Facile Conversion of Toxic Cigarette Butts to N,S-Codoped Carbon Dots and Their Application in Fluorescent Film, Security Ink, Bioimaging, Sensing and Logic Gate Operation

Rajkumar Bandi,† Neela Priya Devulapalli,† Ramakrishna Dadigala, ‡ Bhagavanth Reddy Gangapuram,†,§ and Veerabhadram Guttena*†,§

†Department of Chemistry, Osmania University, Hyderabad 500007, Telangana, India
‡Environmental Consultancy Division, Ramky Enviro Services Private Limited, Ramky Grandiose, Gachibowli, Hyderabad 500032, India
§Department of Chemistry, PG Center Wanaparthy, Palamuru University, Mahabubnagar 509001, Telangana, India

Supporting Information

ABSTRACT: The present work is emphasized on converting toxic cigarette butts (CBs) into highly fluorescent N,S-codoped carbon dots by a facile hydrothermal approach and exploring their multiple applications. The as-produced carbon dots (CBCDs) exhibited bright and stable fluorescence with a quantum yield of 26% and used as a label-free probe for “on-off-on” sequential detection of Fe³⁺ and ascorbic acid (AA). The fluorescence of CBCDs can be significantly quenched by Fe³⁺ ions through static quenching and restored upon the subsequent addition of AA due to the reduction of Fe³⁺ to Fe²⁺ by AA. This nanoprobe presented great selectivity and excellent sensitivity to Fe³⁺ and AA with a detection limit of 0.13 and 0.2 μM, respectively. Furthermore, the nanoprobe was extended to biosystem (intracellular detection) and successfully applied for the detection of Fe³⁺ in real water (tap, bore, and pond) and AA in biological samples (human urine and serum). In addition, we have constructed an IMPLICATION logic gate based on these unique sensing characteristics. The “visible−invisible” and “UV−visible” property explored their use as invisible ink for security applications. Furthermore, highly photostable fluorescent polymer films were prepared by incorporating CBCDs in poly(vinyl alcohol). It is anticipated that the strong and stable fluorescence emission nature of these films might find direct or indirect applications in various optical/optoelectronic devices, ranging from fluorescent displays to light-emitting diodes.

INTRODUCTION

One of the major goals of United Nations Development Programme 2030 is responsible consumption and production of resources. This can be achieved only by efficient management of available resources and proper disposal of toxic waste and pollutants. According to a recent report given by the World Health Organization (WHO 2017), cigarette butts (CBs) and other tobacco wastes make up the major number of individual pieces of litter in the world accounting to more than 40% of all items collected during urban cleanups.1 These butts are washed down by drains and eventually make their way to lakes, rivers, and oceans. Ocean Conservancy also reported similar results in this regard. The present work is emphasized on converting toxic cigarette butts (CBs) into highly fluorescent N,S-codoped carbon dots by a facile hydrothermal approach and exploring their multiple applications. The as-produced carbon dots (CBCDs) exhibited bright and stable fluorescence with a quantum yield of 26% and used as a label-free probe for “on-off-on” sequential detection of Fe³⁺ and ascorbic acid (AA). The fluorescence of CBCDs can be significantly quenched by Fe³⁺ ions through static quenching and restored upon the subsequent addition of AA due to the reduction of Fe³⁺ to Fe²⁺ by AA. This nanoprobe presented great selectivity and excellent sensitivity to Fe³⁺ and AA with a detection limit of 0.13 and 0.2 μM, respectively. Furthermore, the nanoprobe was extended to biosystem (intracellular detection) and successfully applied for the detection of Fe³⁺ in real water (tap, bore, and pond) and AA in biological samples (human urine and serum). In addition, we have constructed an IMPLICATION logic gate based on these unique sensing characteristics. The “visible−invisible” and “UV−visible” property explored their use as invisible ink for security applications. Furthermore, highly photostable fluorescent polymer films were prepared by incorporating CBCDs in poly(vinyl alcohol). It is anticipated that the strong and stable fluorescence emission nature of these films might find direct or indirect applications in various optical/optoelectronic devices, ranging from fluorescent displays to light-emitting diodes.
carbon dots (CDs) from cigarette filters and their application for fluorescence detection of Sudan I. However, sufficient characterization data was not presented (chemical composition of formed CDs is not studied) and the possible formation mechanism of CDs (how the water-insoluble cellulose acetate fibers are converted to water-soluble CDs) was not explained.

