Talanta 153 (2016) 332–339

Contents lists available at ScienceDirect

Talanta

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

A rapid microwave synthesis of nitrogen–sulfur co-doped carbon nanodots as highly sensitive and selective fluorescence probes for ascorbic acid

Junxia Duan [a], Jie Yu [b], Suling Feng [a,*], Li Su [a]

[a] School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007, China
[b] Department of Chemistry, Xinxiang Medical University, Xinxiang 453007, China

ARTICLE INFO

Article history:
Received 1 December 2015
Received in revised form
1 March 2016
Accepted 12 March 2016
Available online 12 March 2016

Keywords:
Microwave
Nitrogen–sulfur co-doped carbon dots
Fluorescence probe
Ascorbic acid

ABSTRACT

A ultrafast one-step microwave-assisted method was developed for the synthesis of nitrogen–sulfur co-doped carbon nanodots (N,S-CDs) by using ethylenediamine as the carbon source and sulfamic acid as the surface passivation reagent. The morphology and the properties of N,S-CDs were explored by a series of techniques, such as high-resolution transmission electron microscopy, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, UV–vis absorption and fluorescence spectroscopy. The prepared N,S-CDs exhibit bright blue photoluminescence with a high fluorescence quantum yield (FLQY) up to 28%, and high stability and excellent water solubility. A N,S-CDs-based fluorescent probe was developed for sensitive detection ascorbic acid (AA) in the presence of Cu^{2+}, based on the mechanism that AA reduces Cu^{2+} to Cu^{+}, then Cu^{+} quenches the fluorescence of N,S-CDs through electron or energy transfer due to the interaction between Cu^{+} and thiol ligand on the N,S-CDs surface. The observed linear response concentration range was from 0.057 to 4.0 μM to AA with a detection limit as low as 18 nM. The probe exhibited a highly selective response toward AA even in the presence of possible interfering substances, such as uric acid and citric acid. Moreover, these promising features made the sensing system used for the analysis of human serum and urine samples.

1. Introduction

Fluorescent carbon dots (CDs) have attracted tremendous interest by virtue of their distinctive superiority including outstanding water solubility, high photostability against blinking and photobleaching, tunable excitation and emission spectra, robust chemical inertness, excellent biocompatibility, and low toxicity [1–4]. And they are very promising in numerous possible applications such as photocatalysis [5], optoelectronic devices [6], bioimaging [7], and optical sensor [1,2,4,8]. To date, a variety of methods have been proposed for preparing CDs, including arc-discharge [9], electrochemical oxidation [10], laser ablation [11], hydrothermal approach [7,12], ultrasonics [13] and microwave pyrolysis approach [14], etc. Among them, microwave pyrolysis has many advantageous features such as high efficiency in heating process, rapid carbonization reactions and simplicity of the instrumentation [15]. Therefore, microwave pyrolysis is a simple, fast and green method for synthesis of CDs with much lower cost.

As one of CDs with heteroatoms, nitrogen–sulfur co-doped carbon nanodots (N,S-CDs) exhibit their fascinating performances in fluorescence, and most of the reported methods for the preparation of N,S-CDs were hydrothermal treatment. For example, Li et al. prepared N,S-CDs with high FLQY up to 73% and excitation-independent emission [3]. Xiong et al. synthesized highly photoluminescence N,S-CDs as fluorescent sensors for Fe^{3+} and cell imaging [7]. Wang et al. fabricated N,S-CDs for highly sensitive and selective detection of methotrexate in human serum [2]. However, the hydrothermal method suffers to some degree from shortcomings such as time-consuming processes, expensive equipment required, and high temperature, which hinder their wide applications. As a “green”, facile and feasible approach, microwave-assisted pyrolysis for N,S-CDs have been barely reported. Choi et al. prepared N,S-CDs by microwave-assisted pyrolysis of rice and N-acetyl-L-cysteine, and the FLQY is only 2.36% [14]. You et al. reported a microwave synthesis of N,S-CDs for bio-imaging of Hg^{2+} in living cells [16]. In addition, although a variety of CDs have been synthesized, it is still desired to diversify the surface group of CDs for enlarging their application in various fields [17]. Thus, to explore new microwave routes for synthesis of highly fluorescent,

* Corresponding author.
E-mail address: slfeng@htu.edu.cn (S. Feng).

http://dx.doi.org/10.1016/j.talanta.2016.03.035
0039-9140/

surface-different N,S-CDs is still a tricky challenge.

Ascorbic acid (AA) as an important anti-oxidant and vitamin, plays an important role in many biochemical processes such as free radical scavenging, cell development and immunity improvement [18,19]. The abnormal concentration levels of ascorbic acid in biological fluids are considered to be associated with some diseases such as cancer and diabetes mellitus [20] etc. Up until now, various methods have been employed for the detection of AA in biological samples, including electrochemistry [21,22], spectrophotometry [23], chemiluminescence [24], HPLC [25] and so on. Among these techniques, electrochemical methods commonly reported for AA, suffered from drawbacks such as high background, rather poor selectivity, weak reproducibility, and complex preparation of electrodes. Spectrophotometric methods showed limited linear range or relatively low sensitivity. Chemiluminescence methods used heavy metal-containing reagent. Chromatographic techniques required complicated sample preparation, and sophisticated and expensive instruments. In recent years, some available fluorescent probes have been employed for the quantitative determination of AA in biological samples [26–33] because of the advantages of high sensitivity, operational simplicity and rapid response. Yan and co-workers reported a CdTe QDs fluorescent probe with $KMnO_4$ as the quencher for the detection of AA in human urine and plasma [26]. Yao and co-workers developed photoluminescent nitrogen-doped carbon nanoparticles for determination of AA in human urine, human blood serum, and human blood plasma samples, based on the synergistic action of the inner filter effect and the static quenching effect [29]. Tang and co-workers demonstrated cobalt oxyhydroxide (CoOOH)-modified luminescence nanoparticles ($Sr_2MgSi_2O_7$:1% Eu, 2% Dy) for detection and imaging of AA in living cells and in vivo [31]. Shao's group synthesized a reversible fluorescent probe by incorporating 4-amino-2,2,6,6-tetramethyl-piperidin-1-ol group into a 7-nitrobenzoxadiazole fluorophore for the cyclic detection of ClO^-/AA in living HeLa cells [32]. However, most of these methods suffer from shortcomings such as usage of toxic heavy metal elements and hazardous reagent, complicated fabrication procedures of the probes, and disturbance of some reductive species including glutathione and cysteine. These shortcomings limited their applications in practical process. Therefore, there is a demand for sensitive, reliable, fast, and inexpensive detection of AA in biological fluids.

