Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 167 (2016) 106–110

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Determination of sunset yellow in soft drinks based on fluorescence quenching of carbon dots

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ARTICLE INFO

Article history:
Received 14 March 2016
Received in revised form 23 May 2016
Accepted 24 May 2016
Available online 25 May 2016

Keywords:
Carbon dots
Sunset yellow
Fluorescence quenching

ABSTRACT

Fluorescent carbon dots was prepared by heating *N*-(2-hydroxyethyl)ethylene diaminetriacetic acid in air. The carbon dots were not only highly soluble in water but also uniform in size, and possessed strong blue fluorescence and excitation wavelength-dependent emission properties with the maximum excitation and emission wavelength at 366 nm and 423 nm, respectively. Food colorant sunset yellow whose excitation and emission wavelength at 303 nm and 430 nm could selectively quench the fluorescence of carbon dots, efficient fluorescent resonance energy transfer between the carbon dots and sunset yellow is achieved. This was exploited to design a method for the determination of sunset yellow in the concentration range from 0.3 to 8.0 μmol L^{-1}, with a limit of detection (3 σ/k) of 79.6 nmol L^{-1}. Furthermore the fluorimetric detection method was established and validated for sunset yellow in soft drinks samples with satisfactory results.

1. Introduction

Food safety problems have attracted worldwide attention and the testing and analysis of various pollutants in foodstuff becomes one of the hot issues of food chemistry [1]. Food colorants, as a special kind of food additives, are usually used to improve appearance, taste, flavour, and color of foodstuffs in order to make them more attractive and appetizing [2]. Sunset yellow (Scheme. 1) is a synthetic azo dye, which is allowed to be added at a maximum limit of 0.1 g/kg in soft drinks (GB2760-2011) in China primarily used in common food products, such as desserts and sweets, beverages, snacks, condiments and spreads, etc. The presence and content of the dyes must be controlled because of their potential harmfulness to human beings. Presently, various methods such as fluorescence emission spectrometry [3], chromatography [4], high performance liquid chromatography-mass spectrometry (HPLC–MS) [5], capillary electrophoresis [6], have been reported for the determination of sunset yellow. However, electrochemical methods [7,8], such as carbon paste electrode (CPE) [9–12] have also been proposed for determination of sunset yellow owing to their advantages of high sensitivity and simplicity. However, it is importantly to control the existence and content of this dye because when ingest large amount of sunset yellow it may cause diarrhea, allergies and puts a dangerous amount of pressure on liver. Therefore, the detection of sunset yellow in foods is of great significance.

Since first discovered in 2004 [13], carbon dots have attracted enormous interest due to their low cost, versatile surface chemistry, stable photoluminescent properties, and good biocompatibility. Fluorescent carbon dots have been extensively applied in analytical assays of distinct analytes, such as metal ions [14–16], non-metallic ions [17–19], pharmaceuticals [20–22], explosives [23,24], food additives [25–27], biomacromolecules [28–30], etc. Furthermore, the analytical methods using carbon dots as donors baded on the fluorescence resonance energy transfer have attracted much attention [31,32].

In this paper, non-fluorescent chelating ligand *N*-(2-hydroxyethyl) ethylenediaminetriacetic acid (HEDTA) is selected as carbon source for the synthesis of fluorescent carbon dots. The fluorescent carbon dots are prepared in air (Scheme. 2). Efficient fluorescent resonance energy transfer between the carbon dots and food colorant sunset yellow is achieved, with which determination of sunset yellow in soft drinks can be accomplished.

2. Experimental

2.1. Preparation of CDs

In detail, 0.5 g HEDTA is weighed and calcined in a quartz crucible. Then the quartz crucible is placed into an electric heating mantle and heated with a working voltage of 220 V for about 6 min until the color of the solids changed from white to reddish-brown. After the reaction was completed, the quartz crucible was cooled down naturally and 10.0 mL ultrapure water was injected into the quartz crucible. The

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http://dx.doi.org/10.1016/j.saa.2016.05.038
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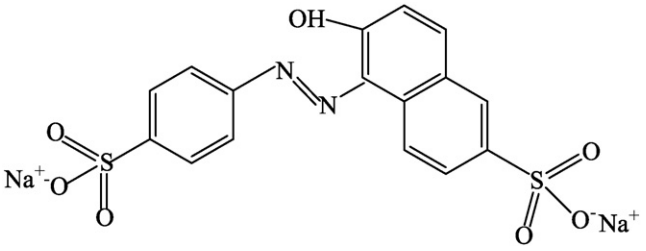


Scheme 1. The structure of sunset yellow.

aqueous solution was centrifuged at 1500 rpm for 15 min to dislodge the non-fluorescent deposits. The upper carbon dots aqueous solution was obtained for use. The reddish-brown solution is further purified through a 0.22 μm membrane filter. The obtained solution was transferred into a 100 mL volumetric flask. Diluted to the mark with ultrapure water and stored in 4 °C for further analysis. The fluorescent quantum yield is measured using a reference method [32], and the value is 4.68%.

