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Carbon dots with tunable emission, controllable size and their application for sensing hypochlorous acid

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ABSTRACT

Optically tunable carbon dots (CDs) were fabricated through a simple one-step microwave-assisted procedure. These carbonaceous nanoparticles exhibited tunable emission under a single wavelength excitation, controllable size without any tedious separation process and stabilities towards photobleaching and high ionic strength. The effects of size difference and surface property on the fluorescence behaviors of CDs were explored through a post-reduction/oxidation method. Experimental results also demonstrated the fluorescence of CDs could be tuned when exposed to H_2O_2/AcOH solutions. Moreover, the use of as-synthesized CDs as a chemical sensor for the quantification of hypochlorous acid (HClO) has been preliminarily tested, showing high sensitivity and selectivity towards HClO over other common ions. The superior optical properties would enable the use of CDs in multiplexed optical coding of biomolecules, light-emitting devices and biological applications.

1. Introduction

The emergence of carbon dots (CDs) has generated enormous excitement due to their great potential in photocatalysis [1], optoelectronic devices [2], bioimaging [3,4], biosensor [5–7] and analytical applications [8–10]. These fluorescent carbonaceous nanoparticles, with a diameter of less than 10 nm, possess fine biocompatibility, high photostability against blinking, excellent upconversion properties and low toxicity, which make them promising alternatives of semiconductor quantum dots (QDs) in chemical and biological analyses. Although the exact origin of luminescence for CDs remains a matter of debate, it is speculated that quantum confinement effect [11], emissive traps [12], aromatic structures [13], and free zig-zag sites [14] contribute to their fluorescence emission.

To date, the synthetic chemistry of CDs has been extensively studied. Various approaches, including discharge [15], laser ablation [12,16,17], electrochemical etching [18,19], strong acid oxidation [20,21], hydrothermal treatment [22,23], pyrolysis of carbon precursors [24], reverse-micelle supported strategy [25] and microwave- [26–28]/ultrasound-assisted [29–31] method, have been explored to prepare CDs. Compared to other synthetic routes, microwave-assisted method would dramatically reduce the fabrication time and greatly improve product yields and purities. The microwave-assisted carbonization of different carbohydrates either in the presence or absence of surface passivating agents has been reported to fabricate CDs [32,33]. CDs prepared by most of these methods mentioned above yield λ_{ex}-dependent emission. Multicolor bioimaging might be obtained by exciting at different wavelengths [27].

Multicolor fluorescent molecular probes which exhibit multi distinguishable emission signals under a single wavelength excitation have shown great promise in vivo optical imaging in biological applications. Strategies towards multiplexed emission include the use of QDs, which provide a controllable emission and wide absorption bands [34], fluorescence resonance energy transfer (FRET)-mediated multicolor fluorescent nanoparticles incorporated two or more energy level-matched fluorescent dyes [35], and post-encoding strategy [36].

Kang's group [11] have obtained CDs with tunable emission by electrochemical cutting of graphite sheets. Hydrothermal treatment of sucrose with different additives (such as HCl, NaOH and hexamine) was also used to prepare CDs with different emission wavelengths [37]. Chen's group [38] have produced multicolor fluorescent CDs via pyrolysis of epoxy-enriched polystyrene photonic crystals. Zhang et al. [39] showed that the emission wavelengths of CDs could be tuned through adjusting N-doping concentration. Zhou et al. [40] have demonstrated a low-temperature solid-phase method with urea and sodium citrate to produce CDs with tunable emission. Intrinsically fluorescent CDs with tunable emission derived from hydrothermal treatment of glucose in the presence of monopotassium phosphate,

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were also reported [22]. Nevertheless, challenges still remain with respect to fabrication of multicolor CDs that could be excited by light of single wavelength and to understanding the driving mechanism in fabricating multicolor CDs.

In this work, we present a rapid one-step microwave-assisted procedure, or combined post oxidation, for the fabrication of water-soluble CDs that allow for fine tuning of the size and emission wavelengths. The resulting CDs could exhibit blue, green and yellow fluorescence under irradiation of an ultraviolet (UV) lamp. The effects of size distributions and surface property on the luminescence behaviors of CDs were explored. Interestingly, the CDs prepared by this method could also have their emission properties altered when exposed to H_2O_2/AcOH solutions. All three types of CDs were examined for the detection of hypochlorous acid (HClO), which expanding the potential applications of these fluorescent nanoparticles.

2. Experimental

2.1. Chemicals

All the reagents were of analytical reagent grade and used without further purification. Chemicals were supplied by Sinopharm Reagent Co. Ltd. (Shanghai, China). The solutions of sodium hypochlorite (NaClO) and hydrogen peroxide (H_2O_2) were prepared daily, and their concentrations were determined using their UV absorbance at 292 nm in basic conditions (pH=12.0, $\varepsilon_{292}=350\ M^{-1}\ cm^{-1}$ for HClO) and 230 nm ($\varepsilon_{230}=81\ M^{-1}\ cm^{-1}$ for H_2O_2) [41].

