Insight into the Modulation of Carbon-Dot Optical Sensing Attributes through a Reduction Pathway

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ABSTRACT: Oxidized/reduced carbon dots (CDs) with tunable optical features have emerged as a new class of CDs having a common “molecular origin” but different fluorescence (FL) behaviors. In the present work, using “banana peel” as a sole carbon source followed by doping with fluorine (F), boron (B), and nitrogen (N) over CDs, banana peel-derived carbon dots (BP-CDs) were synthesized using a well-known hydrothermal synthesis method. Moreover, as-synthesized BP-CDs were further reduced to “rBP-CDs” by NaBH₄. At post reduction, the FL performance (i.e., quantum yield) of rBP-CDs were found to be enhanced compared with the BP-CDs, along with variations in excitation and emission wavelengths. Interestingly, the optical sensing attributes of BP-CDs and rBP-CDs were varied, that is, BP-CDs selectively sense “Co²⁺” with a limit of detection (LOD) value of 180 nM, whereas rBP-CDs detected Co²⁺ (with an LOD value of 242 nM) as well as Hg²⁺ (with an LOD value of 190 nM). To the best of our knowledge, this work presents the very first report on the modulation of CDs’ sensing behavior after reduction. The modulation in the sensing behavior with the common carbon precursor and reduction paves a new possibility for exploring CDs for different commercial applications.

1. INTRODUCTION

Among the various classes of carbon nanomaterials, carbon dots (CDs) have emerged as one of the most exciting nanomaterials, owing to their small size, easy functionalization, and amazing fluorescence (FL) behavior. Carbon-based quantum dots have been established as one of the promising and known candidates in fluorescent sensing applications, enabling the replacement of many toxic quantum dots (QDs) and dyes, owing to their highly tunable luminous properties, water miscibility, and photostability. Since the discovery of QDs, a plethora of luminous quantum dots of semiconductors of the carbon family have been showcased in various sensing applications. So far, surface manipulation of CDs by passivation/functionalization and doping are the two prominent approaches to attain desirable surface features required for the anticipated application. In this respect, heteroatom doping/co-doping may be adopted to provide vivid photophysical features to the CDs as desired. For instance, nitrogen (N) doping, that is, introduction of an n-type impurity, can enrich the electron density in the skeletal structure. Meanwhile, boron (B) may serve the role of a p-type impurity. Co-doping of both these atoms therefore can fine-tune the optoelectronic features of carbon dots (CDs) such as delaying the radiative decay time. Fluorine (F) embellishment on the other hand may be an attractive strategy to increase photostability and biocompatibility.

On the other hand, functionalities such as epoxides, carboxyls, or amides may in fact act as trapping sites for electrons, preventing them from direct recombination with holes. Many groups have reported reduction as a useful strategy to modify the photoelectron transition channels by introducing electron-rich surface groups. For example, Shen et al. reported the reduced form of CDs showing an increase in the quantum yield of CDs upon reduction. Furthermore, the FL performance of reduced CDs was better than that of the original CDs, demonstrating the applicability of reduced CDs for bioimaging and as a biomarker. Similarly, Tiwari et al. reported reduction of CDs co-doped with N, B, and F as an effective strategy to achieve enhanced photophysical properties for bioimaging applications. Apparently, reducing CDs without affecting the size of CDs is an effective approach to augment the electron density at the CD surface. Though the earlier work has shed some light on the photophysical properties of reduced CDs, its applicability in the field of environmental sensing is yet to be explored properly.

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The above-said approaches to regulate FL emission features of CDs have direct implications for tracing water-born pollutants within the heavy-metal family. It is well documented that many of the heavy metals such as Hg$^{2+}$, As$^{3+}$, Cd$^{2+}$, Pb$^{2+}$, Co$^{2+}$, and Cr$^{3+}$/Cr$^{6+}$ serve grounds for fatal health conditions upon long-term exposure above a threshold level.$^{16-20}$ For instance, though the cobalt (Co) ion is known to be an essential micronutrient, the presence of Co in blood above permissible levels can make it a carcinogen and cause respiratory, circulatory, neurological, and allergic diseases.$^{21}$ The prime sources of Co(II) are industries, sewage, and mining,$^{22}$ and hence can directly enter into the aqua life and ultimately into the human body. While only a high concentration of Co is harmful to the ecosystem, the release of even trace amounts of other heavy metals like mercury (II) into water bodies can be fatal. Its release into the ecosystem may happen via either anthropogenic activities, namely, industrial indiscriminate dumping of industrial effluents, coal production, metal extraction, etc., or natural events like volcanic spurt and erosion of minerals deposits.$^{23}$ Mercury (Hg) contagion arises due to its high affinity with diverse biomolecules within the human body. The persistence of Hg in nature makes its tracking crucial to avoid a long-term threat.$^{24}$

