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Facile and green synthesis of fluorescent carbon dots with tunable emission for sensors and cells imaging

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ABSTRACT

Most carbon dots (CDs) conventional fabrication approaches produce single colored fluorescent materials, different methods are required to synthesize distinct carbon dots for specific optical applications. Herein, using one-pot hydrothermal treatment of Syringa obtata Lindl, a facile, low-cost and green assay is achieved in the controllable synthesis of blue and green fluorescent carbon dots. The fluorescent emission of CDs can be well-tuned by adding sodium hydroxide in the precursor solution. Blue fluorescent CDs are applied to Fe^{3+} sensing with a low detection limit of 0.11 μM of linear range from 0.5 to 80 μM, and then further extended to analysis river water samples. Green fluorescent CDs can be applied to pH detection, which show a remarkable linear enhancement in the green fluorescence emission region when the pH is increased from 1.98 to 8.95. Eventually, the detection of Fe^{3+} and pH are applied for the living cells fluorescent images in MCF-7 cells are achieved successfully, indicating as-synthesized CDs potential toward diverse application as promising candidate.

1. Introduction

Fluorescent nanomaterials are important fluorescent probes, Such as quantum dots [1,2], metal nanoclusters [3] and carbon dots [4–6], which can be used to detect different types of target molecules. Due to its high aqueous solubility and photostability, excellent biocompatibility, easy preparation and functionalization, Carbon dots (CDs) have attracted wide attention originate from their applications in photocatalysis [7,8], sensors [9–11], fluorescent ink [12], drug delivery [13,14] and bioimaging [15,16].

Compared to noble metal quantum dots and nanoclusters, carbon dots benefit from their fabrication low cost and simplicity. Various methods or routs have been reported for efficient prepared of this material [17–21]. However, most of these CDs emit blue fluorescence which could interfere with the fluorescent signals from cells and tissues. In recent years, various endeavors have been made toward realizing larger-scale production, improving quantum yield, simplifying operation or lowering the cost of CDs. As far as we know, tunable emission character of CDs has been less reported. Moreover, all these methods have some drawbacks such as using expensive/toxic starting materials and solvents or tedious synthetic methodology [22–26]. So, the development of green and fast methods to synthesis nontoxic CDs with color-switchable fluorescence from natural sources are still challenging.

In recent years, the trend to synthesis CDs from natural biomass has been reported originate from nontoxic, inexhaustible and inexpensive of as-prepared CDs which have various potential applications [10,27,28]. To synthesis tunable fluorescent CDs from eco-friendly natural materials using facile ways have been deeply attracted our attention. Syringa obtata Lindl petals contain carbohydrates, protein, phenylpropanoids and flavonoid [29], which are inexhaustible, low-cost and nontoxic. In the present work, a simply, low-cost and eco-friendly strategy is performed for the first time using one-pot hydrothermal treatment of Syringa obtata Lindl for synthesis of blue and

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green fluorescent CDs (B-CDs and G-CDs). The emission of fluorescent carbon dots can be well-tuned by adding sodium hydroxide. B-CDs are used as Fe^{3+} sensor and G-CDs are applied to pH detection. Eventually, the detection of Fe^{3+} and pH are successfully applied for the living cells fluorescent images in MCF-7 cells.

2. Experimental

2.1. Materials

3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) was purchased from Sigma-Aldrich corporation. $AgNO_3$, KCl, $CaCl_2$, NaCl, $CdCl_2$, $CuCl_2$, $CoCl_2$, $NiCl_2$, $FeCl_2$, $Hg(NO_3)_2$, $PbCl_2$, $MnCl_2$, $MgCl_2$, $ZnCl_2$, $AlCl_3$, $CrCl_3$, $FeCl_3$, NaH_2PO_4 and Na_2HPO_4 were obtained from Shanghai Aladdin Reagent corporation. The Syringa obtata Lindl were picked from Shanxi Medical University (Taiyuan, China) and washed with deionized water and dried at room temperature. All aqueous solutions (≥19 MΩ·cm) were obtained with ultrapure water from a Smart-N system (Heal Force, China).

2.2. Apparatus

UV–Visible absorption spectra were performed by the UV-6100 spectrophotometer (Mapada, China). All photoluminescent (PL) spectra were recorded on the Varian fluorescence spectrophotometer (Cary Eclipse, America) in 1 cm × 1 cm quartz cell. Fluorescence photographs of B-CDs were performed with ZF-6 ultraviolet analyzer under 365 nm UV light (Jiapeng, Shanghai). Fluorescence photographs of G-CDs were obtained by a molecular fluorescence imaging instrument (MFI-10) under excitation of 450 nm. Fourier Transform infrared spectra were performed using Varian FTIR-640 spectrometer. Transmission electron microscopic (TEM) image was obtained using a FEI TECNAI F20 electron microscope at 200 KV. The samples for TEM image were prepared on a super-thin carbon-coated copper grid by coating the CDs dispersion, and dried for 6 h at 50 °C. The particle distribution of as-prepared CDs was obtained by managing about 100 particles. The X-ray diffraction (XRD) patterns, operating at 40 kV and 40 mA with Cu Kα radiation, were performed on an advance Bruker powder X-ray diffractometer. Meanwhile, functional groups and elemental analysis were acquired by an AXIS ULTRA DLD Shimadzu X-ray photoelectron spectrometer using 300 W Al-Kα radiations.

