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## 可视化黄色荧光石油焦基碳量子点高效检测 $\text{Cu}^{2+}$

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**摘要:** 以石油焦为碳源, 采用超声辅助的化学氧化法直接制备可视化黄色荧光碳量子点(CQDs)。作为非标记的探针, 该CQDs无需任何修饰即可成功用于实际水样中 $\text{Cu}^{2+}$ 的检测。该荧光探针制备方法简单、经济, 可快速响应(3 s), 具有良好的选择性、灵敏性和可重复利用性, 并且可实现“混合即检测”的快速检测目的。其线性检出范围较宽, 为0.25~10  $\mu\text{mol/L}$ , 检出限为0.029 5  $\mu\text{mol/L}$ 。光诱导电子转移机理可很好地解释 $\text{Cu}^{2+}$ 猝灭CQDs的过程, 本文提出的CQDs- $\text{Cu}^{2+}$ -EDTA“off-to-on”检测机理为金属离子荧光探针的开发奠定了理论基础。石油焦基CQDs在实际水样 $\text{Cu}^{2+}$ 的检测中具有快速响应性, 在实际传感器应用领域具有很好的实际应用价值。

**关键词:** 石油焦; 碳量子点; 黄色荧光; 快速检测;  $\text{Cu}^{2+}$ 检测

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## Yellow-visual fluorescent carbon quantum dots from petroleum coke for the efficient detection of $\text{Cu}^{2+}$ ions

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**Abstract:** Yellow-visual fluorescent carbon quantum dots (CQDs) were prepared from petroleum coke by ultrasonic-assisted chemical oxidation and were used as label-free probes for  $\text{Cu}^{2+}$  detection in water. The detection of  $\text{Cu}^{2+}$  by CQD probes is related to a quenching of fluorescence by a photo induced electron transfer mechanism. The quenched fluorescence of the CQDs by  $\text{Cu}^{2+}$  can be recovered by adding ethylene diaminetetraacetic acid. The yellow-visual fluorescent CQD probes have a linear detection range from 0.25 to 10  $\mu\text{M}$ , a detection limit of 0.029 5  $\mu\text{M}$ , a response time of 3 s, and a superior sensitivity and selectivity for  $\text{Cu}^{2+}$  detection compared to other fluorescent probes. The CQDs are easy to prepare, economical, reusable, fast to respond and can be used in on-line detection.

**Keywords:** Petroleum coke; Carbon quantum dots; Yellow-visual; Fast response;  $\text{Cu}^{2+}$  detection

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## 1 Introduction

Water pollution caused by heavy metal ions has become a critical issue worldwide. As a kind of heavy metals, a trace amount of copper is essential for many living organisms. However, electroplating wastewater with a plenty of copper is currently becoming a serious threat to human's health and the environment<sup>[1,2]</sup>. Conventional analysis methods, such as atomic absorption spectrometry, electrochemical method, inductively coupled plasma-mass spectrometry and inductively plasma-mass emission spectrometry, have been widely used for the detection of  $\text{Cu}^{2+}$ <sup>[3-5]</sup>. However, the above-mentioned methods are usually time consuming, complicated to prepare sample, even with toxic reagents, and generally unsuitable for on-line application or in-field detection<sup>[6]</sup>. Therefore, it is highly desired to develop a practicable method with a high accuracy and sensitivity for simple, rapid, green, and low-cost tracking of  $\text{Cu}^{2+}$  in environmental, biological and tap water.

Previously, the organic dye/organic complex fluorophore-based and quantum dots (QDs)-based probes, as fluorescent probes, have been proved to selectively respond to  $\text{Cu}^{2+}$  due to their relatively high sensitivity<sup>[7-11]</sup>. However, the employed organic dyes and QDs are easy to be oxidized, toxic and often lack photostability, which restrict their performance in practical applications<sup>[12-14]</sup>.

The emergency of fluorescent carbon quantum dots (CQDs) provides a new way to detect  $\text{Cu}^{2+}$ , which could meet most requirements in  $\text{Cu}^{2+}$  detection. As a new star in QDs family, CQDs show a considerably low toxicity, excellent aqueous solubility, high stability, resistance to photobleaching, and stable fluorescence, which make them promising in fields like fluorescent probe, optoelectrical devices, sensor cell imaging, etc<sup>[15-17]</sup>. Based on the merits mentioned above, CQDs are more suitable as probe for the detection of  $\text{Cu}^{2+}$  than other fluorescent materials.

Some excellent works on CQDs as a probe for  $\text{Cu}^{2+}$  detection have been reported. CQD-based  $\text{Cu}^{2+}$  probe was firstly developed by Liu et al. in 2012<sup>[18]</sup>. They explored the feasibility of photoluminescent polymer nanodots for  $\text{Cu}^{2+}$  detection, which exhibit a blue fluorescent emission. The detection range is from  $5 \times 10^{-11}$  to  $5 \times 10^{-5}$  mol/L with a limit of detection (LOD) of 1 nmol/L, and their response time to  $\text{Cu}^{2+}$  is 10 min. Recently, Wang et al.<sup>[19]</sup> developed a facile approach to prepare the blue-fluorescent graphene quantum dots via a hydrothermal re-oxidation of graphene oxide to detect  $\text{Cu}^{2+}$ , the calibration curve of

which displays a linear region of 0-15  $\mu\text{m}$  with a detection limit of 0.226  $\mu\text{m}$ .

