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Fluorescent carbon dots for glyphosate determination based on fluorescence resonance energy transfer and logic gate operation

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ABSTRACT

Herein, a novel method based on fluorescence resonance energy transfer (FRET) between carbon dots (CDs) and glyphosate (Gly) was designed for Gly detection. CDs were synthesized via a facile and one-step hydrothermal method using citric acid and Tris. The CDs possessed strong blue fluorescence and excitation wavelength-dependent emission behavior with the maximum excitation and emission wavelength at 340 nm and 410 nm, respectively. However, the presence of glyphosate could effectively quench the fluorescence intensity of the CDs through FRET and this phenomenon has been exploited to design an "AND" logic gate for sensitively sensing Gly for the first time. Furthermore, the proposed method has been successfully utilized to detect glyphosate in water samples with satisfactory results. The detection limit for glyphosate was 0.6 μmol L^{-1}(3σ/k), with the linear range of 0.02–2.0 μmol L^{-1}. This is a promising approach for rapid screening of glyphosate in environmental water samples without using any costly instruments.

1. Introduction

Glyphosate (*N*-(phosphonomethyl)glycine) is a broad-spectrum, non-selective, postemergence and systemic organophosphorus herbicide that is used extensively world-wide in various applications for weed and vegetation control [1]. It is used in more than 750 different products for agriculture, forestry, urban, and home applications. Its use has increased sharply with the development of genetically modified glyphosate-resistant crop varieties. Glyphosate has been detected in air during spraying, in water, and in food. However, There is evidence in humans for the carcinogenicity of glyphosate reported by the International Agency for Research on Cancer (IARC), which classified glyphosate as probably carcinogenic to humans [2]. While the EFSA and EU Member States have finalised the re-assessment of glyphosate. In particular, The evaluation considered a large body of evidence, including a number of studies not assessed by the IARC which is one of the reasons for reaching different conclusions. The report concludes that glyphosate is unlikely to pose a carcinogenic hazard to humans and proposes a new safety measure that will tighten the control of glyphosate residues in food [3]. Glyphosate, which shows high herbicidal activity and relatively low toxicity to mammals resulting extensive in agricultural, forestry, and aquatic applications. Although glyphosate presents a lower acute toxicity than other herbicides, recent studies suggest that it is a potential endocrine disruptor [4]. The US Environmental Protection Agency (EPA) has set a maximum contaminant level (MCL) of glyphosate in drinking water at 0.7 μg/mL (4.14 μM) [5]. The maximum residual level (MRL) of glyphosate in most crops is set at 0.1 μg/g by the European Union [6]. In China, the MRL of glyphosate in fruits such as apple was set at 0.5 mg/kg [7].

Therefore, monitoring of glyphosate in crops, fruits, vegetables, and drinking water has become increasingly important. Glyphosate is slightly toxic; recent reports indicate that it is a direct toxic threat to amphibian species [8,9]. Up to now, various analytical methods have been reported such as high performance liquid chromatography (HPLC) [10–12], gas chromatography (GC) [13–15], capillary electrophoresis (CE) [16,17], and mass spectrometry [18]. Although all these methods mentioned above can offer sensitive and accurate detection results, many of them are complicated, time-consuming, or require bulky instrumentation and have to be performed by highly trained technicians. Moreover, they are not cost-effective. Therefore, a simple, sensitive, and cost-effective method was designed for detecting glyphosate, which is based on

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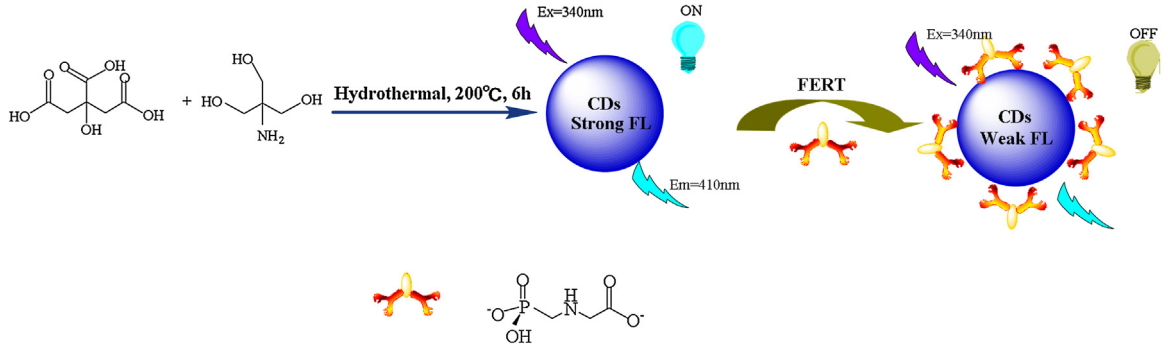

Scheme 1. Illustration of the formation process of CDs and the principle for the response toward.

fluorescence resonance energy transfer (FRET) between CDs and glyphosate (Gly).

