

# Green synthesis of carbon quantum dots from lignite coal and the application in Fe<sup>3+</sup> detection

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**Abstract.** Carbon quantum dots (CQDs) had attracted much attention due to their unique structures and excellent properties. Their green preparation was one of the research frontiers. However, most of the CQDs were prepared by strong acid oxidation, the way of which was not friendly to the environment. In this study, CQDs were prepared by green ozone oxidation of lignite coal, which is abundant and inexpensive. The CQDs were well dispersed, the size distribution of the obtained CQDs centralized from 2 to 4 nm with the average diameter of about 2.8 nm. In addition, the as-prepared CQDs containing rich oxygen functional groups exhibited good water-solubility and optical properties with yield reached 35%. The CQDs showed a highly sensitive and selective quenching effect to Fe<sup>3+</sup> with desirable anti-interference performance. Moreover, the fluorescence intensity of CQDs had a good linear response to the Fe<sup>3+</sup> concentration ranging from 10 to 150 μmol/L with the detection limit of 0.26 μmol/L. This green and facile synthesis method had the prospect of large-scale preparation of CQDs.

## 1. Introduction

As a newly promising member of carbon family, carbon quantum dots (CQDs) have aroused enormous interest due to their stable photochemical properties, excellent chemical stability, low toxicity, excellent biocompatibility, good water-solubility, and easy surface functionalization. CQDs have been displayed important and widespread applications in energy production, catalysis, fluorescence probing, bioimaging, sensing, photoelectric products, and photoelectric catalysis etc.<sup>[1-6]</sup>. At present, several methods have been proposed towards the synthesis of CQDs<sup>[7-12]</sup>, among them, oxidation has become one of the most commonly used methods, however the conventional oxidation process to prepare CQDs usually uses H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> and other strong acids<sup>[11,12]</sup>, which would pollute the environment seriously. Compared with the strong acids, ozone (O<sub>3</sub>) is a common green oxidant since it produces mainly environmental friendly O<sub>2</sub> and H<sub>2</sub>O during oxidation. Additionally, the O<sub>3</sub> oxidation method has been used to large-scale preparation of CQDs in water treatment<sup>[13,14]</sup>.

Various carbon materials have been used to prepare CQDs<sup>[15-18]</sup>, among them, the use of cheap coal can greatly reduce the cost of carbon sources, and has broad application prospects. In particular, lignite reserves are abundant and low price, its internal structure contains a large number of nanometer-sized graphitic crystallites linked by aliphatic amorphous carbon, which make coal an ideal carbon source<sup>[19-21]</sup>. Additionally, the coalification degree of the lignite coal is the lowest, which makes it is easy to



oxidation cleavage in short time. Therefore, it is of great significance to explore a green synthesis method with cheap lignite as a carbon source for the preparation of CQDs.

Herein, we report a green, mild and economical oxidizing approach for the large-scale preparation of CQDs from lignite coal by O<sub>3</sub> oxidation method. The lignite coal is used as the sole carbon source and O<sub>3</sub> is used as the oxidizing agent without the addition of any acid, alkali, salts or organic compounds. The prepared CQDs show superior water dispersibility and blue green luminescence. They also exhibit a good linear response to Fe<sup>3+</sup> in the concentration range from 10 to 150 µM with a detection limit of 0.26 µM. It demonstrated a potential application of the CQDs derived from coal in environmental protection.

## 2. Experimental details.

### 2.1 Synthesis of CQDs from coal

CQDs were synthesized by an environmentally friendly hydrothermal method using lignite coal as the sole reaction precursor. Briefly, 3 g of the lignite coal was dispersed in 200 mL ultrapure water, then ultrasound for 1 h to form a homogenous mixture. Then the mixture was oxidized for 2 h by O<sub>3</sub> (68 mg/L) at 25°C. A brown supernatant was obtained by removing the large particles through centrifugation at 18000 rpm for 30 min. Finally, the supernatant was decompressed to remove water, and the CQDs solid was obtained after drying.