Here we prepared a new kind of yellow fluorescent CQDs from petroleum coke, which show a high selectivity, sensitivity and fast response for  $\text{Cu}^{2+}$  detection. It should be noted that the high value-added utilization of heavy oil is still urgently needed, although lots of efforts have been reported<sup>[20-22]</sup>. As a by-product in oil refining process, petroleum coke used to prepare CQDs can achieve a high value-added utilization. More importantly, the yellow fluorescent CQDs are easier to be distinguished by naked eyes compared with blue fluorescent CQDs. CQDs fluorescent intensity could be recovered by ethylene diamine tetraacetic acid (EDTA) and reused, whereas it could hardly be quenched by other metal ions, such as  $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{6+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Na}^+$ ,  $\text{As}^{3+}$ ,  $\text{K}^+$ ,  $\text{Ce}^{3+}$  and  $\text{Sn}^{4+}$ . Moreover, the proposed CQDs probing system has been successfully applied for the determination of  $\text{Cu}^{2+}$  both in natural water and tap water.

## 2 Experimental

### 2.1 Chemicals and materials

All chemical agents used were analytical-grade pure. 98.0 wt. % sulfuric acid, 65.0 wt. % nitric acid, 28.0 wt. % ammonia, EDTA and all metal salts were provided by Sinopharm Chemical Reagent Company, China. Aqueous solutions of  $\text{Ba}^{2+}$ ,  $\text{Ce}^{3+}$  and  $\text{Na}^+$  were prepared from their nitrate salts, aqueous solutions of  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sn}^{4+}$  and  $\text{K}^+$  were prepared from their chloride salts, aqueous solution of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Al}^{3+}$  were prepared from their sulfuric acid salts. Aqueous solutions of  $\text{As}^{3+}$  and  $\text{Cr}^{6+}$  were prepared from  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{Na}_3\text{AsO}_4$ , respectively. Nitrate and chloride salts of  $\text{Cu}^{2+}$  as well as chloride salts and sulfuric acid salts of  $\text{Na}^+$  were also used. Quinine (97.0 wt. %) was from Aladdin Industrial Corporation at Shanghai of China. Inorganic filter membrane (0.22  $\mu\text{m}$ ) and 3500 Da molecular weight cut off (MWCO) membranes (Amicon Ultra-4, Millipore) were bought from Shanghai Green Bird Science & Technology Development Co. of China. The water used throughout the experiments was deionized (DI) water.

### 2.2 Synthesis and purification of CQDs

CQDs were obtained from petroleum coke via the ultrasonic-assisted chemical oxidation approach<sup>[23]</sup>. In brief, 2 g petroleum coke was added into a mixture of concentrated  $\text{H}_2\text{SO}_4$  (45 mL) and  $\text{HNO}_3$  (15 mL). The solution was sonicated at 700 W in a flask for 2 h and then stirred under reflux in an oil bath at 120  $^\circ\text{C}$

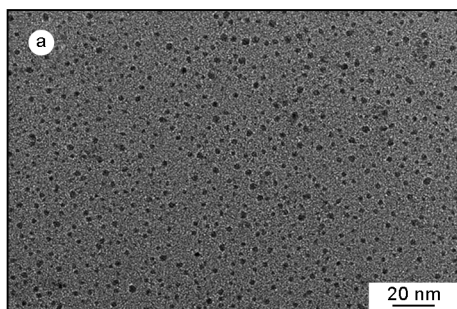
for 24 h. After the reaction, the mixture was cooled to room temperature (RT), then diluted ten times and adjusted to neutral with ammonia. The neutralized mixture was filtered with a 0.22  $\mu\text{m}$  membrane and dialyzed in a dialysis bag (MWCO 3500 Da) for 72 h to remove the remaining salts and tiny fragments to obtain a CQD solution. The CQD solution exhibited a yellow emission under UV light at 365 nm.

### 2.3 Detection of $\text{Cu}^{2+}$

In a typical run, a standard 0.1 mol/L  $\text{Cu}^{2+}$  solution was prepared by dissolving 0.125 g  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in DI water and adjusting the volume to 5.0 mL in a volumetric flask.

A fixed concentration of CQDs (0.02 mg/mL) was transferred to a fluorescent cuvette. The fluorescence intensity of the solution was recorded from 435 to 800 nm with an excitation wavelength of 420 nm. The fluorescence intensity of the solution was then recorded according to the amount of added  $\text{Cu}^{2+}$ . Similar procedure was performed for various predetermined concentrations of  $\text{Cu}^{2+}$ , EDTA and other metal ions. For the sake of comparison, the volume of CQD solution was fixed at 2 mL before the addition of  $\text{Cu}^{2+}$ . All measurements were made at RT.

In this experiment, two kinds of water, i. e. natural water obtained from Tangdao Bay of Qingdao, Shandong province, China and tap water from our lab were used to evaluate the CQD-based probe for  $\text{Cu}^{2+}$  detection. Before analysis, natural water was firstly filtered through a 0.22  $\mu\text{m}$  filtered membrane, then spiked  $\text{Cu}^{2+}$  at different concentrations. The tap water was spiked with different concentrations of  $\text{Cu}^{2+}$  solutions directly without any pretreatment.



### 2.4 Characterization

All fluorescence measurements were carried out with a F-97 Pro fluorescence spectrophotometer (Shanghai Lengguang Technology Co., Ltd., China). UV-Vis absorption spectra were measured by a Gold Spectrumlab 54 UV/Vis spectrophotometer (Shanghai Lengguang Technology Co., Ltd., China). The transmission electron microscopic (TEM) image was obtained by the JEOL JEM-2100UHR microscope with an accelerating voltage of 200 kV. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 spectrometer. The time decay was measured on a Fluoro Max-4 fluorometer (Horiba Jobin Yvon Inc, France). An excitation wavelength of 405 nm was used and emission was collected at 510 nm.

