

Microwave-assisted synthesis of xylan-derived carbon quantum dots for tetracycline sensing

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ABSTRACT

A simple and direct microwave-assisted method was used to prepare nitrogen-doped carbon quantum dots (N-CQDs) in a single step using an ammonia solution of xylan as the precursor at a treatment temperature of 200 °C and an input power of 200 W within just 10 min. It was found that the N-CQDs synthesized by such green, economical, and fast routes possess high crystal quality, favorable photoluminescence properties, and high tolerance for salts and metal ions. More interestingly, we found that the as-prepared N-CQDs without any modification exhibited high selectivity and sensitivity towards tetracycline antibiotics owing to an inner-filter effect. At the optimum conditions, a novel sensing platform for sensitive detection of tetracycline in a linear range of 0.05–20 μM with a detection limit of 6.49 nM was established, suggesting a promising application for the quantification of tetracycline in biomedical analysis.

1. Introduction

Carbon quantum dots (CQDs), which belong to the family of carbon nanomaterials, have attracted considerable attention owing to their superior photoluminescence (PL) [1,2], ease of functionalization [3,4], low toxicity, and biocompatibility [5,6]. These unique physical and chemical properties make CQDs excellent candidates for replacing traditional metal-based semiconductor quantum dots for application in photoelectric devices [7,8], photocatalysts [9], cell imaging [6,10], and fluorescent probes [3,11–14]. In the past few years, a number of synthesis methods have been proposed for CQDs, such as arc discharge treatment [15], electrochemical oxidation [16], laser ablation [17], nitric acid refluxing treatment [18], and ultrasonic processing [19]. Despite intensive efforts, most of the developed approaches are unsatisfactory owing to the high cost of the starting materials, complicated procedures, harsh synthesis conditions, and energy consuming equipment. Unlike the approaches mentioned above, hydrothermal treatment [20,21] is a feasible route in which a mass of low-cost organic substances serve as the carbon source for preparing water-soluble CQDs. However, the greatest disadvantage of this approach is that the processing times are, in general, very long. Thus, it is of great interest to develop a rapid and simple method for the synthesis of CQDs.

As we know, microwave irradiation, which allows for intensive, efficient, and homogeneous energy distribution, is more effective than the traditional hydrothermal treatment in accelerating the reaction rate

in an aqueous phase; there are several reports on the successful application of microwave radiation to synthesize CQDs, which illustrate the feasibility and promising potential of this technique. For instance, Liu et al. reported a microwave pyrolysis route for the preparation of CQDs from glycerol in just a few minutes [22]. Chen et al. synthesized heteroatom-doped CQDs from polyols by microwave pyrolysis in a one-step reaction [23]. Xiao et al. and Gong et al. employed microwave-assisted methods to prepare chitosan-derived CQDs [24,25]. However, using a household microwave oven as a reactor to prepare CQDs (as detailed in previous reports) might be highly energy consuming because its input power is usually greater than 700 W and such equipment is limited to afford ordinary pressure condition for reaction system. Thus, a CEM Discover microwave synthesis system, which has superior and accurate control over temperature, input power, and pressure was used in the present investigation.

Thus far, many different kinds of natural biomass substrates, such as proteins [26,27], carbohydrates [6,28], and alpha hydroxy acids [29–32], have been used to synthesize CQDs. This is highly encouraging, but most food or agriculture-based biomasses are unsuitable for the large-scale synthesis of CQDs. Considering that xylan, which is a main component of hemicellulose in plant cells, is very abundant in nature, we used this biomass as a green and low-cost carbon source to synthesize CQDs using a CEM Discover microwave synthesis system with low energy consumption in an enclosed reaction environment. Additionally, an economical ammonia solution was used as the source of

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nitrogen as well as to disperse xylan; doping with N is an effective method to alter the electronic density of CQDs and further enhance their fluorescence properties [6,25,27]. The polymerization, carbonization, surface functionalization, and nitrogen doping processes are completed simultaneously within just a few minutes in the CEM Discover microwave synthesis system, leading to the formation of nitrogen-doped CQDs (N-CQDs) in a single step. More interestingly, such unmodified nanoparticles can be used as fluorescent probes to detect the presence of tetracycline (TC); such probes exhibit intrinsic properties of simplicity, rapidity, low cost, and high sensitivity.

2. Experimental section

2.1. Materials

Xylan (85%) and quinine sulfate (99.0%) were purchased from Aladdin Biochemical Co., Ltd (Shanghai, China). Purified water (Hangzhou, China) was used for all the experiments, NH_4OH (ammonium hydroxide) was procured from Nanjing Chemical Reagent Co., Ltd. Tetracycline hydrochloride and other biological reagents were purchased from Macklin Biochemical Co., Ltd (Shanghai, China). Phosphate buffer solutions (PBS) of different pH values were obtained from Haibiao Technologies Co., Ltd. All other reagents were purchased from Xilong Chemical Co., Ltd (Shanghai, China). Xylan was purified using sodium hydroxide and all other reagents were used as received.

