A turn-on fluorescent sensor based on coffee-grounds carbon dots for the detection of sodium cyclamate

Junzhe Chen

Chengdu University of Technology

Haiying Du (✉ duhaiying2014@cdut.edu.cn)

Chengdu University of Technology <https://orcid.org/0000-0001-5074-732X>

Yifeng Xu

Chengdu University of Technology

Boyu Ma

Chengdu University of Technology

Zhihong Zheng

Chengdu University of Technology

Pengchan Li

Chengdu University of Technology

Yuqiu Jiang

Chengdu University of Technology

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Abstract

Carbon quantum dots (CQDs) were synthesized by coffee-grounds as carbon source under hydrothermal carbonization treatment for the first time. The obtained CQDs showed a strong emission at the wavelength of 460 nm, with an optimum excitation of 370 nm, and enrichment of the surface functional groups(-OH, -NH₂). Sodium cyclamate in an aqueous solution and the CQDs could form a core-shell structure by hydrogen-bonding and van der Waals bonding to enhance the fluorescent emission. Cyclohexyl sulfamate forms cyclohexyl sulfamate in an aqueous solution and then undergoes dehydration and condensation with the hydroxyl groups on the carbon quantum dots, and finally sodium cyclamate forms a core-shell structure around the carbon quantum dots.

Cyclohexyl sulfamate form a cyclohexyl sulfamic acid in an aqueous solution followed by dehydration condensation with hydroxyl groups on the carbon quantum dots, cyclamate final core-shell structure is formed in the peripheral carbon quantum dot,

1 Introduction

Sodium cyclamate is commonly used as a food additive in the production of cakes, preserved fruits, beverages and other food products because of its high sweetness (sodium cyclamate is 30–80 times sweeter than sucrose), low calories and low price^[1–3]. In GB 2760 – 2014, the national food safety standard for the use of food additives in China clearly stipulated the dosage (0.65-8.0g/kg) of sodium cyclamate in Fig. 1^[4].

Figure 1 Maximum usage of cyclamate in various foods specified in the Fourth National

The scientific committee for food of the European Union stipulated that human acceptable daily intake value of sodium cyclamate was 7mg/(kg bw)^[5]. The use of excessive range and limit of sodium cyclamate can damage the microfilaments and microtubules of osteoblasts, inhibit bone cells activity, the expression of bone morphogenetic protein-2^[6], and even damage to the structure of DNA^[2].

Various techniques including gas chromatography^[1, 7], liquid chromatography^[8], liquid chromatography-mass spectrometry^[9] and so on^[10–12] have been established for the detection of sodium cyclamate. However, new methods with low detection cost, high sensitivity, and short response time are always being established.

Carbon quantum dots (CQDs) are a new kind of nanomaterials, which is to use natural resources or waste materials (papaya, watermelon, tomato, aloe vera, peach and et al.) as carbon sources in order to reduce the environmental pollution^[13–18]. Coffee is a beverage made from roasted and ground coffee beans. As one of the three largest beverages in the world, coffee is consumed around 9 million tons globally each year^[19]. During the production or use of coffee, a lot of coffee-grounds are often produced^[20]. Coffee-

grounds are rich in carbon sources and nitrogen sources, so it can be used as a high-quality carbon source for the production of CQDs^[21]. Up to now, CQDs prepared from the coffee-grounds for the sodium cyclamate detection has been scarcely reported.

In this work, coffee-grounds as carbon source to synthesize CQDs by one-step hydrothermal method could detect sodium cyclamate in food with high efficiency and environment friendly. In the concentration range of 2.8 ~ 56 $\mu\text{mol/L}$, sodium cyclamate was linear with the CQDs of coffee-grounds, and the detection limit was 3.16 $\mu\text{mol/L}$.

2 Experimental

2.1 Chemicals and Materials

Coffee-grounds were obtained from Shanghai, China. Sodium cyclamate, Sucrose, Sorbic acid, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, CuSO_4 and other interfering metals were obtained from Aladdin Reagent Company. All chemicals were at least of analytical grade and used without further purification. Ultrapure water was supplied by a Millipore System throughout the whole experiments.

2.2 Instrumentation

The fluorescence spectra of CQDs were recorded using a fluorescence spectrophotometer(F-4600). X-ray powder diffraction (XRD) patterns of the CQDs were recorded with a D/MAX-IIIC (Japan) operating with Cu K α radiation with a scanning angle (2θ) range from 5° to 80° . The microstructures of the samples were observed by scanning electron microscopy (SEM) (Inspect F50), transmission electron microscopy (TEM) (HT7700). FT-IR was carried out with a Germany Bruker Company TENSOR 27 by means of KBr pellet with the wavelength range of $4000 \sim 400 \text{ cm}^{-1}$.

