

NITROGEN-DOPED CARBON QUANTUM DOTS WITH *PINELLIA TERNATA* AS CARBON SOURCE FOR HIGH SENSITIVE DETERMINATION OF CHROMIUM (VI)

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Abstract. A novel nitrogen-doped fluorescent carbon dots was successfully prepared via a simple one-step hydrothermal method using the medicinal plant *Pinellia ternata* as an environment-friendly carbon-containing precursor for the first time and ethylenediamine as nitrogen source. The diameter, morphology, ultimate composition and optical performance of the prepared *Pinellia ternata* nitrogen-doped carbon quantum dots (N-CQDs) were characterized by a series of analytical characterization techniques. The photostability was also investigated through the conditions of ionic strength, pH, and storage time. The obtained results showed that the particle size distribution of *Pinellia ternata*-based N-CQDs was uniform with the fluorescence quantum yield as high as 21.3%, and it also exhibited good excitation dependence and excellent light stability. Based on the fluorescence quenching mechanism of fluorescent inner filter effect, it has high sensitivity, selectivity and anti-interference ability for chromium (VI). Under optimal working conditions, the nanoprobe showed a good and sensitive linear response ($R^2 = 0.9955$) toward chromium (VI) within the concentration range of 0–200 μM with a low detection limit of 15 nM. This method has been successfully applied to the detection of chromium (VI) in environmental water samples, providing a new idea for the development of green natural compound carbon materials.

Keywords: *N-CQDs, fluorescence quenching mechanism, fluorescent nanoprobe, Cr(VI), environmental samples*

Introduction

Chromium is a steel-gray metal. There is no free state chromium in nature. Chromium (II) is a strong reductant, which is extremely unstable and can be rapidly oxidized to chromium (III) (Abdolmohammad-Zadeh and Sadeghi, 2012; Barrera-Díaz et al., 2012). Therefore, it mainly exists in two forms: chromium (III) and chromium (VI). In addition, as one of the most important micronutrient elements in human body, chromium is an important blood sugar regulator and also one of the components of proteolytic enzymes (Bauer et al., 2013; Broadhurst et al., 2006; Sedman et al., 2006). It plays an important role in the metabolism of glucose and lipid and protein synthesis. The toxicity of chromium was related to its valence (Cosata and Klein, 2006; Gagneten and Imhof, 2009). As a component of glucose tolerance factor, activator of some metabolic enzymes and stabilizer of nucleic acid (Ahmad et al., 2011; Costa, 1997; Kim et al., 2015), chromium (III) could promote insulin to play a role, maintain normal glucose metabolism, promote the production of cholesterol and fatty acids and promote hematopoietic function (Vallejos et al., 2012). Chromium (III) deficiency in human

body could cause diabetes, coronary atherosclerosis and cardiovascular diseases. The toxicity of chromium (VI) was about 100 times higher than that of chromium (III) (Wang et al., 2017). It was also one of the most susceptible metals to allergy. It was second only to nickel, and more easily absorbed and accumulated by human body, causing a series of pathological changes, such as chromium rhinopathy, and even inducing cancer (Ma et al., 2018; Kong et al., 2017; Yuhua et al., 2018). The International Agency for Research on Cancer (IARC) had rated chromium (VI) as a class I carcinogen (Ohira et al., 2015). Therefore, the monitoring of chromium (VI) had attracted the attention of environmental health workers.

Fluorescent carbon quantum dots (CQDs) had been widely used in various research fields due to their advantages of simple preparation, good chemical stability, easy functionalization, good biocompatibility, low toxicity and special optical properties (Wang and Zhou, 2014; Zhang et al., 2014; Zheng et al., 2015; Carrasco et al., 2016). In recent years, many carbon materials had been used to prepare fluorescent carbon quantum dots (Baker and Baker, 2010; Li et al., 2018; Huang et al., 2015). The synthesis of nitrogen-doped carbon quantum dots with excellent optical properties using green natural carbohydrates as precursors had become one of the most popular research topics (Gong et al., 2017; Wang et al., 2018; Gao et al., 2018).

Pinellia ternata is a kind of nourishing medicinal plant. Its raw materials were cheap and easy to obtain. It could be produced on a large scale. Its main bioactive substances included coumarin, alkaloids, amino acids and polysaccharides. *Pinellia ternata* was rich in carbon, nitrogen and oxygen elements. It was one of the ideal carbon materials for preparing carbon quantum dots (Teixeira da Silva et al., 2017; Ng et al., 2012; Zheng et al., 2015).

In this paper, *Pinellia ternata*-based nitrogen-doped fluorescent carbon quantum dots (*Pinellia ternata* N-CQDs) with blue fluorescence were prepared by a simple hydrothermal method using *Pinellia ternata* as precursor and ethylenediamine. The fluorescence quantum yield of *Pinellia ternata*-based N-CQDs was about 21.3%, which had excellent excitation wavelength dependence and optical stability. Based on the fluorescence quenching mechanism (Gunnlaugsson et al., 2005; Alizadeh et al., 2016; Algar and Krull, 2008; Zhang et al., 2017; Wang et al., 2010), a novel fluorescent probe had been developed for the sensitivity and selectivity detection of chromium (VI). This method could be successfully applied to the rapid detection of environmental water and soil samples, as well as subsequent research.

