



Easily synthesized carbon dots for determination of mercury(II) in water samples

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ABSTRACT

In this work, a simple thermal method was used to synthesize carbon dots from citric acid and glycine precursors. It was found that Hg(II) ions can selectively quench the fluorescence emission of these carbon dots. Subsequently, a sensor was designed and optimized for the determination of Hg(II) ions. The limit of detection and quantification of the sensor were found to be 38 and 112 ppb, respectively. The sensor showed good selectivity toward Hg(II) ions and was successfully used for the determination of Hg(II) ions in mineral water samples.

1. Introduction

Over the past two decades, more than a few types of quantum dots (QDs) with high quantum yield, tunable size, and—most importantly—excellent optical properties have emerged. These QDs have been used in applications such as bioimaging [1], cancer therapy [2], and designing of analytical sensors [3]. However, most of these QDs have been shown to be toxic, even in relatively low concentrations [4]. Moreover, compared to their properties in organic solvents, these QDs generally show inferior photophysical properties in water-based solutions; as a result, methods such as surface passivation and incorporation of protective shells have been proposed to overcome these shortcomings. But, such methods are usually time-consuming, elaborate, expensive, and may even reduce the QDs optical quality [5].

As one of the latest discovered quantum dots, Carbon dots (CDs)—also called fluorescent carbon dots (FCDs), carbon nanoparticles (CNPs) or carbon quantum dots (CQDs)—are becoming more and more popular in the recent years [6]. CDs show outstanding properties, such as high chemical stability and inertness, strong fluorescence emissions, low toxicity, environmental compatibility, and relatively low costs; thus, they have found numerous applications in fields like bioimaging [7, 8, 9], catalysis [10], drug delivery [11], and chemical sensing [12]. Several groups of chemicals have been successfully analyzed using CD-based sensors, ranging from bacteria [13], nucleic acids [14], and proteins [15], to small organic molecules [16, 17], pesticides [18, 19], explosives [20], drugs [21], and metal ions [22, 23, 24, 25].

Heavy metal ions are highly toxic to the environment and wildlife;

thus, they had long been at the center of medical and environmental researchers' attention [26]. Among all heavy metal ions, Hg^{2+} —on account of its high mobility, bioaccumulation ability, severe fetal and infant toxicity, and destructive effects on the central nervous system—is one of the most dangerous [27]. Despite its high toxicity, many industrial processes—e.g. electrolytic production of chlorine from saline, production of batteries, and etc.—use extensive amounts of mercury [28]. Thus, there is a high risk of mercury leakage and subsequent contamination of water resources in industrial areas. Consequently, it's crucial to monitor the water resources close to industrial areas for potential mercury contaminations [29].

A number of analytical techniques have hitherto used for detection of the Hg (II); examples including cold vapor atomic absorption spectroscopy (CV-AAS) [30], inductively coupled plasma optical emission spectroscopy (ICP-OES) [31], atomic emission spectroscopy (AES) [32], atomic fluorescence spectroscopy (AFS) [33] and several electrochemical techniques [34, 35]. These techniques—despite being quite valuable and well established—require sophisticated and expensive instruments, have elaborate procedures, and need experienced operators. Carbon dot based fluorescent assays are known to circumvent most of these drawbacks [36]; However, in many cases, CDs have multi-step and time-consuming synthesis procedures [37], need a final functionalization/passivation on their surface [38] or require utilization of sophisticated instruments for preparation [39]. Herein, a facile and one-pot method was used for the synthesis of CDs from glycine and citric acid precursors; these CDs was then used for determination of Hg(II) in mineral water samples.

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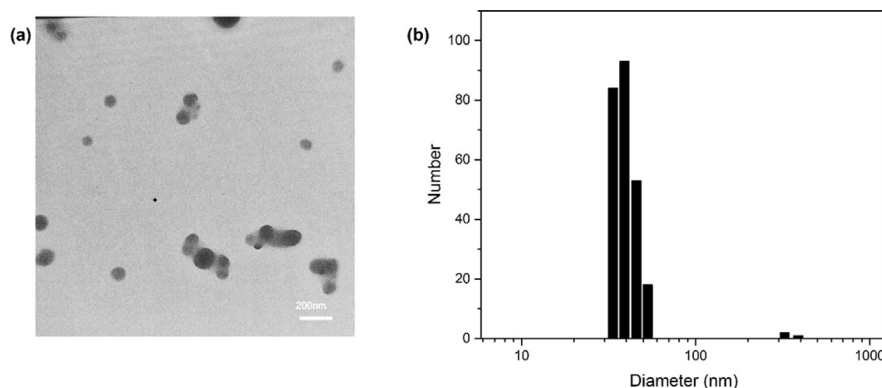


Fig. 1. (a) The TEM image of the glycine-citric acid based CDs which were synthesized at 180 °C (b) DLS Analysis shows CDs' size distribution with a mean size of 43.2 nm.

