Sensors and Actuators B 258 (2018) 580–588

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

One step hydrothermal synthesis of carbon nanodots to realize the fluorescence detection of picric acid in real samples

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ARTICLE INFO

Article history:
Received 11 October 2017
Received in revised form
13 November 2017
Accepted 18 November 2017

Keywords:
Carbon nanodots
Grape skin
Picric acid
Fluorescence spectra

ABSTRACT

In this work, carbon nanodots were synthesized using grape skin as raw material by one step hydrothermal method under optimized experimental conditions. The carbon nanodots were characterized by TEM, fluorescence, UV, IR and XPS. The average particle size of the carbon particles was 4.0 ± 1.5 nm. When excited at 430 nm, the carbon nanodots showed strong green fluorescence of 522 nm which was dependent on the excitation wavelength. The fluorescence quantum yield reached 18.67%. Stability and anti-photobleaching properties were ideal. Picric acid quenched the fluorescence of the carbon nanodots in the phosphate buffer solution at pH = 7.4, and a method of high sensitivity and selectivity to detect picric acid was established. The linear range was 0.06–79.4 μM, the correlation coefficient was 0.998, and the detection limit was 10 nM (S/N = 3). The method was successfully applied to the detection of picric acid in real water samples. The recoveries fell in the range of 95.64%–104.2% and the RSD was 0.26%–0.74%.

1. Introduction

Carbon nanodots (CDs) are a new type of carbon nano particles less than 10 nm in size [1], and are dispersed and quasi-spherical. CDs were first observed by Xu et al., who observed single walled carbon nanotubes by electrophoresis in 2004 [2]. On account of many excellent features, such as small size, tunable emission wavelength [3], strong photostability [4], biocompatibility [5,6], two-photon absorption, optical charge transfer, near infrared photoluminescence and electroluminescence characteristics [7]. CDs are widely used in the field of carbon catalytics, optical devices, fluorescent sensors and bioimaging [8–10]. People are now exploring ways to synthesize CDs, via top-down and bottom-up methods according to different carbon sources [11]. The top-down approach is mainly performed by chemical oxidation or by nodular or mechanical crushing of activated carbon to obtain nano scale precursor carbon–such as nano diamond, carbon black, graphite, carbon nanotubes, ash, and other large candle carbon material. The main methods involved include discharge [12], laser ablation [13], electrochemical [14,15] and the direct synthesis of carbonation [16]. The "bottom-up" method mainly refers to the production of nano particles under different experimental conditions by using small molecules as precursors. These experimental conditions include pyrolysis [17], microwave assisted [18], ultrasonic assisted [19], hydrothermal mechanisms [20,21] and alternatives. The hydrothermal method has been the most widely used because of its simplicity and is also environmentally friendly [22].

Grape skin contains large amounts of anthocyanin, resveratrol, cellulose pectic substances and so on [23]. Anthocyanin is particularly good in preventing various diseases associated with free radicals. Resveratrol can prevent cardiac weakness, cerebrovascular disease, and skin cancer [24]. Therefore, wine, grape juice and other drinks are becoming more and more popular. In this paper, the grape skin was used as a new carbon source to synthesize CDs via an economic and facial synthesis method.

Picric acid (abbreviated PA or TNP, $C_6H_3N_3O_7$), has been widely used in the manufacture of pesticides, chemical fibers, explosives, fireworks, and etc. It could lead to water and soil pollution if discharged into the environment [25]. PA can cause headache, dizziness, nausea, vomiting and other symptoms in humans when breathed in. In addition, it has the hazards of causing contact dermatitis, conjunctivitis, and bronchitis [26]. China's "drinking water health standards" (GB5749-2006) [27] and "surface water environmental quality standards" (GB3838-2002) [28] regulate that the maximum allowable concentration of PA in water is 0.5 mg/L. In general, methods used to detect PA are mass spectrometry [29] surface plasmon resonance (SPR) [30,31], field effect transistor (FET) [32] and fluorescence spectroscopy (FL) [33,34]. Because of the

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https://doi.org/10.1016/j.snb.2017.11.096
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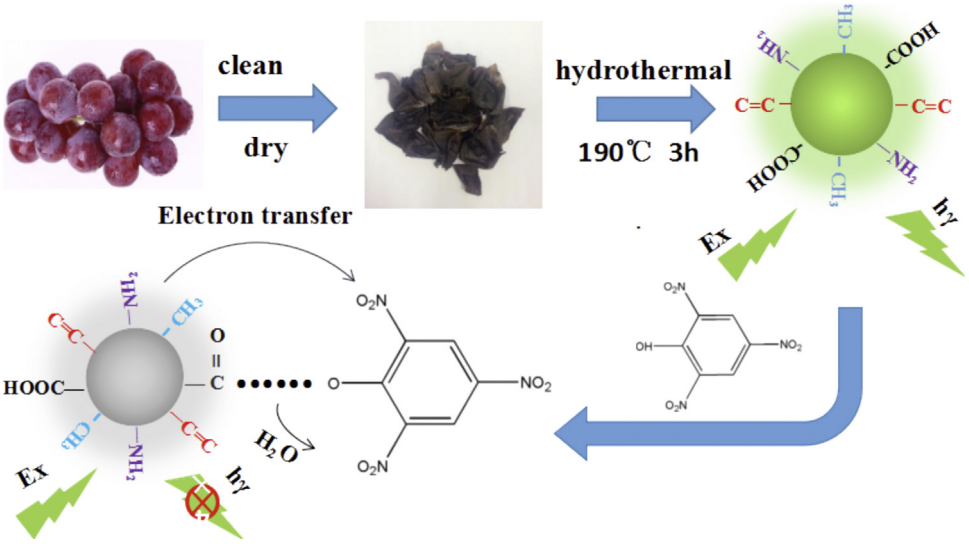