Experiment

Materials and apparatus

Pinellia ternata was purchased from local flower market (Anhui, China); ethylenediamine (EDA) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China); citric acid, sodium hydrogen phosphate (Na_2HPO_4) and sodium hydroxide (NaOH) were purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd. (Tianjin, China). Metal salts mainly include AlCl_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, MgCl_2 , ZnCl_2 , CuCl_2 , CdCl_2 , PbCl_2 , CrCl_3 , CoCl_2 , SnCl_2 , FeCl_3 and FeCl_2 . All solutions were prepared from ultrapure water (18.2 M Ω .cm, 25 °C) of Milli-Q system.

G9800A fluorescence spectrophotometer (Agilent Technologies, USA) was used to determine fluorescence spectrum and its intensity; UV-2600 UV-Visible

spectrophotometer (Shimadzu, Japan) was used to determine the UV-Visible spectrum; Tecnai G2 F30s-Twin high resolution field emission transmission electron microscopy (FEI, Netherlands) was used to detect particle size and morphology characteristics of nitrogen doped fluorescent quantum dots; TENSOR 27 Fourier transform infrared spectrometer (FT-IR, Bruker, Germany) was used to determine the infrared spectrum and the structure of materials; D8-advance X-ray powder diffractometer (XRD, Bruker, Germany) was used to determine the crystal morphology; Thermo Scientific k-alpha X-ray photoelectron spectrometer (Thermo Fisher Scientific Inc. U.S.A.) was used to analyze the proportion of its elements and chemical oxidation state; Z-2000 atomic absorption spectrometer (Hitachi, Japan) was used for the determination of metal ionization; XH-B vortex instrument (Shanghai Hannuo Instrument Co., Ltd., China) was used for vortex blending; 80-2 high-speed centrifuge (Shanghai Surgical Instrument Factory, China) was used for centrifugal filtration; TOP wave microwave digestion device was equipped with PM 60 microwave digestion tank (Jena, Germany) for soil sample digestion; and BPZ-6003 vacuum drying chamber (Shanghai Yiheng Scientific Instrument Co., Ltd., China) was used for vacuum drying.

Preparation of *Pinellia ternata*-based N-CQDs

Pinellia ternata-based N-CQDs were prepared by hydrothermal method according to the reported method. The stems of *Pinellia ternata* were dried naturally at room temperature and ground into fine powder. The powder prepared by weighing 2.0 g was evenly dispersed in 90 mL of hot water at 60 °C. Ethanol (10 mL) and EDA (1 mL) were added to mixture evenly at constant temperature. The powder was transferred to a PTFE lined autoclave (200 mL) and heated at 180 °C for 9 h. After cooling down to room temperature naturally, the bright yellow aqueous solution was centrifuged at 10000 rpm for 15 min to remove large particles of sediment. The sediment was purified by 0.22 μm membrane filtration. The N-CQDs was stored in a refrigerator at 4 °C and diluted with deionized water to the required concentration. The synthetic reaction diagram of *Pinellia ternata* N-CQDs is shown in Figure 1.



Figure 1. The reaction scheme of the synthesis of the *Pinellia ternata*-based N-CQDs

Fluorescence quenching test of chromium (VI)

In 10.0 mL glass centrifuge tube, 30 mL water-soluble *Pinellia ternata*-based N-CQDs solution, 2 mL pH 7.0 citric acid-disodium hydrogen phosphate buffer solution and different concentration of Cr⁶⁺ were added in turn, and then diluted to 4.0 mL with deionized water. At room temperature, the full eddy mixing reaction lasts for 10 min. The slit width of excitation and emission on the fluorophotometer is 5 nm, the excitation wavelength is $\lambda_{ex} = 356$ nm, and the emission wavelength is $\lambda_{em} = 444$ nm. In order to evaluate the influence of coexisting ions on the fluorescence

intensity of N-CQDs and to evaluate the selectivity of Cr⁶⁺, other metal ions (including Zn²⁺, Cu²⁺, Al³⁺, Mg²⁺, Cd²⁺, Pb²⁺, Cr³⁺, Sn²⁺, Co²⁺, Hg²⁺, Fe³⁺ and Fe²⁺) were detected under the same procedure.

Pretreatment of environmental water and soil samples

In this study, three different water samples (tap water, lake water and waste water) were selected for analysis and detection. All water samples were filtered by simple centrifugal filtration to remove solid particles and suspended solids, then filtered by 0.22 µm membrane, and stored in a 4 °C refrigerator for storage. In this study, three different soil samples (parking lot, highway) were selected for analysis and detection. Soil samples of 1.0 g were weighed and added with 1 mL nitric acid and 3 mL hydrochloric acid. They were placed in a microwave digestion tank of polytetrafluoroethylene (PTFE). Microwave digestion was carried out at 140 °C for 15 min, then cooled to room temperature. The digestion was diluted to 50 mL and stored in a refrigerator at 4 °C.