## 3 Results and discussion

### 3.1 Preparation and characterization of the CQDs

With the help from mixed strong acids and ultrasonic treatment for 24 h, yellow fluorescent CQDs could be directly obtained from petroleum coke without any further passivation or modification. The yellow fluorescence intensity of the CQDs was strong enough for  $\text{Cu}^{2+}$  detection, and the quantum yield of as-prepared CQDs was as high as 9.8%.

Fig. 1a shows the TEM image of the CQDs, which exhibits a spherical shape with a narrow size distribution. The corresponding particle size distribution of CQDs in Fig. 1b indicates that their diameters are in the range of 2.0-4.5 nm (averaged 2.8 nm).

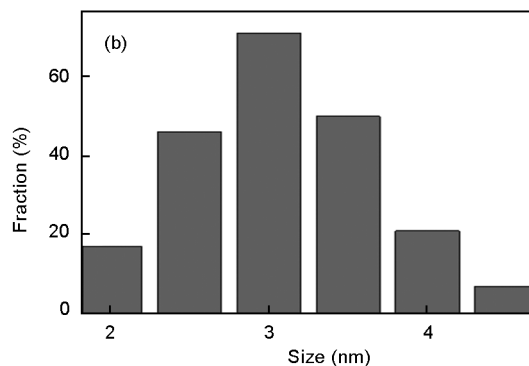


Fig. 1 (a) TEM image and (b) the corresponding particle size distribution of CQDs.

The FT-IR spectra of petroleum coke and the CQDs are shown in Fig. 2. For petroleum coke, no obvious peaks are found except the small peaks at 2 918 and 2 857  $\text{cm}^{-1}$ , which are originated from  $-\text{CH}_2$  vibration. However, rich hydrophilic groups including carboxyl and hydroxyl groups are found in

CQDs. The typical peak at 3 441  $\text{cm}^{-1}$  is assigned to  $-\text{OH}$  group and the small peaks at 2 918 and 2 857  $\text{cm}^{-1}$  belongs to  $-\text{CH}_2$ . The peaks at 1 608 and 1 763  $\text{cm}^{-1}$  arise from the stretching vibration of  $\text{C}=\text{O}$  band in carboxylic moiety. Peak around 1 439  $\text{cm}^{-1}$  belongs to  $\text{C}-\text{OH}$  or  $\text{C}-\text{H}$  stretching

vibration, and peak at  $1\ 128\ \text{cm}^{-1}$  can be identified as C—O stretching vibration<sup>[24,25]</sup>. Obviously, the abundant hydrophilic groups help to greatly improve aqueous solubility of the CQDs, which are beneficial for their applications in water system.

The optical properties of as-prepared CQDs were further explored. The UV—Vis absorption spectrum and fluorescence spectra of the CQDs are shown in Fig. 3. The UV—Vis absorption spectrum of the aqueous CQDs (Fig. 3a) shows an absorption band at ca. 228 nm, attributing to  $\pi$ - $\pi^*$  electron transition of graphitic  $\text{sp}^2$  domains<sup>[26]</sup>. The normalized fluorescence intensities of the CQDs are plotted in Fig. 3b. With the excitation wavelength increases from 300 to 580 nm, the emission peak red-shifts from 480 to 600 nm, indicating the excitation-dependent luminescent behavior of the CQDs. This may be associated with the aromatic C=C bonds and surface defects resulted from C—OH and C=O groups in the CQDs<sup>[27,28]</sup>.

Fig. 4a depicts the comparison of fluorescent spectra before and after 6 months. As shown in Fig. 4a, the fluorescence intensity of the CQDs remains unchanged for 6 months, suggesting the stable fluorescent properties of the CQDs. As molecular

oxygen is regarded as one of the best-known collisional quenchers for fluorescent materials<sup>[19]</sup>, the effect of dissolved oxygen on  $\text{Cu}^{2+}$  detection via the CQD probe was investigated. The dissolved oxygen was removed by filling  $\text{N}_2$  into cuvette for 30 min, detection result without oxygen was then obtained. Fig. 4b shows that the fluorescence intensities of the CQD solutions are almost the same before and after the removal of dissolved oxygen. Therefore, in our case, the effect of dissolved oxygen can be neglected in  $\text{Cu}^{2+}$  detection via the CQD probe, which is an advantage for CQD probing, especially in oxygen existing circumstance.

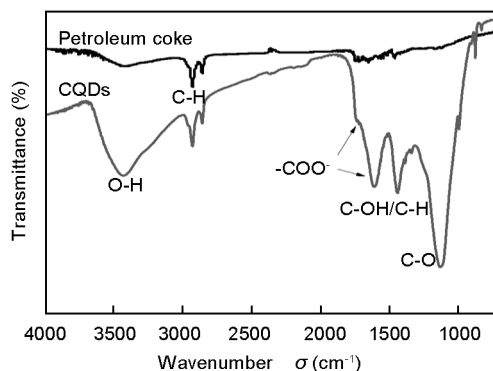


Fig. 2 FT-IR spectra of CQDs and petroleum coke.