Fig. 1. The synthesis process of CDs by grape skin with a simple hydrothermal route and the highly selective and sensitive detection of PA.

structure similarity, it is difficult to distinguish PA from other nitro compounds by photoinduced electron transfer, fluorescence resonance energy transfer, strong electrostatic interaction and internal filtering effect mechanism [35]. These methods are thus limited by poor selectivity or complicated procedures. The sensitivity of these tests still need to be improved so it is of great significance to establish a simple, highly sensitive and fast responding method to test PA in water.

In this paper, we used grape skin as a carbon source and synthesized carbon nanodots using the hydrothermal synthesis method, and had a fluorescence quantum yield of 18.67%. The method of detecting PA was established based on fluorescence quenching of the carbon dots synthesized through picric acid in phosphate buffer solution at pH = 7.4. The procedure is shown in Fig. 1. Additionally, the method was applied to real water samples. Low detection limit, high sensitivity, great selectivity and good anti-jamming capability were obtained.

2. Experimental

2.1. Materials

Grapes (bought from supermarket), rhodamine 6 G was purchased from Beijing Chemical Reagents Company, picric acid (PA, 0.01 M) was purchased from Dalian Dyestuff Factory, PBS buffer solution (concentration was 10 mmoL, pH 1–12), nitro compounds, phenolic compounds and metal ions solutions (concentration was 0.1 M). All these reagents were domestic and pure and were purchased from Beijing Chemical Reagents Company; experimental water was double distilled water.

2.2. Apparatus

The UV absorption spectra of carbon nanodots were obtained on an UV-265 UV–vis spectrophotometer (Tokyo, Japan) with a 1 cm quart cell. IR spectrum of CDs was recorded with a Thermo Scientific Nicolet iS50 Infrared Spectrometer (Thermo Corporation, USA) with solid powder that received by freeze-drying (Ningbo Xinzhi Biotechnology Co., Ltd.). The fluorescence spectra of CDs was collected on a F-4500 fluorescence spectrophotometer (Hitachi, Tokyo, Japan) by a 1 cm fluorescent colorimetric cell. The excitation/emission slits were set to 10 nm/10 nm, and the maximum excitation and emission wavelengths were 430 nm and 522 nm, respectively. The JEM-2100 High Resolution Transmission Electron Microscope (Japan JEOL) scanning electron microscope was used to acquire the scanning electron microscopy (SEM) images at an accelerating voltage of 20 KV. The KQ5200 B ultrasonic cleaning (Kunshan City ultrasound Instrument Co., Ltd.) was taken with gain solution and weighs solid with Analytical Balance (Austrian House Instrument Co., Ltd.). A PHS-3C pH meter (METTLER TOLEDO, Switzerland) was utilized to measu Microscope (Japan JEOL) scanning electron microscope was used to acquire the scanning electron microscopy (SEM) images at an accelerating voltage of 20 KV. The KQ5200 B ultrasonic cleaning (Kunshan City ultrasound Instrument Co., Ltd.) was taken with gain solution and weighs solid with Analytical Balance (Austrian House Instrument Co., Ltd.). A PHS-3C pH meter (METTLER TOLEDO, Switzerland) was utilized to measure the pH values. The elemental composition of CDs was examined by an Axis Ultra Dld X-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD, Britain).

2.3. Synthesis of CDs

The CDs were synthesized from grape skin through a simple, convenient one-step hydrothermal method. The grape skin was cleaned by double distilled water and dried at 40 °C. Then 1.0 g of grape skin and 30 mL of double distilled water were kept in a 50 mL Teflon equipped stainless-steel autoclave and was heated at a constant temperature of 190 °C for 3 h. After cooling to room temperature, the product was filtered and the supernatant fraction was centrifuged at 13000 rpm for 10 min. Dialysis was undertaken with a MW1000 dialysis bag for 24 h and freeze-dried. Then, the solid brown fluorescent CDs were obtained for further characterization and use [20].

2.4. Quantum yield measurement

The quantum yield (QY) of CDs was measured by comparing the fluorescence intensities and absorption values of a CD solution with Rhodamine 6 G[21] (excitation wavelength: 488 nm, quantum yield 0.94, dissolved in ethanol). In an effort to minimize re-absorption effect, the absorbance of the CDs solution was kept below 0.05. The QY of CDs was calculated from the following equation:

$$Yu = Ys * Fu/Fs * As/Au * (\eta u/\eta s)2$$