In the present work, we developed a simple synthesis of N,S-CDs via a one-step microwave-assisted route using ethylenediamine as the carbon source and sulfamic acid as N,S-doped precursors and the surface passivation reagent. The synthesis process can be completed within 2 min. The as-prepared N,S-CDs displayed a relatively high fluorescent quantum yield of 28%. In addition, the N,S-CDs show a highly selective response to AA in the presence of Cu^{2+}. Moreover, the N,S-CDs/Cu^{2+} could be used as a fluorescent probe for detection of ascorbic acid in urine and serum samples, which demonstrates its practical application in biological fluids. In comparison with other fluorescence probes employed for AA detection in urine and serum samples [26,28–30], the developed probe system showed high sensitivity.

2. Experimental

2.1. Chemicals

Sulfamic acid was purchased from Beijing northwest Chemical Reagent Co. Ltd (China). AA was obtained from Beijing Chemical Reagent Co. Ltd (China). Ethylenediamine was bought from Sinopharm Chemical Reagent Co. Ltd (Beijing, China). HOAc and NaOAc were obtained from Shanghai Chemical Reagent Co., Ltd (China). The solution of copper(II) ion (2.5 mM) was prepared from $CuSO_4 \cdot 5H_2O$ (Shanghai Zhenxing Chemical Reagent Co., Ltd (China)). The standard solution of AA (56.8 μM) was prepared and kept in a refrigerator at 4 °C. A HOAc–NaOAc buffer solution was used to maintain the pH of solutions at 5.5. Distilled water was used throughout the experiment. All reagents were of analytical grade and used without further treatment.

2.2. Apparatus and characterization

Transmission electron microscopy (TEM) analyses were carried out using a HITACHI H-8100 transmission electron microscopy (TEM) with an accelerating voltage of 200 kV (Hitachi, Tokyo, Japan). Fourier transform infrared spectra (FTIR) were measured with a Nicolet FTS NEXUS FTIR spectrometer (Nicolet instrument Co., USA). X-ray photoelectron spectra (XPS) were performed by Thermo ESCALAB 250 (Thermo Electron Co., USA). The absorption spectra were recorded on a UV-1700 UV spectrophotometer (Shimadzu, Co., Japan). All fluorescence spectra were performed using a FP-6500 spectrofluorophotometer (JASCO Corp. Japan). The absolute quantum yield (QY) was measured by a FLS-980 fluorescent spectrophotometer employing an integrating sphere (Edinburgh Instrument, UK). The N,S-CDs were centrifuged using a TGL-16G centrifuge (Shanghai anting scientific instrument factory, China). The pH adjustments were monitored using a pHS-3C digital acidity meter (Shanghai INESA Scientific Instrument Co. Ltd, China).

2.3. Preparation of fluorescent N,S-CDs

We developed a green, and simple method for synthesis of N,S-CDs by microwave-heating sulfamic acid and ethanediamine together. In a typical synthesis, 0.25 mL of ethanediamine and 0.5 g of sulfamic acid were dissolved into 10 ml distilled water to obtain a transparent colorless solution. The mixture was heated in a domestic microwave oven (800 W) for 2 min, then cooled to room temperature naturally. The resulting dark brown solid was dispersed in 10 ml distilled water. The obtained suspension was centrifuged at 10,000 rpm for 10 min and filtered through a 0.10 μm membrane. The as-prepared N,S-CDs solution was further diluted to 100 mL with distilled water to obtain a dilute carbon dots solution at a concentration of 4.08 mg/mL. In the control experiments, 0.25 mL of ethanediamine and 0.27 ml of the concentrated H_2SO_4 were placed in 10 ml distilled water and heated in a domestic microwave oven (800 W) for 2 min for preparation of sulfur- doped carbon nanodots (S-CDs). Other procedures were the same as those for N,S-CDs.

2.4. Fluorescence detection of ascorbic acid

0.9 mL of 0.51 mg/mL N,S-CDs, 1.1 ml of 2.5 mM Cu^{2+} and 0.6 mL of the pH = 5.5 HAc–NaAc buffer solution were added to a series of 10 mL volumetric flask, followed by the addition of different concentrations of the standard solution of ascorbic acid or sample solution. They were diluted to the scale with distilled water and mixed thoroughly. Finally, the solution was transferred to a fluorescence cuvette. In order to obtain favorable fluorescence spectra, the excitation and emission slit was set to 5 nm in the case of excitation wavelength at 391 nm. Fluorescence intensity (F) of the solution was recorded under the emission wavelength at 424 nm (the reagent blank was marked as F_0). F_0–F is the decreased fluorescence intensity and marked as ΔF.