2.2. Instruments and materials

The fluorescence spectrum is measured with an F-2500 fluorescence spectrophotometer (Hitachi, Tokyo, Japan) using a 1 cm path length. Absorption spectra are determined on a UV-2450 spectrophotometer (Shimadzu, Japan). A high resolution transmission electron microscope (Tecnai G2 F20 S-TWIN, FEI Company, USA) is used to characterize the morphology of the as-prepared CDs, which is operated at an accelerating voltage of 200 kV. Functional groups analyses is made on a FTIR-8400S Fourier transform infrared spectrometer (Tyoto, Japan). A pHS–3D pH meter (Shanghai Scientific Instruments Company, China) is used to measure the pH values.

All of the regents are all of analytical grade and purchased from Aladdin Reagent (Shanghai, Co., Ltd., China). Ultrapure water was supplied by a Millipore System (18.2 MΩ cm) throughout the whole experiments.

2.3. Typical procedure

350 μL of CDs, 500 μL pH 6.0 Britton-Robinson solution, and the predetermined volume of sunset yellow (SY) solution were transferred to a standard 5 mL calibrated flask in sequence. Then the mixture solution was diluted with ultrapure water to the mark and thoroughly mixed. After 10 min, the fluorescence spectra were recorded against the reagent blank ($\lambda_{ex} = 366$ nm). The fluorescent decrements (ΔF) can be calculated as: $\Delta F = F - F_0$, where F represent for the fluorescence of ion-association complex and F_0 for reagent blank.

2.4. Analysis of real samples

The drink samples were purchased from a local supermarket and used directly without any treatment. 350 μL of CDs, 500 μL of pH 6.0 BR buffer solution, and 0.5 mL of sunset yellow solution were transferred to a standard 5 mL calibrated flask in sequence, and diluted to the mark with ultrapure water. After 10 min, the fluorescence was recorded.

3. Results and discussion

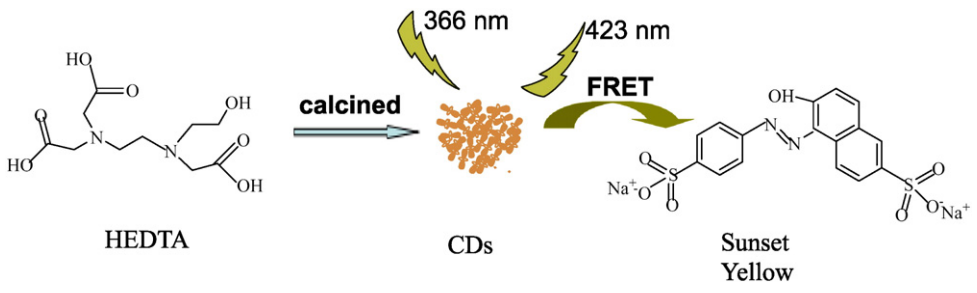
3.1. Characterizations and photoluminescence properties of CDs

Unlike some other preparing approaches, the carbon dots were synthesized by heating HEDTA in air, which is much simpler than some of the reference methods, which typically involved long time pyrolysis using a reaction kettle. It's known that HEDTA is a chelating ligand and it emits no fluorescence. Thus, the appearance of fluorescence of the resulting solid is a definite evidence of the formation of carbon dots. The size and morphology of the as-prepared carbon dots were measured by TEM. The result was shown in Fig. 1. It can be seen that the size and shape of the CDs is uniform. The average size is about 5.9 nm.

As expected, the carbon dots possess wavelength-dependent fluorescent emission properties. As shown in Fig. 2A, when the excitation wavelength increases from 320 to 430 nm, the emission wavelength shifted from 410 to 514 nm. Meanwhile, the emission intensity reached a maximum when excited at 360 nm. Fig. 2B represents the absorption, maximum excitation and emission spectra of the obtained CDs. A wide absorption band rather than an obvious absorption peak is observed, which may attribute to the wide size distribution. The emission peak is slightly lower than the excitation one, indicating that energy loss existed when the excited carbon dots dropped to the lowest vibrational energy level. The composition of functional groups and carbon core is tested by Fourier Transform Infrared Spectroscopy. As shown in Fig. 3, the obtained carbon dots own characteristic absorption bands of O-H stretching vibrations at 3400 ± 100 cm^{-1}, C-H stretching vibrations at 2900 ± 100 cm^{-1}, C═C and C═O stretching vibrations at 1650 ± 200 cm^{-1}, C═N stretching vibrations at 1400 ± 50 cm^{-1}, C-O-C/C-O stretching vibrations at 1200 ± 50 cm^{-1} and C-H bending vibrations at 1100 ± 100 cm^{-1} [33].

3.2. Effects of acidity and reaction time on the detection

Britton-Robinson buffer solution was used to test the influence of acidity on the determination. As shown in Fig. 4, the fluorescence of carbon dots decrease slightly when the pH is above 6.0, while the influence of acidity on the fluorescence of carbon dots with sunset yellow is negligible. Thus, 6.0 are selected as the optimal experiment pH. The Effects of reaction time on the detection is also evaluated, and the results are



Scheme 2. The illustration for synthesis of fluorescence carbon dots and its fluorescent resonance energy transfer with sunset yellow.