2. Experimental

2.1. Materials and instruments

Citric acid and glycine were purchased from Merck (Darmstadt, Germany). All of the solutions were prepared in double distilled water from the salts of $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, KCl , NaCl , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, respectively. All chemicals were of analytical grade.

The fluorescence spectra were recorded by a Perkin-Elmer LS-45 Fluorescence Spectrometer (PerkinElmer, Massachusetts, United States) with an excitation wavelength of 350 nm. Transmission electron microscopy (TEM) was carried out with a Philips CM-300 instrument (Thermo Fisher Scientific, Waltham, United States) using an acceleration voltage of 100 kV. A Zetasizer Nano S90 (Malvern Instruments, UK) instrument used for DLS analysis. Attenuated total reflection Fourier transform infrared spectroscopy (FT-IR) was obtained by a Bruker Equinox 55 instrument (Bruker Optics, Banner Lane, Coventry, United Kingdom). A Metrohm 692 digital pH-meter (Metrohm, Herisau, Switzerland) was used for pH measurements.

2.2. Preparation of CDs

The CDs were synthesized using a procedure similar to a recently reported thermal method [40]. Briefly, 7.68 g citric acid and 0.75 g glycine were dissolved in 30 mL water. The solution was then heated at 180 °C for 3 hours. The resulting solid was dissolved in 25 mL water and filtered through a filter paper. The filtrate was then dialyzed in a 3.5 kD dialysis tube for 24 hours. A rotary evaporator was used for evaporation of water and the final product obtained as a yellow powder and used throughout the experiment without further modification.

2.3. Detection of Hg(II)

A 20.0 ppm stock solution of CDs was prepared and used throughout the experiment. 100 μL of CDs solution and 100 μL of a phosphate buffer solution (0.04 M, pH = 7) was added to a vial. Different amounts of a 100 ppm Hg(II) solution was added to this mixture, and the final volume was adjusted to 4.0 mL by addition of water. After 15 Minutes, the fluorescence spectra were recorded. The reduction in the fluorescence emission intensity at 432 nm, compared to that of a blank solution, was followed as the analytical signal.

2.4. Real sample analysis

Certain amounts of a 100 ppm Hg(II) solution were spiked in 3.0 mL aliquots of a mineral water sample. 100 μL of the CDs solution and 100 μL of a phosphate buffer solution (0.04 M, pH = 7) was added to this mixture, and the final volume was adjusted to 4.0 mL. After 15 Minutes, the fluorescence spectra were recorded and the reduction of the fluorescence emission intensity at 432 nm, compared to that of a blank solution, was followed as the analytical signal.

3. Results and discussion

3.1. Characterization of synthesized CDs

Fig. 1a shows the transition electron microscopy image of the synthesized CDs. According to this TEM image, the obtained nanoparticles have a semispherical morphology. DLS analysis (Fig. 1b) shows that the CDs have a size distribution of 30–60 nm and a mean radius of 43.2 nm. CHN elemental analysis showed elemental weight percents of 42.2% carbon, 4.93% hydrogen, 14.07% nitrogen, and 38.8% oxygen; which shows that nitrogen is successfully doped into the CDs' structure.

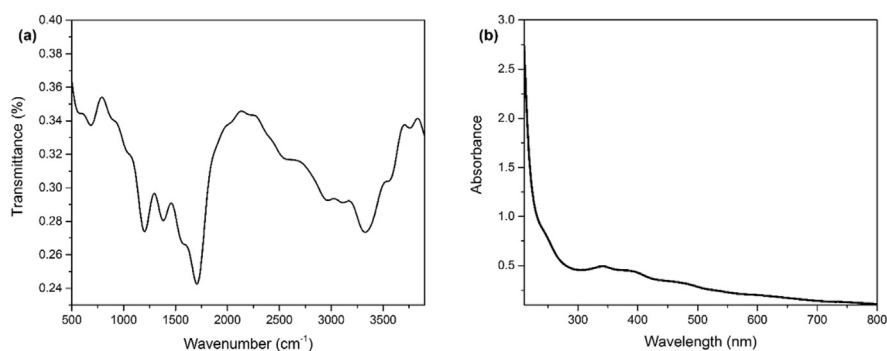


Fig. 2. (a) FT-IR spectrum of the synthesized CDs shows typical absorptions of C=O, NH, OH, and COOH functional groups (b) UV-Vis spectrum of the CDs shows absorptions at 220, 260 and 340 nm.

