### **RESEARCH ARTICLE**

## Simplistic hydrothermal synthesis approach for fabricating photoluminescent carbon dots and its potential application as an efficient sensor probe for toxic lead(II) ion detection

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Abstract The past decade has witnessed a variety of members of the carbon family along with exposure of carbon dots due to their magnificent properties in sensing. bioimaging, catalytic applications, biomedical fields, and so on. Herein, we report the simple hydrothermal method to fabricate photoluminescent doped carbon quantum dots for the detection of noxious lead(II) ions. Lead(II) ion is very venomous for both the environment and human health for which its detection is demanded area in the research field. The as-prepared carbon dots show excellent photostability, low toxicity and significant photoluminescence properties along with good water solubility. Along with these properties, carbon dots have a quantum vield of approximately 15%. In the practical field of application, these carbon dots have been used as sensing probes for the detection of lead(II) ions with a detection limit of 60 nmol·L<sup>-1</sup>. The fluorescence intensity of carbon dots was remarkably quenched in the presence of the lead(II) ion selectively among all the tested metal ions. Furthermore, we have studied the Stern-Volmer relationship for lead(II) quenching along with the explanation of the probable quenching mechanism. Ability of the doped carbon dots in heavy metal ions sensing in an environmental sample was demonstrated.

**Keywords** carbon dots, fluorescence, heavy metal sensing, practical application, photoluminescence

## 1 Introduction

In recent times, there have been many efficient techniques adopted for the determination of heavy metal ions which

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have drawn significant attention from the researchers. The development of new fluorescent nanomaterials with distinctive properties such as low toxicity and good fluorescence features has revealed considerable importance in the biomedical as well as energy applications fields [1,2]. In 2004, Xu et al. [3] accidentally discovered carbon dots (CDs) during the separation and purification of singlewalled carbon nanotubes. Later, Sun et al. [4-6] fabricated CDs with good fluorescence properties with distinctive advantageous properties. Not only does it have this fluorescence emission property, but there are also diverse features such as biocompatibility, good water solubility, low toxicity, and cost-effectiveness which make it unique from the other semiconductor quantum dots and commercial dyes. The important factor is that CDs can be used as a good replacement for semiconductor quantum dots although they have been widely studied [7–9]. Still, it has some serious drawbacks, such as high toxicity because of the use of heavy metals in their preparation method, whereas CDs have low toxicity, photobleaching resistance, non-blinking fluorescence, easy passivation, chemical stability and also good cellular compatibility [10]. So far, a varieties of synthesis methods such as microwave [11], hydrothermal [12], ultrasonic [13], laser ablation [4], have been adopted for the preparation of CDs. As compared to other new-fangled nanomaterials such as carbon nano tubes, fullerenes, nanodiamonds, and graphene, CDs manifest different superior properties like their isotropic shapes with ultrafine dimensions and varieties of surface functionalities that can be modified with different functional groups. Not only do these advantages come, but also along with them, CDs can be synthesized by a very cheap, rapid and facile synthetic procedure. CDs have potential applications in the fields of sensing [14,15], polymerization [16], bioimaging [17], drug delivery [18], tumor invasive biomarker detection [19], catalysis, optoelectronics, solar cells, printing inks, light-emitting diodes, ionic detection, cell labelling, and so on [20,21]. Due to these several advantages and properties with safety hazards from both environmental and biological points of view, CDs are always in the foreground of research activities for the synthesis of non-toxic and environmentally friendly alternatives with the most desirable properties [22,23].

The hydrothermal synthesis method has been widely used for the synthesis of conventional as well as advanced materials. It is defined as the synthesis procedure where the chemical reactions take place above the boiling point of water in an aqueous solution. The most important point is that we can conduct unique synthetic reactions, as well as compounds with very special properties and structure under very mild conditions, which cannot take place in the solid-state pathway because at high-temperature evaporation of reactant, occurs [24]. That's why we used this simple traditional hydrothermal method for the preparation of CDs.

