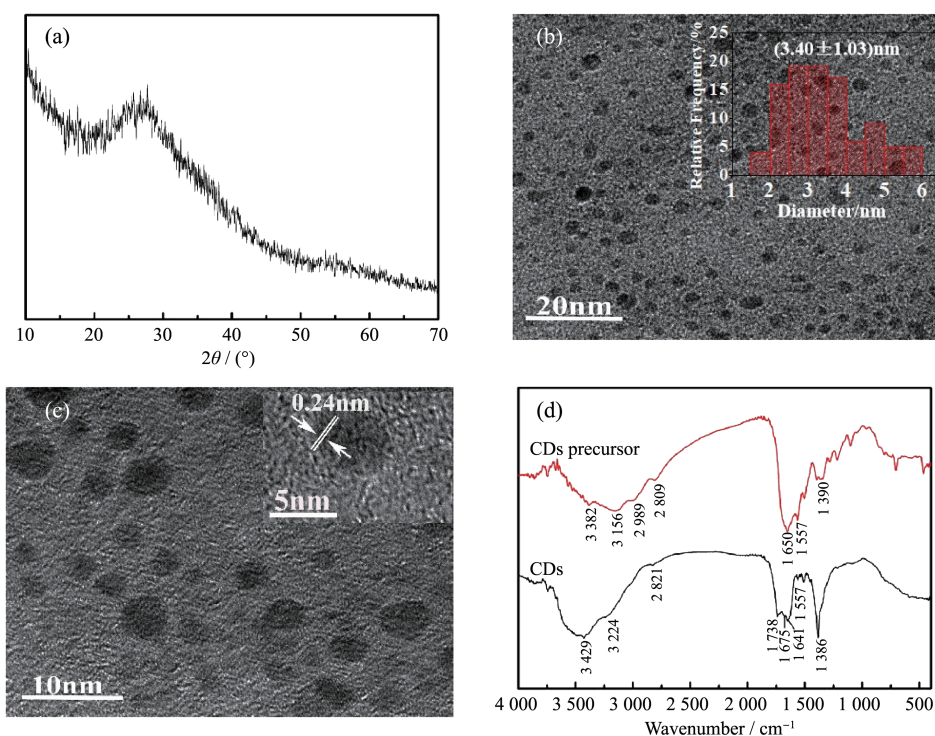
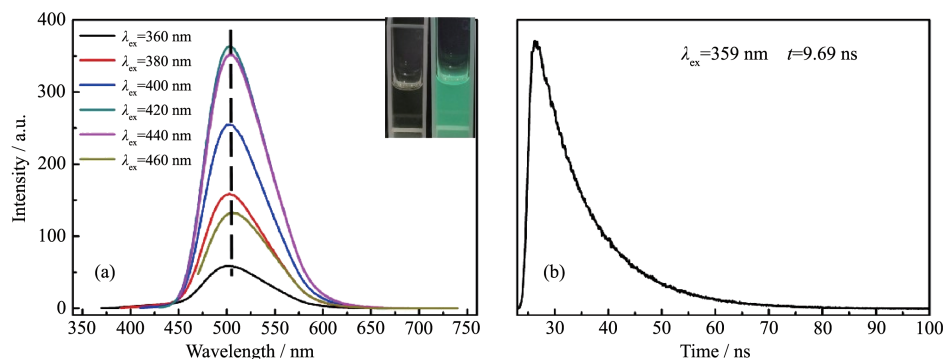


Fig.2 (a) XRD pattern of CDs; (b) TEM image of CDs (Inset: diameter distribution of CDs); (c) HRTEM images of CDs; (d) FT-IR spectra of CDs precursor and CDs

both spectra of CDs and CDs precursors which can be assigned to O-H^[25] and N-H^[26] stretching vibration peaks and the stretching vibration of C-H^[27], respectively. And the peaks at 1 650 and 1 675 cm⁻¹ can be attributed to the stretching vibration of C=O^[28], the absorption peak at 1 557 cm⁻¹ corresponds to the deformation vibration of N-H^[29], which demonstrate that the amide bonds exist in both CDs and CDs precursors. However, unlike the IR spectra of CDs precursors, there was a strong absorption peak at 1 389 cm⁻¹, suggesting the -NO₂ groups on the CDs surface. Another strong absorption peak of CDs at 1 738 cm⁻¹ indicates the carbonyl of the carboxyl groups^[30] existing in the CDs, and the carboxyl groups may be the product of partial hydrolysis of the amide bonds by treating the CDs precursor with concentrated nitric acid. Obviously, there are rich hydrophilic groups such as carboxyl groups, hydroxyl groups and nitro groups on the CDs surface, leading to a good water-solubility of CDs.