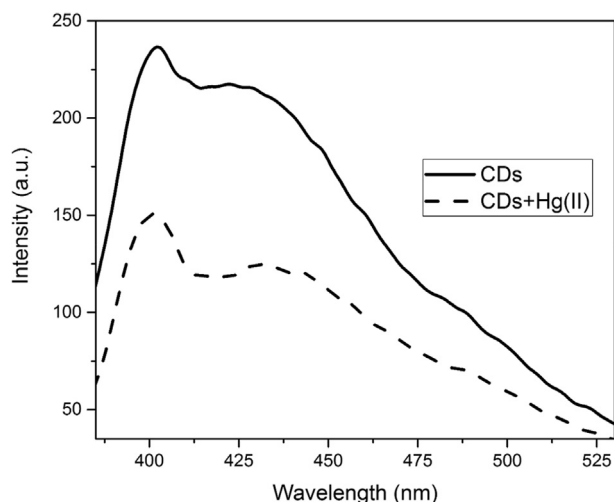


Fig. 3. Quenching of the CDs fluorescence emission in the presence of Hg(II) ions.

Fig. 2a shows the infrared spectrum of the solid CDs. The characteristic peak of C=O stretching vibration, which is a typical observation for CDs, is noticeable at 1713 cm^{-1} . Also noticeable is the broad absorption band around 3000 cm^{-1} which corresponds to the stretching of OH, NH, and carbocyclic acid functional groups; These functional groups typically exist on the surface of CDs [41]. UV-Vis Spectrum of the CDs (Fig. 2b) shows three main absorption bands at 220, 260, and 340 nm, which respectively correspond to carbon-carbon double bond's $\pi \rightarrow \pi^*$, carbonyl double bond's $n \rightarrow \pi^*$, and aromatic ring's $\pi \rightarrow \pi^*$ transitions [42, 43]. Under the normal light conditions, the CDs solution in water had a yellow-pale orange color. The CDs emitted blue light under UV light.

3.2. Quenching effect of Hg(II) ions

Fig. 3 shows the effect of mercury(II) on the intensity of the CDs fluorescence emission. Addition of Hg(II) ions to the aqueous solution of the CDs quenched their fluorescence emission. This quenching ability of Hg(II) ions lays the basis for the determination of mercury in this method. The magnitude of the reduction in fluorescence emission intensity was followed as the analytical signal.

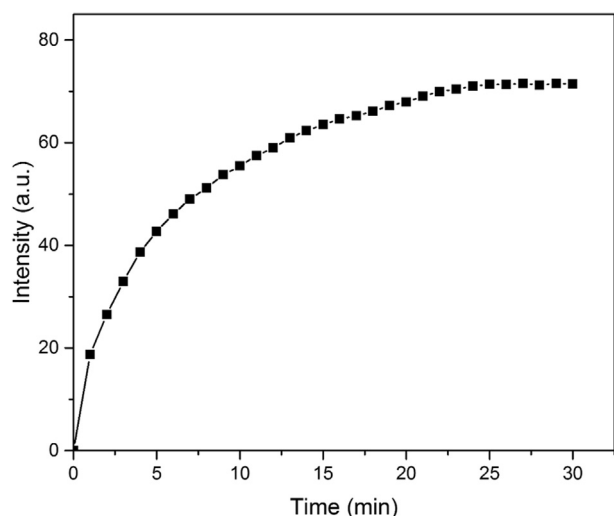


Fig. 4. Effect of time on the sensor's signal development.

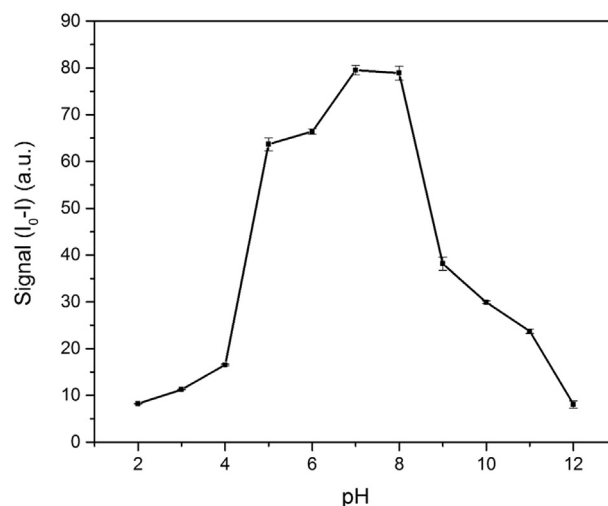


Fig. 5. Effect of pH on the analytical signal (I_0-I).