Fluorescent CDs are a new member of nanocarbon family that comprise discrete, quasi-spherical nanoparticles with sizes below 10 nm. After their serendipitous discovery from carbon nanotubes, they have gained ever-increasing attention due to their fascinating properties like unique optical properties, multiple functional groups, excellent biocompatibility, and chemical and photostability. They are considered as promising alternatives to quantum dots and are advocated for diversified applications such as sensing, bioimaging, optoelectronic conversion, visible-light-activated bactericide, fingerprint detection, dye degradation, solar cells, printing inks, and gene delivery.

Preparation methods of CDs reported so far can broadly be grouped into either top-down or bottom-up. The top-down approach involves the breakdown of bulk carbon sources like graphite, carbon nanotubes, and nanodiamonds into fluorescent CDs by employing techniques like arc discharge, laser ablation, chemical oxidation in strong acid, and electrochemical synthesis. Conversely, in the bottom-up approach, the CDs are formed from molecular precursors by applying solvothermal/hydrothermal methods, ultrasound/microwave treatments, or simple thermal combustion. Although a large variety of techniques and starting materials were employed for the production of CDs, the demand for the sustainable synthetic routes that adhere to the principles of green chemistry is still high. To fulfill this requirement, researchers have explored the use of waste materials like food waste, agriculture waste, waste paper, waste frying oil, etc. as precursors. However, the fluorescence quantum yields (QYs) of the as-produced CDs are less than 10%, limiting the range of their practical applications. Hence, there is a great need of developing facile methods for the large-scale utilization of waste resources toward the production of highly fluorescent CDs.

On the other hand, doping CDs with nonmetals such as N, S, B, and P received a great scientific attention as it can offer CDs with improved properties like resistance to self-quenching, enhanced fluorescence QY, and sensing selectivity. Recently, co-doping with multiple heteroatoms especially N and S has gained extensive consideration because of the improved efficiency resulting from the synergistic effect of the doped N and S atoms.

In the present work, we explored the use of CBs as source material for the production of highly fluorescent N and S-codoped CDs. The as-produced CDs (CBCDs) were systematically characterized by various analytical techniques, and their stability toward diverse environmental conditions like high ionic strength, pH, temperature, storage, and continuous irradiation was evaluated. The CBCDs exhibited bright and stable fluorescence with a QY of 26%. Physicochemical characterizations revealed that the CBCDs are spherical with a mean diameter of 3.7 ± 1.4 nm and composed of graphitic core with amorphous/polar surface functionalities, which impart aqueous solubility. CBCDs were used as “on–off–on” fluorescent probe for the detection of Fe³⁺ and ascorbic acid (AA). The probe was successfully applied for the analysis of real water (tap, bore, and pond) and biological samples (human urine and serum), and a possible quenching mechanism was proposed. In addition, we have constructed an implication logic gate based on these unique sensing characteristics. Excitation-dependent emission behavior coupled with high biocompatibility revealed the multicolor cellular imaging potential of CBCDs. Furthermore, we have prepared fluorescent polymer films by incorporating CBCDs into poly(vinyl alcohol) (PVA). Also these CBCDs were applied as invisible ink for security applications.

**RESULTS AND DISCUSSION**

**Synthesis of CBCDs.** Here, we report a simple hydrothermal method for the production of N, S codoped CDs using cigarette butts as source material. The preparation of CDs from CBs is illustrated in Scheme 1. Cigarette butts are mainly composed of cellulose acetate fibers, and they also contain minor amount of chemicals like nicotine, polycyclic aromatic hydrocarbons (PAHs), N-nitrosamine, aromatic amines, and other tarlike components trapped during smoking. Conversion of cellulose acetate fibers into water-soluble CDs is the critical step. Concentrated sulfuric acid is selected to achieve this conversion due to (1) its strong acid hydroylizing property, which produces cellulose from cellulose acetate and further facilitates the conversion of cellulose into hydrophilic cellulose nanoparticles; (2) its strong dehydrating property, which assists the creation of unsaturated C=C bonds from saturated C−C bonds; and (3) its strong oxidizing property, which facilitates the generation of hydrophilic C=O−H and O=C−O−H from hydrophobic C−H. As CDs predominantly comprise PAHs in their carbon matrix, the presence of PAHs in the reaction mixture is expected to facilitate the formation of CDs. Further, the presence of N-containing compounds (nicotine and other aromatic amines) is known to promote the formation of CDs and improve the QY by N-doping and amine passivation. Furthermore, sulfuric acid can also serve as S dopant to produce S and N-codoped CDs with improved QY. The crucial role of sulfuric acid is evident from the blank experiment (double-distilled (DD) water is used instead of sulfuric acid), which resulted in CDs with very low QY (3%) and insignificant production yield. To obtain the best CDs out of waste CBs, process parameters like reaction temperature,
time, and concentration of acid were optimized (Tables S1 and S2). Under optimal conditions, CDs with QY as high as 26% were obtained with a production yield of 9.6%. A comparison (Table S3) with several previous reports on the production of CDs from waste materials revealed the advantageous features (mild synthetic conditions and higher QY and production yield) of the present method.

