One-step hydrothermal method for preparing carbon dots and its determination of lead (II)

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Abstract. As a new type of carbon nanomaterials, carbon dots have attracted great interest due to their non-toxic, low preparation cost and unique photoluminescence properties. They have been widely studied and shown great potential in many fields. Here, nitrogen doped fluorescent carbon dots were prepared by one-step hydrothermal method using Epiphyllum leaves as raw materials. Ultraviolet-visible absorption spectrometer and fluorescence spectrometer were used to study the optical properties of carbon dots. The elemental composition and morphology of the surface of carbon dots were analyzed by transmission electron microscope, Fourier transform infrared spectroscopy and X-ray photoelectron spectrometer. The results show that the prepared carbon dots are uniformly dispersed in the aqueous solution, emit blue fluorescence, and the average particle size is 4.2 nm. The carbon dots have good light stability and strong anti-photobleaching ability. Continuous spectral scanning of the carbon dots can keep the fluorescence intensity basically unchanged within 30 minutes. In the concentration of 0~1 mol·L⁻¹ NaCl solution, the strength is not affected by the ionic strength. In the pH range of 4~8, the fluorescence intensity of carbon dots is basically stable. The heavy metal ion Pb²⁺ has a quenching effect on the fluorescence of carbon dots, and has a good linear relationship in the range of 0.5~200 μm. Therefore, a simple and green method for Pb²⁺ has been developed.

1. Introduction
Carbon dots are a new type of fluorescent carbon nanomaterials with a size of less than 10 nm and have the advantages of excellent optical performance, low toxicity, and biocompatibility. The application of carbon dots has been widely studied in biological imaging, sensing, environmental testing, photocatalysis, drug delivery, microfluidics and other fields[1,2].

The preparation methods of carbon dots mainly include arc discharge method [3], laser ablation method [4], electrochemical oxidation method [5], combustion method [6], template method[7], hydrothermal method [8], thermal pyrolysis method [9], microwave method [10] and ultrasonic method [11], etc. So far, the use of cheap, readily available, non-toxic natural product materials as carbon sources, and preparing carbon dots using hydrothermal methods have attracted widespread attention, but these carbon sources have problems such as complex preparation steps [12] and long preparation times [13]. Herein, the epiphyllum leaves were used as the carbon source, and the fluorescent carbon dots with excellent performance were prepared by a simple one-step hydrothermal method. The method is cheap raw materials, mild reaction conditions, simple control and fast. The prepared carbon dots have the advantages of wavelength-dependent luminescence, strong resistance to photobleaching, and high optical stability. Their application in the detection of metal ions Pb²⁺ has been further studied.
2. Experimental

2.1. Experimental Materials
Rinse the fresh epiphyllum leaves with water and dry them for later use. Main reagents: Al2(SO4)3, NiSO4, SrSO4, Cd(NO3)2, Cr(NO3)3, Pb(NO3)2, HgCl2, CuCl2, KCl, MnCl2, FeCl3, FeCl2, NaCl, C8H5KO4, NaOH and quinine sulfate, the reagents used in the experiment are analytically pure. The water used in the experiment was ultrapure water.

2.2. Characterization instrument
Fluorescence spectrometer (F-4600, Japan) was used to test the fluorescence performance, and the excitation and emission gap width was set to 5 nm. Ultraviolet-visible spectrophotometer (TU-1901, China) measured the ultraviolet-visible absorption spectrum. Fourier-infrared spectrometer (Vertex 70, Germany) tested the functional groups on the surface of the carbon dots. Transmission electron microscope (F20U-TWIN, Germany) observed the morphology and size of carbon dots. X-ray photoelectron spectroscopy (Escalab 250xi, USA) was used for surface element analysis.

2.3. Preparation of carbon dots
Put 2.58 g of chopped epiphyllum leaves into a 25 mL PTFE-lined reactor, added 10 mL of water, and heated it in an oven at 180 ℃ for 9 hours. After cooling, the sand core was filtered to remove large particles of residue. Then centrifuged at a speed of 10,000 rpm for 20 minutes, and then filtered with a 0.22 μm filter membrane. The obtained carbon dots were stored in the refrigerator for later use.

