Dual-Emissive Carbon Quantum Dot-Tb Nanocomposite as a Fluorescent Indicator for a Highly Selective Visual Detection of Hg(II) in Water

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ABSTRACT: We report very fast, green, and large-scale synthesis of amino-functionalized carbon quantum dots (CQDs) using a domestic microwave to investigate CQD-Tb-based dual emission for visual detection of toxic Hg²⁺. Citric acid and p-phenylenediamine are used as precursor materials to synthesize the CQD, which shows excitation-independent blue luminescence. To achieve the dual emission, Tb-containing CQD is synthesized in a very easy and cost-effective way. These dual-emissive fluorescent materials have been successfully used as a fluorescent indicator for visual detection of toxic Hg²⁺ metal ions. An instant color change from blue to green in the presence of a very low amount of Hg²⁺ under a UV lamp (λ_{ex} = 365 nm) is observed. The material is highly sensitive and selective toward detection of mercury ions in the presence of other metal ions. The photoluminescence quenching mechanism (photoinduced electron transfer process) has been explained using an electronic band diagram supported by zeta-potential and time-correlated single photon counting measurements.

1. INTRODUCTION

Fluorescent carbon quantum dots (CQDs) are a new class of carbon-based nanomaterials with a size of less than 10nm, having emerging potential applications. Carbon dots are more superior than other semiconductor nanomaterials because of their good optical properties, eco-friendliness, lower toxicity, simple synthetic method, low cost, good water solubility, and good photo stability. CQDs have a broad range of applications in many fields such as bioimaging,3–12 drug delivery,13,14 sensing,15–17 catalysis,18 super capacitor,19,20 security ink,21 optoelectronic,22 and so forth. During the last few years, CQDs have been used as sensor materials for sensing heavy toxic metal ions such as Hg²⁺, Pb²⁺, Cd²⁺, Cu²⁺, or explosive nitro aromatics.27–29 Fluorescent quantum dots with dual-emissive colors for visual detection of 2,4,6-trinitrotoluene (TNT) using a UV lamp were reported a few years back.30 A carbon dot-based dual-emission nanohybrid having ratiometric fluorescence has been used for biological imaging of Cu²⁺ ions.31 Very recently, a carbon dot–silicon nanoparticle hybrid has been used for detection of nanometric Cu²⁺ ions.32 Hg²⁺ is one of the most toxic heavy metal ions which seriously affect the human body and the environment. Inorganic mercury salt or organic mercury compound, especially methyl mercury, is the main pollutant of soil and water sources such as river, lakes, or groundwater. Industries and coal-burning power plants are also responsible for Hg pollution. From this contaminated water, mercury directly enters into the food chain, which causes harmful effects on the human body such as brain damage, kidney problem, Minamata disease, pink disease, muscle weakness, and so forth. Therefore, because of this serious problem, people have great concerns about the detection of Hg²⁺-contaminated areas. Different analytical methods are being used to detect Hg²⁺, such as selective cold vapor atomic spectrometry,33 atomic absorption spectrometry/atomic emission spectrometry,34 inductively coupled plasma mass spectrometry,35 and so forth. However, these methods are very selective and sensitive, but some impediments are still present in the sample preparation, such as lack of cost effectiveness and sophisticated instrumentation. Nowadays, luminescence properties of some semiconducting nanomaterials such as CdS,36 CdSe37 nanoparticles, functionalized graphene oxide,38 and MoS₂ quantum dots39 are used to detect Hg²⁺ and nitroaromatics. Carbon-based quantum dots are also used to detect metal ions because of very good water solubility, low toxicity, high quantum yield, and low-cost materials. Hetero atom-doped carbon dots for...
Hg\(^{2+}\) detection are also reported. However, a simple method of sample preparation with visual fluorescence detection of Hg\(^{2+}\) using dual emission is indeed an attractive area of research. Therefore, in the present work, we report a simple, green, and large-scale synthesis of amino-functionalized CQDs using a domestic microwave in which citric acid and \(p\)-phenylenediamine are used as precursor materials. As-synthesized carbon dots show excitation-independent blue luminescence with a high quantum yield of 44.5%. To investigate a carbon dot-based dual-emission nanocomposite for Hg\(^{2+}\) detection, we have synthesized Tb-containing CQD in a very easy and cost-effective way. These dual-emissive fluorescent materials have been successfully used as a fluorescent indicator for visual detection of toxic Hg\(^{2+}\) metal ions. These materials show an instant color change from blue to green in the presence of a very low amount of Hg\(^{2+}\) under a UV lamp (\(\lambda = 365\) nm). It shows very high sensitivity and selectivity toward the mercury ions in the presence of other metal ions with a lower detection limit of...
168.8 ppb. We have also explained the photoluminescence (PL) quenching mechanism [photoinduced electron transfer (PET) process] with an electronic band diagram supported by zeta-potential and time-correlated single photon counting (TCSPC) measurements. The details are reported in this paper.