Hitherto, numerous techniques have been utilized to detect/analyze Co$^{2+}$ and/or Hg$^{2+}$. Among them, highly sensitive and selective techniques such as inductively coupled plasma mass spectrometry (ICP-MS),$^{26}$ atomic absorption spectroscopy (AAS), and so on require complex preparation steps, experienced personnel, and installation of sophisticated instrumentation, making them less reliable for rapid and on-site detection of heavy-metal pollutants. To find out more feasible substitutes to these sophisticated techniques, enormous research has been devoted to alternative tools such as colorimetric detection,$^{27}$ resonance scattering assays,$^{28}$ surface-enhanced Raman scattering (SERS),$^{29}$ and electrochemical methods,$^{30}$ and so on. Nevertheless, a FL sensor renders much more flexibility in terms of simple instrumentation/operation, fast responses, multiple analyses, high sensitivity, and good selectivity with ample scopes to attune CDs as required. Furthermore, a wide range of cheaper sources with green synthesis routes such as hydrothermal methods have also been explored to date for making them more reliable in practical applications.$^{31,32}$

Though many attempts have already been made for sensing of a range of contaminants including heavy metals by differently functionalized CDs, very few works particularize a detailed investigation of physicochemical attributes of CDs responsible for their heavy-metal sensing behavior. Herein, a deliberate attempt has been made to understand how reduction could affect the surface functionalities for tuning useful photophysical attributes to be used for the speciation of heavy metals (Co$^{2+}$ and Hg$^{2+}$) and their dual sensing at trace levels. The CDs required for this study are prepared from banana peel extract, a waste biomass heavily dumped after consumption of edible fruits in household garbage and market places. Cellulose, hemicellulose, lignin, and pectin, which are the main components of banana peel, thus could be effectively used as major carbon sources for synthesizing CDs with varied surface functionalities.$^{33}$ Further, the viability of the said CD systems is tested for real samples. To the best of our knowledge, this work presents the very first report on the modulation of CDs’ sensing behavior after reduction.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterizations of BP-CDs and rBP-CDs. The B, N, and F-doped CDs were hydrothermally synthesized using banana peel as a green precursor and phenylboronic acid (C$_6$H$_7$BO$_2$), ethylenediamine (C$_2$H$_4$(NH$_2$)$_2$), and sodium fluoride (NaF) as doping agents for B, N, and F, respectively. The prepared banana peel-derived carbon dots (BP-CDs) were further reduced at room temperature using sodium borohydride (NaBH$_4$) to tune their photophysical properties and termed as rBP-CDs as shown in Scheme 1.

The optical properties of CDs were further altered through tri-elemental doping with B, N, and F. It is reported that the introduction of new trapped states within an energy level could
be achieved by N-doping, enabling a high yield of radiative recombination while suppressing non-radiative recombination, which contributes to an improved QY (quantum yield) and PL (photoluminescence).\textsuperscript{34,35}\textsuperscript{a} Boron, on the other hand, is integrated into CDs by covalent bonding, modifying the electronic structure and providing more active sites, resulting in CDs with good optical and electrical properties.\textsuperscript{36} Fluorine, being a highly electronegative element, will strongly attract the adjacent electron. This tends to increase the separation between negative and positive charges, thereby altering the electronic structure and excitation and emission characteristics of CDs.\textsuperscript{37,38}\textsuperscript{a} Therefore, heteroatom doping improves the photophysical and electronic properties.\textsuperscript{39,40}\textsuperscript{a} A detailed study on variations in photophysical, surface, and morphological properties between BP-CDs and rBP-CDs was done using spectroscopic and microscopic techniques. Furthermore, the applicability of both CDs was explored toward heavy-metal sensing.