3.3. Kinetics study

In order to find the response time of the sensor, the kinetics of the quenching phenomena was studied. Fig. 4 shows the effect of time on the signal development of a 0.5 ppm CDs solution in the presences of 1.0 ppm Hg(II). It's apparent that as time passed the magnitude of the signal (I_0-I)—and consequently the sensitivity of the method—increased; so, to compromise both the analysis time and its sensitivity, 15 min was chosen as the spectra recording time.

3.4. Effect of pH

The solution's pH can affect the sensor's function in two ways. First, hydroxide ions can form coordination complexes with Hg(II) ions and change its quenching ability. Second, the CDs surface is full of amine, hydroxyl, and carboxylic acid functional groups; A change in the pH value can change the charge of these groups and consequently affect their attitude toward Hg(II) ions. Fig. 5 shows the effect of pH on the analytical signal's magnitude. The spectra were recorded at 15 min, and the concentration of CDs and Hg(II) ions were 0.50 and 1.0 ppm, respectively. In order to maximize the sensor's sensitivity, pH = 7 was chosen as the optimum pH value.

3.5. Quenching mechanism

Quenching mechanism is most probably of a nonradiative electron transfer type; where recombination of excitations is restrained by an electron transfer from the charged groups, mostly carboxylates on the surface of the CDs, to a Hg(II) ion in the solution [44, 45]. Such a mechanism also explains the pattern of signal change that's observed in Fig. 5. When pH is very low, there is a small number of negatively charged groups on the CDs' surface, thus their affinity toward Hg(II) ions is very low. As a result of these conditions, Hg(II) ions' ability to quench the fluorescence emission is very low. By increasing the pH, the number of ionized carboxylates on the CDs' surface rises; thus the CDs affinity toward the Hg(II) ions increases and more quenching is observed. On the other hand, when the pH is very high, hydroxide ions and the surface carboxylates compete for binding the Hg(II) ions and, less quenching is observed.

3.6. Calibration curve

Further studies revealed that under the optimal conditions (pH = 7 and 15 min incubation time) the concentration of Hg(II) ions could be

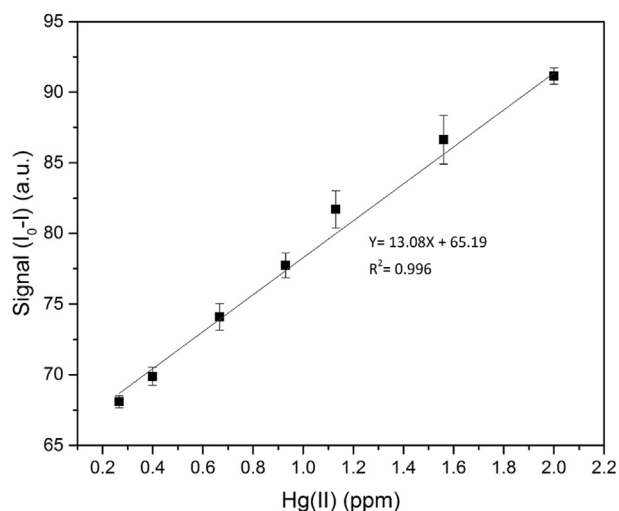


Fig. 6. Calibration curve of Hg(II) sensor under the optimal conditions (pH = 7, record time = 15 min).

linearly related to the extent of CDs' fluorescence quenching. Fig. 6 depicts the linear relationship between mercury's concentration and magnitude of quenching ($I_0 - I$), Where I_0 and I are the fluorescence intensity of the CDs' solution before and after addition of Hg(II),

Table 1

Figures of merit for some of the previously reported CDs based Hg(II) fluorescence sensors.