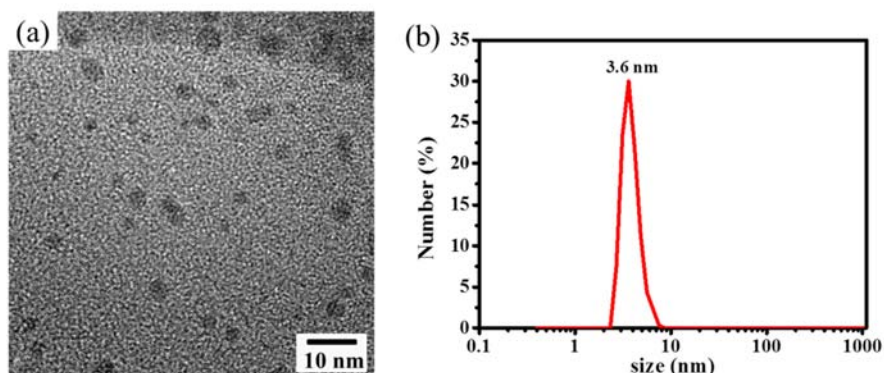
### 2.2 Apparatus and characterization

Transmission electron microscopy (TEM) was characterized by a FEI-Tecnai G2 F30 transmission electron microscope with an accelerating voltage of 300 kV. Size distribution of the CQDs was observed using a Zeta sizer Nano ZS instrument (Malvern, UK). Fourier transform infrared spectrometry (FTIR) was conducted on a Nicolet iN10 MX & iS10 spectrophotometer using KBr pellets. X-ray photoelectron spectroscopy (XPS) analysis was performed on an Escalab 250Xi spectrometer equipped with an Al Kα exciting source. All luminescence spectra were recorded on an F97pro fluorescence spectrophotometer with the scan speed of 1000 nm min<sup>-1</sup>. The excitation wavelength was set at 360 nm. The ultraviolet–visible (UV–vis) absorption spectra were acquired on a UV2900 UV–vis Spectrophotometer.

## 3. Results and discussion

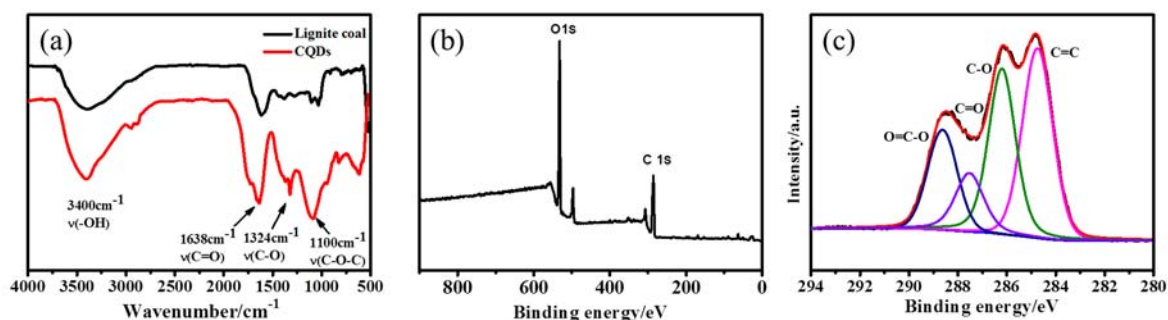
### 3.1 Structural characterization of CQDs

TEM and DLS were used to characterize the morphology, microstructure and size distribution of the CQDs sample. As shown in Figure 1a, the TEM images of the CQDs showed that the obtained CQDs were uniform and monodisperse with an average size of 2.8 nm. Revealing that lignite coal was oxidative cleavage into 2-4 nm dots and well dispersed. The size distribution of CQDs was also measured by light scattering, as shown in Figure 1b, the size distribution of CQDs was in the range of 2-7 nm in which the content of CQDs with a diameter of 3.6 nm reached 30%. The diameter from DLS was little a larger than that from TEM results may because that the size tested by DLS measurement was the average hydrodynamic diameter.



**Figure 1.** (a) TEM images of the CQDs, (b) Size distributions of the CQDs samples measured by DLS

In order to analyze the functional groups of the as-synthesized CQDs sample, the FTIR spectra of the as-prepared CQDs were given in Figure 2a. The CQDs showed four main absorption bands at  $3400\text{ cm}^{-1}$ ,  $1638\text{ cm}^{-1}$ ,  $1324\text{ cm}^{-1}$ , and  $1100\text{ cm}^{-1}$ , which can be indexed to the stretching vibrations of O-H, the symmetric stretching vibration of C=O, the vibration of C-O, and the symmetric stretching vibration of C-O-C<sup>[22]</sup>. These functional groups could improve the hydrophilicity and stability of the CQDs in an aqueous system. The chemical composition of the as-synthesized CQDs sample was characterized by XPS. As shown in Figure 2b, the XPS results showed the presence of O and C, and O content was approximated 41.89%, corresponding C1s and O1s peaks were located at 285.0 and 532.1 eV, respectively. The high-resolution spectrum of C1s (Figure 2c) displayed four peaks at 284.6 eV, 285.8 eV, 286.7 eV, and 288.5 eV, which were corresponding to C=C, C-O, C=O, and -COOH groups, respectively<sup>[23]</sup>. In a word, the above XPS characterization results confirmed that the synthesized CQDs sample possessed a rich surface carboxy group and carbonyl group functional groups, which was consistent with the corresponding FTIR spectra.

