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Green and simple turn off/on fluorescence sensor for mercury (II), cysteine and histidine

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ABSTRACT

In this study, microwave-assisted synthesized nitrogen and sulfur co-doped carbon dots (N-S-CDs) were used Hg^{2+} ions, cysteine and histidine sensor. The optimum pH was 7 and detection limit and linear range were 8 nM and 0.01–50 μM, respectively. Fluorescence of N-S-CDs-Hg^{2+} system was recovered after addition of cysteine and histidine and this effect was used for the determination of these amino acids. The fluorescence recovery of the N-S-CDs–Hg^{2+} (25 μM) system was linearly increased with increasing the concentration of cysteine or histidine from 5 to 50 μM and LODs were 0.4 μM and 0.6 μM for cysteine and histidine, respectively. Simple and green synthesis, solubility in water, no need to any organic solvent and very fast response time were good properties of the new sensor.

1. Introduction

Mercury exists as elemental, organic and inorganic forms [1]. Industrial wastes are important sources of the ecosystem contamination and exposure to mercury may damage to brain, kidney and neurological system [2–5]. Several analytical techniques such as atomic absorption spectrometry [6], inductively coupled plasma mass spectrometry [7], X-ray fluorescence spectrometry and gas chromatography–mass spectrometry [8] were reported for Hg^{2+} determination. Although these methods have low detection limit and wide dynamic range, but they have some difficulties such as expensive instrumentation, problems associated with sample preparation, long analysis time and procedure complexity. Thus, it is essential to develop new methods to overcome these limitations. Different colorimetric or fluorescent sensors were also developed in recent years [9,10]. In the most of the reported colorimetric sensors, organic reagents were used in organic media that had not sufficient selectivity and sensitivity in aqueous media [11,12]. Fluorescence quenching based sensors were also designed for mercury ion [13–15].

In recent years, carbon dots have been considered because of their unique properties such as size-tunable luminescent, broad excitation spectrum, narrow emission spectrum and good capability to functionalization in order to increase selectivity [16]. Among several synthesis methods for the carbon dots preparation, microwave-assisted techniques is simple, low-cost, one-step, environmentally friendly and energy-saving [17–18]. Fluorescence efficiency and selectivity of carbon dots can improve with co-doping of them with nitrogen, sulfur, boron.

The main objectives of this work were synthesis of nitrogen sulfur co-doped carbon dots by microwave-assisted method, development of a turn off fluorescent sensor for Hg^{2+} ions and selective determination of cysteine and histidine by a turn on carbon dots–Hg^{2+} system.

2. Experimental

2.1. Reagents and instruments

Chemicals with highest purity available were obtained from Merck (Darmstadt, Germany). $HgCl_2$ salt was used to prepare stock solution of Hg^{2+} (10 mM). Different ions and molecules were used for interference study. Desired pH values were adjusted by Britton–Robinson universal buffers (0.01 M).

Varian Cary 300 Bio, Vertex 70 FT-IR and Varian Cary were used for UV/vis, FT-IR and fluorescence study. High resolution transmission electron microscope (HRTEM; MC30 Philips) was used for size determination.

2.2. Synthesis of nitrogen sulfur co-doped carbon dots

Microwave-assisted synthesis as an easy and fast method that provides homogeneous heating and uniform size distribution was used for nitrogen sulfur co-doped carbon dots preparation. Citric acid (1 g) and ammonium thiocyanate (1 g) were dissolved in deionized water (10 mL). and heated for 5 min in a microwave oven at 600 W. Brown

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solid was dissolved in 10 mL water, centrifuged to remove impurities and evaporated until dryness at room temperature. Then, it was re-dissolved in distilled water (4.41 mg/mL).

2.3. Fluorimetric and real samples analysis

In typical analysis, different concentrations of Hg^{2+} were added to N-S-CDs solution (75 μL) and Britton–Robinson universal buffer (3 mL, pH = 7, 0.01 M) and fluorescence was measured (1-cm quartz cuvette, $\lambda_{excitation} = 400$ nm, $\lambda_{emission} = 480$ nm, excitation slit width = 10 nm and emission slit width = 5 nm).

Real water samples (river, mineral and tap water) were analyzed by new method. The river water samples were filtered by 0.45 μm membrane filters and then centrifuged for 15 min at 4000 rpm. The water samples were spiked by different Hg^{2+} concentrations and then analyzed with the proposed method.

3. Result and discussion

3.1. Characterization of nitrogen-sulfur co-doped carbon dots

In N-S-CDs absorption spectra (Fig. 1A), there are two absorption peaks (290 and 350 nm) that absorption peak at 350 nm was related to $\pi \rightarrow \pi^*$ transition [19]. When carbon dots were excited at 410 nm, strong fluorescence emission was seen at 490 nm (Fig. 1A). N-S-CDs fluorescence intensity changed (without significant shift) when excitation wavelength increased from 400 to 460 nm (Fig. 1B).

As shown in HRTEM image (Fig. 2A), carbon dots were well dispersed and had diameters about 30 nm. FT-IR was used to determine the main functional groups of the N-S-CDs (Fig. 2B). Bands at 3202, 1717 and 2063 cm^{-1} was assigned to O—H and N—H, carbonyl and azide group vibrations, respectively. These polar groups increase the hydrophilicity of CDs. C—N stretching and C—S and S—N stretching vibrations were observed at region 1192–1406 and 500–700 cm^{-1}, respectively [20].