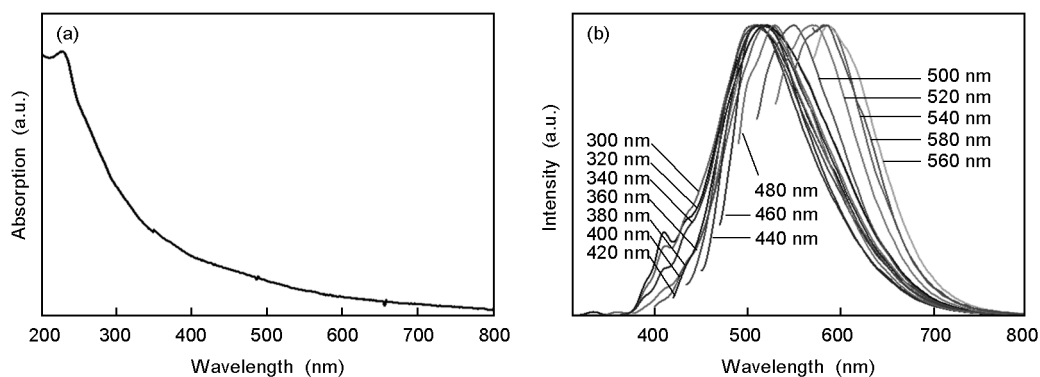


Fig. 3 (a) UV-Vis absorption spectrum and (b) normalized fluorescence spectra of CQDs.

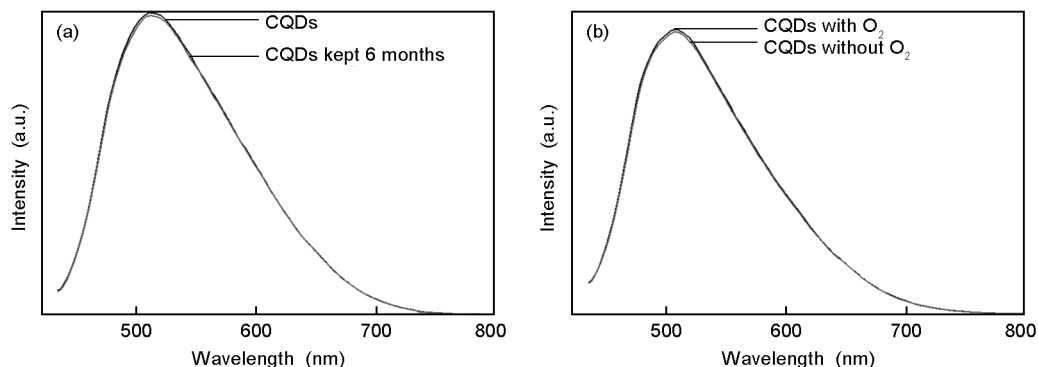


Fig. 4 (a) The stability of CQDs and (b) the effect of dissolved oxygen.

### 3.2 Detection of Cu<sup>2+</sup>

To confirm the quenching is solely caused by Cu<sup>2+</sup> and not due to the associated anions, various salts with different types of anions were added and investigated (Fig. 5a). All solutions containing Cu<sup>2+</sup> and different salts show similar quenching effect, proving that Cu<sup>2+</sup> is responsible for fluorescence quenching of the CQDs (Fig. 5b). To prove that the

quenching is not due to a synergistic effect of ions and their counter anions, the similar experiments were carried out by various Na<sup>+</sup> salts substituting above mentioned Cu<sup>2+</sup> salts (Fig. 5c). Interestingly, none of the Na<sup>+</sup> salts show fluorescence quenching of the CQDs, further confirming that it is Cu<sup>2+</sup> that solely cause the fluorescence quenching of the CQDs. (Fig. 5d).

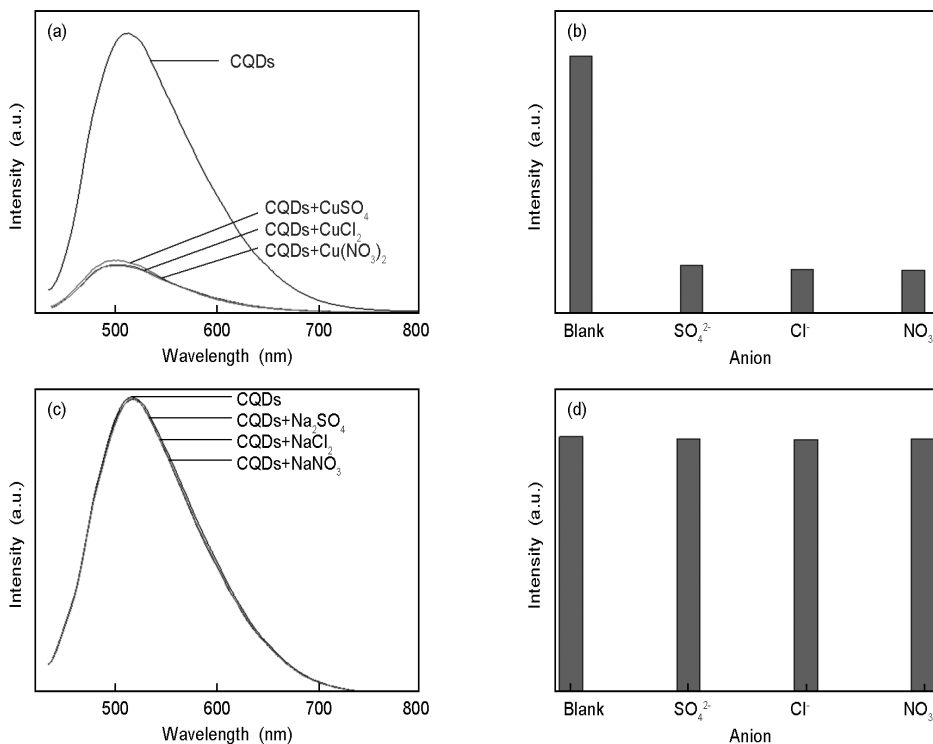


Fig. 5 (a, b) Fluorescent intensity responses of CQDs towards different salt solutions of Cu<sup>2+</sup>(50 μmol/L) and (c, d) Na<sup>+</sup>(50 μmol/L).