2. RESULTS AND DISCUSSION

2.1. Material Characterization. High-resolution transmission electron microscopy (HRTEM) is used to investigate the morphology of as-synthesized CQDs. Figure 1a shows the transmission electron microscopy (TEM) image of CQDs. It is seen that the carbon dots are well dispersed with the size varying from 2 to 6 nm. The HRTEM (Figure S1) image of CQDs shows the crystalline nature with lattice spacing of 0.216 nm, suggesting the formation of CQDs.40 The size distribution curve of the as-synthesised carbon dots is shown in Figure 1b. The Gaussian-fitted curve shows the average size of quantum dots as 3.4 nm with a standard deviation of 0.16 nm.

The X-ray diffraction (XRD) pattern of the CQDs in Figure 1c shows that a broad diffraction peak appears at 30.1° with a poor hump at 19.4° corresponding to an interlayer spacing of 3.29 and 5.07 Å, respectively, suggesting that an amorphous structure is formed with more oxygen and a nitrogen-rich group. A broad maximum intense peak occurs at 44.2 nm when excited at 360 nm. This excitation-independent PL property is observed because of the functionalization of the amino-benzene group rather than the doping of the nitrogen atom in the carbon dots.41

The Fourier transform infrared (FT-IR) spectra of pure carbon dots and composite materials are shown in Figure 1d. Pure carbon dots show a broad absorption peak at 3100–3500 cm⁻¹ (3257 and 3430 cm⁻¹) for N–H and O–H bond stretching vibrations. The peaks at 1721 and 1880 cm⁻¹ correspond to stretching vibrations of C=O and C=N bonds, respectively. Peaks appear at 1198 and 1130 cm⁻¹ because of C–N and C–O stretching vibrations.42,43 The peak for COO⁻ stretching vibration appears at 1386 cm⁻¹ and C–O–C symmetric and asymmetric stretching vibrations occur at 1062 and 1302 cm⁻¹, respectively. The peak for the aromatic C–H bond appears in the range of 600–800 cm⁻¹. The CQD-Tb composite material also shows the same spectral nature as pure CQD but the peaks for C=O, C–O, COO⁻, C=N are shifted to 1710, 1112, 1405, and 1572 cm⁻¹, respectively.44,45 This indicates that Tb is coordinated with the functional group of carbon dots (low-range FT-IR spectra of both materials are shown in Supporting Information Figures S2 and S3).

The zeta-potential value of carbon dots is −17.5 mV, shown in Figure S4. It indicates that more electron-rich functional groups (−NH₂, −OH, −CONH₂) are present at the surface of the carbon dots.46

X-ray photoelectron spectroscopy (XPS) is used to understand the elemental composition of CQD-Tb composite materials. X-ray photoelectron spectra of the sample are presented in Figure 2a, which consist of four elements C 1s at 286 eV, N 1s at 400 eV, O 1s at 534 eV, and Tb 3d and 4d at 1242, 1274 and 148 eV, respectively, with the atomic percentage of C–58.59%, N–16.37%, O–20.75%, and Tb–4.29%. The high-resolution deconvoluted spectra of C 1s (Figure 2b) are assigned to four different peaks at 284.3, 285.7, 287.6, and 289.2 eV for C–C/C–C of graphitic carbon, C–N, C–O, and C=N bonds, respectively. In the deconvoluted spectra of N 1s, the peaks at 398.3, 399.6, and 400.7 eV are assigned to graphitic N, N–H (amino), and C–N bonds, respectively (Figure 2c). This indicates that the electron-rich amino group is present at the surface of the carbon dots. Figure 2d shows two separated peaks of O 1s at 531.8 and 535.5 eV assigned to C–OH and C–O=C bonds, respectively. Figure 2e,f shows the high-resolution spectra of Tb 3d and 4d. Peaks at 1241 and 1276 eV correspond to Tb 3d5/2 and 3d3/2 and 146.8 and 152.7 eV for Tb 4d.47 It is seen that the binding energy for Tb 4d of the CQD-Tb composite material decreases to 146.8 eV (ΔE = 4.8 eV) as compared to TbCl₃ (151.6 eV).47 However, the binding energies for C–O (531.8 eV) and C–OH (535.5 eV) of CQD-Tb increase by ΔE=0.7 eV and ΔE=3.2 eV as compared to the reported binding energy of NCOQD.45 This result suggested that the Tb³⁺ ion gets coordinated with the O-containing functional group of the carbon dots. Because of the coordination, the electron density of the O atom decreases and the Tb³⁺ ion increases as obtained from XPS data.