Inset: image of CDs under natural light and UV light

Fig.3 (a) Fluorescence spectra of CDs; (b) Fluorescence lifetime decay profile of CDs

2.3 Valuation of applications of as-prepared CDs

2.3.1 CDs for fluorescent ink in anti-counterfeiting

The above results confirm excellent fluorescence characteristics of the as-prepared CDs. When it was used as ink to write words on a piece of paper, the written words emerged clearly with green fluorescence under 365 nm UV light and were invisible in natural light (Fig.4a). This property highlights its promising application in fluorescent ink and anti-counterfeiting.

2.3.2 CDs for pH measurement

Unlike most of reported carbon dots, the fluorescence intensity of as-prepared CDs varied with the pH

2.2 Analysis of fluorescence performance of CDs

The green fluorescent CDs is essentially colorless under natural light and can emit bright green fluorescence under UV light (Fig.3a inset). From its fluorescence spectra (Fig.3a), it is obvious that as the excitation wavelength ranged from 360 to 460 nm, the CDs kept emitting green fluorescence with maximum peak around 500 nm, revealing an excitation-independent PL behavior. When the excitation wavelength was 420 nm, the fluorescence intensity reached the maximum. By choosing rhodamine 6G as the reference substance, its relative QY was measured as high as 44.2% in water.

Fig.3b is the fluorescence lifetime decay profile of the as-prepared CDs. Apparently, the fluorescence lifetime of the as-prepared CDs was single exponential decay with only one fluorescence lifetime of 9.69 ns. The result indicates that the green CDs is relatively uniform in structure^[11], which might be the reason for its excitation-independent PL behavior mentioned above.

values of the CDs solution. As shown in Fig.4b and 4c, the fluorescence intensity of CDs got stronger as the pH value varied from 1 to 4, and it reached the maximum when the pH value was 4. The fluorescence intensity of CDs solution decreased rapidly as the pH value continued increasing; particularly, the normalized fluorescence intensity decreased linearly as the pH increased from 4.5 to 8.5 (Fig.4d), and the corresponding equation was $y=1.4866-0.1634\text{pH}$ with the linear correlation coefficient $R^2=0.9723$. In extreme alkaline environment, the fluorescence of CDs almost became hard to be detected. The possible reasons are as fol-

