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Sensors and Actuators B: Chemical

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

Metal-ion-mediated fluorescent carbon dots for indirect detection of sulfide ions



SENSORS

ACTUATORS

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ARTICLE INFO

Article history: Received 13 October 2015 Received in revised form 15 February 2016 Accepted 17 February 2016 Available online 22 February 2016

Keywords: Carbon dots Fluorescence probe Sulfide detection Inner filter effect (IFE) Metal ion mediated probes

ABSTRACT

Because of the fact that carbon dots (CDs) generally do not show satisfied fluorescence activities, developing indirect approaches to use these nanomaterials as fluorescence probes is of increasing interest. In this study, two novel metal-ion-mediated fluorescent probes based on CDs for the indirect detection of sulfide ions are presented. The first probe was established using CDs in the presence of Hg^{2+} ions and utilized as a fluorescence-enhancement probe. In this case, Hg^{2+} efficiently quenched the fluorescence of the CDs and subsequent addition of sulfide ions removed them from the surface of CDs resulting in regenerating the fluorescence. This probe was used for detection of sulfide over a linear concentration range of $2-10 \,\mu$ M and a detection limit of $0.32 \,\mu$ M. In the second probe, CDs in the presence of Ag⁺ was utilized as a fluorescence-quenching probe. Here, the fluorescence intensity of CDs. The quenching process was found to be based on the inner filter effect (IFE) of the formed Ag₂S particles which absorb both the excitation wavelength and emission spectrum of CDs. This probe allowed detection of sulfide over the range of $1-100 \,\mu$ M and a detection limit of $0.43 \,\mu$ M. We validated the practicality of this probe for determination of sulfide ion concentration in tap and mineral waters with good recoveries.

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1. Introduction

Hydrogen sulfide and its ionization products bisulfide (HS⁻) and sulfide (S²⁻) ions frequently appear in many natural and waste waters, mainly owing to extensive use of sulfide in different fields like sulfur and sulfuric acid production, dyes and cosmetic manufacturing and, precipitation of metals in wastewater treatment [1]. Sulfide ions are also formed in anoxic waters by heterotrophic, microbial reduction of sulfate by anaerobic bacteria and by geochemical processes in hydrothermal systems. Sulfide is known as a toxic pollutant with [2] several harmful influences on the human health [3,4]. As example, high concentrations of sulfide anions cause various physiological and biochemical problems such as suffocation, personal distress, unconsciousness or even permanent brain damage [3]. Hydrogen sulfide is also extremely corrosive to most metals and can cause cracking of drill pipe and tubular goods

http://dx.doi.org/10.1016/j.snb.2016.02.075 0925-4005/© 2016 Elsevier B.V. All rights reserved. [5]. Therefore, detection of sulfide is of high importance from industrial, environmental and biological points of view.

Up to now, a variety of analytical methods for determination of sulfide in different media has been developed [6]. Among these methods, fluorescence-based sensors have recently attracted high attention due to offering higher sensitivity and a wide range of measurement techniques such as direct fluorescence measurement, energy transfer, and ratiometric methods. Correspondingly, several elegant displacement approaches [7–9] and reaction-based organic dye fluorescent probes [10–13] have been developed for sulfide detection.

Today, nanomaterials have been emerging as a simple and cost effective sensing strategy. On this subject, several types of semiconductor quantum dots (QDs) and other novel nanomaterials have been introduced as colorimetric or fluorescent probes for simple and rapid detection of sulfide ions [14–29]. For example, JamesáYang et al. [25] utilized glutathione capped silver nanoclusters for selective detection of sulfide with a limit of detection of 2 nM based on fluorescence quenching. Xiong et al. introduced Au-Ag core–shell nanoparticles as a sulfide sensor with a detection limit of 0.1 μ M in balk solution based on the induced shift in the absorption spectrum of nanoparticles in the presence of sulfide ions

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[26]. However, they dramatically improved the performance of the sensor via single-particle spectral imaging [27].

Fluorescent carbon dots (CDs) with a number of unique optical properties such as water solubility, biocompatibility, high quantum yield, and excellent optical and chemical stability, are established as promising substitutes of the heavy-metal-containing QDs. Consequently, more and more attention has been paid to these emerging nanomaterials with respect to their syntheses, properties, and applications [30]. Recently, many effort has been made to fabricate CDs-based fluorescent probes and sensors for chemical and biochemical sensing. Accordingly, some CDs based sensing system for sulfide detection have also been introduced [28,31,32]. For example, Yu et al. describe the first example of a CDs-based FRET ratiometric hydrogen sulfide sensor in aqueous solution by conjugating a naphthalimide azide derivative, as a sulfide sensitive probe, to the surface of CDs. The sensor worked based on the concept of H₂S-mediated reduction of azides to amines that resulted in FRET between CDs and the reduced azide ligands on the surface [31]. In a later report, they linked a Cu²⁺ sensitive-ligand on CDs surface. Here, the binding of Cu²⁺ ions to ligands quenched the fluorescence of CDs, and subsequent addition of sulfide extracted them from the system, resulting in fluorescence turn-on sensor for sulfide ions [32]. Wang et al. prepared a nanosilver-CDs composite to propose a new method for detection of sulfide using the electrochemiluminescence of a nanosilver-CDs composite in an aqueous solution [28].