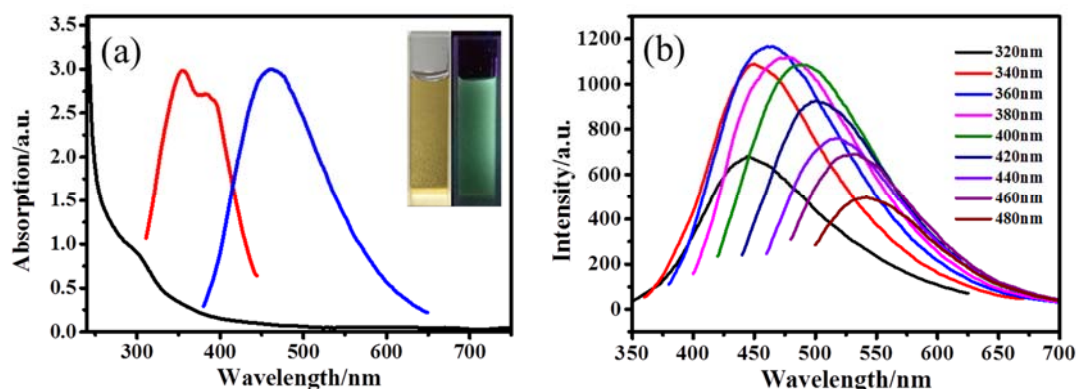


**Figure 2.** (a) FTIR spectra of lignite coal (black) and the CQDs (red), (b) XPS survey spectrum of CQDs, (c) high-resolution XPS spectra of C1s.

### 3.2 Optical properties of CQDs

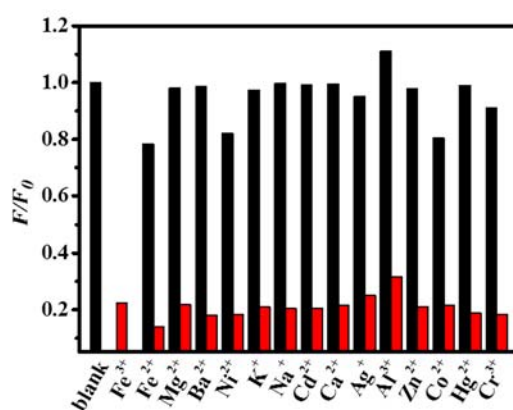
The optical properties of as-prepared CQDs were investigated by UV-vis absorption spectra, FL excitation spectra, and emission spectra. CQDs showed a broad absorption band at 280-310 nm (Figure 3a). This was the absorption from the aromatic system, which was a typical characteristic of the fluorescent CQDs<sup>[24,25]</sup>. The aqueous suspension was achromatous and transparent in the daylight, but the emitted obvious blue luminescence under the irradiation of a 365 nm lamp (Figure 3a inset). The emission wavelength of as-prepared CQDs was strongly dependent on the excitation wavelength from 320 to 480 nm (Figure 3b). We could obviously observe that the emitted fluorescence intensity increased from 320 to 360 nm and then decreased from 360 to 480 nm. The fluorescent intensity reached the highest value when excited at 360 nm, the emission wavelength showed red shift, the

excitation dependent PL behavior of the CQDs reflected the effect of particles of different sizes and the distribution of the different surface state<sup>[26,27]</sup>.



**Figure 3.** (a) UV-vis absorption of CQDs (black), PL excitation (red,  $\lambda_{\text{ex}} = 360$  nm), and PL emission spectra (blue,  $\lambda_{\text{em}} = 460$  nm) of CQDs, Inset: the photographs taken under daylight (left) and 365 nm UV light (right), (b) Emission spectra of the CQDs recorded at different excitation wavelengths in the range of 320-480 nm.