2.2. Optical Properties of Quantum Dots. UV–vis spectra of the solution containing CQDs shown in Figure S5 give two absorption peaks at 260 and 330 nm corresponding to π → π* transition of C≡C, C≡N and n → π* transition of C≡N and C≡O, respectively. The PL spectra of as-synthesized CQDs are shown in Figure 3a. With tuning excitation wavelength from 295 to 415 nm, an excitation-independent PL behavior is observed. The maximum intense peak occurs at 442 nm when excited at 360 nm. This excitation-independent PL property is observed because of the narrow distribution of particle size and a lesser number of defect states present in the quantum dots. This lower value of defect states created in the present quantum dots arises because of the functionalization of the amino-benzene group rather than the doping of the nitrogen atom in the carbon dots.48 The fluorescence quantum yield of the as-synthesized carbon dots is calculated to about 44.5% with respect to quinine sulfate as a reference.
The PL spectra of the CQD-Tb composite material (Figure 3b) show the excitation-independent PL properties but because of the attachment of the Tb$^{3+}$ ion on the carbon moiety through the oxygen and nitrogen atoms of the surface group of carbon dots, some additional narrow peaks appear at 490, 546, 587, and 622 nm. As a result of the attachment of Tb in the carbon dots’ moiety, another energy state ($^5$D$_4$) is generated near the valence band of the carbon dots and transition from this level to a lower level emits light in the green region. The emission bands at 490, 546, 587, and 622 nm correspond to $^5$D$_4$$\rightarrow$ $^7$F$_6$, $^5$D$_4$$\rightarrow$ $^7$F$_5$, $^5$D$_4$$\rightarrow$ $^7$F$_4$, and $^5$D$_4$$\rightarrow$ $^7$F$_3$ transition, respectively.49

### 2.3. Visual Detection of Hg$^{2+}$ in Aqueous Solution.

Our as-synthesized CQD-Tb composite materials have dual-emission bands in the blue and green regions. Therefore, we have successfully used this material for visual detection of Hg$^{2+}$ in aqueous solution using a hand UV lamp ($\lambda$ 365nm). To perform the quenching experiment, 4 mL of this material is taken in a quartz tube and PL spectra are recorded at 365 nm excitation after addition of 10 $\mu$L of 400 $\mu$M Hg$^{2+}$ solution, shown in Figure 4a. We have seen that after gradual addition of Hg$^{2+}$ solution, the color of the luminescent quantum dots changes from intense blue to bright green because of the gradual PL quenching corresponding to the 442 nm peak. It is seen that about 97% PL quenching (442 nm) occurs in the presence of only 3 ppm Hg$^{2+}$ in aqueous solution. Figure 4b shows the Commission Internationale de l’Eclairage (CIE) index with the color change from blue to green after addition of Hg$^{2+}$ at a 365 nm excitation. A digital photograph of the color change of the CQD-Tb solution in the presence of different concentrations of Hg$^{2+}$ under a UV lamp ($\lambda$365nm) is shown in Figure 4. Therefore, this material is highly sensitive for visual detection of Hg$^{2+}$ in aqueous solution.