Hydrothermal synthesis is referred to as a synthesis method where a chemical reaction occurs in an aqueous solution above the boiling point of water. In the solidstate reaction, diffusion of raw materials takes place at the interface whereas in hydrothermal the reaction occurs through the solution phase which is a better alternative and mild synthetic method than solid state reaction relatively at a lower temperature because in the solid state the evaporation of solvent occurs at very high temperature. Many compounds or materials which cannot be prepared by solid-state reaction due to their special or complex structure and property can be obtained by simple hydrothermal reaction. The nonideality and nonequilibrium are the most important part of any hydrothermal reaction. In this hydrothermal synthesis method, the aqueous solution is activated under high pressure as well as at high temperature. For the manufacture of most inorganic functional materials, the condensed state with particular morphology, nano and ultrafine powders, nanocrystalline state and single crystal hydrothermal method become extremely predominant methods due to their unique specificity and superiority [12].

Pb is a naturally occurring toxic metal in the earth's crust. Its worldwide use results in fatal environmental pollution and also remarkable health issues in the world. It is a very high poisonous element that affects almost every organ in the human body. Among all living bodies, Pb most affect the nervous system in both children and adult body. Living bodies become exposed to Pb through environmental sources mainly through drinking water [16]. That's why researchers show their anxious interests in the progress of unique nanoparticles for the detection of heavy metals in drinking water. Among the sensors, these luminescence-based sensors are more advantageous due to their unique sensitivity and specificity towards the metal, ease of preparation, and rapid response time [17].

In recent years CDs can be used in heavy metal ion detection due to their several advantageous properties such as low cost, portability, versatility. There is a wide variety of analytical techniques that are reported for detecting Pb ions namely atomic absorption spectrometry, atomic emission spectrometry, inductively coupled plasma mass spectrometry, and stripping voltammetry (SV) which are very efficient for identification of  $Pb^{2+}$ ion in water samples [16,17]. Though the abovementioned methods are very efficient still expensive difficult instrumentation, long testing period, involvement of hazardous chemicals with laborious chemical procedures along with the need for a professional operation restrict their application. Therefore, researchers developed many modern strategies that are easy to handle in the field of application. They are fluorescence, electrochemistry, surface-enhanced Raman scattering, and dynamic light scattering [18,19]. The development of these modern technologies opened up a new era for the detection of heavy metal ions by breaking through conventional analytical methods. Among these allmodern techniques, fluorescence has gained popularity due to its authenticity, ease of visualization, and sensitivity to the metals, as well as the fact that it is a simple and cost-effective method [20,21].

In this present work, we demonstrated a facile approach for the preparation of luminescence CDs from boric acid, citric acid, and cysteine by a simple hydrothermal method and its analysis for selective sensing of the poisonous  $Pb^{2+}$  ions which is a potential pollutant. As per the U.S. Environmental Protection Agency, the permissible amount of Pb in drinking water is 72 nmol·L<sup>-1</sup> [25]. This newly developed sensor probe showed good linearity with a limit of detection (LOD) as low as 60 nmol $\cdot$ L<sup>-1</sup> which is much lower than the permissible amount. When  $Pb^{2+}$  ion was added to the aqueous solution of CDs, the fluorescence intensity was drastically reduced, which we can explain through the electron transfer process. The Pb<sup>2+</sup> ion has a very strong affinity toward the carboxyl and hydroxyl groups present on the surface of CDs which results from fluorescence quenching via the inner filter mechanism. Though previously many explanations are reported for this Pb<sup>2+</sup> ion quenching herein we tried to explain in a different way with a new precursor for CD preparation relatively with high quantum yield (QY) along with low detection limit, which is a novelty in our work. Based on this quenching mechanism, an economically efficient, non-sophisticated nanoprobe was designed for the selective and sensitive detection of  $Pb^{2+}$  ion.

### 2 **Experimental**

#### 2.1 Materials

Boric acid (> 99.0%), citric acid (> 99.0%), and cysteine

(> 95%) were acquired from Sigma Aldrich, Germany and used without further treatment. Lead acetate, sodium chloride, cobalt chloride, barium chloride, aluminum nitrate, cadmium chloride, chromium nitrate, and calcium chloride were acquired from Merck, Germany, and many others and used without further purification and separation. All the other chemicals used in this experiment were of reagent grade.