2.2. Synthesis of multicolor CDs

Sucrose (1.0 g) was added into different concentration of phosphoric acid to yield 20 mL transparent solution. The solution was heated in a 200 W domestic oven for varying time periods. When cooled down to room temperature, the supernatant was retained after centrifugation at 10,000 rpm for 5 min. The resulting CDs solution was neutralized by sodium hydroxide solution and then further purified by dialyzing against de-ionized water using a membrane with 1000 MWCO for 3 days.

2.3. Synthesis of reduced CDs

The reduced CDs were synthesized according to a previously reported method [42]. Sodium borohydride ($NaBH_4$, 0.5 g) was added to 5 mL CDs aqueous solution and stirred gently overnight at room temperature. The product was subjected to dialysis to completely remove the excess reductant.

2.4. Synthesis of oxidized CDs

In a typical oxidized process, 100 μL of the as-prepared CDs was mixed with 6 mL of H_2O_2/AcOH ($v/v=2:1$) solution, and the solution was stirred gently for different hours at room temperature. Excess oxidant was removed by dialysis as mentioned above.

2.5. HClO assays

20 μL CDs was added into 2 mL PBS buffer (pH 5.0). The resulting solution was incubated with different concentrations of HClO for 5 min and their fluorescence spectra were measured.

2.6. Fluorescence measurements

Fluorescence emission spectra were recorded on RF-5301PC fluorescence spectrophotometer (Shimadzu). Time-resolved fluorescence measurements were carried out on a FluoroMax-4 TCSPC (HORIBA Jobin Yvon) fluorescence spectrophotometer. Decay data analysis was performed using the DAS6 software (HORIBA Jobin Yvon IBH).

2.7. Quantum yields measurements

The quantum yields of CDs were measured by the comparative method, according to the following equation:

$$\Phi_x = \Phi_{std} \times \frac{I_x}{I_{std}} \times \frac{A_{std}}{A_x} \times \frac{n_x^2}{n_{std}^2}$$

where Φ is the quantum yield, I is the integrated area of the corrected emission spectrum, A is the absorbance at the excitation wavelength, n is the refractive index, and the subscripts x and std refer to CDs and the standard, respectively.

Quinine sulfate in 0.1 M sulfuric acid ($\Phi=0.54$) was used as the reference fluorophore for determination of the quantum yield of bCDs. Fluorescein in 0.1 M sodium hydroxide aqueous solution ($\Phi=0.95$) was selected as the reference fluorophore for determination of the quantum yields of gCDs and yCDs. In order to minimize re-absorption effects, absorbencies in the 10 mm cuvette were kept under 0.05 at the excitation wavelength (excited at 390 nm for bCDs, 410 nm for gCDs and yCDs).

2.8. Materials characterization

Absorption spectra were characterized by Hitachi U-3900 UV–vis spectrophotometer (Hitachi Ltd., Japan). Fourier transform infrared (FTIR) spectra were measured on a Nicolet IR330 spectrophotometer (KBr disc). Transmission electron microscopy (TEM) images were performed in a TECNAI F-30 (Netherlands). X-ray photoelectron spectroscopy (XPS) was carried out on a Quantum 2000 Scanning ESCA Microprobe system (Physical Electronics, USA), for determining the composition and chemical bonding configurations.

3. Results and discussion

As a member of carbohydrates that widely distributed in living organisms, sucrose has been chosen for carbon source in this work. With assistance of microwave irradiation the thermal pyrolysis finished within several minutes and strongly fluorescent CDs were obtained without post-passivation. What makes this work more significant is that blue, green and yellow emission CDs were obtained in presence of phosphoric acid of various concentrations (Fig. 1). Qu's group [26] has reported a microwave synthesis route for CDs in the presence of several to tens mM of phosphate salt. The results showed that the amount of phosphate salt affected the formation rate and quantum yield but not the photoluminescence characteristic of the prepared CDs. And phosphate salt was thought to act as an inorganic ion-based catalyst in catalyzing the formation of CDs. Other inorganic ions, cations and anions, including monovalent, divalent, and trivalent as well, have also been explored and showed ability to catalyze carbohydrate carbonization and CDs formation. In the present work, we use phosphate acid of various concentrations in the process of carbonation. By increasing the concentration of phosphoric acid from 0.01 M, 6.0 M to 13.0 M, CDs with blue (bCDs), green (gCDs) and yellow (yCDs) emission under a 365 nm UV lamp were obtained (Fig. 1). The as-prepared CDs exhibited a red shift in both the optimal emission and excitation maximum wavelengths with increasing concentration of phosphate acid (Fig. S1). When sulfuric acid instead of phosphate acid was used in the pyrolysis of carbohydrate, maximum emission peaks of the produced CDs