Results and discussion

Characterization of Pinellia ternata-based N-CQDs

In order to further study the nanostructure characteristics of *Pinellia ternata*-based N-CQDs, the morphology and particle size of *Pinellia ternata*-based N-CQDs were characterized by transmission electron microscopy (TEM). As shown in *Figure 2*, the *Pinellia ternata*-based N-CQDs were uniformly dispersed without agglomeration and were spherical carbon nanoparticles. In addition, the particle size distribution of biomass-based N-CQDs is narrow, mainly between 5 and 6 nm, and the average particle size is about 5.2 nm.

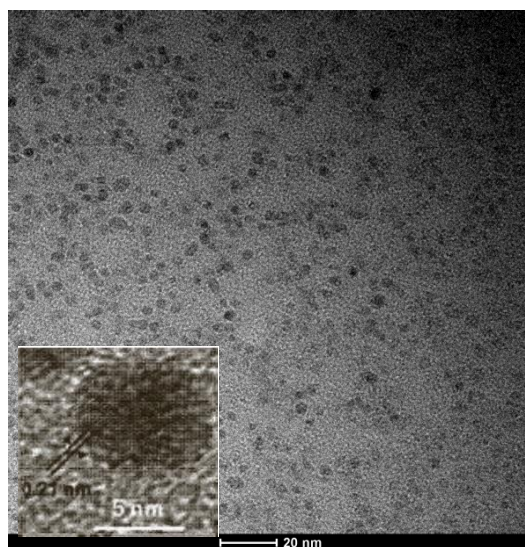


Figure 2. The TEM image of the synthesized N-CQDs

The composition and surface chemical structure of *Pinellia ternata*-based N-CQDs were determined by Fourier transform infrared spectroscopy (FT-IR) and X-ray electron

spectroscopy (XPS). *Figure 3* is the infrared spectra of N-CQDs. The broad and strong absorption peaks at 3442 cm^{-1} are attributed to the stretching vibration absorption peaks of O-H and N-H; the peak at 1637 cm^{-1} is attributed to the stretching vibration absorption peak of O = C-NH; the absorption peaks at 1467 cm^{-1} are attributed to the stretching vibration peak of COOH; and the absorption peaks at 1119 cm^{-1} and 1078 cm^{-1} are attributed to the C-N bend. Bending vibration peak and C-O stretching vibration peak. The results show that the *Pinellia ternata* N-CQDs have abundant hydrophilic functional groups, such as hydroxyl, carboxyl and carbonyl groups, which have good water solubility and broad application prospects.

The elements of *Pinellia ternata*-based N-CQDs were characterized by XPS, as shown in *Figure 4*. XPS elemental analysis is consistent with FT-IR results, which proves that the functional groups containing oxygen and nitrogen, such as hydroxyl, carboxyl, amino groups, etc.