Quenching efficiencies are analyzed by the Stern–Volmer plot using the following equation

$$I_0/I = K_{sv}[Q] + 1$$

where $I_0$ and $I$ are the fluorescence intensities of quantum dots in the presence and absence of Hg$^{2+}$, [Q] is the concentration of the Hg$^{2+}$ ion, and $K_{sv}$ is the quenching constant. From Figure 5a, it is seen that for a lower concentration range from 0.2 to 0.8 ppm, the curve rises linearly but with increasing the concentration of Hg$^{2+}$, the linearity gets deviated and rises exponentially. This nonlinearity $S$–$V$ curve is due to the coordination of the Hg$^{2+}$ ion with the surface functional groups (–NH$_2$, –OH, –CONH$_2$) of carbon dots. We have calculated the quenching constant ($K_{sv}$) for Hg$^{2+}$ as $1.59 \times 10^{5}$ M$^{-1}$ using the fitting equation $I_0/I - 1 = 0.268 + 0.0854 \exp(1.862 -$
The detection limit is calculated using a lower concentration of the linear portion of the curve and the detection limit for Hg\(^{2+}\) is found to be 168.8 ppb. Detailed calculations are shown in the Supporting Information (Figure S6). The detection limit and linear response range for Hg\(^{2+}\) detection are compared with other various reported methods and listed in Table 1. This lower detection limit and lower linear response range reveal the high sensitivity of CQD-Tb materials toward Hg\(^{2+}\) detection.

2.4. Selectivity Analysis. We have also performed the same PL quenching experiment in the presence of different metal ions such as Na\(^{+}\), Mg\(^{2+}\), Al\(^{3+}\), Fe\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\), Zn\(^{2+}\), and so forth. The presence of different metal ions with a 3 ppm concentration causes very poor PL quenching, but after addition of the same amount of Hg\(^{2+}\) in this mixture, significant PL quenching occurs. Therefore, this result indicates that our CQD-Tb composite material is highly selective toward the Hg\(^{2+}\) ion, it can be selectively detected in the presence of other metal ions, and the selectivity is about 90%. Figures 5b and 6a show the PL quenching efficiency of different individual metal ions and also in the presence of the Hg\(^{2+}\) ion.

2.5. PL Quenching Mechanism for Hg\(^{2+}\) Detection. It is seen that the material CQD-Tb is highly superior for selective Hg\(^{2+}\) detection. Initially, the presence of 0.2 ppm of Hg\(^{2+}\) causes 10% PL quenching. As Hg\(^{2+}\) has high affinity to coordinate with the N-atom, the Hg\(^{2+}\) ion is attached with the surface functional groups, viz., \(-\text{NH}_2\), \(-\text{CONH}_2\) and pyridinic nitrogen of quantum dots as shown in Scheme 1. This has also been verified by the zeta-potential value where the zeta potential of CQD-Tb changes from \(-15.1\) mV to \(-10.1\) mV after addition of Hg\(^{2+}\) (Figure 6b). This indicates that the surface negative charge of quantum dots decreases because of the attachment of Hg\(^{2+}\) with the surface functional group, as Hg\(^{2+}\) has a strong binding affinity with the N-atom of quantum dots. PET is possible from the electron-rich CQD-Tb to the electron-deficient Hg\(^{2+}\) ion, which is the possible explanation for this PL quenching behavior in the quantum dots.

To explain the PET mechanism, we have performed TCSPC measurements, from which we have understood the relative population of the excited states of the quantum dots in the presence and absence of Hg\(^{2+}\) ions. The average lifetime of CQD-Tb is obtained as 8.61 ns, but in the presence of 2 ppm of Hg\(^{2+}\), the average lifetime decreases to 6.21 ns as shown in Figure 7a. The average lifetime calculation is shown in the Supporting Information.
Supporting Information. This decrease in decay lifetime explains the PET process as because of the presence of electron-deficient Hg$^{2+}$, excited-state electrons are immediately transferred to the Hg$^{2+}$ state, causing a decrease in lifetime. Figure 7b shows the band diagram of probable PL quenching in the presence of Hg$^{2+}$ ions. Therefore, after gradual addition of Hg$^{2+}$ ions in the composite solution, the peak (blue) intensity at 442 nm decreases for the PET process, but this Hg$^{2+}$ ion does not affect the transition because the Tb ion and the emission color change from blue to green accordingly.

2.6. Detection of Hg$^{2+}$ in a Lake Water Sample. We performed the same fluorescence quenching experiment using lake water as lake water has different metal ions with different micro-organisms. We collected water from Rabindra Sarobar lake, Kolkata, India. This water was filtered using a Whatman filter paper to remove big particles if present. Using this water, we prepared a 400 μM Hg$^{2+}$ solution and performed a similar PL quenching experiment at pH 7. It is seen that the presence of a 3 ppm concentration of Hg$^{2+}$ causes 96% PL quenching. Therefore, our materials selectively detect Hg$^{2+}$ ions in lake water in the presence of different metal ions and also various micro-organisms. The experimental PL spectrum is shown in Figure S7 (Supporting Information).