**Physicochemical Properties.** The structure and morphological features of CBCDs were explored by transmission electron microscopy (TEM) analysis. As presented in Figure 1.
the (002) lattice spacing of graphitic carbon, indicating the introduction of oxygen-containing functional groups or owing (0.37 nm) is larger than that of graphite (0.34 nm), articulating integrated intensity ratio of D and G bands (carbon atoms in a two-dimensional hexagonal lattice). The neighboring sp3 defect. The G band corresponds to the E2g vibration phonon that is only activated in the presence of stretching vibrations of N\(^{164}\). To the presence of − bonds and chemical composition of CBCDs was obtained from the sense that it corresponds to the A1g (zone-edge) breathing mode of graphite and is related to the vibration of sp2-bonded molecule center, respectively. Similar to several previous reports, aqueous solution of CBCDs exhibit bright blue emission under 365 nm UV light, and it appeared transparent which designates the existence of pyridinic N s, 1\(^{a}/2\)\(^{b}\) amino N s (399.0 eV), and pyrrolic N s (400.7 eV). S 2p spectrum (Figure 2d) can be resolved into three distinct peaks at 167.5, 168.7, and 169.5 eV, which designates the existence of C−SO\(_x\) (x = 2, 3, 4) on the surface of CBCDs. \(^{27}\) ζ potential of the as-prepared CBCDs suspension was found to be −14.9 mV, demonstrating the negative surface charge of CBCDs (Figure S2). All of these results manifested the occurrence of multiple functional groups like −OH, −C=O, −COOH, and −NH and successful doping of N, S elements in the CB-derived CDs.

**Optical Properties.** The UV−vis absorption, excitation, and emission spectra are represented in Figure 3a. As shown in the figure, the absorption spectrum displays two poorly resolved bands around 270 and 320 nm, which can be ascribed to the π−π* transition of carbonic core center and n−π* transition of heteroatomic surface functionalities or molecule center, respectively.\(^{22}\) Similar to several previous reports, aqueous solution of CBCDs exhibit bright blue emission under 365 nm UV light, and it appeared transparent and pale yellow under daylight (inset of Figure 3a). The corresponding excitation spectrum shows two peaks, which can be ascribed to core and surface excitations. Like most of the fluorescent CDs, CBCDs also exhibited excitation tunable emission behavior. A steady increase in λ\(_e\) from 300 to 480 nm resulted in a red shift in the emission peak position along with a concurrent first increase and then decrease in the emission intensity (Figure 3b). This red shift can be clearly observed in the corresponding normalized emission spectra (Figure S3). This tunable emission is considered to be the versatile characteristic of CDs and has been most prominently ascribed to the selective excitation of subsets of CDs within the CD ensemble.\(^{52}\) The maximum emission peak centered at 430 nm was observed under the excitation of 360 nm with a large Stokes shift of 70 nm. As presented in Figure S4, the fluorescence QY of CBCDs at room temperature was calculated to be 26% (using quinine sulfate (QS) as reference), which is greater compared to various previous reports (Table S3). The reason for this higher QY may be due to the synergistic effect of doped N and S atoms.\(^{33}\)

**Figure 3.** (a) Absorption (black), excitation (red), and emission (blue) spectra of CBCDs (inset: CBCDs aqueous solution under daylight (left) and UV light (right)). (b) Excitation wavelength-dependent emission spectra of CBCDs.
Stability. In view of the fact that fluorescence emission of many fluorescent probes can be disrupted by the complex environmental conditions, we have examined the emission spectra of CBCDs under diverse conditions to verify their practical applicability. The effect of ionic strength was examined by recording the emission spectra under various KCl concentrations. As depicted in Figure S5a, only a slight diminution in the photoluminescence (PL) intensity is observed even at a high KCl concentration of 2 M, which verifies the excellent stability of CBCDs under high-ionic-strength environments and outspreads their usage to identical ion-rich biological conditions. As shown in Figure S5b, change in the solution pH did not alter the peak position, but caused fluctuations in the emission intensity. No significant alteration in the emission intensity is recorded over a pH range of 5–9, which is a beneficial property for the fluorescent probe to be used in complex biological system and practical applications. Photostability studies revealed their excellent property of resistance to photobleaching (Figure S5c). As presented in Figure S5d, the fluorescence intensity of CBCDs was found almost stable in the temperature range of 25–45 °C representing their thermal stability. Further, the storage stability of CBCDs was examined by keeping those under (1) ambient conditions and (2) refrigerator for 60 days. Virtually no fluctuations in their emission intensity and no obvious precipitation were observed in both the cases (Figure S6), demonstrating their great stability and long shelf life.