#### 2.2 Synthesis and functionalization of CDs

The CDs were prepared from boric acid, citric acid, and cysteine through hydrothermal treatment. In brief, 1.5 g of citric acid, 0.6 g of boric acid, and 0.6 g of cysteine were dissolved in 15 mL of deionized water and stirred for 20 min to mix up these ingredients homogeneously. After that, the aqueous solution was transferred to a Teflon-lined steel autoclave and heated for 4 h at a constant temperature of 180 °C. A light yellow-colored product was obtained at the end of this reaction, which was then cooled down at room temperature. Then this obtained solution was poured into a beaker containing 20 mL of deionized water and the pH of the solution was adjusted to 7 using an aqueous NaOH (aq.) solution. Subsequently, this solution was centrifuged at 8000 r min<sup>-1</sup> for 20 min for separating the large carbonaceous particle through precipitation from it and the supernatant of clear dispersion of CDs was collected. After that, for the final purification method, the solution was dialyzed through a dialysis bag (molecular weight cut off: 1000 Da) for 3 d. The distilled water was changed every 6 h. In the end, 1.5 g of purified B, N, and S-doped CDs were obtained.

#### 2.3 Instrumentation of the experiment

The UV-visible absorption spectrum of the produced CDs was detected by a UV spectrometer (PerkinElmer, model-2 Singapore, Lambda35). Fourier transform infrared (FTIR) spectrum was obtained by an FTIR spectrophotometer (Perkin Elmer, model-Spectrum-2, Singapore) of the prepared CDs with a resolution of 4 cm<sup>-1</sup> and 16 scans within the range of 500–4000 cm<sup>-1</sup>. Fluorescence experiments of CDs aqueous solution were measured in a Fluoromax. The fluorescence lifetime was measured by a time-resolved fluorescence spectrometer, FL3-P-TCSPC (Horiba Jobin Jvon, France). The elemental composition of the prepared CDs was estimated by an energy dispersive X-ray study (EDX, INCA PentaFET x3, Oxford Instrument UK). The distribution of the composition was recorded by mapping in this X-ray The morphological structure and detailed study. microstructure of the CD were measured by a highresolution transmission electron microscopy (HRTEM) (JEOL, Japan operating voltage 200 kV with filament LaB6). An X-ray diffractometer (XRD, Panalytical High-Resolution XRD-I, PW 3040/60) was used to measure the

interlayer spacing and amorphous characteristics of CDs. The X-ray photoelectron spectroscopy (XPS) of the CDs was measured by a VG Scientific ESCALAB MK II spectrometer (UK) with an Mg K $\alpha$  excitation source (1253.6 eV) and a five-channeltron detection system.

#### 2.4 Analysis of fluorescence QY of CDs

The QY of the CDs was measured by using the equation given by:

$$Q_{x} = Q_{\rm std}(I_{x}/A_{x})(A_{\rm std}/I_{\rm std})(\eta_{2x}/\eta_{2\rm std}),$$
 (1)

here, Q represents the QY, I stands for the integrated fluorescence intensity of the fluorescent sample, A stands optical density measured by UV visible for spectrophotometer and n corresponds to the refractive index. The subscript x represents the unknown CDs and std refers to the standard reference. The QY of the prepared CDs can be measured by comparing the fluorescence emission intensity and optical density with the standard reference quinine sulfate. From the literature survey, it is known that the QY of the quinine sulfate is 54% when dissolved in 0.1 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> ( $\eta = 1.33$ ). This is the standard method for measuring the QY of unknown CDs sample. By using this standard technique we found that the QY of the as-prepared CDs was approximately 15%, which is higher than the other reported methods [26].

## 3 Results and discussion

3.1 Morphological, structural and compositional characterizations of as-prepared CDs

HRTEM was executed to understand the morphology and structure of the prepared CDs and the corresponding figures are depicted in Fig. 1. Figure 1(a) represents the HRTEM image, demonstrating that it is well dispersed in phase with its spherical shape without any apparent aggregation. HRTEM image of CDs was also shown in Fig. 1(b). CDs have a narrow particle size distribution, with an estimated average particle size of 2–3 nm, and the maximum population in this region is shown in the histogram (Fig. 1(a)).