Herein, we have developed two simple and fast responding fluorescence probe for indirect determination of sulfide ions based on the high fluorescent CDs. As shown in Scheme 1, the simple addition of Hg²⁺ and Ag⁺ ions to CDs solution were employed to develop two metal ion mediated fluorescence enhancement and quenching probes for sulfide detection. In the case of CD/Hg²⁺ system, the Hg²⁺ ions bound to the surface of the CDs and quenched their fluorescence, and sulfide ions removed them from the surface, resulting in free CDs and regenerating of the fluorescence. In the second strategy, the CDs in the presence of Ag⁺ were used to introduce CD/Ag⁺ as a turn-off probe for sulfide detection. In the presence of sulfide, fluorescence of CD/Ag⁺ probe significantly quenched based on the inner filter effect (IFE) of produced Ag₂S particles. The combination of strong binding of Ag⁺-sulfide and optical properties of Ag₂S resulted in higher selectivity of CD/Ag⁺ probe toward sulfide as it compared to the CD/Hg²⁺ probe that suffers from interfering of iodide and biothiols.

2. Material and methods

2.1. Materials

Ammonium bicarbonate, $AgNO_3$ and $Hg(NO_3)_2.H_2O$ were obtained from Merck and $Na_2S.9H_2O$ from Sigma–Aldrich. Fresh limes were purchased from the local market. Other routine chemicals were of analytical grade and used without further purification. Double-distilled water was used throughout all experiments.

2.2. Apparatus

Fluorescence measurements were performed using a Varian Cary Eclipse spectrofluorometer equipped with a xenon flash lamp. The slit widths of 5 nm were used as excitation and emission slit widths. All measurements were performed in a 1 cm quartz cell. UV–vis spectra were collected by an Agilent 8453 diode array spectrophotometer. Transmission electron microscopy (TEM) images were obtained on a Zeiss-EM10C transmission electron microscope with an accelerating voltage of 80 kV (K.N.Toosi University of Technology, Tehran, Iran).

2.3. Synthesis of CDs

The CDs were synthesized from lime juice through a one-pot hydrothermal method reported in our previous work [33]. Briefly, the fresh crude lime juice, was centrifuged at 6000 rpm for at least 30 min and supernatant was passed through a filter paper with slow filtration speed. 10 mL of the filtrate juice and 1.8 g ammonium bicarbonate, as nitrogen source, were transferred into a Teflonlined stainless steel autoclave and heated at 180 °C for 7 h. After heating, the autoclave was cooled to room temperature and the resulting dark solution was centrifuged at 10,000 rpm for 30 min to remove large and agglomerated particles. The final product solution was filtered through 0.2 μ m microporous membranes and dialyzed in a dialysis bag (retained molecular weight: 500 Da) for 6 days (deionized water was changed every 12 h).

2.4. Measurements

The typical detection measurements were carried out as follows. A desired volume of CDs from its stock solution was diluted to 3 mL using HEPES buffered solution (0.01 M, pH 7.4) in the quartz cell to achieve the final concentration of 1.0×10^{-5} mg/mL of CDs. Then, the suitable volumes of Ag⁺ or Hg²⁺ ion stock solutions were added into the quartz cell gradually by using a micropipette to generate the metal-ion-mediated CDs fluorescence probes. Fluorescence data were recorded at 5 min after the addition of the sulfide ions. The excitation wavelength was fixed at 340 nm and emission spectra were collected from 350 to 650 nm.

2.5. Real sample measurements

To assess the practical applicability of the present system, tap and mineral waters were analyzed as real samples. The water samples were first filtered through 0.2 μ m microporous membranes and then 5 mL of the water samples were diluted by HEPES buffered solution (0.01 M, pH 7.4) to 15 mL. Appropriate concentration of CDs (1.0×10^{-5} mg/mL) and Hg²⁺ (4μ M) or Ag⁺ (0.6 mM) were added to 3 mL of this solution and mixed thoroughly. Then, known amounts of S²⁻ were spiked into these water samples and the resulting mixtures were finally analyzed with the proposed methods and the percent recovery values were obtained.

3. Results and discussions

3.1. Optical properties of synthesized CDs

Several characterization of the prepared CDs were provided in our previous work [33], some of them being mentioned here. The TEM image of CDs shows nearly spherical nanoparticles with the average diameter of about 7.6 nm (Fig. 1a). Atomic force microscopy (AFM) images was also used to probe CDs (Fig. 1b). The AFM image shows that the heights of the CDs are in the range of 0.9–1.62 nm, with average heights of 1.2 nm. The XRD pattern of CDs (Fig. S1) displays a broad peak centered at about $2\theta = 30^\circ$, indicate a graphitic nature with highly disordered carbon atoms. In the FTIR spectra shown in Fig. 1c, the broad band at 3200-3550 cm⁻¹ and peaks at 2800-2950 cm⁻¹ are assigned to C-OH and N-H, and C-H stretching vibrations. The bending vibrations of the N-H groups could appear at $1400\,cm^{-1}$ and peaks at about 1600 and $1400\,cm^{-1}$ indicate the presence of C=O and C-NH-C (or C=C) groups, respectively and the band at around 1100 cm⁻¹ present the existence of C–O as hydroxyl, ester, epoxide or ether groups. The absorption and emission spectra of CDs are shown in Fig. 1d. As can be seen, CDs possess UV-vis absorption spectrum with a peak at 345 nm and a shoulder at 235 nm. According to the previous studies, these peaks could be attributed to π - π ^{*} and *n*- π ^{*} transitions of C=C and Download English Version:

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