2.3. Preparation of CDs

The B-CDs were obtained using Syringa obtata Lindl as carbon precursor via one-pot hydrothermal method. The Syringa obtata Lindl were first grounded into powder. Syringa powders (1.0 g) were added in ultrapure water (20 mL), and then the mixture was moved into a Teflon autoclave (25 mL), afterwards heated at 200 °C for 4 h in an oven. Finally, the suspension of CDs was performed for centrifugation (12,000 rpm, 10 min) and filtered through a 0.22 μm millipore filter, the obtained CDs solutions were dialyzed against ultrapure water passed through a 1000 MWCO dialysis membrane for 48 h. The G-CDs were obtained using Syringa obtata Lindl as carbon precursor via a hydrothermal method by adding sodium hydroxide in the precursor solution. Typically, Syringa powder (1.0 g) and sodium hydroxide (0.5 g) were added into deionized water (20 mL) and then the mixture was moved into a Teflon autoclave, afterwards heated at 200 °C for 4 h. And the suspension of CDs was performed for centrifugation (12,000 rpm, 10 min) and filtered through a 0.22 μm millipore filter, the pH of CDs solutions was neutralized, then the obtained CDs solutions were dialyzed passed through a 1000 MWCO dialysis membrane for 48 h.

2.4. Determination of Fluorescence QY

Quinine sulfate is used as a standard (QY = 54%) in the measure. The QY of B-CDs was calculated by the established procedure. Absorbencies were kept under 0.1 to decrease the re-absorption effects at the 360 nm wavelength. The QY of the B-CDs was determined using the following equation:

$$Q = Q_R \times \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{n^2}{n_R^2}$$

where Q is the QY, A refers to the absorbance, I is the measured integrated fluorescent emission intensity, and the solvent refractive index is showed by n. The subscript R refers to the corresponding parameter of the known fluorescent standard.

Rhodamin 6G was chosen as a standard in ethanol for determining the QY of G-CDs with a QY of 0.94 at 488 nm.

2.5. Fluorescence Assay of Fe^{3+}

In a typical assay, the Fe^{3+} detection was tested in 10 mM PBS buffer solution at room temperature (pH = 7.40). 20 μL of B-CDs (1.2 mg/mL) were added into 2000 μL of PBS buffer, and followed with the addition of different concentrations of Fe^{3+}. To determine the selectivity for Fe^{3+} sensing, same method was performed by the addition of different other metal ions instead of Fe^{3+}. The fluorescence was performed under 340 nm excitation wavelength.

In order to evaluate the N-CDs-based sensor for Fe^{3+} ion detection in an artificial system, the present method was examined by the river water samples to replace ultrapure water for real water sample analysis. Water samples were centrifuged for 10 min at 12000 rpm, filtered through the 0.22 μm micron filter. Aliquots (1000 μL) of the CDs solution were spiked with Fe^{3+} standard solutions. And the spiked samples containing B-CDs were determined by the above described strategy and inductively coupled plasma optical emission spectrometer (ICPE-9000, Shimadzu).

2.6. Fluorescence Assay of pH

The detection of pH was determined at room temperature in the Britton-Robinson buffer (B-R buffers, pH 1.98, 2.87, 3.29, 4.10, 5.02, 6.09, 7.00, 7.96, 8.95, 9.91, 10.88, 11.20, 11.92). 100 μL of CDs solution (1.6 mg/mL) was transferred into 1900 μL B-R buffer at different pHs.

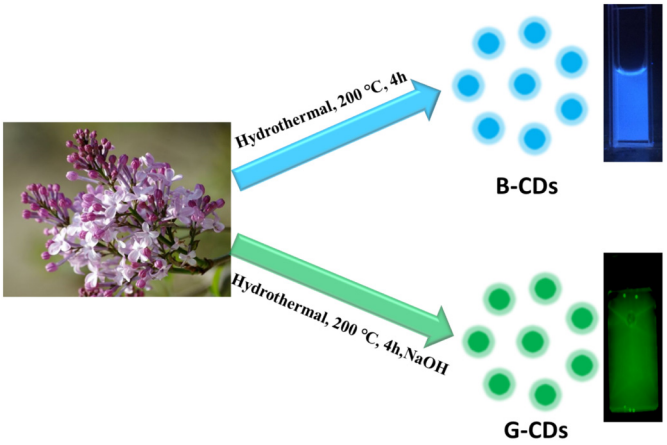

Fig. 1. Diagram for as-synthesized CDs from Syringa obtata Lindl, along with graphic of the corresponding B-CDs of under irradiating 365 nm UV lamp (top) and G-CDs of 470 nm excitation (bottom).