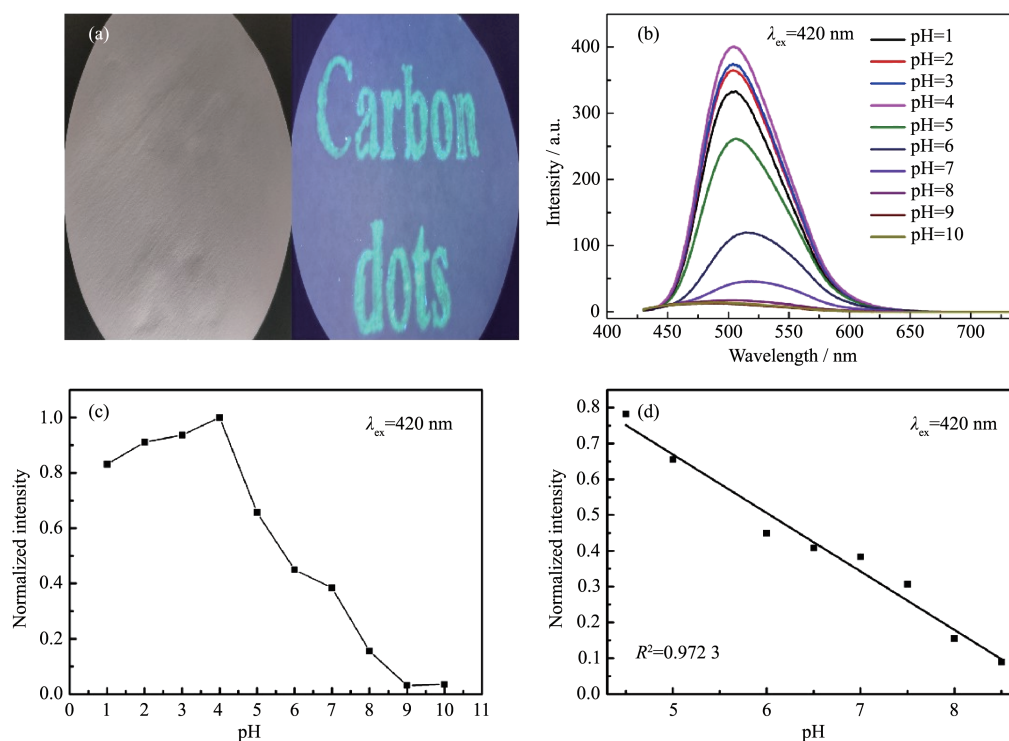


Fig.4 (a) Photos of text written with CDs solution under natural light (left) and UV light (right); (b) Emission spectra of as-prepared CDs solutions at different pH values; (c) Normalized fluorescence intensity of as-prepared CDs solutions at different pH values; (d) Linear relationship between normalized fluorescence intensity of as-prepared CDs solutions and pH value in a range of 4.5~8.5

lows: with the change of pH value of solution, the protonation and deprotonation^[31] of carboxyl functional groups on the surface of CDs may change the Fermi^[32] level of CDs, resulting in the pH dependence of CDs. The above results show that the as-prepared CDs may have potential application as fluorescent sensors for pH measurement, especially in the physiological pH range.

2.3.3 CDs for Fe³⁺ ions detection

As shown in Fig.5a, a concentration of 20 mmol·L⁻¹ Fe³⁺ ions might significantly quench the bright green fluorescence of CDs, indicating the as-prepared CDs may be applied in Fe³⁺ ions detection. Some common metal ions (Mⁿ⁺=Fe³⁺, Ba²⁺, Ag⁺, Cd²⁺, Cr³⁺, Hg²⁺, Mg²⁺, Ni²⁺, Pb²⁺, Sn²⁺ and Zn²⁺) were chosen as research subjects to investigate the selectivity and specificity of CDs in Fe³⁺ ions detection. The corresponding results are shown in Fig.5b. Clearly, when the concentrations of the selected metal ions were 20 mmol·L⁻¹, three kinds of ions (Fe³⁺, Cr³⁺ and Sn²⁺) had a considerable effect on the fluorescence of CDs. The fluorescence quenching efficiency of Fe³⁺, Cr³⁺ and Sn²⁺ to CDs was

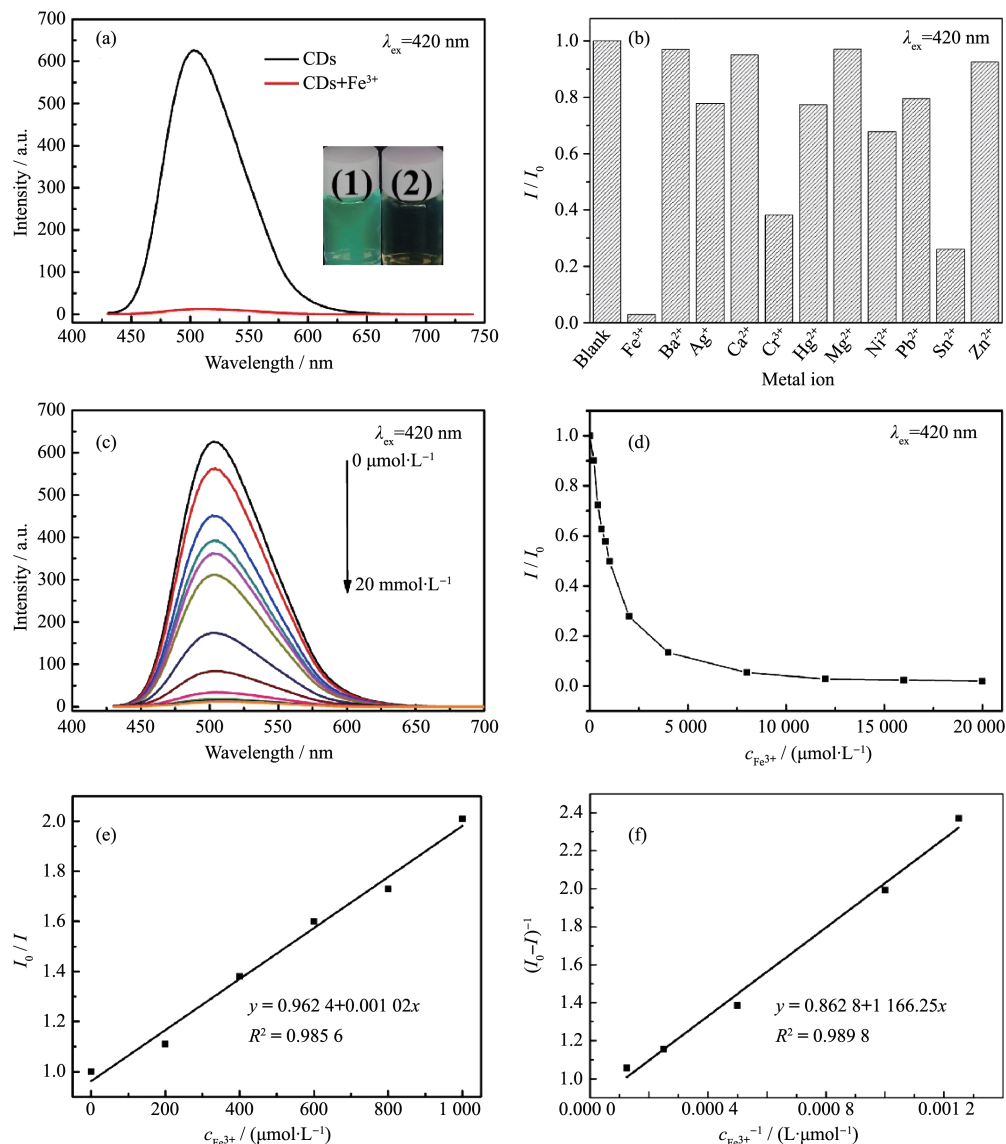
calculated to be 98%, 62% and 70%, respectively. In comparison, the fluorescence of CDs can be almost completely quenched by Fe³⁺, indicating good selectivity and specificity of CDs in Fe³⁺ ions detection, especially in an environment without Cr³⁺ and Sn²⁺.