The fluorescence intensity of the CQD solution versus scan time at 513 nm of emission wavelength are given in Fig. 6. After a fast titration of Cu<sup>2+</sup>, the fluorescence intensity at 513 nm immediately decreases to the lowest value within 3 s, then reaches a constant value, which indicates a fast and completed reaction between CQDs and Cu<sup>2+</sup>. It is noted that the response time is 3 s, which is the fastest response probe compared to other CQD probes reported in literatures<sup>[18,19,29,30]</sup>. Therefore, the on-line detection and “mix-and-detect” protocol can be realized.

The insets of Fig. 7a show the photographs of the CQD aqueous solution (left) and the CQDs with 50 μmol/L Cu<sup>2+</sup> (right) under UV light. Compared with other CQD probes (blue emission)<sup>[18,19,31]</sup>, petroleum coke-based CQDs prepared here show a long wavelength (yellow fluorescence), which could be easier to be distinguished by naked eyes. After the titration of Cu<sup>2+</sup>, it can be clearly seen that the yellow-visual fluorescent CQDs is effectively quenched by

Cu<sup>2+</sup>. The fluorescence intensity ( $F/F_0$ ,  $F_0$  and  $F$  are the fluorescence intensities before and after the addition of Cu<sup>2+</sup>) gradually decreases by about 93% of its initial value when the concentration of added Cu<sup>2+</sup> increases to 50 μmol/L (Fig. 7b). Particularly, with the addition of Cu<sup>2+</sup>, an obvious blue shift is observed (Fig. 7a). The fluorescence intensity of the CQDs versus Cu<sup>2+</sup> concentration in the range of 0.25-10 μmol/L exhibits a good linearity (inset of Fig. 7b). Under the current experimental conditions, the LOD of Cu<sup>2+</sup> is estimated to be 0.0295 μmol/L based on  $3S_b/k$  (here  $S_b$  is the standard deviation of the corrected blank signals of CQDs and  $k$  is the slope of the calibration curve), which can meet the limit of Cu<sup>2+</sup> in drinking water (20 μmol/L) set by U. S. Environmental Protection Agency<sup>[6]</sup>, and is comparable to or even better than most previous reported nanoparticle-based probes<sup>[19,32-34]</sup>. Recently, modified carbon dots or doped CQDs have been reported with a high LOD<sup>[18,30,35,36]</sup>, which make us believe that the LOD



of as-made CQDs from petroleum coke can be increased in near future in our lab.

The different  $F/F_0$  ratios of the CQD solutions in the absence and presence of various metal ions were also calculated. The  $F/F_0$  ratios of other metal ions are almost 4-5 times as high as that of  $\text{Cu}^{2+}$ . In order to assess the selectivity of the proposed probing method on  $\text{Cu}^{2+}$ , the possible interferences of coexisting cations in  $\text{Cu}^{2+}$  aqueous solution were also tested (Fig. 8). Those employed ions include  $\text{Ba}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sn}^{4+}$ ,  $\text{K}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{As}^{3+}$  and  $\text{Cr}^{6+}$  common in our living environment. Notably,  $\text{Cu}^{2+}$  can substantially quench the fluorescence intensity of the CQDs, and the effect of other metal ions can be neglected. Such results directly illustrate that the CQDs can be developed as a rapid

response fluorescent probe for detection of  $\text{Cu}^{2+}$  with a high sensitivity and selectivity.

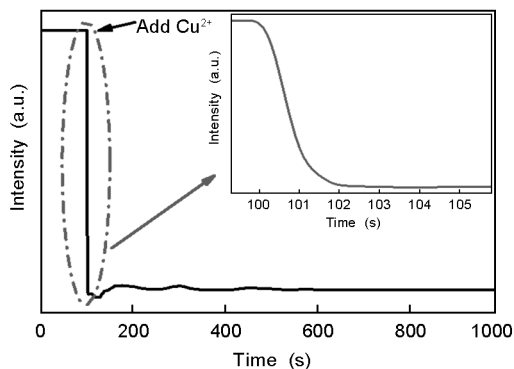


Fig. 6 The fluorescence intensity of CQD solution versus scan time at room temperature (inset: the enlarged drawing of selected area just after the addition of  $\text{Cu}^{2+}$ ) (excitation at 420 nm, emission at 513 nm;  $[\text{Cu}^{2+}] = 25 \mu\text{mol/L}$ ).

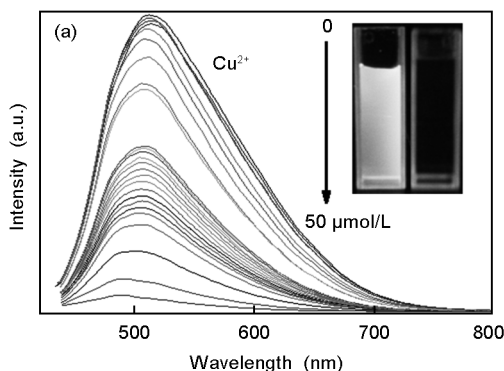


Fig. 7 (a) Fluorescence spectra of CQDs in the presence of  $\text{Cu}^{2+}$  concentrations ranging from 0 to  $50 \mu\text{mol/L}$ . (inset: photographs of CQD aqueous solution (left) and CQDs with  $50 \mu\text{mol/L}$   $\text{Cu}^{2+}$  (right) under UV light). (b) Fluorescence intensity response of CQDs to the concentration of  $\text{Cu}^{2+}$  (inset: fluorescence intensity response of CQDs versus the concentration of  $\text{Cu}^{2+}$  from 0.25 to  $10 \mu\text{mol/L}$ ).

