Facile Synthesis of Tomato-Based Carbon Nanodots and Its Utilization in Sensitive Detection of Tartrazine

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Abstract

Carbon nanodots (CDs) with superior fluorescence performance were obtained by hydrothermal method using tomatoes as raw materials. When the ultraviolet absorption band of tartrazine and the fluorescence spectrum of CDs have complementary overlaps, the fluorescent internal filter effect (IFE) occurred. Furthermore, the degree of quenching of fluorescence intensity of CDs has an excellent linear correlation with tartrazine concentration. And based on this principle, a method for detecting tartrazine was established. As the decrease of fluorescence intensity, tartrazine can be measured in the linear range of 0.1 \( \mu \text{M} \) ~ 40 \( \mu \text{M} \). The detection limit is 39 nM, and the recovery rate is 90.7%~114.5%. The established protocol was also effectively employed to assay tartrazine in beverage samples, indicating that it has great potential for food color analysis.

1 Introduction

Tartrazine is a water-soluble azo food pigment with the advantages of stability, brightly colored, strong coloring power, cheap cost, and so on, but azo pigments in the body can be reduced to aromatic amines, may cause headaches, asthma, and other diseases.[1] Tartrazine also has neurotoxicity, genotoxicity and carcinogenicity, and other toxicity.[2] Studies have shown that tartrazine may affect children's intellectual development. Due to safety considerations, many developed countries have banned the addition of tartrazine to foods. However, tartrazine is still widely added to foods, so it is essential to develop a reliable detection strategy for tartrazine sensing. At present, there are many ways of sensing tartrazine, such as capillary electrophoresis,[3] thin-layer chromatography (TLC) method,[4] spectrophotometry,[5] high-performance liquid chromatography,[6, 7] electrochemical strategy,[8–10] etc. Although these methods have been widely applied in pigment detection, there are still some problems such as low sensitivity, complex sample processing, and high application cost. Compared with the above-mentioned methods, the fluorescence analysis method has excellent advantages in detection due to its simple preparation and high sensitivity.

Carbon dots (CDs), one of the most valuable nanomaterials, are mainly composed of a carbon core and heteroatoms in organic functional groups.[11] CDs have many advantages, such as good biocompatibility, good aqueous solubility, and environmental friendliness. Because of the unique photochemical properties and environmentally friendly characteristics of CDs, they have been widely used in pollutant monitoring,[12, 13] bioimaging,[14, 15] photocatalysis,[16, 17] anti-counterfeiting marks, [18, 19] and other fields. From the emergence of organic matter to biological evolution, it can be proved that elemental carbon is the fundamental component of life, and carbon-based materials have always occupied important position in the area of chemical study. Since the discovery of carbon nanoparticles in the work of Xu et al in 2004, they have attracted more and more attention.[20] At present, there are many methods to synthesize CDs, such as electrochemical synthesis, chemical oxidation, microwave, hydrothermal, combustion and so on. Among them, the hydrothermal method is simple, the reaction conditions are easy to control, green and environmentally friendly, which is one of the most popular methods. Currently, natural substances such as silk, pepper and petals were used as carbon sources to
synthesize carbon dots. These methods are favored because the raw materials are cheap and readily available. Inspired by these works, it is still necessary to find new raw materials to synthesize a different kind of carbon nanoparticles.

In this study, we developed a facile and inexpensive hydrothermal strategy for the synthesis of carbon nanodots used tomatoes as new raw materials. The synthesized carbon dots shown superior salt resistance and optical stability. On the basic of inner filter effect (IFE) between CDs and tartrazine, a sensitive and selective detection method for tartrazine was proposed. There was a linear response between the fluorescence quenching of CDs and tartrazine concentrations ranging from 0.1 µM to 40 µM. This developed monitoring method offered a low detection limit of 39 nM. This strategy was also utilized for sensing tartrazine in real beverages with satisfactory results.

2 Experiment

2.1 Materials

Orange juice and cola beverages were procured from a local supermarket. Rhodamine B, tartrazine, brilliant blue, lactose, fructose, saccharose, glucose, malachite green, citric acid and ascorbic acid were procured from the Aladdin reagent company (Shanghai). Tomatoes were purchased from local supermarket. All other chemicals used were of analytical grade and had not been purified in any way. Ultrapure water was used throughout the experiment.

2.2 Equipment

The F-4700 fluorescence spectrophotometer from Hitachi of Japan was utilized to record fluorescence spectra; UV-vis absorption were obtained from UV-1801 spectrophotometer from Beijing Beifen Ruili Analytical instrument Co., Ltd. was used to measure UV-vis spectrum. Transmission electron microscope (TEM) images were recorded from Tecnai G2 F30 (FEI, USA). The fluorescence lifetime was measured by the FLS 920 spectrometer from Edinburgh Instruments.