The different types of functional groups and their respective linkages present on the surface of CDs were determined by using FTIR spectroscopy (Fig. 1(c)). The band at 3559 cm<sup>-1</sup> is attributed to the O–H and N–H stretching vibrations. The presence of a peak at 2952 cm<sup>-1</sup> refers to the C–H stretching vibration. The asymmetric and symmetric stretching vibrations of carboxylate groups give peaks at 1712 and 1390 cm<sup>-1</sup>, respectively. The band at 1058 cm<sup>-1</sup> can be ascribed due to the stretching vibration of the C–O–C bond [19]. The presence of such polar groups at the surface of the CDs



**Fig. 1** (a) TEM image of the prepared CDs and particle size distribution histogram in the inset; (b) HRTEM image of CDs showed spherical shape nature; (c) FTIR spectra of the CDs; (d) EDX data of the as-prepared CDs; (e) and (f) are the three-dimensional (3D) and two-dimensional (2D) atomic force microscopy (AFM) images of the CDs, respectively.

improves its water dispersibility and makes it more hydrophilic in nature. Thus, FTIR spectral data mainly demonstrated that an oxygen-rich functional group is present on the surface of CDs.

The EDX analysis (Fig. 1(d)) demonstrates the presence of C, O, B, S, and N. It also proves the presence of carbon in the nanodot structure. The silicon wafer was used for the atomic force microscopy image of the prepared CDs. The AFM image proves CDs with globular

shape along with their very good water dispersibility character. The 3D and 2D images of this AFM study of the prepared CDs are shown in Figs. 1(e) and 1(f).

The XPS spectrum of the as-prepared CDs is demonstrated in Fig. 2 with all element's deconvolution spectra. The XPS spectrum shows the peaks of C 1s, O 1s, N 1s, B 1s, and S 2p at 285, 531.2, 400.9, 194.2, and 163.2 eV, respectively. The convoluted short scan spectra of C 1s of CDs include three peaks at 287.7, 285.0, and



**Fig. 2** (a) XPS survey scan spectra of CDs (inset: elemental atomic percentage of CDs obtained from XPS scan); deconvoluted spectra of (b) C 1s, (c) N 1s, (d) O 1s, (e) S 2p, and (f) B 1s, respectively.

284.0 eV correspond to the O–C=O (sp<sup>2</sup>), C=O (sp<sup>2</sup>), C–N (sp<sup>3</sup>), and C–C (sp<sup>3</sup>), respectively [27,28]. The same is true for O 1s, with peaks at 533.5 and 531.6 assigned to C–O–C and C=O bonds, respectively. The N 1s peak includes 401.1 and 400.3 eV due to the N–H (sp<sup>3</sup>) and C–N (sp<sup>3</sup>) bonds, respectively [29]. The B 1s shows the deconvoluted peaks at 188.9, 191.5, and 192.4 due to the formation of BC<sub>3</sub>, BC<sub>2</sub>O, and BCO<sub>2</sub> bonds, respectively. Here, for S 2p the peaks are located at 162 and 168 eV for  $2p_{3/2}$  and  $2p_{1/2}$ , two spin-orbit states, respectively. The overall XPS data and the deconvolution spectra of all elements are shown in Fig. 2. The XPS analysis described the successful doping of B, N, and S in the CDs.

The XRD pattern picture and optical properties with stability of prepared CDs are manifested in Fig. 3. The XRD pattern (Fig. 3(a)) clearly demonstrates that the asprepared CDs possess an amorphous carbonaceous structure within them [30]. The pattern shows the peak at 24° which reveals that there is diffraction of X-rays occurring from the (002) plane of the amorphous carbon core of the graphitic structure with a d-spacing of 0.37 nm. This type of specific structure clearly substantiates the shedding graphitic structure of the material which conveys the more graphite-type character of the prepared carbon quantum dots (CQDs) [31,32].

#### 3.2 Optical characteristics

Under UV illumination, the aqueous solution of CDs shows fluorescence. The UV–visible absorption spectrum of the prepared CDs shows a maximum absorption peak

at 294 nm. This peak is specified to the  $\pi$ - $\pi$ \* electronic transition of the sp<sup>2</sup> skeleton structure (C=C and C=O bonds) [33,34]. A tail at 334 nm is also observed, which corresponds to the n- $\pi$ \* transition of the functional groups containing lone pairs over the CDs surface. The optical absorbance spectrum of CDs was shown in Fig. 3(b).