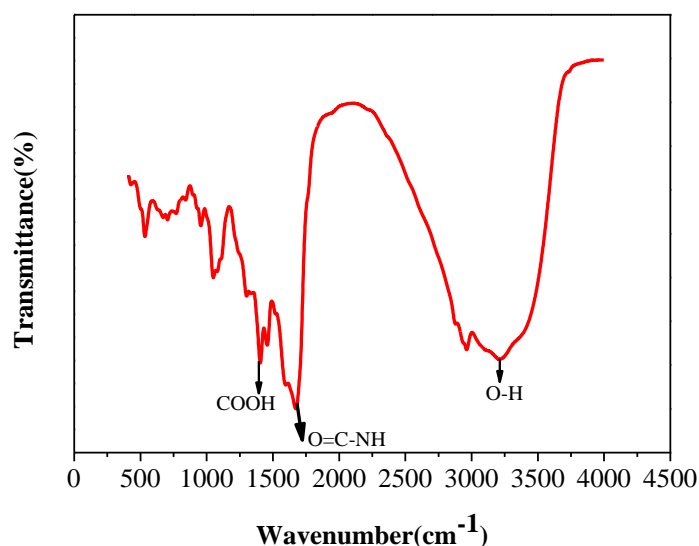


Figure 3. The FT-IR spectrum of the *Pinellia ternata*-based N-CQDs

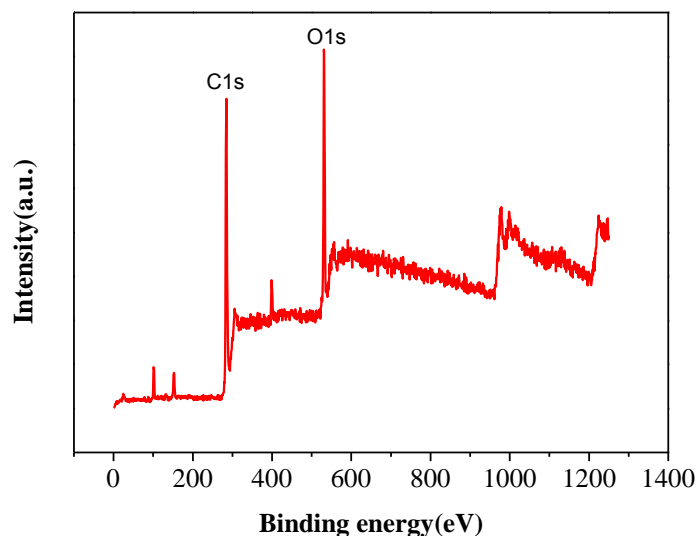


Figure 4. The XPS spectra of the synthesized N-CQDs

Optical properties of *Pinellia ternata*-based N-CQDs

The optical properties of *Pinellia ternata*-based N-CQDs were characterized by UV-Vis absorption spectra and fluorescence emission spectra. In addition, the illustrations in *Figure 5A* show that *Pinellia ternata*-based N-CQDs are golden in natural light (left) and bright blue fluorescence in 365 nm ultraviolet light (right). Benefiting from its narrow size distribution, *Pinellia ternata*-based N-CQDs exhibit relatively symmetrical fluorescence spectra, as shown in *Figure 5B*. Under 356 nm excitation light, the maximum emission wavelength is 444 nm. The principle of fluorescence depends mainly on the bandgap transition formed by conjugated pion electrons and the surface defects of fluorescent carbon quantum dots. *Figure 5C* is the fluorescence emission spectra of *Pinellia ternata*-based N-CQDs at different excitation wavelengths, showing good excitation wavelength-dependent fluorescence behavior. The results shown that nitrogen doping can adjust the intrinsic electronic and surface properties of CQDs, enhance their effective surface defects and internal carbon core structure, and thus significantly improve their optical properties.

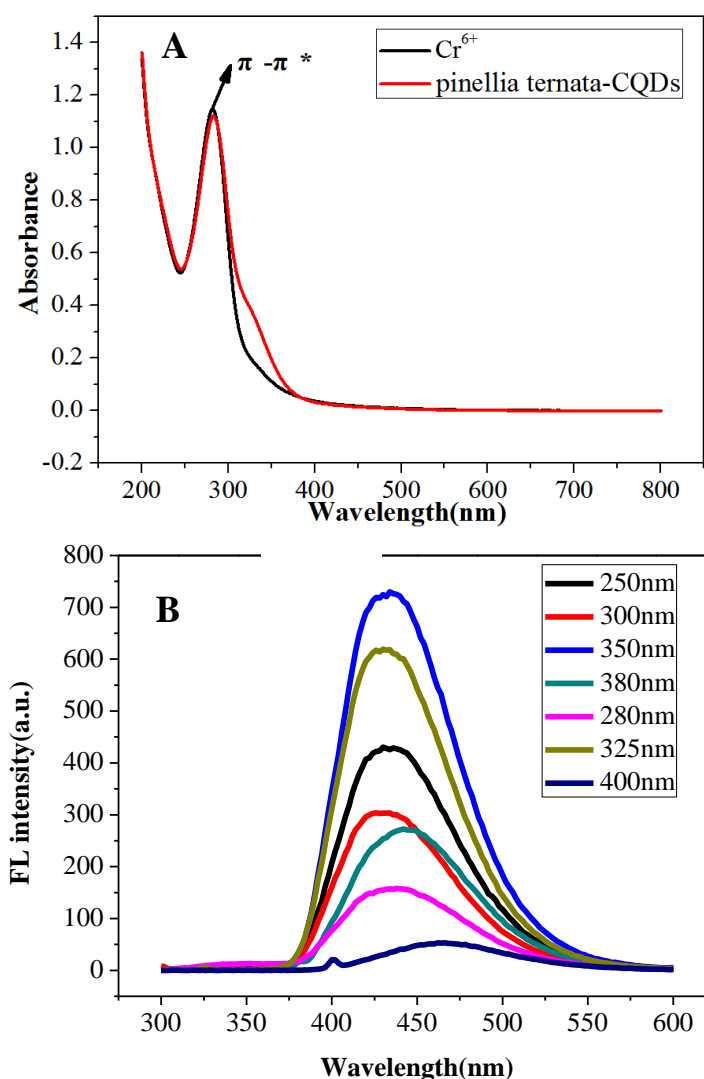
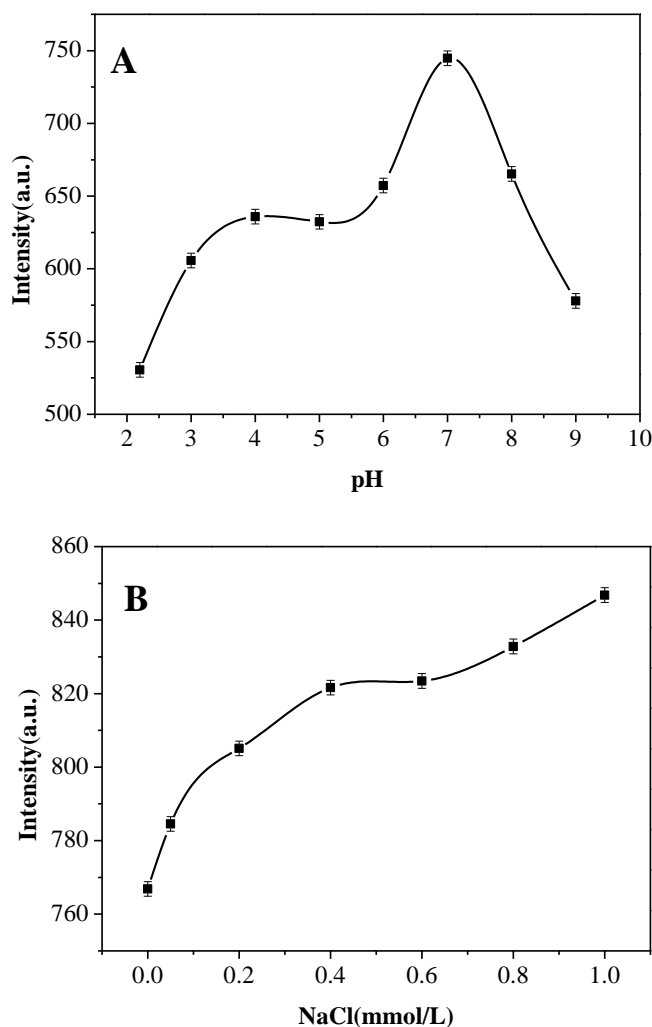