In view of this, the sensitivity of CDs in Fe³⁺ ions detection was further explored. The results are shown in Fig.5c and d. Obviously, the fluorescence intensity of CDs decreased rapidly when the concentration of Fe³⁺ increased from 0 to 1 mmol·L⁻¹, and a slowly fluorescence decrease behavior appeared as the concentration of Fe³⁺ continued to rise from 1 to 20 mmol·L⁻¹. When the concentration of Fe³⁺ ions reached 8 mmol·L⁻¹, the fluorescence intensity of CDs was substantially quenched. Further investigation reveals that there is a good linear relationship between the quenching efficiency of green fluorescence CDs (I_0/I) and the concentration of Fe³⁺ within a range of 0~1 000 μmol·L⁻¹ (Fig.5e), which is consistent with the Stern-Volmer^[13] equation.

$$I_0/I=1+K_{sv}c_Q \quad (2)$$

where I_0 is the fluorescence intensity of CDs without Fe^{3+} ; I is the fluorescence intensity of CDs after adding Fe^{3+} ; K_{SV} is the Stern-Volmer quenching constant; c_0 is the concentration of Fe^{3+} ($\mu\text{mol}\cdot\text{L}^{-1}$). Taking the Fe^{3+} concentration as the abscissa and I_0/I as the ordinate, the equation of Stern-Volmer was obtained as follows: $y = 0.962\,4 + 0.001\,02x$, and the linear correlation coefficient R^2 was 0.985 6. The detection limit was $9.8\,\mu\text{mol}\cdot\text{L}^{-1}$ based on $3\sigma/k$ (σ is the standard deviation of the blank measurements of the CDs and k is the slope of the fitting line). The above results indicate potential application of the CDs in low concentration Fe^{3+} detection.

From the above results, it can be found that the



Inset: fluorescence photographs of CDs in the absence (1) and presence (2) of Fe^{3+} upon excitation under a UV lamp

Fig.5 (a) Emission spectra of CDs solution before and after adding Fe^{3+} ($20\text{ mmol}\cdot\text{L}^{-1}$); (b) Fluorescence responses of CDs in the presence of different metal ions (I and I_0 correspond to the fluorescence intensity with and without metal ions, respectively; the metal ion concentration is $20\text{ mmol}\cdot\text{L}^{-1}$); (c) Emission spectra of CDs in the presence of Fe^{3+} with different concentrations; (d) Plot of fluorescence intensity ratio (I/I_0) of CDs versus concentration of Fe^{3+} ; (e) Stern-Volmer plot of CDs in the presence of Fe^{3+} with different concentrations ($0\sim 1\,000\,\mu\text{mol}\cdot\text{L}^{-1}$); (f) Lineweaver-Burk double-reciprocal plot of CDs in the presence of Fe^{3+} with different concentrations ($800\,\mu\text{mol}\cdot\text{L}^{-1}\sim 8\text{ mmol}\cdot\text{L}^{-1}$)