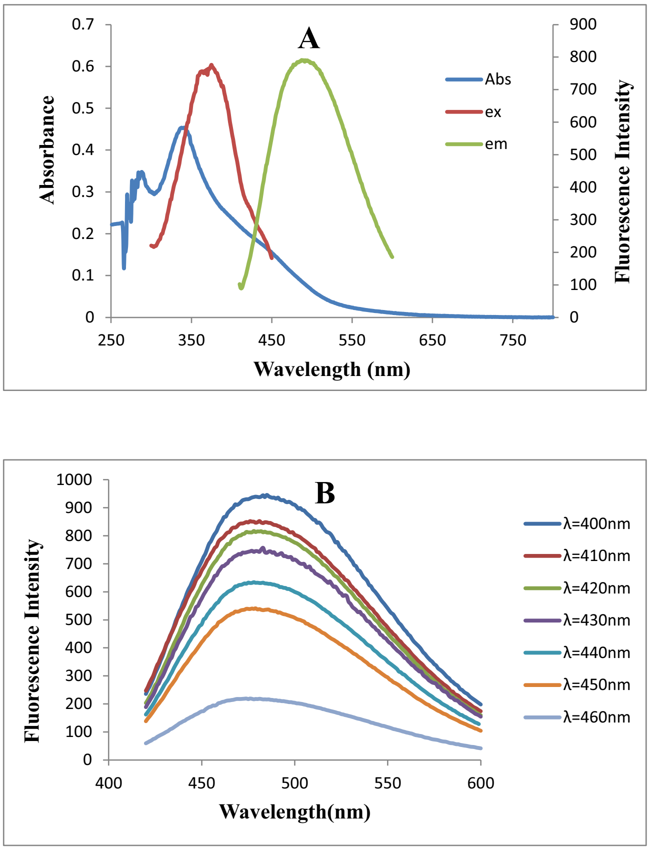

Fig. 1. (A) UV–vis absorption, excitation and emission spectra of CDs in aqueous solutions (4.42 mg/mL), $\lambda_{ex} = 400$ nm and $\lambda_{em} = 490$ nm. (B) FL spectra at different excitation wavelength.

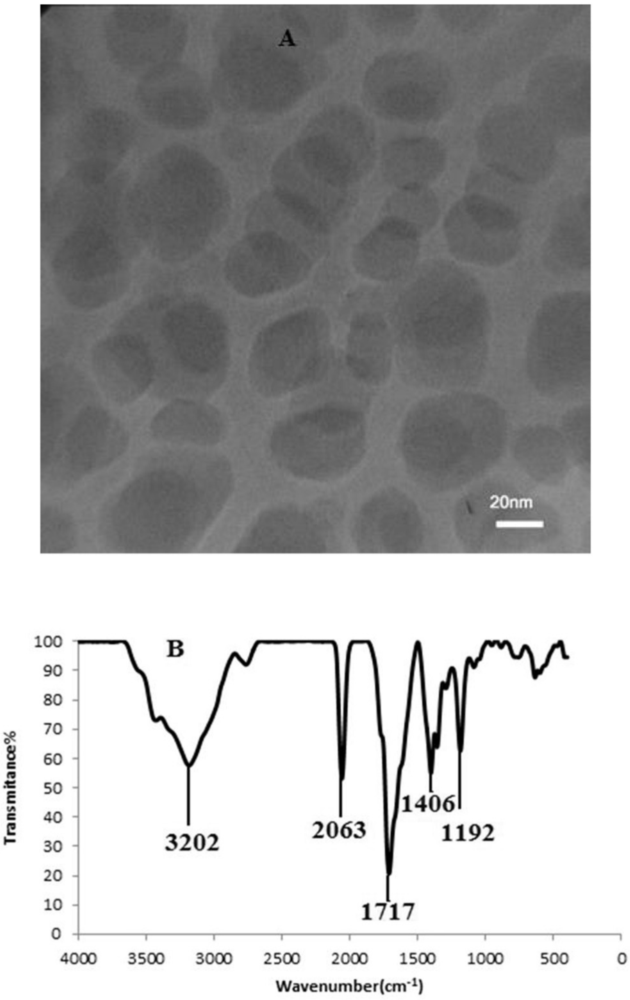

Fig. 2. (A) The typical HRTEM image. (B) FT-IR spectrum of N-S-CDs.

3.2. Effect of pH and time

One of the most effective parameter is pH that influences the solubility of metal ions and fluorescence intensity of carbon dots (protonation or deprotonation of the functional groups on the surface in acidic and alkali media) [19,21]. The effect of pH in the range of 2–10 on the fluorescence quenching of CDs in the presence of Hg^{2+} (25 μM) was studied. When pH increased from 2 to 7, the relative fluorescence intensity was increased and had maximum value at pH = 7 and then decreased at higher pH (Fig. 3A).

Time effect (1 to 30 min) on the relative fluorescence intensity was studied after addition of Hg^{2+} at room temperature and pH = 7. As shown in Fig. 3B, relative fluorescence reached to maximum after 5 min. This property is one of the requirements for an effective chemical sensor.

3.3. Calibration

At optimized conditions, Fluorescence intensity of N-S-CDs was gradually decreased with increase in the concentration of Hg^{2+} ion in