The foremost and distinctive characteristic of CDs is their fluorescence property which is very important and effective in several applications. Figure 3(c) shows that the emission wavelength of a CD solution in water has a peak at 420 nm, while the excitation wavelength is 350 nm. The excitation-dependent emissive profile of the prepared CDs shows a broad region of different wavelengths in the visible zone when excited with individual different wavelengths. The reason behind this excitation-dependent wavelength has already been discussed in the literature [35]. In CDs surface divergent types of functional groups are present which is mainly responsible for their excitation-dependent behaviour. Several functional groups present on the surface react with different energy traps, giving rise to different absorption and corresponding emission wavelength. Hence, they show excitation-dependent emission behaviour (Fig. 3(d)). In addition to this explanation, the different groups present on the CDs surface choose different photoluminesence decay pathways, as the functional groups are different; they react with different energy traps with the various exciting species. Irradiation by a specific wavelength a particular emissive trap on the surface of CDs dominants, and when the other excitation wavelengths are used, the other energy trap becomes



**Fig. 3** (a) XRD pattern of the as-prepared CDs; (b) UV–visible absorption spectra of CDs; (c) excitation and emission spectra of the CDs; (d) excitation dependent fluorescence behaviour of prepared CDs; (e) photostability done under UV exposure on the FL intensity of prepared CDs.

dominant than others. Thus, the photoluminescence behaviour of CDs is very much dependent on their surface topography morphology.

By using quinine sulphate in 0.1 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> (OY 54%) as a reference, the QY value of the prepared CDs was found to be 15% higher than other reported values of CDs [28]. The fluorescence-based CD can be employed for the identification of several heavy metals due to the presence of several functional groups on its surface which can bind respective metal ions, resulting in fluorescence quenching. Here, we studied the effect of pH on the fluorescence intensity of CDs within the range of 2-12 (Fig. S1, cf. Electronic Supplementary Material, ESM). From the spectra, it can be concluded that the intensity was relatively low in the lower pH range, whereas in the ranges of 6 to 10, the fluorescence intensity remains almost constant, and after that, it decreases again with increasing pH up to 12. In consideration of that result, we can conclude that the as-prepared CD is most stable within the pH range of 6 to 10 in which region the fluorescence intensity remains at its maximum. Therefore, we can carry out the experiment with CD solution by setting the pH  $\sim$ 7.0 where we got the maximum fluorescence intensity.

The stability factor of CDs is an important facet in their empirical field of application. The photostability of CDs was manifested through continuous UV light irradiation for up to 3 h. From Fig. 3(e), we can see that it shows almost the same fluorescence intensity throughout the whole time or it shows no considerable reduction in fluorescence intensity after 3 h of the experiment. From this, we can conclude that the as-prepared CD possesses good photostability. For further confirmation of this stability part, we checked it in salt condition. From the spectra (Fig. S2, cf. ESM) we observed that 1.5 mol· $L^{-1}$  NaCl did not exhibit much effect on the fluorescence intensity of CDs, referring to the outstanding stability in high ionic conditions.

## 3.2.1 Selective sensing of $Pb^{2+}$ ion constructed on fluorescence quenching mechanism

The fluorescence quenching spectra of CDs in presence of Pb<sup>2+</sup> ion with Stern–Volmer plot as well as result obtained from interference study of Pb<sup>2+</sup> ion on fluorescence quenching in presence of other metal ions are displayed in Fig. 4. The fluorescence-based selectivity test was done with different metal ions such as Cr(III), Cd(II), Ba(II), Co(II), Na(I), Al(III), Ca(II), Pb(II). Among these all-metal ions, CDs show selective and sensitive detection towards Pb<sup>2+</sup> based on fluorescence quenching property (Fig. 4(c)). For the sensitive study of any metal ion with CDs based on fluorescence quenching, there must be some useful mechanism between them. For an improved understanding of the quenching mechanisms, the fluorescence titration studies were performed by titrating the various concentrations of metal ions ranging from 0.002 to 100 micromolar of the prepared CDs (Fig. 4(a)). From the photoluminescence spectroscopy spectrums, it is clear that FL intensity changes with the changing concentration of Pb<sup>2+</sup> ions. The FL intensity of the aqueous CD solution decreases with increasing the concentration of these metal ions at the excitation wavelength of 350 nm. The quenching efficiency of prepared CDs was calculated as 30.82% upon the addition