2.3 Preparation of carbon nanodots (CDs)

Carbon nanodots were prepared by the hydrothermal technology of tomatoes. 2 g of tomatoes was added to 20 mL of water, and then the mixture was added into a 25 mL autoclave lined with Teflon, and heated at 200°C for 8 h. After the reaction, the autoclave was naturally cooled to room temperature. The resulting solution was centrifuged for 30 min at 10000 rpm, and then the supernatant was filtered through 0.22 µm membrane. Afterwards, the filtrates containing carbon nanoparticles were collected and preserved at 4°C for further application.

2.4 The detection of tartrazine with CDs

The testing procedures for tartrazine were as follows. Firstly, 500 µL of CDs solution was blended into 500 µL of PBS buffer at pH 6.0. Then, 500 µL of varied concentrations of tartrazine solution were spiked into the aforementioned solution. Finally, the resulting solution was reconstituted to 2 mL using ultrapure
water and mixed thoroughly. The fluorescence spectrum was recorded at excitation wavelength of 350 nm, slits width of 5/5 nm, and a voltage of 600 V.

2.5 Assay of tartrazine in real samples

Orange juice and cola drinks were provided by local supermarket. The drinks were well shaken and then diluted to 10 times with water. The dilution was purified through a 0.22 µm filter membrane and the filtered solution was recovered for use. Subsequently, various concentrations of tartrazine standard solutions were injected into the filtered beverage samples. The tartrazine in the beverage samples was tested according to the procedure in 2.4.

3 Results And Discussion

3.1 Characterization of CDs

Transmission electron microscopy (TEM) was employed to explore the morphology of the prepared carbon dots. As presented in Fig. 1, the prepared CDs exhibited good dispersity in aqueous solution with narrow distribution of particle size. The morphology of the CDs was spherical, and the average diameter of the particles was calculated to be 2.61 nm through TEM images analysis. UV-visible and fluorescence spectroscopy were utilized to study optical characteristics of CDs. Fig. 2 presented the UV-Vis absorption curve, which had peak at 325 nm owing to the n-π* transition of C=O bond.[24] It can be observed from Fig. 3 that the maximum excitation and emission wavelengths of prepared CDs were 350 nm and 437 nm, respectively. The prepared CDs were light brown solutions under natural light conditions, and emitted strong blue fluorescence under 312 nm ultraviolet lamp (illustration of Fig. 3). The quantum yield (QY) of prepared CDs in water solution was estimated as 53% taking rhodamine B as parameter. The detailed calculation protocol was depicted in the supporting documentation. In addition, the fluorescence stability of the obtained CDs was studied. The fluorescence emission of CDs did not vary significantly after 120 minutes of excitation at 350 nm (Fig.S1), indicating that the CDs solution has good photostability. Even though the NaCl concentration was up to 3.0 M, the fluorescence intensity of the CDs changed negligibly (Fig.S2), indicating that the prepared CDs have superior salt tolerance. These results revealed that the obtained CDs could be suitable as excellent candidate for optical testing.

3.2 Principle of tartrazine detection

To understand the fluorescence quenching principle of tartrazine on CDs, the UV-Vis absorption of tartrazine and the fluorescence spectrum of CDs were studied. As shown in Fig. 4, there was a large degree of overlap between the UV-Vis absorption spectral curve of tartrazine and the fluorescence emission spectral curve of carbon nanoparticles, which indicated that their interaction could be fluorescence resonance energy transfer (FRET) or inner filter effect (IFE). In order to farther demonstrate the principle of interaction between CDs and tartrazine, the fluorescence lifetime was surveyed. As observed in Fig. 5, the fluorescence lifetimes of CDs and CDs/tartrazine mixtures were 1.26 ns and 1.28...
ns, respectively. The fluorescence lifetime did not change obviously with and without tartrazine, indicating that the quenching mechanism was IFE.

### 3.3 Exploration of tartrazine assay conditions

To investigate the sensitivity and precision of this analytical method, we optimized the parameters of medium pH, use level of CDs and response time. The affection of pH on the quenching efficiency of the analytical platform was shown in Fig. S3(a). The fluorescence quenching rate was defined as \((F_0 - F)/F_0\), \(F\) and \(F_0\) were fluorescence intensity of CDs in the presence and absence of tartrazine, respectively. The fluorescence quenching efficiency increased with the increase of pH firstly, reaching the maximum when the pH = 6, while farther increase of pH resulted in a gradual decrease of quenching efficiency. Therefore, we chosen buffer solution with pH 6 for the experiment. As seen in Fig. S3(b), the affection of the dosage of CDs on the tartrazine assay was studied. As the dosage of CDs increased from 200 µL to 500 µL, the fluorescence quenching efficiency of the analytical platform gradually increased. However, the quenching efficiency gradually decreased when the amount of CDs exceeded 500 µL. Hence, 500 µL of CDs was used as the optimal experimental condition. Fig. S3(c) exhibited the influence of response time on tartrazine analysis. These results showed that when 15 µM of tartrazine was introduced to the carbon dots solution, the fluorescence quenching reached a stable level after 2 minutes. Thus, 2 min was the optimal incubation time for tartrazine assay.