CDs applied for ion detection is based on the fluorescence quenching of CDs by Fe³⁺. Generally, fluorescence quenching can be divided into dynamic quenching and static quenching^[33]. The Stern-Volmer equation (2) and the Lineweaver-Burk equation (3)^[34] are usually employed to describe the dynamic and static quenching behavior, respectively.

$$(I_0 - I)^{-1} = (I_0)^{-1} + K_{LB}^{-1} (I_0)^{-1} c_Q^{-1} \quad (3)$$

where K_{LB} is the binding constant of Fe³⁺ and CDs during static fluorescence quenching. As mentioned above, the fluorescence quenching efficiency of CDs by the Fe³⁺ at a concentration range of 0~1 000 $\mu\text{mol} \cdot \text{L}^{-1}$ is consistent with the Stern-Volmer equation, indicating a dynamic quenching behavior involved. Yet, when the concentrations of Fe³⁺ increased from 800 $\mu\text{mol} \cdot \text{L}^{-1}$ to 8 $\text{mmol} \cdot \text{L}^{-1}$, the plot of I_0/I versus Fe³⁺ ion concentration can be fitted with a conventional linear Lineweaver-Burk equation (Fig. 5f), suggesting a static quenching processes occurred. Hence, the fluorescence quenching effect of Fe³⁺ to CDs involves both dynamic and static quenching in the entire test concentration range.

The possible fluorescence quenching mechanism by Fe³⁺ is analyzed. The IR spectra of CDs reveal that there are a large number of hydroxyl, carboxyl groups and nitro groups on the CDs surface. The Fe³⁺ ions may be quickly absorbed on the surface of CDs and coordinate with carboxyl groups and hydroxyl groups due to their stronger binding force and faster chelation kinetics with carboxyl and hydroxyl groups than other metal ions^[35]. These behaviors result in the severe aggregation of CDs with each other^[35]. Meanwhile, the Fe³⁺ ions possess half-filled 3d orbits (3d⁵) and they are very strong electron acceptors. The electrons in the excited state of CDs may transfer to the unfilled orbital of Fe³⁺ because of the above coordination interaction and result in non-radiative electron/hole recombination^[27], which causing significant fluorescence quenching of CDs. Additionally, by analyzing the solubility product constant (K_{sp}) data of $\text{M}(\text{OH})_n$, we find that there is a certain correlation between the quenching efficiency and the value of K_{sp} . Compared with other metal ions, three kinds of ions (Cr³⁺, Sn²⁺, and Fe³⁺) with greater fluorescence quenching effect on CDs are all possess-

ing smaller K_{sp} ($K_{sp, \text{Cr}(\text{OH})_3} = 6 \times 10^{-31}$, $K_{sp, \text{Sn}(\text{OH})_2} = 1.4 \times 10^{-28}$, $K_{sp, \text{Fe}(\text{OH})_3} = 4 \times 10^{-38}$). It seems the higher the quenching efficiency is, the smaller the K_{sp} is. Yet, it is not an absolute positive correlation. In a word, the fluorescence quenching of CDs by Fe³⁺ is a complicated process and may cause by cumulative impact of the above mentioned factors, which needs to be further improved.

3 Conclusions

In summary, we successfully synthesized a water-soluble green fluorescence CDs with good fluorescence properties by using citric acid, formamide and concentrated nitric acid as raw materials. The as-synthesized CDs shows an excitation-independent PL behavior and a high quantum yield (44.2%), which can be applied in anti-counterfeiting technique. The fluorescence intensity of CDs is pH sensitive, making it a potential candidate for pH measurement, especially in the physiological pH range. In addition, the green fluorescent CDs exhibits excellent selective response and a relative low detection limit (9.8 $\mu\text{mol} \cdot \text{L}^{-1}$) as well as a good linear relationship with Fe³⁺ in a concentration range of 0~1 000 $\mu\text{mol} \cdot \text{L}^{-1}$, which endows its potential applications in Fe³⁺ detection.

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