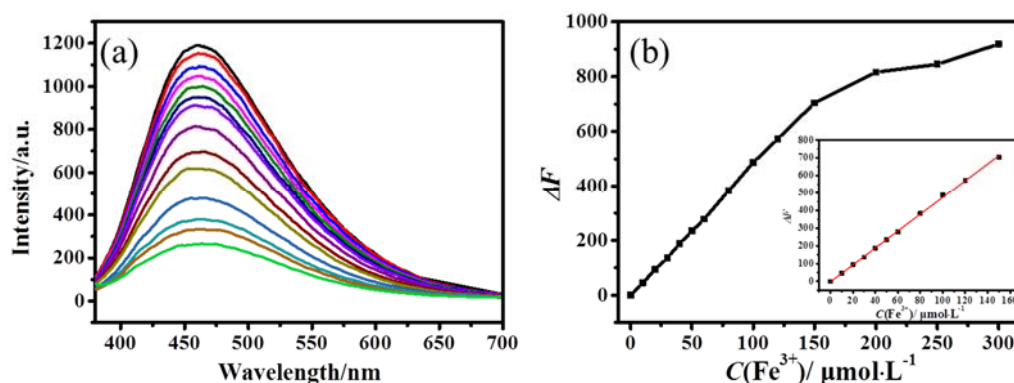
Oxygen rich functional groups over the surface of CQDs made the CQDs be a kind of potential fluorescent probe for the detection of metal ions since they may interact with metal ions to form complex compounds<sup>[28,29]</sup>. So we take into account the selectivity of CQDs towards different metal ions, including  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{2+}$  and  $\text{Hg}^+$  with the same concentration of 300  $\mu\text{mol/L}$ . As shown in Figure 4, we can clearly observe that only  $\text{Fe}^{3+}$  gave significant quenching effect on the fluorescence of CQDs upon addition of  $\text{Fe}^{3+}$ .  $F_0$  and  $F$  were the FL intensities of the CQDs in the absence and presence of different ions, respectively. The selectivity of the CQDs toward  $\text{Fe}^{3+}$  in the presence of other ions were also observed. The quenching effect of CQDs to  $\text{Fe}^{3+}$  don't disturbed in the presence of other ions. This illustrated the CQDs had highly selective and anti-interference to  $\text{Fe}^{3+}$ .



**Figure 4.** Corresponding  $F/F_0$  of CQDs before (black) and after (red) the treatment with  $\text{Fe}^{3+}$

Finally, we explored the feasibility of CQDs for detecting  $\text{Fe}^{3+}$  in aqueous solution, the fluorescence spectra of CQDs in the presence of  $\text{Fe}^{3+}$  with different concentrations were investigated. As shown in Figure 5a, PL intensities of CQDs at 360 nm gradually quenched with the increasing of concentrations of  $\text{Fe}^{3+}$ . It could be clearly seen that the fluorescence quenching efficiency ( $\Delta F = F_0 - F$ ) decreased as the concentration of  $\text{Fe}^{3+}$  increases. A good linear correlation from 10  $\mu\text{mol/L}$  to 150  $\mu\text{mol/L}$  was obtained, where  $F$  and  $F_0$  stood for the PL intensities at 360 nm in the presence and absence of  $\text{Fe}^{3+}$ , respectively. And the linear regression equation was  $\Delta F = 4.766C - 2.354$  with a correlation coefficient of 0.999, where  $C$  was the concentration of  $\text{Fe}^{3+}$ . The limit of detection was

estimated to be  $0.26 \mu\text{mol/L}$  according to  $3\delta/S$  [30], where  $\delta$  was the standard deviation of the blank signal and  $S$  was the slope of the linear calibration plot. This consequence suggested that the CQDs were suitable as fluorescent probes and exhibits higher sensitivity to detection  $\text{Fe}^{3+}$ .



**Figure 5.** (a) PL spectra of CQDs in the presence of different concentrations of  $\text{Fe}^{3+}$  (from top to bottom:  $0\text{--}300 \mu\text{mol/L}$ ), (b) The curve of the fluorescence quenching between  $\Delta F$  and  $\text{Fe}^{3+}$  concentration from  $0\text{--}300 \mu\text{mol/L}$  (inset: the low level linear relationship for the  $\text{Fe}^{3+}$  detection).

#### 4. Conclusion

In conclusion, the green fluorescent CQDs with different sizes were prepared using lignite coal as the carbon source with  $\text{O}_3$  chemical oxidative method. The exfoliated CQDs from lignite coal exhibited superior optical properties and excellent water-solubility due to many oxygen-rich functional groups on the surface of CQDs. The CQDs could be used as a highly selective and sensitive FL probe for detecting  $\text{Fe}^{3+}$  with a lower detection limit of  $0.26 \mu\text{M}$  from  $10$  to  $150 \mu\text{M}$ . The method of fabricating CQDs is simple and green, which is feasible for large-scale industrial applications.

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