### 3.4 Response of CDs to tartrazine

To measure the variations in the fluorescence quenching rate of the system, various concentrations of tartrazine were injected to the CDs solution under optimal conditions. As revealed in Fig. 6A, the fluorescence intensity of CDs slowly decreased as the increase of tartrazine concentration. As displayed in the illustration of Fig. 6B, the fluorescence quenching rate was linearly related to tartrazine concentrations ranging from 0.1 to 40 µM. The linear relationship equation was \((F_0 - F)/F_0 = 0.013[C] + 0.0319\) (C is the concentration of tartrazine, µM), and the correlation coefficient was 0.9914. The detection limit for tartrazine was 39 nM (S/N = 3). A comparison of our method for the detection of tartrazine with other methods was shown in Table S1, indicating that our method offered comparable or even superior detection limit and linear range. In addition, to prove the specificity of the sensing platform, we tested the fluorescence signal of CDs to 14 substances that may be found in drinks including K⁺, Ca²⁺, Zn²⁺, Na⁺, HCO₃⁻, Cl⁻, glucose, ascorbic acid, citric acid, lactose, fructose, saccharose, malachite green, and bright blue. According to Fig. 7, the fluorescence intensity of the analytical platform was significantly quenched by tartrazine, whereas fluorescence changes caused by coexisting substances were almost negligible, even if their concentrations were 10 times that of tartrazine. The outcomes confirmed that the developed test approach has high specificity for the detection of tartrazine.

### 3.5 Application in real samples

Orange juice and cola drinks were chosen as actual samples to assess the availability of the developed strategy. Tartrazine standard solutions of various concentrations were spiked into the beverage samples and the established approach was used for the measurement of tartrazine according to the procedure in
2.5. As mentioned in Table 1, the outcomes validated that the recoveries of tartrazine for orange juice samples were 96.8~ 97.3% and 90.7 ~ 114.5% for cola samples. The relative standard deviation (RSD) of the tartrazine assay ranged from 1.32–4.83%. All the experimental data confirmed the accuracy and practicability of the developed method for tartrazine sensing in drinks.

4 Conclusion

In this paper, we proposed a facile, green one-step hydrothermal technique to manufacture CDs utilizing tomatoes as a natural source. The synthesized CDs displayed excellent optical properties and high stability. On the basis of the IFE between tartrazine and CDs, a sensitive and selective analytical technique for tartrazine assay was proposed, which offered detection limit as low as 39 nM. Excitedly, this approach has also been utilized for tartrazine sensing in real beverage samples with satisfactory results. In the future, this technique might be used for the monitoring of colorants in the field of food safety.

Declarations

Author Declarations

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Availability of data and material

All data in this research are presented in this paper and its supporting information.

Code availability

Not applicable

Conflicts of interest

There are no conflicts of interest to declare.

Ethics Approval

Ethical approval was not applicable in this study.
Consent to participate

The authors all agreed to participate in this study.

Consent for publication

The authors all approved their participation in the publication of this study.

Authors’ contributions

Haijian Liu conceptualized and wrote this manuscript. Zhenxiang Li, Wei Zhang, and Ying Liu carried out relevant experiments. Rongkai Pan and Guofu Huang implemented the analysis and discussion of the experimental data.

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Tables

Table 1 Determination results of tartrazine in actual drink samples

| Samples        | Detected (µM) | Spiked (µM) | Found (µM) | Recovery (%) | RSD (%) |
|----------------|---------------|-------------|------------|--------------|---------|
| Cola           | 1.50          | 1.36        | 90.7       | 4.83         |
|                | ND            |             |            |              |         |
| Orange juice   | 10.00         | 11.45       | 114.5      | 2.53         |
|                | 1.50          | 4.98        | 97.3       | 3.62         |
|                | 3.62          |             |            |              |         |
|                | 10.00         | 13.18       | 96.8       | 1.32         |

ND: Not detectable

Figures
Figure 1

TEM pictures and histograms of particle size distribution of CDs
Figure 2

UV-Vis absorption curve of the CDs
Figure 3

Fluorescence excitation (black line) and emission (red line) spectra of the CDs. The inset shows pictures of CDs solution under natural light (a) and ultraviolet light (b).
**Figure 4**

Overlapping between fluorescence emission spectra of CDs (black line) and the UV-vis absorption curve of tartrazine (red line).
Figure 5

The fluorescence lifetime of CDs (black line), CDs and tartrazine (red line).

Figure 6

Fluorescence emission of the CDs after the addition of various concentrations of tartrazine (A) and linear response between fluorescence quenching rate and tartrazine concentrations (B).
Figure 7

(A) Fluorescence spectra and (B) the corresponding fluorescence quenching rate of the CDs in the presence of tartrazine (15 μM) and coexisting substances (150 μM).

Supplementary Files

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- Scheme1.png
- Supportinginformation.docx