2.3 Synthesis of CQDs

The hydrothermal treatment of coffee-grounds was used to prepare CQDs in Fig. 2. Firstly, coffee-grounds were washed with the mixture of ultrapure water and ethanol, and dried at 80°C for 12h. Then, about the weight (0.25g, 0.125g, 0.0625g) of the coffee-grounds powder was dispersed in 40mL ultrapure water. After ultrasonication for 30min, the dispersed solution was transferred into a steel kettle and reacted at the constant temperature (120°C , 160°C , 200°C) for a fixed time (6h, 10h, 14h). The final brown hydrothermal products were centrifuged at 6000 rpm for 5 min to wipe out the large particles. Finally, the CQDs solution was purified in a 500 Da dialysis bag in ultrapure water, and then the remaining solution was put into the oven to obtain solid powder CQDs.

2.3.1 Effects of the reaction concentration

The effect of coffee-grounds concentration was investigated. As displayed in Fig. 3a, the fluorescence intensity presented the best with 0.125g coffee-grounds in 40mL ultrapure water.

2.3.2 Effects of the reaction time

The effect of the reaction time was investigated. As displayed in Fig. 3b, the fluorescence intensity presented the best in 10 h.

2.3.3 Effects of the reaction temperature

The effect of reaction temperature on the fluorescence intensity of the system also was studied. As depicted in Fig. 3c, the intensity of this system reached a maximum and was stable at 120 °C.

All in all, the best fluorescence properties of CQDs synthesized from coffee-grounds were obtained under optimal conditions(0.125g, 120°C and 10h).

2.4 Fluorescence sensing of sodium cyclamate

0.0561g of sodium cyclamate was dissolved in 100mL ultrapure water as standard reserve solution. The concentration gradient of sodium cyclamate was set at 0, 2.8, 9.4, 11.8, 28, 56 and 112 μ mol/L. 1mL of the as-prepared CQDs solution was added in the corresponding pH buffer solution (pH = 2.18, 3.25, 4.23, 5.39, 6.08, 7.01, 7.61, 8.53, 9.45,10.94). The final fluorescence spectra of the tested samples were recorded under the excitation of 370 nm.

3 Results And Discussion

3.1 Structure analysis and characterization

3.1.1 XRD and FT-IR

Figure 4 XRD (a) and FT-IR (b) of the CQDs.

The structures of the obtained CQDs are detected by the XRD and FT-IR. As shown in Fig. 4a, the primary XRD peaks of the obtained CQDs showed a broad diffraction peak at 23.5°, which was associated with the diffraction of the (002) crystal plane, as a graphite structure.

The surface groups of CQDs were measured via FT-IR spectroscopy in Fig. 4b. It can be confirmed that a broad peak at about 3310 cm^{-1} resulted from the vibrations of O–H and N–H, and abundant hydroxyl and amino groups are integrated on the surface of CQDs, promoting water solubility of CQDs. The peak at 2941 cm^{-1} was associated with the stretching vibrations of $-\text{CH}_3$ and $-\text{CH}_2$. A characteristic peak at about 1670 cm^{-1} belonged to the typical vibration of the C = O group. Other two peaks were observed at around 1395 and 1365 cm^{-1} , which resulted from the characteristic vibrations of C–N and C–O–C, respectively.

3.1.2 TEM

Figure 5 TEM image (a), corresponding size-distribution (b) of the CQDs

The morphology of the as-prepared CQDs was characterized via TEM. As seen in Fig. 5a, CQDs exhibited a spherical structure and a well-dispersed state. The size-distribution revealed that the size of CDs ranged from 1.9 to 5.9 nm with the average diameter of about 4.0 nm (Fig. 5b).

3.2 The spectral properties of CQDs

The spectral properties of CQDs are shown in Fig. 6a. The absorption band observed at 320nm was attributed to the $\pi-\pi^*$ transition of the C = C bond. The increase of excitation wavelength from 340–400nm, emission peaks are red-shift from 440–470nm. When the excitation of CQDs is at 370nm, CQDs exhibited the maximum fluorescence emission intensity at 460nm in Fig. 6b.

3.3 Fluorescent response toward sodium cyclamate

Figure 7 Fluorescence emission spectra of CQDs in the presence of sodium cyclamate of different concentrations, which are 2.8, 9.4, 11.8, 28, 56 and 112 μ mol/L from bottom to top, respectively (λ_{ex} = 370nm)

Under optimum conditions, a calibration curve was drawn by conducting a series of similar experiments at various concentrations of sodium cyclamate and the results were depicted in Fig. 7. Calibration curve was linear in the range of 2.8 ~ 112 μ mol/L with the correlation coefficient of 0.992. Fluorescence sensing between CQDs of coffee-grounds and sodium cyclamate belongs to the “turn on” type. This synergistic system may be due to the formation of cyclohexyl aminosulfonic acid from cyclohexyl aminosulfonate in aqueous solution, and then sodium cyclamate and the CQDs forms a core-shell structure by hydrogen-bonding and van der waals bonding, which stabilizes or even strengthens the morphology of the surface groups of CQDs in the original solution and reduces unnecessary energy transfer in Fig. 8.