**Fig. 4** (a) Fluorescence quenching spectra of CDs with increasing the concentration of  $Pb^{2+}$  ion; (b) relationship of  $F/F_0$  vs. concentration of  $Pb^{2+}$  ion, inset shows the linear relationship FL intensity and  $Pb^{2+}$  ion; (c) the difference in the fluorescence intensity of CDs of different metal ions in the excitation wavelength 350 nm; (d) the interference experiments study of CDs with  $Pb^{2+}$  along with other metal ions.

of the highest concentration (100  $\mu$ mol·L<sup>-1</sup>) of quencher Pb<sup>2+</sup> ion. By using the Stern–Volmer equation, the quenching mechanism becomes more understandable. The dynamic quenching originates from the collisional interaction between the quencher and fluorophore. In the case of this dynamic quenching, the Stern–Volmer equation is employed, which is given below [36]:

$$F_0/F = \tau_0/\tau = 1 + K_q \tau_0[Q], \qquad (2)$$

where  $F_0$  and F are the fluorescence intensities in the absence and presence of quencher, respectively.  $\tau_0$  and  $\tau$ are the fluorescence lifetime in the absence and presence of a quencher, respectively and  $K_q$  is the dynamic constant of the reaction and [Q] is the quencher concentration. In the case of static quenching, a nonfluorescence complex is formed between the fluorophore and the quencher. In static quenching, the used Stern–Volmer equation is given as follows:

$$F_0/F = 1 + K_{\rm SV}[Q],$$
 (3)

where  $K_{SV}$  is the association constant for the complex formation. Here, in the case of static quenching the

formed complex is non-fluorescent in nature and it eliminates the fraction of fluorophore, but the lifetime of the fluorophore is unperturbed here. Thus, in this case,  $\tau_0/\tau = 1$ , because the fluorophore lifetime is unperturbed. The dependence of the  $F/F_0$  on the concentration of Pb<sup>2+</sup> is shown in Fig. 4(b). The log value of  $F_0/F$  against the various concentration of Pb<sup>2+</sup> (Fig. 4(b)) shows that it does not fit the traditional linear Stern-Volmer plot. The plot deviates from the traditional plot which clearly indicates that both static and dynamic quenching occur for this prepared nanoprobe. From the plot, the correlation coefficient  $R^2$  value was determined, and it was found to be 0.9791. The high value of  $R^2$  indicates a good correlation between the plots. After that, we calculated the LOD using the standard deviation rule  $(LOD = 3\sigma/s, \sigma \text{ is the standard deviation of the blank})$ measurements, and s is the slope of the curve), which is found to be 60 nmol  $L^{-1}$  that is adequate compared to other reported methods [37,38]. The selectivity of this nanosensor was checked in the presence of various metal ions. It can be shown that (Fig. 6) among the all-metal

ions, the Pb<sup>2+</sup> ion shows immense quenching intensity towards CDs. The Pb<sup>2+</sup> ion has a very much high affinity towards the -OH and -COOH groups present on the surface of CQDs, That is why CDs can be used for a potential lead sensor [26,39]. UV-vis spectroscopy studies of CDs with quencher Pb2+ metal ion with different concentrations are also shown (Fig. S3, cf. ESM). The interference experiments study was also done on CDs with Pb2+ ions along with other metals (Fig. 4(d)). The addition of  $Pb^{2+}$  in the CDs quenched the fluorescence intensity in presence of other metal ions clearly revealing that the presence of other metals did not have any remarkable effect on the quenching property of the respective metal ion. Thus, the fabricated CDs showed a selective and discriminatory quenching effect on the  $Pb^{2+}$  ion in the aqueous medium.