Figure 5. UV absorption spectra of the *Pinellia ternata*-based N-CQDs and Cr^{6+} (A); fluorescence excitation and emission spectra of the *Pinellia ternata*-based N-CQDs (B)

Photostability of *Pinellia ternata*-based N-CQDs

In order to explore the anti-interference ability of *Pinellia ternata*-based N-CQDs to the external environment, the light stability test was carried out, and the conditions of ion strength, pH and storage time were investigated. As shown in *Figure 6A*, when the pH value of citric acid-disodium hydrogen phosphate buffer changes from 2.2 to 8.0, its fluorescence intensity does not change obviously under acidic and neutral conditions of pH 2.2-7.0, but decreases sharply under alkaline conditions of pH 8.0, which indicates that the probe can be used as a fluorescent nanoprobe in acidic medium. *Figure 6B* investigated the effect of ion strength on the fluorescence intensity of *Pinellia ternata*-based N-CQDs. As can be seen from the figure, the fluorescence intensity only fluctuates slightly with the increasing concentration of NaCl solution, and there is no obvious change. Therefore, *Pinellia ternata*-based N-CQDs still have strong stability in high ionic strength environment. As shown in *Figure 6C* and *D*, *Pinellia ternata*-based N-CQDs with the same concentration were stored in refrigerator at room temperature for 3 h or even 4 °C for 3 months under the same experimental conditions. The fluorescence intensity of *Pinellia ternata*-based N-CQDs remained basically unchanged and stable, and no floating or sediment could be seen in its aqueous solution by naked eyes. The above experimental results show that the *Pinellia ternata*-based N-CQDs have excellent optical stability.



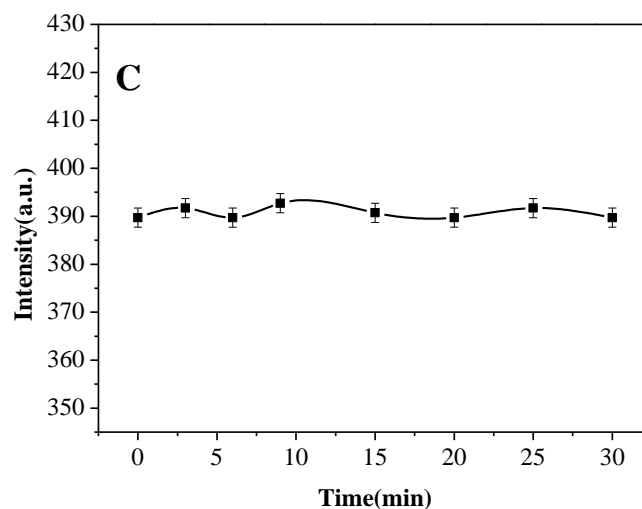


Figure 6. Effects of various conditions on the fluorescence intensity of the *Pinellia ternata*-based N-CQDs: (A) pH; (B) NaCl concentrations; (C) storage time

Selective investigation test

In order to investigate the selectivity of *Pinellia ternata*-based N-CQD fluorescence intensity to different metal ions, 12 metal ions with the same concentration of Al^{3+} , Mg^{2+} , Zn^{2+} , Cu^{2+} , Cr^{6+} , Cr^{3+} , Cd^{2+} , Co^{2+} , Sn^{2+} , Ag^+ , Pb^{2+} , Fe^{3+} , Fe^{2+} , were investigated. As shown in *Figure 7*, only Cr^{6+} can effectively quench the fluorescence intensity of *Pinellia ternata*-based N-CQDs, while the introduction of other metal ions does not cause significant changes in the fluorescence intensity of *Pinellia ternata*-based N-CQDs. This indicates that *Pinellia ternata*-based N-CQDs have high selectivity to Cr (VI) and can be used as nanoprobe for fluorescence quenching detection of Cr (VI). In addition to Cr^{6+} , other metal ions will coexist with the actual samples. Therefore, this study further investigated the ion interference problem in the detection of Cr^{6+} through competitive experiments, that is, in the presence of other metal ions, the detection of Cr^{6+} was carried out. As shown in *Figure 7*, the experimental results show that the presence of interfering ions has little effect on the detection of Cr^{6+} . In particular, the potential interference ion Cr^{3+} , although causing a slight reduction in the fluorescence intensity of the detection of Cr^{6+} , has a negligible effect, and can be used to distinguish between Cr^{3+} and Cr^{6+} , which is a characteristic that some fluorescent nanoprobe for the detection of Cr^{6+} do not possess. In conclusion, *Pinellia ternata*-based N-CQDs have good selectivity and anti-interference ability as a fluorescent nanoprobe for detection of Cr(VI).