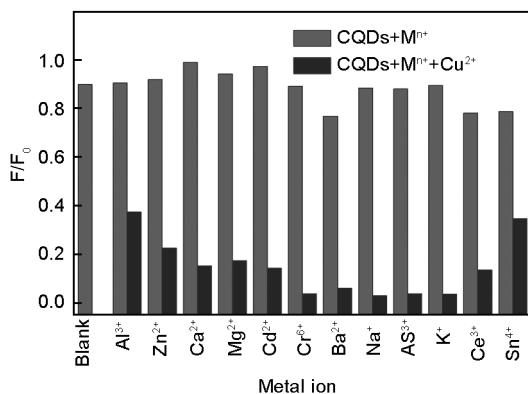
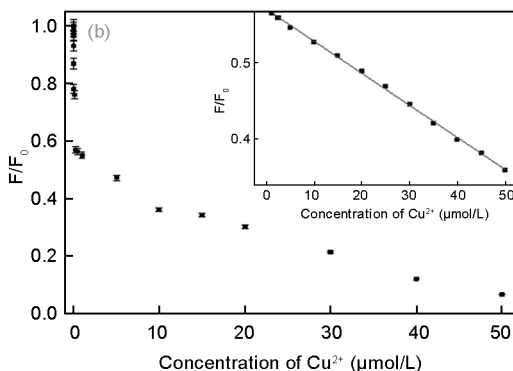


Fig. 8 Selective fluorescence intensity responses of aqueous CQD solution towards  $50 \mu\text{mol/L}$  non-copper metal ions (gray bars), and the mixed solution of  $50 \mu\text{mol/L}$   $\text{Cu}^{2+}$  and other metal ions (red bars) (excitation at 420 nm).

### 3.3 Possible sensing mechanism

The sensing mechanism is not yet completely understood, even there are several suggested mechanisms in literature<sup>[37-39]</sup>, such as inner filter effect,

non-radiative recombination pathways, electron transfer process, ion binding interaction and hole-trap.

Herein, a photoinduced electron transfer (PET) mechanism is proposed to explain the fluorescence quenching of the CQDs caused by  $\text{Cu}^{2+}$ . The photoluminescence excitation (PLE) and fluorescence spectra of the CQDs have been detected in the absence and presence of  $\text{Cu}^{2+}$ .

CQDs with conjugate aromatics and many oxygen-containing groups are considered to be the electron donors. Due to the unfilled d shell,  $\text{Cu}^{2+}$  are regarded as electron acceptors, which have a higher binding affinity and faster chelating kinetics with  $-\text{COO}^-$  on the surface of the CQDs than other transition-metal ions<sup>[35]</sup>. After the addition of  $50 \mu\text{M}$   $\text{Cu}^{2+}$  into CQD aqueous solutions, the strong fluorescence intensity of the CQDs is quickly quenched and the corresponding PLE intensity is simultaneously reduced (Fig. 9a). These phenomena indicate that there is

electron transfer from the CQDs to  $\text{Cu}^{2+}$  at the excited state<sup>[34]</sup>. To further implore the energy transfer and exciton recombination process of the CQDs in the presence and absence of  $\text{Cu}^{2+}$ , the fluorescence decays of the CQDs by a time-correlated single-photon counting (TCSPC) in the absence and presence of  $\text{Cu}^{2+}$  have been measured (Fig. 9b). The fluorescence lifetime of the CQDs (the black line) is 3.86 ns, reflecting a fast exciton recombination process. After the addition of  $\text{Cu}^{2+}$  (the red line), the lifetime of the CQDs decreases to 2.87 ns. This significantly shortened lifetime further confirms that there is an ultrafast electron transfer process in the CQDs- $\text{Cu}^{2+}$  system.

In addition, EDTA is a kind of metal ion chelators, which can prevail over the CQDs, and form coordination complex with  $\text{Cu}^{2+}$ <sup>[40]</sup>.  $\text{Cu}^{2+}$ -quenched CQD aggregates could be dissociated after the introduction of EDTA because  $\text{Cu}^{2+}$  display a higher affini-

ty to the oxygen-donor atoms in EDTA than the carboxylate groups and conjugate aromatics of the CQDs<sup>[41]</sup>. When EDTA (a strong  $\text{Cu}^{2+}$  chelator) was added into the  $\text{Cu}^{2+}$ -quenched CQDs solution, the fluorescence intensity of the CQDs can recover as high as 96.0% (Fig. 10a). Moreover, repetitive experiments on the same CQD solution by added EDTA or  $\text{Cu}^{2+}$  three times were also measured. It is easily seen that the fluorescence intensity of the CQDs can recover to 94.4% in the third cycle, indicating that CQDs are reusable (Fig. 10b).

Fig. 11 illustrates the “off-to-on” mechanism of CQDs- $\text{Cu}^{2+}$ -EDTA. Based on the above detection mechanism and “mix-and-detect” protocol, CQD probe can be used for the detection of  $\text{Cu}^{2+}$  in real water. Meanwhile, the proposed “off-to-on” mechanism of CQDs- $\text{Cu}^{2+}$ -EDTA may aid in the development of serial fluorescent probes for the detection of different metal ions.