2.1.1. Surface and Morphological Studies. For further assessing the surface functionalities upon reduction of original CDs, Fourier transform infrared (FTIR) spectra were acquired for BP-CDs (Figure 1a, black spectrum) and rBP-CDs (Figure 1a, red spectrum). Since the stretching vibrations in absorption of C=\text{C} and C=\text{O} are analogous, a small peak at 1636 cm\textsuperscript{-1} in BP-CDs is assigned for C=\text{C}/C=\text{O} stretching vibrations. However, this peak disappeared in the rBP-CD, signifying its effective reduction. The peak at 1048 cm\textsuperscript{-1} corresponds to C−O−C (epoxide ring), which is present in BP-CDs, and is evidently diminished in rBP-CDs.\textsuperscript{41} Apparently, stretching vibrations of O−H at 3440 cm\textsuperscript{-1} and C−H at 2930 cm\textsuperscript{-1} were found to be largely enhanced in the reduced form. A similar trend was observed in N−H bending vibrations, probably from an amide group, positioned at 1577 cm\textsuperscript{-1}.\textsuperscript{42,43}\textsuperscript{a} Both imply the emergence of a large number of surface O−H/N−H functionalities upon reduction.\textsuperscript{14,41}\textsuperscript{a} To further support the reduction of BP-CDs, X-ray photoelectron spectroscopy (XPS) analysis of both BP-CDs and rBP-CDs was performed (Figure 1b,c). The major peaks that appeared in the survey spectra from both samples were assigned to specific elemental orbitals, conferring binding energies of 192.8 eV (\text{B 1s}), 285.6 eV (\text{C 1s}), 399.2 eV (\text{N 1s}), 532.0 eV (\text{O 1s}), and 688.2 eV (\text{F 1s}).\textsuperscript{44,45}\textsuperscript{a} This confirmed doping of B, N, and F in the initial BP-CD sample to an extent of 0.1%, 1.4%, and 0.5%, respectively, as calculated from their respective peak areas. It is estimated that the percentage of doping remains roughly the same in rBP-CDs even after reduction. The C 1s high-resolution spectra of BP-CDs and rBP-CDs (Figure S2a,b) could be resolved into three peaks, centering at 284.5 eV (C=\text{C}), 285.9 eV (C=O/C−N/C−O−C), and 288.4 eV (C=\text{O}). A significant diminishing of the peak area at 288.4 hints the prominent hydrogenation of C=\text{O} functionalities upon reduction.\textsuperscript{46,47}\textsuperscript{a} The results obtained indicating the X-ray diffraction (XRD) patterns of both CDs have broad peaks at 23.5° and 23.2° for BP-CDs and rBP-CDs, respectively, as shown in Figure S3a,b. The broadness of these peaks may have arisen from the amorphous carbon phase of CDs.\textsuperscript{48}\textsuperscript{a} Furthermore, the Raman spectra of the BP-CD and rBP-CD were acquired (Figure S4a,b) to further confirm their physicochemical structures. It is evident that both Raman spectra display two broad peaks at approximately 1373 and 1588 cm\textsuperscript{-1}, which are attributed to the “disorder” D band (sp\textsuperscript{3}) and “crystalline” G band (sp\textsuperscript{2}), respectively. The I\textsubscript{D}/I\textsubscript{G} value calculated from integrated intensities of deconvoluted I\textsubscript{D} and I\textsubscript{G} bands\textsuperscript{49,50} for BP-CD was 0.9, and that of rBP-CD was 1.2. These values signify the introduction of more defects with a partially disordered crystal structure arising from the sp\textsuperscript{3} carbon core upon reduction of BP-CDs. Also, the observed broadness in the region of 1540−1690 cm\textsuperscript{-1} could be attributed to the attachment of other functional groups to the sp\textsuperscript{3} carbon atom of BP-CDs and rBP-CDs.\textsuperscript{51,52}\textsuperscript{a}

![Figure 1](https://doi.org/10.1021/acsomega.2c04766)
Furthermore, the morphology and shapes of CDs were obtained by high-resolution transmission electron microscopic (HR-TEM) imaging. The low-resolution TEM image of BP-CDs given in Figure 1d and its histogram (Figure 1e) describe the narrow size distribution of spherical BP-CDs with particle sizes of 1.8–3.4 nm. The corresponding selected area electron diffraction (SAED) pattern shows diffused rings as shown in Figure 1f, suggesting the amorphous nature of CDs. The HR-TEM image of BP-CDs in Figure 1g reveals the lattice fringes of the (002) plane with a d spacing of 0.33 nm. Similarly, the TEM image of rBP-CDs shown in Figure 1h indicates the presence of evenly dispersed spherical CDs. The size distribution histogram of rBP-CDs shows particle sizes in the range of 2.0–3.8 nm (Figure 1i). The diffused rings observed in the SAED pattern (Figure 1j) support the amorphous nature of rBP-CDs. The prominent lattice fringes seen in Figure 1k correspond to the (002) plane with a d spacing of 0.34 nm. TEM results were regarded as the primary determinant of the CD FL.

2.1.2. Photophysical Properties. To start with the optical behavior, the absorbance and emission of BP-CDs and rBP-CDs were studied using ultraviolet–visible (UV–vis) and FL spectrometers (Figure 2).

The BP-CDs showed two absorbance peaks as shown in Figure 2a. The main peak obtained at 288 nm can be attributed to the π–π* transition of the sp² carbon (C═C), which redshifted to 290 nm upon reduction as shown in Figure 2b. Meanwhile, a shoulder peak obtained at 370 nm, assigned to the n–π* transition of C═O, disappears after reduction due to a decrease in concentrations of carbonyl and epoxide. The FL spectra of BP-CDs at various excitation wavelengths (λex) from 290 to 390 nm are shown in Figure 2c. The BP-CDs exhibited an excitation-dependent emission behavior where they showed enhancement in the FL in the beginning followed by the subsequent decrease. This could have arisen from variable emissive states of CDs as reported earlier. The blue shift of 10 nm in λex of BP-CDs was observed after the reduction with an emission at 456 nm when excited at 360 nm. Interestingly, a blue shift in the FL maxima along with an increase in the FL intensity upon reduction of BP-CDs to rBP-CDs was observed due to the reduction of carbonyl and epoxide. Obviously, surface states were regarded as the primary determinant of the CD FL.