Detection of Fe^{3+} and AA. The aforementioned optical merits, along with the existence of abundant surface functional groups encouraged us to further investigate the possible sensing applications of CBCDs. According to several previous reports, the surface functional groups of CDs can selectively interact with metal ions and produce a fluorescence change; thus, we have studied the fluorescence response of CBCDs toward various biologically and environmentally important metal ions, such as Fe^{2+}, Ca^{2+}, Na^{+}, Pb^{2+}, Cu^{2+}, Mn^{2+}, Cd^{2+}, Sn^{2+}, Cr^{3+}, Al^{3+}, Ni^{2+}, Hg^{2+}, Mg^{2+}, Ba^{2+}, K^{+}, Zn^{2+}, and Fe^{3+}. As shown in Figure S7, among all ions, only Fe^{3+} caused a severe decline in the PL intensity, which unveiled the applicability of CBCDs as highly selective turn-off fluorescent probes for Fe^{3+} detection. This discrimination effect for Fe^{3+} can be credited to the special coordination between electron-deficient Fe^{3+} ions and electron-rich surface functional groups of CBCDs. 46 In the course of developing an efficient probe, some critical parameters, including usage concentration of CBCDs, incubation time, and solution pH, were optimized. In general, in the presence of quencher of a given concentration, lower concentration will achieve a broader detection range; 53 hence, through comprehensive consideration of both sensitivity (limit of detection (LOD)) and linear detection range, 0.05 mg mL⁻¹ of CBCDs was selected as optimum. Quenching kinetic investigations (Figure S8a) revealed that 2 min of interaction with Fe^{3+} is sufficient to produce maximum fluorescence response, which remained stable in the following 20 min of observation, suggesting the complexion between Fe^{3+} and CBCDs is quick and stable, which is useful in rapid sensing without strict time control. 54 As presented in Figure S8b, Fe^{3+} ions were able to produce decent response in the pH range of 6–9, which is beneficial as most environmental and biological samples lie in this pH scale and maximum response is achieved at pH 7, which is taken as optimum.

Under optimal circumstances, sensitivity was inspected by computing the fluorescence response of CBCDs to several concentrations of Fe^{3+} in the range of 0–100 μM. As depicted in Figure 4a, the PL intensity gradually dwindled with
increasing concentrations of Fe\textsuperscript{3+}. The plot of quenching efficiency (F\textsubscript{0}/F) versus Fe\textsuperscript{3+} concentration (Figure 4b) displayed a good linearity (R\textsuperscript{2} = 0.998) in the range of 0–100 μM, where F\textsubscript{0} and F are the PL intensities of CBCDs at 430 nm in the absence and presence of Fe\textsuperscript{3+}, respectively. The detection limit (LOD) was estimated to be 0.13 μM based on the equation 3σ/m, where σ is the standard deviation of the blank signal (n = 6) and m is the slope of the linear fit. The LOD presented by our method (0.13 μM) is much lower than the maximum permissible limit (5.36 μM) stipulated by World Health Organization (WHO) and LOD presented by other researchers for Fe\textsuperscript{3+} in drinking water.

Comparison of analytical performance of CBCDs nanoprobe with several chosen probes in the literature (Table S4) revealed the superiority of the present sensor in terms of linear range, LOD, and applicability to real samples.

With inherent complexity, metal-ion detection in real samples poses a great challenge to the analytical methods not only in terms of sensitivity but more importantly in selectivity. Hence, to further explore the applicability of the proposed nanoprobe to real samples, selectivity and competition experiments were carried out. The black bars shown in Figure 4c depict the PL response (F/F\textsubscript{0}) of CBCDs to various metal ions each at a concentration of 200 μM. It is evident that none of these metal ions caused a considerable decline in the PL intensity. Competition experiments were conducted by subsequently adding 100 μM of Fe\textsuperscript{3+} to the above solutions. As represented by the red bars in Figure 4c, no substantial change in the PL response (F/F\textsubscript{0}) appeared in the co-presence of Fe\textsuperscript{3+} and other metal ions in comparison to that of Fe\textsuperscript{3+} alone. All of these results clearly demonstrated the excellent selectivity of CBCD-based nanoprobe and motivated us to investigate their practical applicability in real samples.