3. CONCLUSIONS
In summary, we have explored a technique for rapid production in the gram scale of CQDs free from further purification using a domestic microwave. The as-synthesized CQD-Tb nanocomposite shows dual-emission peaks in the PL spectra. This dual-emissive CQD-Tb nanocomposite is highly selective to detect trace amounts of Hg$^{2+}$ ion in water and the change of fluorescence color from blue to green in is observed by the naked eye under a UV lamp in the presence of the Hg$^{2+}$ ion. This nanocomposite material shows a very high quenching efficiency of about 97% in the presence of 3 ppm Hg$^{2+}$ with a selectivity of about 97% with respect to other metal ions.

4. EXPERIMENTAL SECTION
4.1. Materials. Citric acid, mercury(II) acetate, cobalt(II) chloride hexahydrate, nickel(II) chloride hexahydrate, cadmium(II) chloride, copper(II) chloride dihydrate, iron(II) sulfate heptahydrate, manganese(II) acetate tetrahydrate, lead nitrate, zinc(II) sulfate heptahydrate, sodium chloride, and sodium hydroxide were purchased from Merck, India. 3-Phenylenediamine was purchased from Loba Chemie, and terbium(III) chloride and dialysis bags (1 kDa) were purchased from Sigma-Aldrich. All reagents were of analytical grade and used without further purification. Milli-Q water was used for all the experiments.

4.2. Synthesis of CQD. Citric acid (0.8 g) and 0.1 g of 3-phenylenediamine are dissolved in 1.2 mL Milli-Q water. The solution is heated in a domestic microwave oven at 800 W for 50 s. The solidified dark colored sample is then cooled to room temperature and dissolved in 20 mL of Milli-Q water and sonicated for 2 min. After sonication, a white glossy solid is separated from the solution because of coagulation of carbon dots in the acidic medium. The residue is filtered and washed with Milli-Q water and dried. Finally, the material is dissolved in 0.1 N alkaline water and used without further purification.

4.3. Synthesis of the CQD-Tb Composite. To synthesize Tb-containing CQD (CQD-Tb), 8 mg of carbon dots is dissolved in 4 mL of alkaline water. TbCl$_3$ (4.2 mg) is dissolved in 4 mL of carbon dot solution, and the pH is adjusted to pH 7 by using NaOH solution followed by addition of 2 mg of sodium citrate as shown in Scheme 2. The solution is then stirred at 80 °C for 3 h, then cooled to room temperature, and dialyzed through a 1 kDa dialysis bag overnight to remove all free ions.
4.4. Detection of Hg²⁺ Ions in the Water Sample.
CQD-Tb composite solution (4 mL, 0.1 mg/mL) is taken in a quartz tube. The PL spectrum is recorded at a 365 nm excitation upon gradual addition of 400 µM Hg²⁺ solution. This measurement is performed in a neutral pH 7 medium. The same experiment is performed using different metal ions for a selectivity test.

4.5. Characterizations. To characterize the carbon dots, TEM is carried out using a JEOL-2011 Transmission Electron Microscope. XRD spectra are studied using an X-ray diffractometer (RICH SEIFERT-XRD 3000P with an X-ray Generator-Cu, 10 kV, 10 mA, and wavelength 1.54 Å). FT-IR spectroscopy is performed by a NICOLET MAGNA IR 750 System. The XPS is investigated using an OMICRON-0571 system. The zeta-potential measurement was carried out using a Malvern instrument. The PL spectra are measured by a PTI fluoromax QM-400 spectrophotometer using a quartz tube with a 1 cm path length. The UV-vis absorption spectra are recorded using a Cary UV 5000 spectrophotometer. The time-resolved PL measurements of carbon dots are measured by an Edinburgh FLS980 spectrometer using a 375 nm picosecond diode laser.

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**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01159.

Quantum yield calculations of as-synthesized CQDs, detection limit calculations, UV-vis spectra of CQDs, zeta potential of CQDs, PL quenching experiments of a Hg²⁺ lake water sample, and the pH effect on the PL properties (PDF)

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**Notes**

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