Moreover, an approximately 30% increase in the QY for BP-CDs was also observed upon reduction to rBP-CDs from 10.39% to 13.28%, respectively. After the reduction with NaBH₄, more defects were created when the carbonyl and epoxide groups were reduced to hydroxyl groups. The appearance of these defects infers the influx of the π electron density, and due to which, radiative recombination rates increased, which ultimately increased the QY and also led to an enhancement in the FL. The fluorescence lifetimes of BP-CDs and rBP-CDs were calculated through a time-correlated single-photon counting (TCSPC) technique as shown in Figure 2e. The BP-CDs and rBP-CDs were excited with a 334 nm diode laser, and the emissions were monitored at 506 and 456 nm, respectively. The FL decay curves fit well with two exponential decay functions. The change in the FL lifetime was observed from 3.48 to 3.81 ns for BP-CDs to rBP-CDs. The average lifetimes of BP-CDs and rBP-CDs were approximately the same. The FL radiative rate constant of the CDs was also computed with the help of eq 1

\[ K_{r} = \Phi_{r} / T_{r} \]  

where \( K_{r} \) is the FL radiative rate constant, \( \Phi_{r} \) is the QY of CDs, and \( T_{r} \) is the FL lifetime of CDs. The \( K_{r} \) values for BP-CDs and rBP-CDs were found to be \( 2.9 \times 10^7 \) and \( 3.4 \times 10^7 \) s⁻¹, respectively. As the value of \( K_{r} \) increased, the number of
radiative transition centers increased, while the number of non-radiative transition centers was reduced in rBP-CDs compared to BP-CDs, which is in accordance with the advanced unified defect model (AUDM) theory’s prediction. Notably, the increase in the PL and QY of rBP-CDs indicates that the FL intensity, emission wavelength (\(\lambda_{\text{em}}\)), and QY can be favorably tuned simply by the reduction of as-synthesized CDs. A consolidation of optical properties of BP-CDs and rBP-CDs is shown in Table 1 for comparing the changes that occurred in the optical properties of CDs before and after reduction.

### Table 1. Optical Properties of BP-CDs and rBP-CDs

| Sample | \(\lambda_{\text{ex}}\) (nm) | \(\lambda_{\text{em}}\) (nm) | \(\Phi\) (%) | \(\tau_{\text{ave}}\) (ns) |
|--------|----------------|----------------|---------|-------------|
| BP-CD  | 370            | 506            | 10.39   | 3.48        |
| rBP-CD | 360            | 456            | 13.28   | 3.81        |

#### 2.2. Study of the Fluorescence Stability

Since the fluorescent nature of these CDs has proven applications in the areas of optical sensing, validating the stability of their FL properties in different harsh conditions is crucial. Accordingly, the FL stability of BP-CDs and rBP-CDs was investigated under different conditions, and the results are summarized in Figure S5. The obtained results showed that both BP-CDs and rBP-CDs’ FL spectra were stable, suggesting their usefulness in sensing applications. Since the main aim of the present work was to check the FL sensing nature of the synthesized carbon dots (BP-CDs) and their reduced counterparts (rBP-CDs), the following subsections discuss the sensing attributes of BP-CDs in detail and followed by rBP-CDs. After having excellent photophysical properties for both BP-CDs and rBP-CDs, we were prompted to explore their sensing behavior.

#### 2.3. Selectivity Studies of BP-CDs and rBP-CDs for Metal Ions

The selectivity of BP-CDs and rBP-CDs toward various metal ions such as Co\(^{2+}\), Pb\(^{2+}\), K\(^{+}\), Al\(^{3+}\), Ca\(^{2+}\), Cr\(^{3+}\), Na\(^{+}\), Zn\(^{2+}\), Sn\(^{2+}\), Hg\(^{2+}\), Zr\(^{4+}\), Ni\(^{2+}\), PO\(_4\)\(^{3-}\), Se\(^{4-}\), I\(^{-}\), S\(^{2-}\), and vitamin B6 (Vit B6), l-tyrosine (l-tyr), histidine (His), and nicotinamide (Nico) was also checked. As represented in Figure S6a, Co\(^{2+}\) showed the strongest quenching effect on the FL intensity of BP-CDs among all the metal ions, amino acids, and Vit B6. Meanwhile, in the case of rBP-CDs, both Hg\(^{2+}\) and Co\(^{2+}\) showed profound quenching in the FL intensity (Figure S6b). The error bar on both the bar graphs indicates the uncertainty in the measurement, which is very low as shown in Figure S6a,b.

