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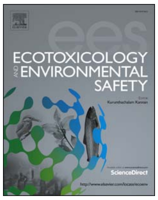

Microwave assisted synthesis of doped carbon dots and their application as green and simple turn off–on fluorescent sensor for mercury (II) and iodide in environmental samples

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ABSTRACT

A novel, green, facile and dual turn-off/on sensor for detection of Hg^{2+} and I^- was developed based on carbon dots. Carbon dots were synthesized from citric acid, urea, and thiourea by microwave-assisted method. The size of the carbon dots (CDs) was about 10 nm and the synthesized CDs showed a strong emission at 523 nm upon excitation at 416 nm. The fluorescence quantum yield was 19.2%. Mercury (II) quenched the fluorescence of carbon dots. This turn off sensor had linear response for Hg^{2+} over a concentration range from 0.1 to 20 µM with detection limit as low as 62 nM. The carbon dots/Hg^{2+} system was also used as a turn on sensor for detection of iodide. Linear concentration range for I^- was 0.1–10 µM with detection limit as low as 72 nM. The proposed method showed good sensitivity and selectivity with respect to interference ions. Finally, this system was successfully used for the detection of Hg^{2+} and I^- in tap, river and mineral waters and fish samples.

1. Introduction

Mercury is one of the hazardous pollutants that found throughout the environment. Its mobile nature allows it to diffuse through the air, soils and ultimately into water systems and food chain. It is confirmed that Hg^{2+} can lead to DNA and central nervous system damage because it can easily pass through skin and respiratory (Bera et al., 2014). Iodide is an essential trace element and biological anion that is vital for normal growth and development. It is known because of its essential and important role for thyroid function. In fact, without iodide, thyroid hormones could not even be synthesized. Thus, dietary iodide deficiency can lead to several different problems, including poor thyroid function, goiter, neurological damage and paralysis. However, an excess of iodine can also lead to thyroid disorders, especially in infants. Hence, it is very important to approach the method to facile, rapid, sensitive and selective detection of mercury and iodide.

Up to now, several methods have been developed for the determination of trace mercury and iodide. cold-vapor atomic absorption spectroscopy, inductively-coupled plasma atomic emission spectroscopy (Grazyna and Jerzy, 2011), inductively coupled plasma mass spectrometry (Hsu et al., 2013), spectrophotometry (Rofouei et al., 2012), cyclic voltammetry with electrochemical liquid-phase microextraction (Zhu et al., 2010), flow injection spectrophotometric analysis (Kamavisdar and Patel, 2010) have been developed for detection of I^-. These methods require expensive and sophisticated instrumentation and/or complicated sample preparation processes.

In recent years, detection of ions by fluorescent sensors has earned enormous attention because of their advantages over other techniques, such as ease detection, simple handling, high sensitivity and selectivity. New member of the carbon family is carbon dots (CDs) that is an important class of fluorescent sensors (Farka et al., 2017; Goryacheva et al., 2017; Sharma et al., 2017; Tuerhong et al., 2017; Walekar et al., 2017; Zu et al., 2017). Owing to its proper properties such as high chemical stability, low toxicity, good photo-stability, and excellent biocompatibility were used as fluorescent sensors for detection of ions (Sachdev and Gopinath, 2015; Sun et al., 2016). Different methods for CDs preparation such as arc discharge, laser ablation, electrochemical oxidation, and microwave methods were established. Among these methods microwave-assisted techniques can prepare CDs with fluorescence efficiency and high selectivity in short time.

In this study, new CDs was synthesized by microwave-assisted method and used for mercury (II) and iodide detection in aqueous solution. The assay principle is shown in Fig. 1. Fluorescence of CDs was quenched after addition of Hg^{2+}. Because of higher affinity between Hg^{2+} and iodide, after addition iodide to Hg^{2+}-CDs system, Hg^{2+} ions released from surface of CDs and fluorescence of CDs were recovered. This process was successfully employed for determination of Hg^{2+} and iodide in real water and fish samples. Selectivity of synthesized CDs for

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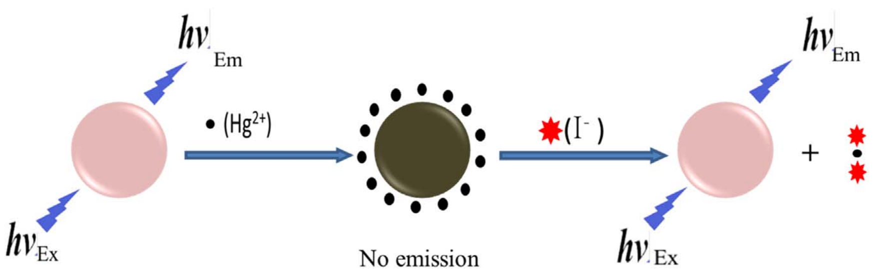

Fig. 1. The schematic illustration of the detection process for Hg (II) and I^-.

Hg^{2+} and iodide was also studied.

2. Methods

2.1. Chemicals and instruments

All chemicals were analytical grade and obtained from Merck (Germany). Britton–Robinson buffers (0.04 M) were used in the range pH = 2–10. Stock solutions (10 mM) of Hg^{2+} and I^- ions were prepared from $HgNO_3$ and KI in ultrapure water. By diluting standard stock solutions, different concentrations of Hg^{2+} and I^- ions were obtained. Stock solutions (10 mM) of metal ions (Na^+, K^+, Cu^{2+}, Zn^{2+}, Ca^{2+}, Fe^{3+}, Hg^{2+}, Mg^{2+}, Ni^{2+}, Fe^{2+}, Ag^+, Cd^{2+}, Co^{2+}, Cr^{3+}, Ti^{3+}, Bi^{3+}, Ba^{2+}, Si^{4+}) were prepared with ultrapure water from their salts.