2.4. Pb2+ detection
Diluted Pb2+ standard solutions of different concentrations with potassium hydrogen phthalate-sodium hydroxide buffer solution (pH=6) to 3 mL, added 30 μL carbon dot solution, mixed well, and placed at room temperature for 1 min. The fluorescence spectrum of the solution was measured under the excitation wavelength of 360 nm, and each sample was measured 3 times in parallel.

3. Results and discussion

3.1. Research on the optical properties of carbon dots
Under high temperature conditions, different organic matter in the leaves of the epiphyllum is carbonized to form carbon dots. As shown in the figure1 (A), the carbon dots are yellow in an aqueous solution and emit blue fluorescence when irradiated with ultraviolet light with a wavelength of 365 nm and the ultraviolet-visible absorption spectrum of carbon dots has an absorption peak at 279nm, which is caused by the absorption of the n-π* transition of C=O[14]. From figure1 (B), it is shows that the emission wavelength of carbon dots gradually redshifts with the change of excitation wavelength, when the excitation wavelength increases from 300 nm to 440 nm, the emission wavelength covers the violet to green part of visible light, while the fluorescence of the emission spectrum first increases and then decreases. This excitation wavelength-dependent characteristics of the carbon dots may be related to the difference in the particle size of the carbon dots [15]and the existence of energy traps on the surface of the carbon dots [16]. When the excitation wavelength is 360 nm, the maximum emission wavelength is 440 nm as shown in the figure1 (C).
The fluorescence stability of carbon dots was further studied. Under continuous and uninterrupted conditions, the carbon dots were spectrally scanned. As shown in the figure 2 (A), the intensity remained unchanged within 30 minutes. The results showed that carbon dots had strong resistance to light bleaching strong.

At the same time, the fluorescence stability of carbon dots in high ionic strength solutions was studied. The carbon dots were added to NaCl solutions of different concentrations, and the fluorescence intensity of carbon dots was measured respectively. As shown in the figure 2 (B), when the ion concentration of NaCl changes from 0 to 1 molꞏL⁻¹, the intensity of the carbon dots remained almost unchanged, indicating that the fluorescence stability of the carbon dots was high and not affected by the ionic strength.

In addition, the effect of pH on the fluorescence intensity of carbon dots was also studied. As shown in the figure 2 (C), when the pH is very low, the fluorescence is almost quenched. When the pH increases from 4.0 to 7.0, the fluorescence intensity of carbon dots is basically stable. When the pH value is greater than 8.0, the fluorescence intensity of the carbon dots significantly weakened. This is due to protonation reaction in strong acidic condition and deprotonation reaction in strong alkaline condition. Therefore, the -OH, -NH and -COOH groups on the surface of the carbon dots will interact with each other, resulting in the aggregation of carbon dots and fluorescence quenching.

3.2. Morphology and surface analysis of carbon dots
The morphology of the prepared carbon dots was show in figure 3 (A). The transmission electron microscope (TEM) image shows that the carbon dots are spherical with a particle size of 4.2 nm (based on statistical analysis of more than 100 dots). Disperse uniformly in the aqueous solution without agglomeration.
Fourier transform infrared spectrometer was used to analyze the surface functional groups of carbon dots. As shown in the figure3 (B), the carbon dot has a wide absorption band near 3358 cm$^{-1}$, which is attributed to the stretching vibration of N-H and O-H; there is a strong peak at 1599 cm$^{-1}$, which is attributed to the stretching vibration of the C=O bond; 1423 cm$^{-1}$ is the stretching vibration of C-N and C-O; the weak absorption at 1081 cm$^{-1}$ is the bending vibration absorption peak of C-O; the absorption peak at 678 cm$^{-1}$ corresponds to the bending vibration of the O-H bond.