#### 2.4. Sensing Behavior of BP-CDs toward (Co\(^{2+}\))

As the next step, the fluorescent sensing behaviors of different metal ions were explored with the BP-CDs. It showed a sensing response toward Co\(^{2+}\). The sensitivity was monitored through quenching of the FL intensity of BP-CDs for Co\(^{2+}\) ions. After addition of 10 mM Co\(^{2+}\) with a concentration range of 50–1000 \(\mu\)M in an aqueous solution of BP-CDs, a visible decrease in the FL intensity was noticed as shown in Figure 3a. For the linearity study, \(F/F_0\) was plotted against the concentration of Co\(^{2+}\) (50–1000 \(\mu\)M) (Figure 3b). A good linear correlation is obtained for a 50–250 \(\mu\)M concentration range with a linear correlation coefficient, \(R^2 = 0.9986\) with error bars, which indicates the precision in measurements. The limit of detection (LOD) for BP-CDs with the Co\(^{2+}\) ion was calculated as 180 nM.

#### 2.5. Sensing Behavior of rBP-CDs toward Co\(^{2+}\) and Hg\(^{2+}\) Ions

Furthermore, the reduced form of CDs (rBP-CDs) was used to investigate their FL sensing behavior toward several metal ions, and these rBP-CDs were found to be specific toward sensing of Co\(^{2+}\) and Hg\(^{2+}\) at different concentrations. The sensitivity was monitored through quenching of the FL intensity of rBP-CDs toward Co\(^{2+}\) and Hg\(^{2+}\). The Co\(^{2+}\) and Hg\(^{2+}\) solutions in the concentration range of 50–1000 \(\mu\)M were added in the rBP-CDs separately and showed a turn-off behavior and decrease in the FL intensity of rBP-CDs as shown in Figure 3c,e, respectively. Superior correlations were obtained for Co\(^{2+}\) (Figure 3d; \(R^2\) value of 0.9942 within the 50–250 \(\mu\)M range) and Hg\(^{2+}\) (Figure 3f; \(R^2\) value of 0.9876 within the 50–200 \(\mu\)M range) with rBP-CDs with uncertainty in measurements indicated by error bars. The LODs for both Co\(^{2+}\) and Hg\(^{2+}\) ions were found to be 242 and 190 nM, respectively, with rBP-CDs.

#### 2.6. Competitive Selectivity Studies of BP-CDs and rBP-CDs for Metal Ions

Furthermore, competitive selectivities of BP-CDs and rBP-CDs were investigated by combining...
them with other anions, cations, amino acids, and Vit B6. Despite the presence of various foreign components, BP-CDs showed upright sensing behaviors for Co\(^{2+}\) and rBP-CDs showed a good sensing response toward Co\(^{2+}\) and Hg\(^{2+}\) (Figure S7a,b). The performance of the present CD system was found to be superior in comparison to the other earlier reported FL-based Co\(^{2+}\) and Hg\(^{2+}\) sensors. Moreover, the simple and environment-friendly synthesis of the current CDs makes them superior compared to the other sensors. (Tables S1 and S2). Our samples show good detection capabilities in a broad linear range as well as better LODs. Their applicability for real-sample analysis makes them valuable for practical applications. Therefore, the current work presents a facile preparation route to a multifaceted heavy-metal ion sensor with impressive sensitivity.

2.7. Real-Sample Analysis with BP-CDs. Furthermore, regular tap water, milk, vegetable juice, and a urine sample were utilized as solvents to assess the reliability of as-developed CDs as analytical tools for real-time examination. The abovementioned samples were tested with the as-prepared fluorescent probe. All of the samples were spiked with different concentrations of metal ions (i.e., Co\(^{2+}\) and Hg\(^{2+}\)), and recovery assays with rBP-CDs were performed (Tables S4 and S5). The recovery of the Co\(^{2+}\) ion was 96–97\%, and that of Hg\(^{2+}\) ions was 97–104\% with tap water. The recovery of Co\(^{2+}\) and Hg\(^{2+}\) ions in milk was found to be in the range of 93–94\% and 98–103\%, respectively. The recovery rate for Co\(^{2+}\) ions in vegetable juice was found to be 101–103\%, and for Hg\(^{2+}\), it is 99–102\%. The recovery of the Co\(^{2+}\) ion from a urine sample was 101–102\%, and that of Hg\(^{2+}\) ion was 101–102\%. Thus, the sensor’s utility in real-world applications was established by its high recovery rate as well as its precision and reliability. For comparison, a summary of reduced CDs explored so far for multifarious applications such as tuning of the FL property, catalysis, synthesis of nanoparticles, utilization as a drug carrier, and bioimaging agent is listed in Table S6, which indicates that the reduced form of CDs has been utilized for metal-ion sensing for the very first time.