It is observed that the quenched fluorescence of CBCDs/Fe\textsuperscript{3+} can be recovered by the addition of AA. This can be attributed to the (i) antioxidant nature of AA, which can reduce Fe\textsuperscript{3+} to Fe\textsuperscript{2+} and (ii) the high selectivity of CBCDs toward Fe\textsuperscript{3+} over Fe\textsuperscript{2+}. Moreover, AA did not exhibit any significant effect on the fluorescence of CBCDs alone. Hence, the CBCDs/Fe\textsuperscript{3+} system can be employed as a turn on fluorescent probe for the detection of AA (Scheme 2). Kinetic investigations disclosed that, 10 min of interaction with AA recovered the emission of CBCDs/Fe\textsuperscript{3+} system to a stable value (Figure S9), and this 10 min is taken as the incubation time for the assay. Sensitivity of CBCDs/Fe\textsuperscript{3+} system toward AA is evaluated by recording its fluorescence response to various concentrations of AA. As presented in Figure 4d, the emission intensity of CBCDs/Fe\textsuperscript{3+} nicely recovered with increase in the concentration of AA, and the plot of F/F\textsubscript{0} versus AA concentration (Figure 4e) demonstrated a good linearity (R\textsuperscript{2} = 0.996) in the range of 0.5–100 μM, where F\textsubscript{0} and F are the emission intensities of CBCDs/Fe\textsuperscript{3+} at 430 nm in the absence and presence of AA, respectively. The detection limit (LOD) was estimated to be 0.2 μM based on the equation 3σ/m, where σ is the standard deviation of the blank signal (n = 6) and m is the slope of the linear fit. Selectivity of the probe is evaluated by studying the interference of various amino acids, anions, and sugars. As depicted in Figure 4f, the probe presented greater selectivity, which opened their further applicability to real samples. The sensing performance (linear range and limit of detection) of the present probe is compared to that of several reported methods (Table S5), which revealed that the presented method is among the best methods reported so far.

**Analysis of Real Samples.** Practical applicability of CBCDs nanoprobe was assessed by detecting Fe\textsuperscript{3+} in real water (tap, bore, and pond) and AA in complex biological (human urine and serum) samples. To avoid the particulate matter, real water samples are subjected to centrifugation and filtration (0.45 μm membrane filter). Serum and urine samples are subjected to a 100-fold dilution with PBS before analysis. Then, the water samples were spiked with various concentrations of standard Fe\textsuperscript{3+} solution, and the serum and urine samples were spiked with AA and analyzed by the proposed method. As shown in Tables S6 and S7, good recoveries (98–102) and high analytical precision with RDS 3.2 (n = 6) were obtained. Furthermore, the nanoprobe is validated by comparing the results of Fe\textsuperscript{3+} and AA detection in a real sample to those of a standard method (atomic absorption spectrometry for Fe\textsuperscript{3+} and high-performance liquid chromatography–UV for AA). These results confirm the reliability and feasibility of the proposed nanosensor for monitoring Fe\textsuperscript{3+} in environmental and AA in biological samples.

**Possible Mechanism of Fluorescence Quenching.** In general, several sorts of molecular interactions between the fluorophore and quencher such as electron or energy transfer, excited-state reaction, collisional quenching, and ground-state complex formation can lead to fluorescence quenching.\textsuperscript{56} The quenching mechanisms are typically classified into (1) dynamic quenching, involving the transfer of electron from excited-state fluorophore to ground-state quencher by means of collision and (2) static quenching resulting from the formation of a nonfluorescent ground-state complex between the fluorophore and quencher.
To explore the possible mechanism of quenching of CBCDs fluorescence by Fe$^{3+}$ ions, the standard Stern−Volmer equation is applied.

$$K_{sv} = \frac{F_0}{F} = 1 + K_{sv}[Q] = 1 + k_q \tau_0 [Q]$$

where $F_0$ and $F$ refer to the fluorescence intensities of CBCDs in the absence and presence of quencher (Fe$^{3+}$), respectively; $K_{sv}$ and $k_q$ represent the Stern−Volmer quenching constant and bimolecular quenching constant, respectively; $[Q]$ is the concentration of quencher (Fe$^{3+}$); and $\tau_0$ is the average lifetime of CBCDs in the absence of quencher.