Optimization of experimental conditions

The fluorescence quenching mechanism can be used for rapid detection of Cr (VI). In order to obtain the best fluorescence response signal, some key experimental factors such as solution pH and reaction time were further investigated and optimized. Firstly, the fluorescence intensity of *Pinellia ternata*-based N-CQDs was studied in different pH ranges (2.0-12.0). It can be seen from *Figure 8A* that the fluorescence quenching efficiency is the highest when the pH value is 7.0. The influence of pH value on the quenching process may be related to the form and distribution of acid-base equilibrium

groups on *Pinellia ternata* N-CQDs surface and Cr (VI) in solution (Vaz et al., 2017). Cr(VI) exhibits a pH-dependent dynamic equilibrium in aqueous solution: $2\text{CrO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + 2\text{H}_2\text{O}$. Cr(VI) mainly exists in the form of chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$). Although it has the same charge number, it has higher molar volume, so it has lower electron density and lower effective interaction with *Pinellia ternata*-based N-CQDs. Its fluorescence quenching efficiency is lower than that of chromite (CrO_4^{2-}). In acidic medium, Cr (VI) mainly exists in the form of dichromate ($\text{Cr}_2\text{O}_7^{2-}$), so its fluorescence quenching efficiency is low, and gradually increases with the increase of pH.

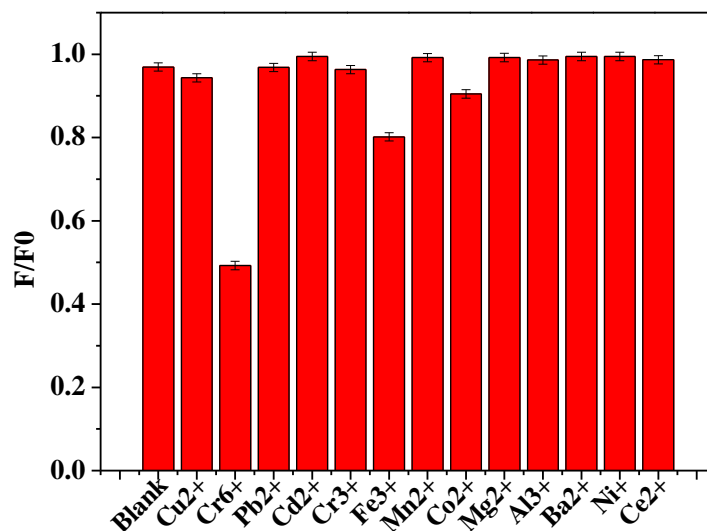


Figure 7. Evaluation of method selectivity against possible interferences

In addition, in alkaline medium, the oxygen-containing functional groups on *Pinellia ternata*-based N-CQDs are mainly in the form of chromate (CrO_4^{2-}), which is easy to dephosphorize and increase the negative charge on the surface. The interaction between Cr (VI) and negatively charged chromite (CrO_4^{2-}) is weakened due to electrostatic repulsion, which shows that the fluorescence quenching efficiency begins to decrease gradually. Therefore, pH 7.0 is defined as the optimum determination condition.

In order to determine the quenching response time of Cr^{6+} to *Pinellia ternata* N-CQDs, the reaction time was also discussed in this study. Figure 8B shows the fluorescence intensity of *Pinellia ternata* N-CQDs with time after adding Cr^{6+} . The fluorescence intensity of *Pinellia ternata*-based N-CQDs decreases sharply in 0-2 min, and reaches the lowest fluorescence intensity in 2 min. Later, the fluorescence intensity of *Pinellia ternata*-based N-CQDs decreases slightly but tends to stabilize gradually with the extension of time. Therefore, the optimal fluorescence quenching response time is 2 min.

Study on methodological performance

Under the optimum experimental conditions, the relationship between the fluorescence quenching intensity of *Pinellia ternata* N-CQDs and the concentration of Cr^{6+} was studied, and a quantitative analysis method for the fluorescence quenching of Cr^{6+} was established. As shown in Figure 9A, the fluorescence intensity of N-CQDs

decreases gradually with the increase of the concentration of Cr^{6+} and changes regularly, which further proves the feasibility and application prospects of N-CQDs as a fluorescent probe for the detection of Cr^{6+} . As shown in *Figure 9B*, the fluorescence quenching efficiency (F_0/F) has a good linear relationship with the concentration of Cr^{6+} in the range of 0-200 μM . The linear equation is $F_0/F = 1.0218 + 0.1156 C (\text{Cr}^{6+})$, $R^2 = 0.9955$, and the detection limit is 15 nM ($S/N = 3$).