2.8. Real-Sample Analysis with rBP-CDs. In addition, to check the reliability of as-developed rBP-CDs as an analytical tool for real-time examination, a similar fluorescent analysis was performed as discussed in the case of the non-reduced form. For this, the normal tap water, milk, vegetable juice, and urine sample were used as solvents. Metal ions were not present initially in any of the solutions as ensured by analyzing using the as-prepared fluorescent probe. All of the samples were spiked with different concentrations of metal ions (i.e., Co\(^{2+}\) and Hg\(^{2+}\)), and recovery assays with rBP-CDs were performed. The recovery of the Co\(^{2+}\) ion was 96–97\%, and that of Hg\(^{2+}\) ions was 97–104\% with tap water. The recovery of Co\(^{2+}\) and Hg\(^{2+}\) ions in milk was found to be in the range of 93–94\% and 98–103\%, respectively. The recovery rate for Co\(^{2+}\) ions in vegetable juice was found to be 101–103\%, and for Hg\(^{2+}\), it is 99–102\%. The recovery of the Co\(^{2+}\) ion from a urine sample was 101–102\%, and that of Hg\(^{2+}\) ion was 101–102\%. Thus, the sensor’s utility in real-world applications was established by its high recovery rate as well as its precision and reliability. For comparison, a summary of reduced CDs explored so far for multifarious applications such as tuning of the FL property, catalysis, synthesis of nanoparticles, utilization as a drug carrier, and bioimaging agent is listed in Table S6, which indicates that the reduced form of CDs has been utilized for metal-ion sensing for the very first time.

2.9. Mechanism of Sensing by BP-CDs and rBP-CD for Co\(^{2+}\) and Hg\(^{2+}\). The fluorescence sensing mechanism usually include static quenching, dynamic quenching, inner filter effect (IFE), and photoinduced electron transfer (PET). The plausible quenching mechanism in the case of BP-CDs and rBP-CDs toward metal ions has been revealed by UV–vis studies and the FL lifetime curve. According to the results shown in Figure S8a–c, the absorption spectrum of Co\(^{2+}\) and Hg\(^{2+}\) did not overlap with the excitation spectrum of BP-CDs and rBP-CDs, respectively. Therefore, Co\(^{2+}\) and Hg\(^{2+}\) ions were not able to shield the excitation light for BP-CDs and rBP-CDs, respectively, and also did not absorb the emission light of both the CDs. Therefore, the inner filter-effect quenching mechanism was not possible in both the cases. Moreover, the dynamic and PET mechanism is easily distinguished from the static quenching mechanism by TCSPC curves because the FL lifetime of fluorophore remains constant in the case of static quenching, but it gets altered in the case of dynamic quenching. Therefore, the FL lifetime decay curves for BP-CDs in the presence and absence of Co\(^{2+}\)
were recorded to point out the quenching phenomenon and are presented in Figure 4a. The decay curves with and without Co$^{2+}$ remain unaltered in both cases, which elucidate the static quenching with the ground-state complex formation as the plausible mechanism for Co$^{2+}$ ion sensing by BP-CDs. Further, the corresponding absorbance spectra were acquired to further confirm the sensing mechanism. As shown in Figure 4b, after addition of Co$^{2+}$ in BP-CDs, the peak of absorption at 288 nm was shifted to 358 nm, confirming that Co$^{2+}$ changes the electronic structure of BP-CDs by forming a non-fluorescent stable complex between the surface functional groups such as the carbonyl/pyridinyl N of BP-CDs and Co$^{2+}$. The gradual color change in the BP-CDs' colloid before and after addition of Co$^{2+}$ under visible and UV (365 nm) light was captured and is presented in digital photographs shown in Figure 4c, indicating the quenching of BP-CDs by Co$^{2+}$. The obtained results confirmed that the static quenching is the sole mechanism for Co$^{2+}$-induced FL quenching. Figure 4d illustrates the schematic of cobalt ion sensing (Figure 5a). The UV absorption spectra were obtained to further confirm the static mechanism. The absorbance peak at 290 nm in rBP-CDs was redshifted to 358 nm upon the addition of Co$^{2+}$, as shown in Figure 5b, suggesting the formation of a complex between the surface functional groups such as carbonyl/pyridinyl N groups of rBP-CDs and Co$^{2+}$. Additionally, the color change in the rBP-CD solution before and after addition of Co$^{2+}$ under visible and UV (365 nm) light was captured and is exhibited in digital images shown in Figure 5c, indicating the quenching of FL.

Likewise, with emphasis on further exploring the mechanism for Hg$^{2+}$ ion sensing by rBP-CDs probe, similar studies were carried out. The similar lifetime decay curves of rBP-CDs in the presence and absence of Hg$^{2+}$ with almost no change in their PL lifetime further confirm rBP-CDs undergoing a ground-state complex formation with static quenching as a possible mechanism (Figure 5d). Furthermore, the red shift in the absorbance peak of rBP-CDs from 290 to 313 nm (Figure 5e) suggested the formation of a ground-state complex between amine and hydroxyl surface functional groups of rBP-CDs and Hg$^{2+}$. The moderate change in color of rBP-CDs is depicted in Figure 5f in the presence and absence of Hg$^{2+}$.
under UV light (365 nm) and visible light, indicating the quenching in FL. Our above findings clearly show that rBP-CDs undergo static quenching with both Co\(^{2+}\) and Hg\(^{2+}\), which is further illustrated through the schematic representation in Figure 5g.