As depicted in Figure 4b, the plot of $F_0/F$ versus $[Q]$ exhibited a good linear correlation (correlation coefficient, $R^2 = 0.998$) and the Stern−Volmer quenching constant ($K_{sv}$) was found to be $2.2 \times 10^4$ M$^{-1}$. The excellent linear correlation infers that the observed quenching is either purely dynamic or purely static and rules out the possibility of static−dynamic combination. In principle, fluorescence lifetime measurement is the most definitive method to distinguish dynamic and static quenching processes. In light of this, fluorescence lifetime quenching analysis is carried out to confirm the nature of quenching. Figure 5a reveals that the PL lifetime of CBCDs is not quenched by Fe$^{3+}$ ions, which rule out the possibility of dynamic quenching. The bimolecular quenching constant ($k_q$) calculated from $K_{sv}$ and average lifetime $\tau_0$ (5.26 ns) is found to be $4.18 \times 10^{13}$ M$^{-1}$ s$^{-1}$, which is higher than the diffusion-controlled limit ($10^{10}$ M$^{-1}$ s$^{-1}$) and further supports the static quenching mechanism involving the ground-state complex formation. Decrease in the quenching constant with rise in the temperature (Figure 5b) further supported the static quenching process. All of these findings designate that the quenching caused by Fe$^{3+}$ ions is a result of nonfluorescent complex formed between the surface functional groups of CBCDs and Fe$^{3+}$ ions. FTIR spectral analysis was further used...
to verify this assumption. As shown in Figure S10, evident changes (especially at the characteristic peaks of C=O, C=N, and SO\(^2\)) were observed in the FTIR spectrum of CBCDs after the addition of Fe\(^{3+}\), which further confirmed that Fe\(^{3+}\) indeed coordinated with these surface functional groups of CBCDs.

**Cytotoxicity and Cellular Imaging.** With the grander optical properties like bright fluorescence (QY = 26\%), high ionic strength, and tolerance to photobleaching and complex environmental conditions, the CBCDs showcase a great potential to serve as bioimaging agents. However, like various biological applications, low cytotoxicity is the key requirement for a material to be used as bioimaging agent also. Hence, we have evaluated the inherent cytotoxicity of CBCDs toward human normal (HEK-293) and human cancerous (HeLa) cells. Standard 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) cell viability assay is employed for this purpose. As shown in Figure S11, CBCDs did not exhibit substantial toxicity on both cancerous and noncancerous cells and the cell viabilities remain 85% even at a concentration of 1000 \(\mu\)g mL\(^{-1}\), denoting their excellent biocompatibility. An important observation is that, at the dosage used for bioimaging (200 \(\mu\)g mL\(^{-1}\)), virtually no toxicity is witnessed (cell viability is over 95\%), which indicated that the CBCDs have great potential for biomedical applications such as in vivo imaging, cellular labeling, and medical imaging.\(^{59}\) These results are in agreement with similar studies carried out earlier.\(^{59}\) Further, it is interesting to note that CDs derived from toxic CBs did not exhibit any toxicity toward human normal and cancerous cells demonstrating their versatility.

Cellular imaging potential of CBCDs was evaluated by performing the in vitro cellular uptake experiments with HeLa cells. After incubating with 200 \(\mu\)g mL\(^{-1}\) CBCDs for 6 h, the cells were imaged under a confocal laser scanning microscope. As shown in Figure 6, the cells were brightly illuminated with blue, green, and red colors under the excitation of 408, 488, and 543 nm, respectively. Nevertheless, the control cells did not display any detectable fluorescence under the same exposure conditions. A closer observation of the images revealed that the fluorescence glow is mainly confined to cell membrane and cytoplasmic area while the nucleus had only a weak glow. These results indicate that, similar to some previous reports,\(^{60}\) CBCDs were also having difficulties in labeling the nucleus, while the cytoplasm and cell membrane are easily stained.

**Intracellular Detection of Fe\(^{3+}\) and AA.** It has been reported that overload and deficiency of Fe\(^{3+}\) can disturb the cellular homeostasis, resulting in various diseases.\(^{61}\) Hence, developing a simple and sensitive probe for monitoring intracellular Fe\(^{3+}\) is of great importance. Impressed by the favorable biocompatibility, cell imaging ability, and high selectivity, CBCDs were further applied for monitoring Fe\(^{3+}\) in live cells by introducing exogenous Fe\(^{3+}\) into the CBCD-pretreated HeLa cells. As expected, the confocal microscopic images taken after supplementing cells with 200 \(\mu\)M Fe\(^{3+}\) in the growth medium exhibited very weak intracellular fluorescence (Figure 6). Further treatment of cells with AA resulted in the nicely recovered intracellular fluorescence indicating that emission of CBCDs/Fe\(^{3+}\) in the cells can be recovered by AA. It can be observed that the fluorescence emission of the cells is in the order of CBCDs > CBCDs/Fe\(^{3+}\) treated. All of these results elucidate that CBCDs could serve as efficient fluorescent probe for “on-off-on” detection of Fe\(^{3+}\) and AA in living cells.