Fluorescent carbon dots (CDs) have shown great promise for bioanalysis and biomedical applications in recent years due to their unique optical properties, excellent water dispersibility, chemical and photo stability, the low cost of fabrication, and good biocompatibility [19–24]. Due to these superior properties, CDs have been used extensively to replace the use of other fluorescent nanoparticles for various applications including bioimaging [25,26] photocatalysis [27,28] fluorescence sensors [29,30] optoelectronic devices [31] and drug delivery [32]. Since 2006, Sun et al. found a new fluorescent nanoparticle named as carbon dots, many approaches have been found to prepare CDs [33]. To date, a series of methods for obtaining carbon-based materials have been developed, such as chemical oxidation method [34], ultrasonic method [35], hydrothermal synthesis [30,36,37], solvothermal method [38], microwave method [39] and laser ablation method [33]. However, it is still a problem for progress in controlling the morphology, particle size, and surface chemistry of the resultant products with high quantum yields [33]. Inspired by the above information, we suppose that CDs-Gly might be superior energy donor–acceptor pairs for fabricating FRET-based homogeneous assays. To explore the usefulness of the above concept, herein, we construct a FRET-based sensing platform using CDs-Gly as the energy donor-acceptor pairs. The as-fabricated probe further demonstrates an application for the detection of Gly, Herein, a facile and highly photoluminescent strategy is demonstrated for hydrothermal synthesis of CDs that by using citric acid and Tris as precursor (Scheme 1). This method is highly reproducible and the sources of the CDs have the advantage of being relatively cheap and environmental friendly. The prepared CDs exhibit strong fluorescence within ultrapure water in the presence of Gly, which can bind with the CDs and quench the fluorescence of CDs with high sensitivity.

2. Experimental

2.1. Apparatus

The fluorescence spectrum was recorded with an F-2500 fluorescence spectrophotometer (Hitachi, Tokyo, Japan) using a 1 cm path length. A UV-2450 spectrophotometer (Shimadzu, Japan) was used for acquiring absorption spectra and measure absorbance. A high resolution transmission electron microscope (Tecnai G2 F20 S-TWIN, FEI Company, USA) was used to characterize the morphology of the CDs, which was operated at an accelerating voltage of 200 kV. Fourier transform infrared spectrometer (FTIR-8400S, Kyoto, Japan) was employed to identify functional groups of the CDs. A pH S-3D pH meter (Shanghai Scientific Instruments Company, China) was used to measure the pH values.

2.2. Chemicals

The sodium citrate and Tris(hydroxymethyl)methyl aminomethane (Tris)was purchased from Jinshan Chemical Reagent Factory (Chengdu, China), glyphosate was purchased from Adamas Reagent Co., Ltd. (Shanghai, China), The Britton–Robinson (BR) buffer solutions at different pH values were prepared by mixing the mixed acid (composed of 2.71 mL 85% H_3PO_4, 2.36 mL HAc and 2.47 g H_3BO_3) with 0.2 mol L^{-1} NaOH in different proportions. The buffer solutions were used to control the acidity. All reagents were of analytical reagent grade and were used without further purification, and doubly distilled water was used throughout.

2.3. Synthesis of fluorescence CDs

CDs were prepared by hydrothermal synthesis [40]. First, 0.21 g citric acid and 0.12 g Tris were dissolved in 10 mL ultrapure water thoroughly to form a clear solution. Then, the solution was transferred into a poly(tetrafluoroethylene) (Teflon)-lined autoclave (15 mL) and heated at a specific temperature (200 °C) for 6 h. After the reaction, the reactors were cooled down at room temperature. The deep-brown aqueous dispersion formed was centrifuged at high speed (12,000 rpm/min) for 15 min in order to remove any insoluble particulates. Then the supernatant was dialyzed through a dialysis bag (1000 MWCO) to remove the precursors that did not participate in the reaction and resulting small molecules. At last, the product in the dialysis membrane was dried by a freezing dryer. The drying product was dissolved into a certain amount of solution (1 mg/mL) and stored in the refrigerator for further research.

2.4. Quantum yield measurements

The fluorescence quantum yield (Φ) is defined as the ratio of photons absorbed to photons emitted through fluorescence. In other words, the quantum yield gives the probability of the excited state being deactivated by fluorescence rather than by another, non-radiative mechanism. The quantum yield of CDs was calculated using the following equation [41]:

$$\Phi_u = \Phi_s \cdot \frac{F_u}{F_s} \cdot \frac{A_s}{A_u}$$

where *Fu* and *Fs* referred to the areas under the fluorescence curves of CDs and standard, respectively. *Au* and *As* were absorbance of the sample and standard at the excitation wavelength, respectively. Briefly, quinine sulfate (0.1 M H_2SO_4 as solvent), which QY is about 54.2%, was chosen as a reference standard. The absorbance for the quinine sulfate and the CDs at the 340 nm excitation and the fluorescence spectra of the same solutions at the same excitation were measured respectively. Then the integrated fluorescence intensity