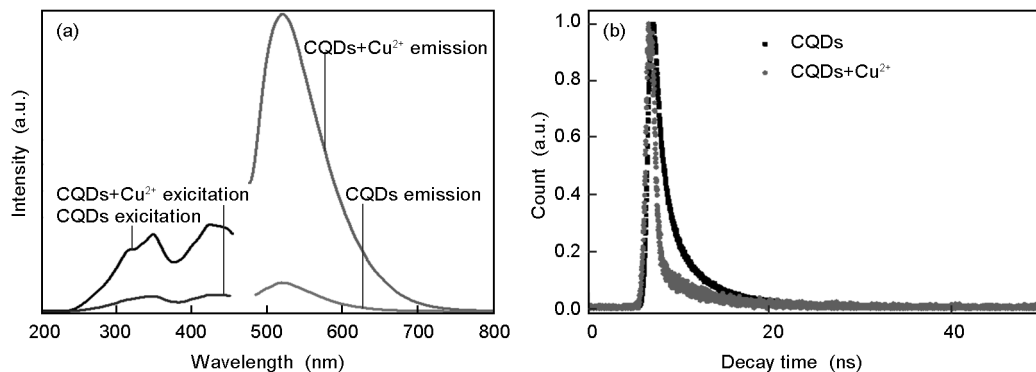


Fig. 9 (a) Comparisons of PLE and fluorescence spectra of CQDs with and without 50  $\mu\text{mol/L}$   $\text{Cu}^{2+}$ , and (b) fluorescence decay curves of CQDs by TCSPC in the absence and presence of  $\text{Cu}^{2+}$ .

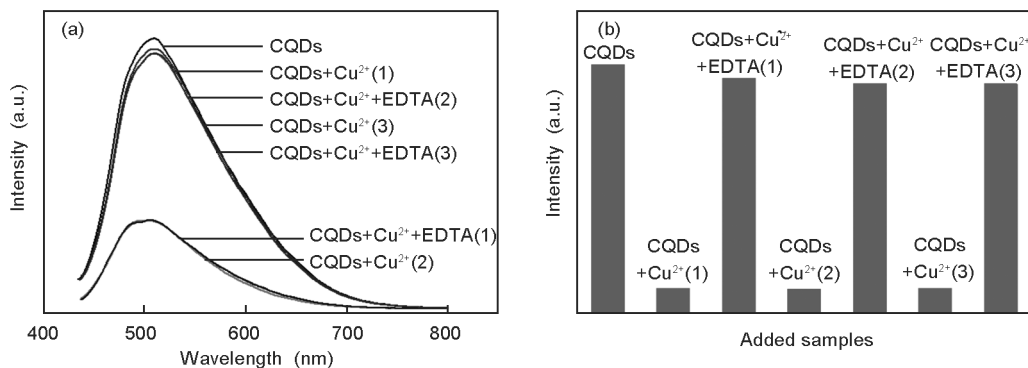


Fig. 10 (a, b) Repetitiveness of the fluorescence intensity responses of aqueous CQD solution ( $[\text{Cu}^{2+}] = [\text{EDTA}] = 25 \mu\text{mol/L}$ , excitation at 420 nm).

### 3.4 The feasibility of CQDs for sensing $\text{Cu}^{2+}$ in real water

Fig. 12 shows the fluorescence response of the CQDs in natural water (Fig. 12a) and tap water (Fig. 12c) with different concentration of  $\text{Cu}^{2+}$ . The

relationship between  $F_0/F-1$  and the concentration of  $\text{Cu}^{2+}$  of natural water (Fig. 12b) and tap water (Fig. 12d) are also given. It can be clearly seen that the fluorescence intensity gradually decreases with the concentration of  $\text{Cu}^{2+}$  both in tap water and natural

water. The calibration curve for determining  $\text{Cu}^{2+}$  in tap water and natural water can be obtained in the range of 0-50 nmol/L. In spite of the interference from numerous minerals and organics/inorganics possibly existed in different water sources, the lowest detection concentration of  $\text{Cu}^{2+}$  via the CQDs can reach

5 nmol/L, which meet the requirement of the  $\text{Cu}^{2+}$  detection in real water. These results make us believe that CQD-based probe can be applied for an accurate analysis of  $\text{Cu}^{2+}$  in a wide range including natural water and tap water.

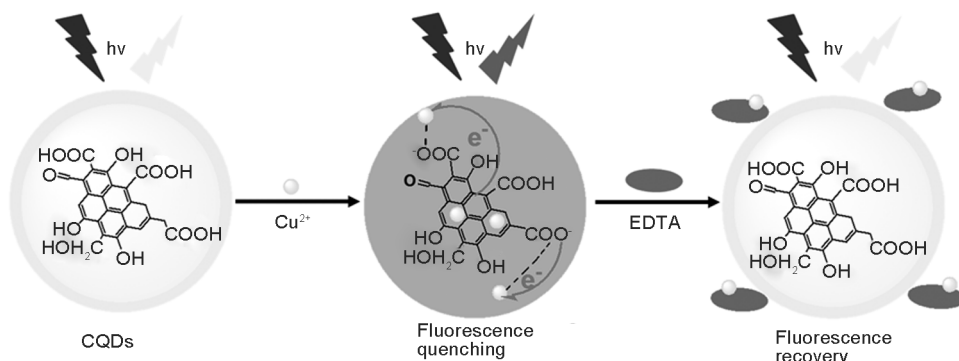


Fig. 11 Mechanism schematic of  $\text{Cu}^{2+}$  detection via the fluorescence response of CQDs.