**Logic Operations of CBCDs.** The fluorescence switching behavior of CBCDs in the presence of Fe\(^{3+}\) and AA can be employed as multiple molecular logic gates, performing the Boolean algebraic logic operations.\(^{62}\) The simple single input molecular logic gate NOT can be constructed using Fe\(^{3+}\) as single input signal (Figure 7a). The multiple input logic gate IMPLICATION can be realized by taking Fe\(^{3+}\) and AA as input 1 and input 2, respectively. The presence of Fe\(^{3+}\) or AA is taken as 1 and their absence as 0. For output, the maximum fluorescence was taken as 1 and the corresponding quenched fluorescence as 0. As shown in Figure 7b, only in the presence of Fe\(^{3+}\) and absence of AA, i.e., input (1, 0), significant

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**Figure 7.** Logic operations using CBCDs: (a) logic symbol and truth table of NOT logic gate; (b) logic symbol and truth table of IMPLICATION logic gate; and (c) fluorescence response of CBCDs under different inputs.
fluorescent quenching is observed and provided output as 0, while in the case of other inputs (0/0, 0/1, 1/1), the output remains 1. The logic symbol, truth table, and output fluorescence intensity at 430 nm are shown in Figure 7.

**Fluorescent Ink and Polymer.** Finding novel applications to emerging materials like CDs is always important. Here, CBCDs possess unique properties, including strong and stable fluorescence and good transparency in the visible region, which makes them suitable candidates for fluorescent ink applications. To explore this, a sketch pen is filled with CBCDs aqueous solution (Figure S12) and employed for writing some text on commercial filter paper. As shown in Figure 8, the words “Osmania University” are clearly visible (showing blue fluorescence) under UV light, whereas the filter paper appeared as blank under daylight. It is worth mentioning that the information on the filter paper remained consistent and can be reproducible even after 30 days (when stored under ambient conditions) (Figure S13). These observations suggest that the CBCDs can be used as invisible ink for loading important information for secret communications and have a great potential for anticounterfeiting applications. Furthermore, with their high biocompatibility (low/nontoxic nature), CBCDs can be safely used as ink pads to form human fingerprints that do not contaminate the fingers. Figure 8c characterizes the CBCDs-formed fluorescent fingerprint on commercial filter paper, which could reflect human fingerprint clearly. Thus, the water-soluble CBCDs-based fluorescent ink could serve as an alternative to the traditional inks to form a clear, adelomorphic, long-lasting, and blue fluorescent fingerprint that can be easily cleaned with water and is pollution free.

Further extending their applicability to solid-state optic-related fields is interesting and challenging. Efficient solid-state PL emission of CDs is extremely important for light-emitting diode (LED) applications. However, CDs in the solid state generally suffer from self-quenching because of the aggregation-caused quenching effect, which might be a result of excessive Forster resonance energy transfer among adjacent CD particles in the aggregated state or direct \( \pi-\pi \) interaction. Dispersing CDs in the polymer matrix is considered to be an effective strategy to avoid this. Here, we have prepared solid-state films by dispersing CBCDs in poly(vinyl alcohol) (PVA). PVA was selected as polymer host because of its known high optical quality and desirable film properties. The as-fabricated films are highly transparent (about 90% transmittance in the entire visible region) under daylight, while exhibited bright blue fluorescence under UV illumination (Figure 9). The absorption spectra (Figure S14a) of CBCDs in the polymer film is similar to those in solution, and the emission spectra (Figure S14b) also exhibited a similar excitation-dependent behavior.