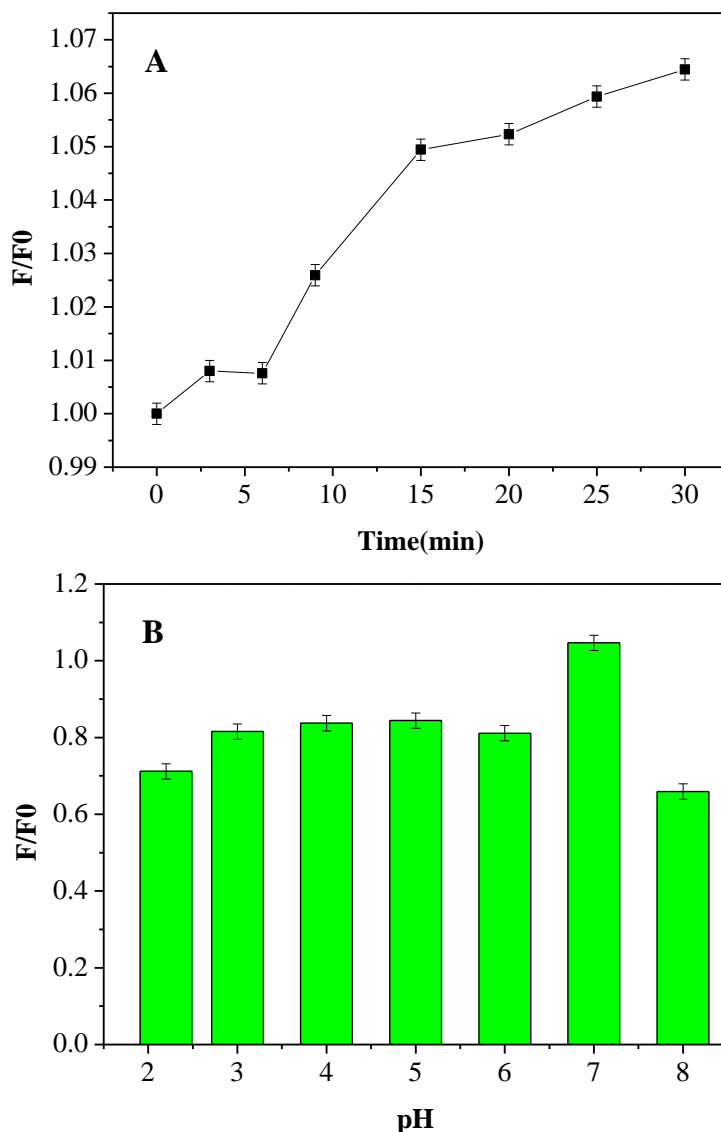


Figure 8. Effect of reaction time (A) and pH (B) on the fluorescence intensity of the *Pinellia ternata*-based N-CQDs

Analysis of fluorescence quenching mechanism

The fluorescence quenching mechanism of *Pinellia ternata*-based N-CQDs for detecting chromium (VI) is similar to that of polyacrylamide-based N-CQDs for detecting Hg^{2+} . It is caused by the synergistic effect of fluorescent inner filter effect (IFE) and electron transfer. As shown in *Figure 10*, at pH 7.0, the ultraviolet-visible absorption spectra of Cr (VI) show two absorption peaks at 272 and 371 nm,

respectively, while *Pinellia ternata*-based N-CQDs have ultraviolet absorption peaks at 337 nm, and the maximum excitation and emission wavelengths are 356 and 444 nm, respectively. It is obvious that the absorption spectra of Cr (VI) overlap with the excitation and absorption spectra of *Pinellia ternata*-based N-CQDs. Therefore, Cr (VI) partially shields the excitation spectra of *Pinellia ternata*-based N-CQDs and partially absorbs the light emitted by *Pinellia ternata*-based N-CQDs, resulting in the fluorescence endofiltration effect between *Pinellia ternata*-based N-CQDs and Cr⁶⁺, resulting in the quenching of the fluorescence of *Pinellia ternata*-based N-CQDs. In addition, Cr⁶⁺ has strong electron acceptance and affinity, and it is easy to capture electrons. When the excited state molecule of *Pinellia ternata*-based N-CQDs collides with Cr⁶⁺, the nitrogen and oxygen functional groups on its surface can combine with Cr⁶⁺ to form complexes, which lead to electron transfer and non-radiative transition, leading to fluorescence quenching.