The XPS test further characterized the chemical state and element composition of the carbon dots surface. The figure4 (A) shows the XPS scan full spectrum of the carbon dots. There are 3 binding energy peaks at 532.08, 400.08, and 286.08 eV, corresponding to the 1s of oxygen, nitrogen and carbon atoms. In which the carbon content is 66.68%, the oxygen content is 28.11%, and the nitrogen content is 5.21%, indicating that the surface of the carbon dots contains oxygen, nitrogen and carbon elements. Figure4 B is the narrow sweep spectrum of C1s, which can be divided into 4 peaks at 284.5, 285.4, 286.3, 288.2 eV, respectively, representing the C element with C=C / C-C, C-N, C-O, -COO' bonds exist on the surface of carbon dots. The N1s spectrum of carbon dots (Figure4 C ) shows that the N element exists in the form of C-N (399.7eV) and N-H (400.59eV). In the O1s spectrum of carbon dots (Figure4 D), the peaks at 531.5eV and 532.8eV are attributed to C=O/C-O-C and C-OH, respectively.

The above results show that the carbon dots are nitrogen-doped fluorescent carbon dots. There are a large number of hydrophilic active groups such as hydroxyl, carboxyl and amino groups on the surface,
thus having better dispersal in an aqueous solution. It is conducive to the application of carbon dots in the fields of analysis, sensing and cell imaging.

3.3. Research on the response of Pb$^{2+}$

The prepared carbon dots are rich in hydroxyl, carboxyl and amino groups on the surface, and these functional groups have the ability to recognize and coordinate metal ions, based on this, the metal ion response of carbon dots was discussed.

![Figure 5. (A) Fluorescence intensity of carbon dots with different concentrations of Pb$^{2+}$ (from 0 to 200 µm); (B) Linear equation of carbon dots for the detection of Pb$^{2+}$. $F$ and $F_0$ correspond to fluorescence intensity of carbon dots with and without Pb$^{2+}$, respectively.](image)

The experimental results (figure 5 (A)) show that the fluorescence intensity of carbon dots decreases with the increase of Pb$^{2+}$, and fluorescence quenching occurs. As shown in the figure 5 (B), when the concentration of Pb$^{2+}$ is 0.5~200 µm, the relative fluorescence quenching intensity ($F/F_0$) of carbon dots is linear with the concentration of Pb$^{2+}$, and the linear equation is $F/F_0 = -0.001x + 0.971$, a good linear relationship (linear correlation coefficient $R^2=0.9941$). The detection limit was calculated according to $3s/K$ (where $s$ is the standard deviation of the blank sample and $K$ is the slope of the fitted curve) by performing 7 tests on the blank samples, and the detection limit is 0.34 µm. It can be seen that the method has a wide linear range and high sensitivity.

The selectivity of carbon dots for the determination of Pb$^{2+}$ was further studied. Under the same experimental conditions, the effects of interfering ions K$^+$, Mn$^{2+}$, Sr$^{2+}$, Cr$^{3+}$, Ni$^{2+}$, Al$^{3+}$, Cd$^{2+}$, Hg$^{2+}$, Cu$^{2+}$, Fe$^{2+}$, Fe$^{3+}$ were investigated with the concentration of 200 µM, respectively. The experimental results are shown in Figure 6. It is found that only Fe$^{3+}$ has a certain effect, while other metal ions have almost little quenching. The carbon dots have highly selectivity for Pb$^{2+}$, as the active groups on the surface of the carbon dots are prone to coordination reaction with the Pb$^{2+}$ to form highly stable complexes, leading to the aggregation of carbon dots and fluorescence quenching. However, other metal ions are not prone to forming complexes, so there is almost no quenching effect.

![Figure 6. Response of different metal ions to carbon dots](image)
4. In conclusion
In summary, a one-step hydrothermal method was proposed to prepare N-doped carbon dots using epiphyllum leaves as a carbon source. The prepared carbon dots have good fluorescence properties and stability, and their surface contains active groups such as hydroxyl, carboxyl and amino groups. In addition, a method based on fluorescence quenching for the detection of Pb²⁺ has been developed, which provides new possibilities for the development of environmentally friendly, low-cost, high-sensitivity detection methods, and has potential application prospects.

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