3. CONCLUSIONS

In conclusion, B, N, and F-doped carbon dots (BP-CDs) were synthesized by using banana peel as an economically viable carbon precursor. A simple reduction with NaBH\(_4\) resulted in reduced BP-CDs (rBP-CDs) with an enhanced QY, which tuned its optical properties. Interestingly, rBP-CDs also revealed similar compositions but with different optical features. A visible change in the sensing behavior was observed between the original BP-CDs and its reduced form (rBP-CDs). Surprisingly, rBP-CDs showed a dual-sensing behavior toward both Co\(^{2+}\) (LOD value of 242 nM) and Hg\(^{2+}\) (LOD value of 190 nM), whereas BP-CDs sensed only Co\(^{2+}\) (with an LOD value of 180 nM). Despite the variation in surface and optical features, both the CDs were showing a consistent QY and excellent stability under diverse harsh conditions such as of temperature, salinity, and pH. Furthermore, the present CD probes showed excellent detection ability of Hg\(^{2+}\) and Co\(^{2+}\) in various real samples such as milk, tap water, vegetable juice, and urine. Our results clearly highlight the importance of the above probes toward the fabrication of a new and efficient sensor for real-sample analysis. To the best of our knowledge, this is the first report in which a comparative study has been attempted toward a sensing application of both as-synthesized carbon dots and their reduced form as fluorescent probes. Our present study paves a new pathway for designing multiple sensors based on single carbon dots synthesized through tailoring surface states by a reduction method.

4. EXPERIMENTAL SECTION

4.1. Materials and Reagents. The purchasing of bananas (ripe bananas) was done in a local market. Ethylenediamine and sodium fluoride were procured from SRL chemicals. Phenylboronic acid and sodium borohydride were procured from Spectrochem. The various metal salts of Co\(^{2+}\), Pb\(^{2+}\), K\(^{+}\), Al\(^{3+}\), Ca\(^{2+}\), Cr\(^{3+}\), Na\(^{+}\), Zn\(^{2+}\), Sn\(^{2+}\), Hg\(^{2+}\), Zr\(^{4+}\), Ni\(^{2+}\), PO\(_4\)^{3-}, Se\(^{4+}\), I\(^{-}\), S\(^{2-}\), and vitamin B6 (Vit B6) and amino acids like L-tyrosine (L-tyr), histidine (His), and nicotinamide (Nico) were procured from SRL, Sigma-Aldrich, and Merck, and their details (including CAS numbers) are given in the Supporting Information. All the chemicals were utilized without any further purification. All the experiments were performed using deionized water (DI) obtained from Sartorius Milli-Q system (Germany).

4.2. Instrumentation. A Rigaku RINT smart lab 2500 V X-ray diffractometer with Cu Ka radiation (1.5406 Å) was used for performing X-ray diffraction (XRD). Raman spectra were recorded using a Horiba Jobin Yvon micro-Raman spectrometer with a 633 nm excitation laser with minimum power to avoid any laser-induced heating. Transmission electron micrographs (TEM), high-resolution TEM (HR-TEM) images, and SAED (selected area electron diffraction) of BP-CDs and rBP-CDs were captured in an FEI Tecnai 30 G2S-TWIN transmission electron microscope at an accelerating voltage of 300 kV. The SAED pattern was acquired to know the crystallinity of carbon dots. To know more about the atomic compositions and changes in chemical functionalities of CD samples, survey spectra and high-resolution spectra were recorded on a Thermoscientific NEXA Surface analyzer X-ray photoelectron spectrometer (XPS). A model 3000 Hyperion microscope with a Vertex 80 Fourier transform infrared (FTIR) system was used for recording FTIR spectra (4000–400 cm\(^{-1}\)). The UV–visible spectroscopic studies were conducted on a Varian UV–vis spectrophotometer ( Carry 100 Bio). The FL spectra of BP-CDs and rBP-CDs were obtained by using a Fluoromax-4 spectrophotometer (HORIBA Jobin Yvon, model FM100) with an excitation and emission slit width at 2 nm. FL lifetime studies were performed using time-correlated single-photon counting (TCSPC) on a HORIBA Jobin Yvon system of model Fluorocube-01-NL.

4.3. Synthesis of BP-CDs and rBP-CDs. BP-CDs were synthesized using a simple one-step hydrothermal method. The banana peels were cleaned with tap water and soaked in 500 mL of distilled water for 2 h. The obtained peels were then chopped and ground using a domestic mixer. The obtained thick extract was then diluted with 15 mL of distilled water. To this solution, 5 mL of ethylenediamine, sodium fluoride (0.8 M in 5 mL), and phenylboronic acid (0.4 M in 5 mL) was added. The obtained mixture was then sonicated for 15 min to get a homogeneous solution. This solution was poured into Teflon-lined autoclave and reacted hydrothermally at 180 °C for 12 h. The autoclave was cooled down to room temperature, and the obtained solution was centrifuged at 5000 rpm to remove any solid remains. The rBP-CDs were prepared from BP-CDs by adopting an earlier reported study. Briefly, 0.35 g of NaBH\(_4\) was added into BP-CDs and stirred for 6 h at room temperature to obtain the rBP-CDs. Any unwanted NaBH\(_4\) was removed by heating the solution at 80 °C.