2.2. Synthesis of N-CQDs

Xylan (0.5 g) was dissolved in 10 mL of purified water, followed by the introduction of 100 μL NH_4OH (25–28 wt %). The mixture was then treated in a CEM Discover microwave system (MATTHEWS.NC, USA) at 200 W and 200 °C for 10 min. The synthesis route is schematically illustrated in Fig. 1. When exposed to microwave radiation, the color of the solution changed from pale yellow to brown, indicating the formation of N-CQDs; the supernatant of the obtained reaction mixture was simply filtered using a 0.22 μm syringe filter to remove the precipitate after cooling to ambient temperature. Prior to further characterization, the aqueous solution containing N-CQDs was freeze-dried. Additionally, CQDs without N-doping were synthesized in conditions similar to those described above.

2.3. Characterization

High-resolution transmission electron microscopy (HR-TEM) images were generated using a TECNAI G2 F20 microscope (FEI, USA) operating at an accelerating voltage of 200 kV. The Raman spectra of the synthesized N-CQDs were recorded using a DXR532 Raman spectrometer (Thermo Scientific, USA) at an excitation wavelength of 532 nm using an argon ion laser. The infrared spectra of the synthesized CQDs were recorded on a Vertex 80V FTIR spectrometer (Bruker, Germany). Absorption spectra were obtained using a Lambda 950 UV–Visible spectrophotometer (PerkinElmer, USA). X-ray photoelectron

spectroscopy (XPS) experiments were performed on an AXIS UltraDLD spectrometer (Shimadzu, UK) with an ultrahigh vacuum generator. All fluorescence spectral measurements were performed on an F-7000 spectrophotometer (Hitachi, Japan) with excitation and emission slit set at a 10-nm band pass in 1 cm \times 1 cm quartz. The surface charge of the N-CQDs was measured using a ZEN3600 Zeta Plus (Malvern, United Kingdom) instrument with a He-Ne laser source. Time-resolved fluorescence decays were measured using a FLS 980 spectrometer (EI, UK) and the obtained lifetime decay curves were fitted using a double-exponential function $Y(t)$ (eq (1)) and the average lifetime was calculated according to eq (2).

$$Y(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (1)$$

$$\tau^* = (A_1 \tau_1^2 + A_2 \tau_2^2)/(A_1 \tau_1 + A_2 \tau_2) \quad (2)$$

Here, A_1 and A_2 are the fractional contributions of time-resolved fluorescence decay lifetimes τ_1 and τ_2 , respectively, and τ^* refers to the average lifetime.

2.4. Quantum yield calculation

Quinine sulfate in 0.1 M H_2SO_4 ($\Phi = 54\%$) was chosen as the standard and the quantum yield (QY) of N-CQDs was determined at an excitation wavelength of 360 nm using a comparative method as follows.

$$Q_x = Q_{st} (\text{Grad}_x / \text{Grad}_{st}) (\eta_x^2 / \eta_{st}^2) \quad (3)$$

Here, Q stands for quantum yield. Grad refers to the gradient of the plot of integrated fluorescence peak area against absorbance. The refractive index (η) of the solvent is 1.33. The subscripts x and st correspond to N-CQDs and quinine sulfate, respectively. In particular, the absorbance was adjusted to less than 0.05 to prevent re-absorption by both N-CQD and quinine sulfate solutions.

2.5. Detection of TC and interference experiments

The as-prepared N-CQDs were mixed with PBS buffer (0.10 M, pH = 5.0) in a 10 mL volumetric flask to create solutions of 0.3 mg/mL concentration. Subsequently, different amounts of TC were added to the N-CQD solutions. Unless otherwise stated, all the samples had an N-CQD concentration of 0.3 mg/mL and they were used for fluorescence measurements. Interference experiments were performed to confirm whether the detection system is selective; analysis was carried out based on the principle of fluorescence quenching. Specifically, various of representative metal ions, such as Ag^+ , Al^{3+} , Ba^{2+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Cr^{2+} , Cu^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Zn^{2+} , and Fe^{3+} were added into PBS buffer (0.10 M, pH = 5.0) at a concentration of 50 μM . In addition, several biological agents, including chlorotetracycline, oxytetracycline, L-ascorbic acid, L-histidine, amoxicillin, ibuprofen, glutathione, streptomycin, penicillin G Na, melamine, glucose, lincomycin, and L-cysteine were dissolved in purified water to create solutions of 50 μM . The fluorescence response characteristics of N-CQDs in the

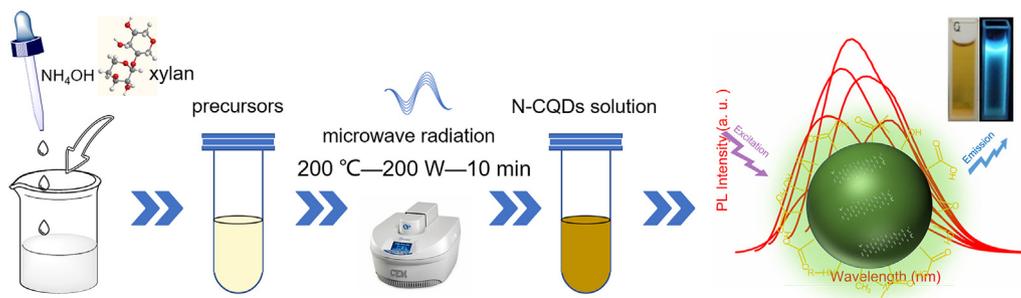


Fig. 1. Synthesis of N-CQDs by microwave treatment.

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