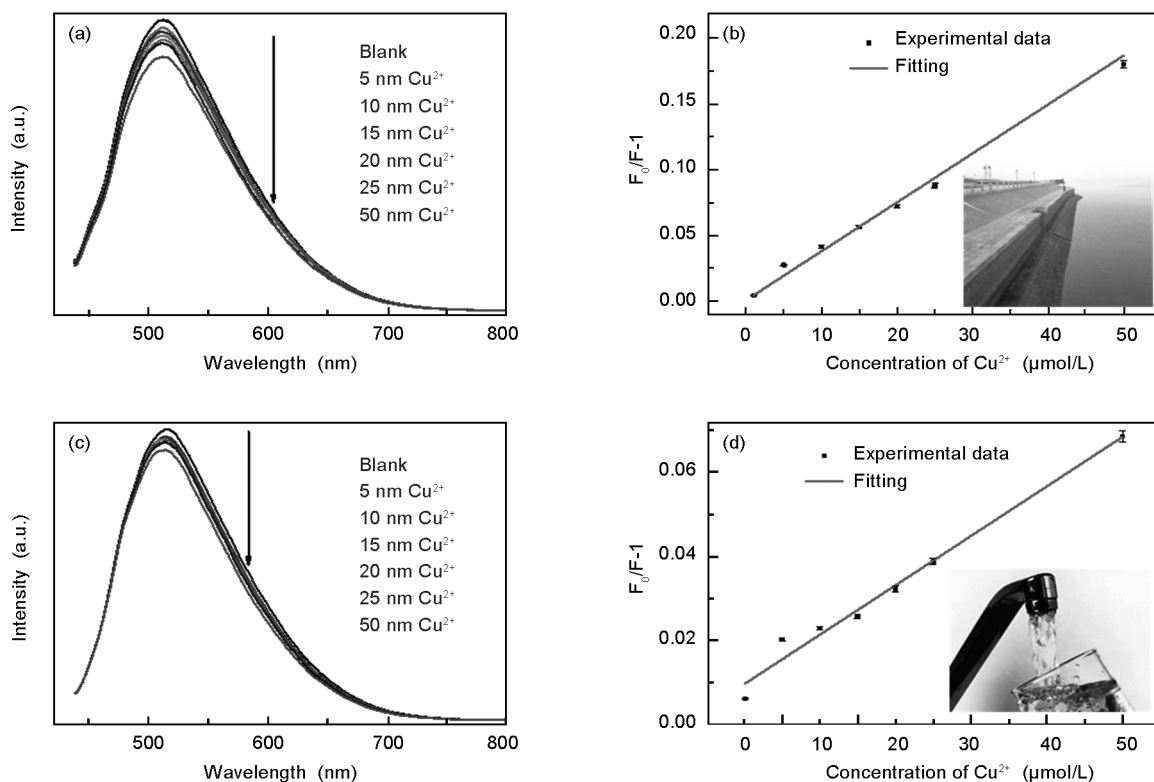


Fig. 12 CQDs to detect  $\text{Cu}^{2+}$  in real water: fluorescence spectra of CQDs in the presence of (a) natural water and (c) tap water with different concentrations of  $\text{Cu}^{2+}$ . Relationship between  $F_0/F-1$  and the concentration of (b)  $\text{Cu}^{2+}$  of natural water, and (d) tap water (excitation at 420 nm).

### 4 Conclusions

In summary, a simple and effective yellow-visual fluorescent CQD probe for  $\text{Cu}^{2+}$  detection was developed. CQDs were prepared from petroleum coke by an ultrasonic-assisted chemical oxidation method

without any subsequent chemical modification. The reusable as well as “mix-and-detect” CQD probe with a unprecedentedly rapid response compared with reported CQDs, is highly selective and hardly interfered by other metal ions. The CQD is fluorescence turn-off probe for a reliable detection of  $\text{Cu}^{2+}$  in water with a



response time as fast as 3 s, evidenced by the analysis of real water samples. The fluorescence intensity of the CQDs versus the concentration of  $\text{Cu}^{2+}$  has a very good linearity from 0.25 to 10  $\mu\text{mol/L}$ , and the detection limit is as low as 0.029 5  $\mu\text{mol/L}$ . Theoretically, the detection mechanism of  $\text{Cu}^{2+}$  via CQD probe is basically originated from a photoinduced electron transfer. The petroleum coke-based CQDs hold a great promise for real-world sensing applications.

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## 书 讯



天津大学教授王成扬撰写的《碳质中间相理论与应用》专著已由科学出版社正式出版,全书 55.6 万字。该书系“十二五”国家重点图书出版规划项目:材料科学技术著作丛书,并得到中国科学院科学出版基金项目的资助。

该书是著者及其研究团队 30 多年来在碳质中间相理论与应用研究方面部分工作的总结。主要包括:稠环芳烃的液相炭化理论、碳质中间相的形成机理、中间相沥青基炭材料的可控制备等内容。该书从稠环芳烃液相炭

化的物理化学角度系统地阐述了均相成核和非均相成核碳质中间相的形成和形态发展规律,提出了碳质中间相形成和形态发展的“颗粒基本单元构筑”理论,完善了沿用已久的传统理论对中间相结构形成过程的解释。

本书可作为从事炭素材料研究、制造与应用工作的科学技术人员的参考书,亦可作为相关专业本科生、研究生的教学参考书。

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