3.4 Effect of pH

In the 100mL mixed solution(phosphoric acid, acetic acid, boric acid, concentration of 0.04mol/L), the corresponding pH buffer solution was obtained by adding 0.2mol/L NaOH. Ten buffer solution values of 2.18, 3.25, 4.23, 5.39, 6.08, 7.01, 7.61, 8.53, 9.45 and 10.94 were set up, and the fluorescence intensity of CQDs with and without sodium cyclamate was measured at each fixed value.

3.5 Fluorescence emission studies with analyte

From Fig. 10, it can be seen that the fluorescence sensing between the CQDs of coffee-grounds and sodium cyclamate belongs to “turn on” type, and the CQDs of coffee-grounds and copper ions is “turn off” type. However, there is no fluorescence sensing response for other metal ions, indicating that the CQDs of coffee-grounds is high selective for the detection of sodium cyclamate.

3.6 Calculation of Detection Limit

Firstly, fluorescence intensity of 10 times CQDs solution and the first addition of sodium cyclamate solution were measured respectively. The average fluorescence intensity of F_0 was calculated and the data were brought into formula (1) to get the standard deviation value S_0 . The difference of fluorescence intensity was obtained according to $\Delta F = F - F_0$. At the same time, the sensitivity S was obtained by introducing formula (2), in which ΔC is the concentration change of enhancer in the whole solution system after adding sodium cyclamate. Finally, the detection limit(DL = 3.16 $\mu\text{mol/L}$) was obtained by formula (3). The latest National Food Safety Standard for the determination of sodium cyclamate (GB 5009.97–2016) is 0.010g/kg. As the concentration of dilute solution is approximately regarded as the concentration of aqueous solution 1 kg/L while the DL of the national standard is 49.7 $\mu\text{mol/L}$ after conversion. The DL of our method is far lower than that of the national standard method.

Table 1 Fluorescence intensity of adding 10 times CQDs solution and cyclamate solution										
□□	1	2	3	4	5	6	7	8	9	10
F_0	4528	4517	4535	4494	4505	4498	4503	4499	4591	4556
F	5304									

$$S_b = \sqrt{\frac{\sum_i^n (F_i - \bar{F}_0)^2}{n - 1}} \tag{1}$$

$$S = \frac{\Delta F}{\Delta C} \tag{2}$$

$$DL = \frac{3S_b}{S} \tag{3}$$

4 Conclusions

A new type of CQDs using coffee-grounds as carbon source was synthesized by one-step hydrothermal method. The obtained CQDs were used to detect the sodium cyclamate with highly sensitive and selective. Under the optimum conditions, calibration curve was linear in the range of 2.8 ~ 112mmol/L with the correlation coefficient of 0.992, the DL of sodium cyclamate was 3.16 $\mu\text{mol/L}$. The CQDs of coffee-grounds can be used for the rapid and selective detection of sodium cyclamate, and provide a reference for food safety supervision and detection.

Declarations

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Figures

Figure 1

Maximum usage of cyclamate in various foods specified in the Fourth National

Figure 2

Schematic illustration for the preparation process of CQDs

Figure 3

Fluorescence spectra of the optimum conditions ((a) concentration, (b) time, (c) temperature)) of the reaction

Figure 4

XRD (a) and FT-IR (b) of the CQDs.

Figure 5

TEM image (a), corresponding size-distribution (b) of the CQDs

Figure 6

UV-Vis absorption spectra and fluorescence spectra of the CQDs(a), emission spectra of the CQDs at different excitation wavelengths(b)

Figure 7

Fluorescence emission spectra of CQDs in the presence of sodium cyclamate of different concentrations, which are 2.8, 9.4, 11.8, 28, 56 and 112 μmol/L from bottom to top, respectively ($\lambda_{\text{exc}}=370\text{nm}$)

Figure 8

The mechanism of the turn-on fluorescent sensor

Figure 9

Fluorescence responses of CQDs in the presence 5.6 μmol/L sodium cyclamate at different pH values

Figure 10

Sensing results of sodium cyclamate and commonly found interferents, including sorbic acid, KCl, MgSO₄, FeCl₃, CuSO₄, CaCl₂ and surose to the fluorescence emission of the CQDs.

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