# 3.2.2 Analysis of toxic $Pb^{2+}$ ions in the environmental sample

The result obtained from fluorescence quenching study of CDs in presence of Pb<sup>2+</sup> ion in environmental sample with Stern-Volmer plot is illustrated in Fig. 5. The magnificent sensitivity and selectivity performance of this nanoprobe has also been utilized for the detection of toxic  $Pb^{2+}$  ions in environmental samples. Therefore, we applied this prepared nanoprobe for the sensing of  $Pb^{2+}$ ions in river water. For evaluation of the sensing performance of  $Pb^{2+}$ , first, we collected the water sample from the local river, Kharagpur, West Bengal, India. Before starting the analysis, the river water sample was filtered through a 0.20 micromolar membrane and then centrifuged at 10000 r min<sup>-1</sup> for 30 min. After that, the obtained water sample was spiked with various concentrations of  $Pb^{2+}$ , and then evaluation was done by following the proposed mechanism. The fluorescence intensity of the CDs in presence of the river water containing lead ion drastically decreases with increasing the concentration of lead ions which is shown here in (Fig. 5(a)). The  $F/F_0$  relationship with the concentration of Pb<sup>2+</sup> ion is also shown here (Fig. 5(b)). Although there are many metals ions present in environmental water, this prepared nanoprobe can selectively detect the lead ion, which is very beneficial and advantageous.

#### 3.2.3 Elucidation of probable sensing mechanism

From the present inquisition analysis, it can be revealed that the turn-off phenomena fluorescence mechanism can be ascribed to a different pathway such as the electron transfer process, inner filter effect, non-radiative recombination, and ion binding interaction [40]. Though this type of quenching mechanism is well established for semiconductor quantum dots but does not have any direct information for CDs or in other words this does not have a very clear mechanism. Though both are more or less same in the size and the physicochemical properties are also the same. So, the explanation will be the same for both semiconductor dots and CDs [41].

The main plausible mechanism for fluorescence quenching by Pb<sup>2+</sup> ions is attributed to the electron transfer process. As the carboxyl and hydroxyl groups present on the surface of the CDs have a great affinity towards Pb<sup>2+</sup>, that's why these groups on the CD surface form chelate complexes with  $Pb^{2+}$  ions. As a result,  $Pb^{2+}$ is very much susceptible to forming complexes with CDs which can quench the fluorescence intensity efficiently [27]. Herein, no noteworthy shift in emission peak was observed suggesting the most possible mechanism is related to electron transfer [38]. Also, the selectivity of the  $Pb^{2+}$  ions can be ascribed to the high binding affinity between the vacant d-orbital of the Pb<sup>2+</sup> ions and the nitrogen functionalities present at the surface of the CDs compared to other metals. In general, the N atom of the amine functionalities contributes an electron pair to the unoccupied d-orbital of Pb ions via a nonradiative type of electron-transfer process, enabling more facile surface complexation than other metal ions. A similar kind of



Fig. 5 (a) FL quenching data of CDs of environmental water sample (river water) at different concentrations; (b) relationship between  $F/F_0$  vs. concentration of Pb<sup>2+</sup> ion, inset shows the dependence that is the linear relationship of  $\log(F_0/F)$  vs. concentration of Pb<sup>2+</sup> ion.

observation was also reported by Kumar et al. [42]. The fast electron transfer mechanism is prime for heavy metal, and since lead is a heavy metal, they show the effect of relativistic contraction. In this effect, the metal ion has the tendency to draw the electron toward its nucleus [38]. Non-radiative electron-hole recombination occurs via the electron transfer process in which the excited state electrons of CDs are dragged by the metal ion towards itself; once this takes place near the surface of the CDs, the original fluorescent process is disrupted, leading to decreased or no fluorescence. So, in the combination of all these processes, the quenching of fluorescence takes place. Moreover, we have studied the time-resolved photoluminescence spectra of the CDs before and after the addition of metal ions which are shown in Fig. 6. From the spectra, as shown in Figs. 6(a) and 6(b), the average lifetime for CD is found to be approximately 6.34 ns, and after the addition of the quencher metal ion, it is approximately 6.33 ns, confirming the result that static quenching occurs here through fluorescence quenching mechanism. This result further proves the quenching property of prepared CDs by the  $Pb^{2+}$  ion.