Report	LOD	Linear Range	Modification
Li et al. [46]	7.0 ppb	0–0.2 ppm	Thymine
Huang et al. [47]	16.7 ppb	0–6.0 ppm	None
Haiyan et al. [48]	0.094 ppb	0–0.01 ppm	CdSe quantum dots
Yan et al. [49]	5.6 ppb	0–0.1 ppm	Gold nanoclusters
Ghaedi et al. [50]	93 ppb	0.16–5.7 ppm	PVC
Liu et al. [51]	4.0 ppb	0.01–1.0 ppm	PEG ₂₀₀
Yan et al. [52]	49 ppb	0.8–3.6 ppm	None
Sharma et al. [53]	20 ppb	0.2–3.6 ppm	None

respectively. Considering the linear equation depicted in Fig. 6, the limit of detection (LOD, 3σ) and limit of quantification (LOQ, 10σ) of this method are 38 and 112 ppb, respectively. Also, the linear range of this sensor is 0.12–2.0 ppm. Table 1 shows the figures of merit for some of the previously reported CDs based Hg(II) fluorescence sensors; Considering its ease of synthesis and the fact that it doesn't need any post-synthesis modifications, the sensor that's proposed in this work has acceptable figures of merit.

3.7. Selectivity study

In addition to sensitivity, selectivity is another critical factor that shows the value of a sensing method. Thus, the effect of 13 other metal ions—in addition to mercury—on the signal was also studied. All of these experiments were carried out in the optimal conditions, and the concentration of all metallic ions was 2.0 μ M. Fig. 7 shows the results of this study. As Fig. 7 clearly demonstrates, the proposed analytical method has an acceptable selectivity toward Hg(II) ions.

3.8. Real sample analysis

In order to further demonstrate the applicability of the proposed method, a mineral water sample was analyzed. Table 2 summarizes the results of this study. As Table 2 shows, the obtained recovery values ranged from 97 to 105 percent, and the method was successfully used for the determination of mercury(II) in mineral water samples.

Table 2

Results of analyzing a mineral water sample that was spiked with Hg(II).

Spiked (ppm)	Found (ppm)	Recovery (%)	RSD (%)
0.60	0.63	105	2.16
1.00	0.97	97.0	3.27
1.40	1.43	102.1	2.3

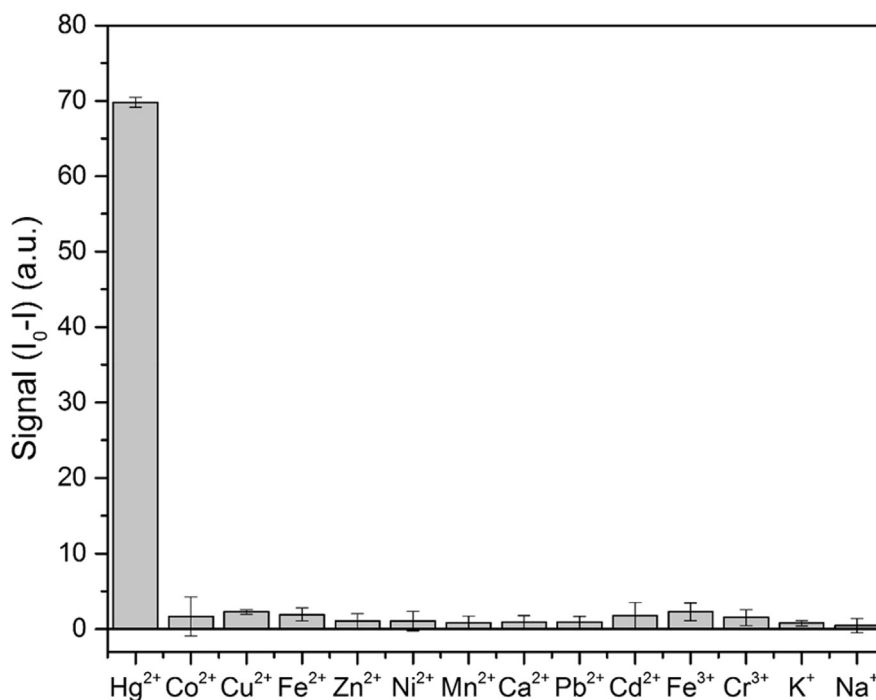


Fig. 7. Selectivity study of the proposed sensor, all of the experiments are carried out under the same optimal conditions and all metallic ion concentrations are 2.0 μ M.

4. Conclusion

In summary, blue emitting CDs were derived from citric acid and glycine by a facile thermal method. The synthesis method is simple and does not require any sophisticated instrument. Furthermore, there is no need for additional modification/passivation of the CDs. These CDs were successfully used for the determination of mercury in mineral water samples. The LOD(3 σ) and LOQ(10 σ) of the proposed method are 38 and 112 ppb, respectively. In addition, the proposed method has an acceptable selectivity toward Hg(II) ions.

Declarations

Author contribution statement

Ehsan Yahyazadeh, Farzaneh Shemirani: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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