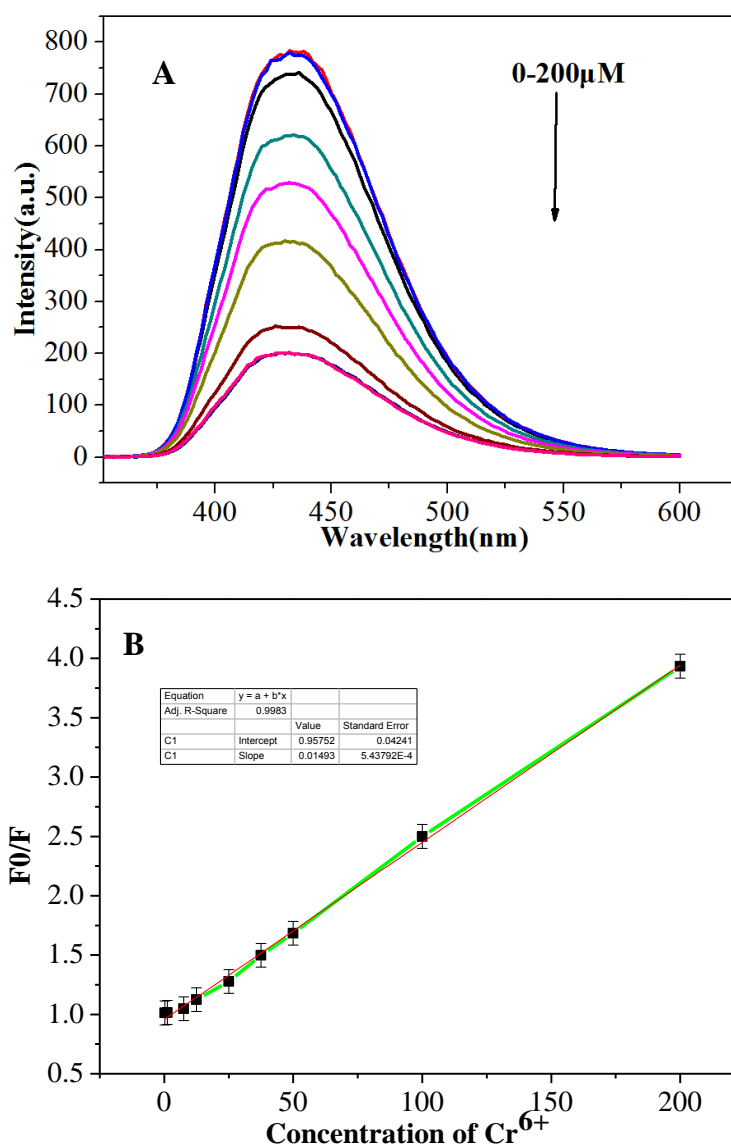


Figure 9. The fluorescence response of the *Pinellia ternata*-based N-CQDs upon the addition of different concentrations of Cr⁶⁺ (A) and a linear correlation of F₀/F values versus the concentration of Cr⁶⁺ over the range from 0 to 200 μM (B)

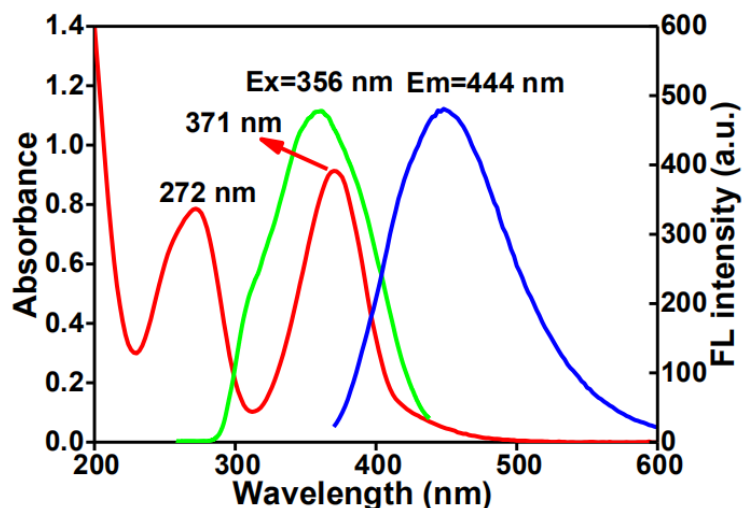


Figure 10. UV-Vis absorption spectra of Cr (VI) and fluorescence excitation/emission spectra of the *Pinellia ternata*-based N-CQDs

Detection of actual samples

In order to verify the practicability of this method, the content of Cr⁶⁺ in different water samples was investigated. As shown in *Table 1*, the recoveries of water samples were 94.2-102.5% and RSD was less than 5.8%. In order to evaluate the accuracy of this method, FAAS method was used to detect the content of Cr in water samples with the same concentration. The results show that in *Table 1*, the results of the two methods are very close, so, this method can be used for the rapid analysis and detection of Cr⁶⁺ in environmental water samples, and can be effectively applied to further research.

Table 1. Analytical results of Cr (VI) in the water samples (n = 3)

Samples	Spiked (μM)	Found (μM)	Recovery (%)	RSD (% , n = 3)	FAAS Found (μM)
Tap water	0	-	-	-	-
	5	4.71	94.2	4.3	4.82
	20	19.3	96.5	3.6	19.3
Lake water	0	-	-	-	-
	5	4.92	98.4	5.8	4.98
	20	20.5	102.5	2.5	20.1
Waste water	0	-	-	-	-
	5	5.10	102.0	5.3	5.04
	20	20.05	100.3	4.7	19.75

“-” not detected

Conclusion

In this study, for the first time, *Pinellia ternata* was used as a carbon precursor and ethylenediamine as a nitrogen source. Nitrogen-doped fluorescent carbon quantum dots with excellent optical properties and fluorescent quantum yield of 21.3% were prepared

by a simple one-step hydrothermal method. The morphology, particle size, crystalline form, chemical element composition and optical properties were characterized by TEM, FT-IR, XPS, UV-Vis and FS. The results show that *Pinellia ternata* N-CQDs have uniform size distribution, rich oxygen and nitrogen functional groups on their surface, and show good excitation wavelength dependence and tunability. Based on the quenching mechanism of fluorescence internal filter effect, Cr⁶⁺ has high sensitivity, selectivity and anti-interference ability. It can be used as a fluorescent nanoprobe for the analysis and detection of Cr⁶⁺ in complex environmental samples. The method has good linear relationship, fast reaction, simple operation, high sensitivity, high selectivity and low detection limit. It provides a new idea for developing carbon quantum dot fluorescent nanoprobe for detecting Cr⁶⁺ and has broad application prospects.

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