In Table 1, we have summarized different methods of Pb sensing within their detection limits, sensing mechanisms, as well as sensing probes based on fluorescence CDs. Several methods are available for the recognition of Pb ions, such as error number increase, absorbance reduction, fluorescence intensity increment,

as well as reduction. The CD-based luminescence sensors have excellent fluorescence properties, which are the lowcost method, ease of preparation and the most advantageous property is that they have fluorescence without any photobleaching and photo blinking. This chemosensor displays a remarkable change in optical, electronic, and magnetic properties when it gets attached to a particular guest part [27,28]. Among the sensors, luminescence chemosensors have distinctive advantageous properties like unique specificity, rapid response time along with excellent sensitivity beneficial for metal ion detection. This chemosensor also gives a cheap, easy, less time-consuming, and accurate way to find out what kind of metal ions are present [43].

## 4 Conclusions

In summary, we successfully prepared CDs from boric acid, citric acid, and cysteine for the first time using the facile hydrothermal method and utilized them as selective and sensitive chemosensors for Pb<sup>2+</sup> based on a turn-off fluorescence mechanism. HRTEM studies confirm the formation of spherical CDs with particle size ranges within 2–3 nm, along with FTIR and XPS results which indicate the presence of hydroxyl and carboxyl groups on the surface of prepared CDs. The presence of different



**Fig. 6** (a) Time resolved photoluminescence spectra of CDs and (b)  $CDs + Pb^{2+}$  ion.

| Table 1     Different types of evaluation results of $Pb^{2+}$ detection in real water and their detection | n limit |
|--|---------|
|--|---------|

| Serial No. | Sensing probe                  | Mechanism              | LOD                                    | Real water sample | Ref.      |
|------------|--------------------------------|------------------------|--|-------------------|-----------|
| 1          | Compact disc method            | Error number increase  | $10 \text{ nmol} \cdot \text{L}^{-1}$  | River water       | [44]      |
| 2          | Fluorescent gold nanoparticle  | Fluorescence increment | $10 \text{ nmol} \cdot \text{L}^{-1}$  | Drinking water    | [45]      |
| 3          | Gold nanoparticle              | Absorbance decrease    | $50 \text{ nmol} \cdot \text{L}^{-1}$  | Drinking water    | [46]      |
| 4          | Magnetic/colorimetric          | Fluorescence increase  | $50 \text{ nmol} \cdot \text{L}^{-1}$  | Drinking water    | [47]      |
| 5          | Colorimetric gold nanoparticle | Absorbance reduction   | $100 \text{ nmol} \cdot \text{L}^{-1}$ | Tap, river water  | [28]      |
| 6          | Fluorescent CD                 | Fluorescence quenching | $0.5 \ \mu mol \cdot L^{-1}$           | Drinking water    | [48]      |
| 7          | Fluorescent CD                 | Fluorescence quenching | $5.05 \ \mu mol \cdot L^{-1}$          | Drinking water    | [43]      |
| 8          | Fluorescent CD                 | Fluorescence quenching | $60 \text{ nmol} \cdot \text{L}^{-1}$  | River water       | This work |

functional groups leads to the formation of several surface traps resulting in the excellent fluorescence properties of CDs. The fabricated CDs displayed excellent optical properties, very low toxicity, and longlive photostability along with fluorescence property alternation upon the addition of  $Pb^{2+}$  ions in the aqueous medium. This result indicates that the as-prepared CDs can be applied for the detection of  $Pb^{2+}$  ions in the environmental water sample. The addition of  $Pb^{2+}$  in an aqueous solution transforms the fluorescence CDs into non-fluorescent or turn-off fluorescent materials. Good linearity was obtained between the concentrations of Pb<sup>2+</sup> ions and fluorescence signal within the range of 0.002 to 100  $\mu$ mol·L<sup>-1</sup> having a detection limit of 0.06  $\mu$ mol·L<sup>-1</sup>. The interference study also demonstrates the excellent sensitivity and selectivity toward Pb<sup>2+</sup> ions in the presence of other metal ions. A simple, fast, and economically favourable fluorescence quenching technique was demonstrated here by using these doped CDs as fluorescent nanosensors. Finally, it can be concluded that with all of these supremacies, this nanoprobe will be beneficial with low cost and unique sensitivity properties for the sensitive and selective detection of heavy metals in environmental samples.

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