4.4. Quantum Yield (QY) and Limit of Detection (LOD) Evaluation. The FL QY (Φ) of BP-CDs and rBP-CDs were calculated by the procedure stated in the manual Guide to Recording Fluorescence Quantum Yields by HORIBA Jobin Yvon IBH Ltd. and also the published procedure. The BP-CDs and rBP-CDs FL quantum yield was calculated by eq 2, keeping quinine sulfate (with 0.54 quantum yield) dissolved in 0.1 M H\(_2\)SO\(_4\) as a standard.

\[
Φ = \frac{Φ_s \times S_s \times A_s \times n_s^2}{S \times A \times n^2}
\]

(2)

Here, Φ, Φ\(_s\) and Φ\(_a\) stand for sample and standard QYs. S\(_s\) and S\(_a\) are the sample and standard slopes from the plot of the FL integrated intensity versus the absorbance shown in Figure S1, respectively. A\(_s\) and A\(_a\) are absorbance of the standard and the sample at λ\(_{ex}\) respectively. n\(_s\) and n\(_a\) are the solvent refractive index of the sample and standard, respectively. The LOD was calculated by eq 3.

\[
LOD = 3.3 \times (σ/S)
\]

(3)

where S is the slope of the calibration plot and σ is the error.

4.5. Selectivity Studies, Detection of Co\(^{2+}\) and Hg\(^{2+}\), and Interference Studies. The selectivity of BP-CDs toward various analytes such as, metal ions, amino acids, and Vit B6 (10mM) was determined by adding various metal ions, amino acids, and Vit B6 in 2 mL of the BP-CD solution bearing a concentration of 120 mg/mL, which was kept for 5 min in static conditions for equilibration, and same conditions were followed throughout the experiment, and then the FL spectra at λ\(_{ex}\) 370 nm were recorded. Then, for the sensitivity study, different concentrations of Co\(^{2+}\) solutions were added and the
FL spectra at $\lambda_{em}$ 370 nm were recorded by setting the maximum obtained intensity as a control ($I_0$). Next, the interference study was performed. For that purpose, the other metal ions, amino acids, and Vit B6 were mixed with BP-CDs. Then, in the same system, the Co$^{2+}$ solution was added. Then, the FL spectra were recorded. The concentration of the Co$^{2+}$ solution was kept as 10 mM. The selectivity study of rBP-CD toward different metal ions, amino acids, and Vit B6 solution of 10 mM was performed. The FL spectra for rBP-CDs were taken at $\lambda_{ex}$ 360 nm, and emission spectra were recorded. Further, for the sensitivity study, different concentrations of mercury ion and cobalt ion solutions were added to a 2 mL rBP-CDs solution of a 132 mg/mL concentration followed by FL measurements. The interference study was performed with rBP-CDs containing various metal ions, amino acids, and Vit B6. In this solution, the Hg$^{2+}$ was mixed and, at $\lambda_{ex}$ 360 nm, the emission spectrum was recorded. The 10 mM Hg$^{2+}$ solution was used for all interference studies. The selectivity and sensitivity experiments were performed three times, and the error bar was calculated. All the experiments were performed under identical conditions unless otherwise mentioned.

4.6. Detection of Analytes in Real Samples. All the samples (the tap water (corporation water, Simrol area, Madhya Pradesh), milk (Amul, India), vegetable juice (spinach, local market, Simrol, Madhya Pradesh), and urine (female, human)) were utilized after pre-treatment. These samples were spiked with different concentrations of metal ions, and sensing in the same conditions was performed by following the procedure stated in the previous section, and recovery was calculated. All the samples were utilized after pre-treatment. The sensors’ (BP-CD and rBP-CD) efficiency were studied by spiking the real samples with 20, 40, and 60 μM metal ion concentrations as shown in Tables S3–S5. The BP-CDs were added to prepared real samples spiked with Co$^{2+}$ and rBP-CDs to samples spiked with Co$^{2+}$ and Hg$^{2+}$. The FL spectra at $\lambda_{em}$ = 370 and 360 nm for BP-CD and rBP-CD, respectively, were recorded, and recoveries were calculated.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsomega.2c04766.

Measurements of the quantum yield of BP-CDs and rBP-CDs, powder X-ray diffraction pattern of BP-CDs and rBP-CDs, Raman spectra of BP-CD and rBP-CD, deconvoluted C 1s spectra of BP-CDs and rBP-CDs, stability test of BP-CDs and rBP-CDs under various conditions such as NaCl, pH, and temperature, FL spectra of BP-CD and rBP-CD upon addition of various interference metal ions, performance comparison table of various FL-based Co$^{2+}$ and Hg$^{2+}$ ion sensors, real sample spiked with Co$^{2+}$ and Hg$^{2+}$ analyzed through BP-CDs and rBP-CDs, and comparison table of carbon dots and their reduced form for various applications (PDF)

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Notes

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