In comparison to CBCDs aqueous solution, the optimal emission spectra of CBCDs/PVA film exhibited a blue shift of 6 nm and a slight red shift (3 nm) in the optimal excitation wavelength (Figure S15), which might be due to the fact that PVA environment is different from aqueous solution. The fluorescence QY of CBCDs in PVA matrix determined using QS as reference was found to be 33% (Table S8), which is higher than that in aqueous solution. This enhancement in the QY can be ascribed to the formation of hydrogen bonds between PVA and surface functional groups of CDs, which provide a stabilization effect on the electrons and holes for more efficient radiative recombination.
solution was neutralized with Na$_2$CO$_3$, centrifuged, and solution was centrifuged to remove large particles. Then, the obtained samples were well characterized and explored for multiple applications. Bright and stable fluorescence coupled with high biocompatibility made CBCDs a potential candidate for bioimaging applications. They were successfully applied as a fluorescent probe for the sequential detection of Fe$^{3+}$ and AA concentrations were added to 1 mL of CBCD solution, shaken varying concentrations. For the detection of ascorbic acid solution and then 1 mL of AA with varying concentrations was added to 1 mL of CBCDs aqueous solution. At room temperature, 1 mL of DD water is added to 1 mL of CBCDs aqueous solution. Cu K$_\alpha$ X-ray, $\lambda = 1.5406$ Å.

**Calculation of QY.** QYs of all of the CBCD samples were calculated by using the slope method in which quinine sulfate (QS) is chosen as standard ($\Phi = 54\%$). This particular method first involves the preparation of several concentrations of CBCDs aqueous solutions and QS 0.1 M H$_2$SO$_4$ solutions by maintaining the absorbance values less than 0.1 at their excitation wavelengths. Subsequently, the integrated emission intensities of all of the samples were recorded by exciting at 360 nm. Afterward, the integrated emission intensities were plotted against corresponding absorbance values and the slope values of the obtained linear plots were computed. Finally, quantum yields were calculated by using the following equation

$$\Phi_x = \Phi_s \left( \frac{\text{Grad}_s}{\text{Grad}_x} \right) \left( \frac{\eta_x^2}{\eta_s^2} \right)$$

where $\Phi$ is the quantum yield, Grad is the gradient of the plot of integrated emission intensity versus absorbance, and $\eta$ is the refractive index of the solvent (1.33 for both solvents). The subscripts st and x denote standard (QS) and CBCDs, respectively.

**Detection of Fe$^{3+}$ and Ascorbic Acid.** Solutions of all metal ions used in this experiment are prepared from corresponding salts in DD water. At room temperature, 1 mL of DD water is added to 1 mL of CBCDs aqueous solution (0.1 mg mL$^{-1}$), the emission spectra of this sample are recorded at an excitation wavelength of 360 nm, and the emission intensity is denoted as $I_0$. In a similar manner, 1 mL of different metal ion solutions of 200 μM concentration were added to 1 mL of CBCD solution, shaken well, and incubated for 2 min and thereafter the emission intensity is recorded as $F$. A similar procedure was followed for the quantitative determination of Fe$^{3+}$. In a typical assay, 1 mL of CBCDs solution was mixed with 1 mL of Fe$^{3+}$ solution of varying concentrations. For the detection of ascorbic acid (AA), first, 0.5 mL of Fe$^{3+}$ is added to 0.5 mL of CBCDs solution and then 1 mL of AA with varying concentrations was added. The final concentrations of Fe$^{3+}$ and CBCDs are 100 μM and 0.05 mg mL$^{-1}$, respectively. After 10 min of incubation, fluorescence response in recorded.

**Cytotoxicity and Cellular Imaging.** Standard MTT assay was employed for evaluating the in vitro cytotoxicity of cigarette butt-derived CDs. Experimental studies were performed on both normal (HEK-293) and cancerous (HeLa) cell lines. Complete details are provided in the Supporting Information.

**Preparation of Fluorescent Films (CBCDs/PVA Composite Films).** Poly(vinyl alcohol) (PVA) (1 g) is added to 10 mL of DD water under constant stirring, and the mixture was heated to dissolve PVA. After that, 1 mL of 1 mg mL$^{-1}$ CBCDs were well characterized and explored for multiple applications. Bright and stable fluorescence coupled with high biocompatibility made CBCDs a potential candidate for bioimaging applications. They were successfully applied as a fluorescent probe for the sequential detection of Fe$^{3+}$ and AA. Furthermore, the optical properties of CBCDs/PVA films promise their applicability in anticounterfeiting. CBCDs/PVA film/phosphor material in solid-state lighting systems.
aqueous solution was added to 9 mL of PVA solution and stirred gently for 10 min. Finally, the mixture was drop-casted onto a clean glass slide and dried in an oven. After drying, the film was peeled off from the glass substrate to get a freestanding film.

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**AUTHOR INFORMATION**

*Corresponding Author*

E-mail: gvbhadram@gmail.com.

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