Fourier transformed infrared spectroscopy (FT-IR) study was conducted with a Vertex 70 FT-IR. The UV–vis absorption and the fluorescence spectra were measured with a Varian Cary 300 Bio UV/vis spectrometer and Cary eclipse fluorescence spectrophotometer, respectively. To characterize the morphology and size of carbon dots, high resolution transmission electron microscopy (HRTEM) was performed by a MC30 transmission electron microscope (TEM; Philips).

2.2. Carbon dots synthesis

The carbon dots were synthesized by microwave-assisted method. Citric acid (1 g), urea (1 g) and thiourea (1 g) were dissolved in 10 ml distilled water and subsequently was stirred. The solution was irradiated for 5 min in a microwave oven at 450 W. The resulting brown solid was dissolved in 20 ml water and centrifuged at 12000 rpm for 15 min and then filtered by a 0.2 µm membrane filter. The resulting clear solution was evaporated until dryness for 3 days at room temperature. Then, solid re-dissolved in 50 ml water.

2.3. Spectrofluorimetric assay for mercury

In a typical assay, a suitable volume of Hg^{2+} solution and 100 µl of carbon dots (0.298 mg/ml) were added to 3 ml of universal buffer (pH = 9). The fluorescence was recorded at λ_{em} = 523 nm and λ_{ex} = 416 nm in a 1-cm quartz cuvette at room temperature. Slit widths for the excitation and emission were 10 and 10 nm, respectively. The selectivity of the proposed sensor for Hg^{2+} was evaluated by addition of other metal ions in a similar way.

2.4. Spectrofluorimetric assay for iodide

To prepare of carbon dots/Hg^{2+} mixture for iodide sensing, 20 µl Hg^{2+} solution (0.001 M) and 100 µl of carbon dots were added to 3 ml of universal buffer (pH = 9). Then, a suitable volume of I^- solution was added to carbon dots/Hg^{2+} mixture. The fluorescence was recorded at λ_{em} = 523 nm and λ_{ex} = 416 nm in a 1-cm quartz cuvette at room temperature with slit widths of 10 and 10 nm for the excitation and emission, respectively.

2.5. Quantum yield measurement

The fluorescence quantum yield of N/S co-doped carbon dots was calculated by comparing their integrated fluorescence intensities (excitation at 416 nm) and absorbance values at 416 nm with those of quinine sulfate using the following equation (Lakowicz, 1999):

$$\phi = \phi_R \times \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{\eta^2}{{\eta_R}^2} \tag{1}$$

where the subscripts R denote standard (quinine sulfate with known fluorescence quantum yield of 0.54) and ϕ is the fluorescence quantum yield. I, η and A are the measured integrated emission intensity, refractive index of the solvent and optical density, respectively.

2.6. Determination of Hg^{2+} and I^- in real samples

The proposed method was used for determination of Hg^{2+} and I^- concentrations in river, tap and mineral water samples and canned fish samples. The river water samples were filtered through a 0.45 µm membrane filter and then centrifuged at 4000 rpm for 5 min. The tap water and mineral water samples did not need to any pretreatment. Different Hg^{2+} and I^- concentrations were spiked and then analyzed with the proposed method.

One gram of canned fish in a 100-ml beaker was mixed with 15 ml of HNO_3 and 3 ml $HClO_4$. The mixture was heated for 10 min at 130 °C. Again, 2 ml H_2SO_4 and HNO_3 was added to it. The resulting solution was then heated to reach minimum volume and after cooling at room temperature, transferred into a 25 ml volumetric flask. The pH was adjusted to 9.0 by NaOH solution and diluted to mark by universal buffer (pH = 9). A 0.5 ml portion of the final solution obtained was analyzed for mercury content with the proposed method.

3. Result and discussion

3.1. Characterization of carbon dots

New water-soluble N/S co-doped CDs had three UV–vis absorption peaks at 215, 281and 342 nm (Fig. 2A). These peaks at 215 and 281 nm were related to electron transitions from π (or n) to π* of C=C, C=N, and C=O (Wang et al., 2010). The fluorescence spectra of the N/S co-doped CDs are shown in Fig. 2A. As shown, when the N/S co-doped CDs were excited at 416 nm, strong fluorescence emission at 523 nm was seen. The maximum fluorescence peak shifted from 523 to 550 nm with change of excitation wavelength from 416 to 496 nm, respectively (Fig. 2B).

The high resolution transmission electron microscopy (HRTEM) image of the N/S co-doped CDs was shown in Fig. 3A and the CDs size was about 10 nm. The surface functional groups of C-dots were characterized by FT-IR study (Fig. 3B). A broad peak at 3433 cm^{-1} was indicative of OH stretching. Absorption bands at 3329 and 3188 cm^{-1} were attributed to NH_2. The absorption bands at 3050, 1720, 1400–1600 and 1666 cm^{-1} were characteristics of the aromatic C-H stretching vibrations, C=O from acid carbocyclic, C-N and stretching vibration band of C=O indicate the formation of –CONR, respectively.