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Cooking oven produced carbon is incorporated into polyaniline without any further purification or chemical modification. The product shows excitation-independent triple-band photoluminescence, as well as sensitive and selective ion detection (Fe$^{3+}$) ability. Clearly, it would add up to the green nanotechnology area, beneficiary to the society.
Green Nanotechnology from Waste Carbon–Polyaniline Composite: Generation of Wavelength-Independent Multiband Photoluminescence for Sensitive Ion Detection

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This study reports on the qualitative analysis of photoluminescence effect generated from waste carbon of cooking oven by facile cost-effective material engineering. The waste carbon product as a form of carbon nanoparticles (CNPs) is incorporated within a conjugate polymer, namely, polyaniline (PANI) to produce CNP-PANI composites that have shown excitation-wavelength-independent triple-band photoluminescence emission effect and highly sensitive Fe$^{3+}$ ion detection ability. Herein the waste carbon material, while functionalized within the conjugated polymer, needs no further acid treatment or surface modification thus making the process cheaper, environmentally benign, and useful for green nanotechnology. The excitation-wavelength-independent unique triple-band photoluminescence spectrum is the direct consequence of carbon–polyaniline synergy in $\pi$–$\pi$ transition and the surface passivation of CNPs by the $-\text{NH}_2$ group rich aniline during in situ polymerization. The current scenario has been studied for the samples prepared with different CNP concentrations for different reaction times and discussed in details with supportive physico-chemical characterizations. Moreover, the present study has demonstrated that the current material can be used as a fluorescent sensing platform for Fe$^{3+}$ ions with high sensitivity and selectivity criteria where the detection limit of the sensing probe has a value as low as $12 \times 10^{-9}$.

1. Introduction

With global interest, carbon-based nanomaterials having significant implications for the development of optoelectronic devices,[1–3] energy conversion,[4] photocatalysis,[5] biomedical imaging,[6–8] sensing probe,[9–14] and many more,[15,16] are receiving great attention from both experimentalists and theorists. They have become the new-generation luminescent materials being superior to conventional organic dyes and semiconductor quantum dots, while compared in terms of chemical inertness, large two-photon excitation cross sections, lack of blinking, low cytotoxicity, and biocompatibility.[17] However, proper understanding of the photoluminescence (PL) origins in carbon nanoparticles is still inadequate, which is actually lowering the speed of major development and abundant use of carbon-based materials with desired PL characteristics. Different mechanisms have been proposed so far, respectable ones are, for example, quantum confinement effect or conjugated $\pi$-domains determined by carbon core, surface state determined by hybridization of carbon backbone and connected chemical groups, molecule state determined by solely fluorescent molecules connected on surface or inside the carbon particles as well as the cross-link enhanced emission effect. Though the mechanisms based on particle size distribution, surface traps and quantum effects, charge transfer, intramolecular H-bonds, electronic conjugate structure, defects, etc., are more popular in this case, till now, the actual PL mechanism is still an open debate for related researchers.[18–22] On the other side, conjugate polymers are also of great interest because of their ability to control the energy gap and electronegativity through molecular design that has made possible the synthesis of conducting polymers with a range of ionization potentials and electron affinities.[23,24] More interestingly, most of the conjugated polymer shows PL quenching upon oxidation, while developing oxidation-resistance can lead to an increment of PL emission. The excellent properties of $\pi$-electron delocalization at the backbone of conjugate polymer can be an initiator of charge transfer mechanism with carbon nanoparticles (CNPs) resulting oxidation-resistance. This unique combination of two types of materials has the ability to expand the...
class of novel composite materials with controlling their properties through rational chemical synthesis.\textsuperscript{[25,26]} In this work, we have used the idea of surface passivation indirectly by the incorporation of CNPs within polyaniline (PANI) during in situ polymerization. CNPs that were collected from normal cooking oven produced waste carbon, feature significantly simpler acquisition and low cost, but have rarely been studied as photoluminescence material. A simple and feasible wet chemical route has been followed using ethanol-water as the reaction and dispersion medium. Aniline monomer acted as the key factor for polymerization and in a late run also providing the surface amino groups for passivating surface traps. As-synthesized product has shown highly intense triple-band photoluminescent peaks, interestingly with excitation-wavelength-independent behavior. Different concentrations of CNPs have been incorporated into the conjugated polymer, driving to the development of oxidation-resistant polymers that show a significant outcome on PL emission. On the other hand, a progressive study on the PL emission with functionalization time of CNPs within PANI was carried out to understand the influence of interaction between them. Our findings can be considered among the few reports, which have achieved the excitation-independent luminescence in carbon-based materials. Though both excitation-dependent and excitation-independent emissions have been observed, the excitation wavelength-dependent emission behavior is most common and it may arise from the wide distributions of differently sized dots and surface chemistry, different emissive traps, or some other currently unresolved source.\textsuperscript{[27]} But, the excitation-independent PL behavior has been seldom achieved and the reason behind it is still unclear. Researchers are mostly doing their part for improving quantum yield of CNPs,\textsuperscript{[28,29]} though widening the area of comprehensive understanding of emission origins and finding out the controlling factors or criteria are also very much significant for more successful applications in future. Even after all these yet to be clear concepts about the PL of CNPs, several research groups have accepted the idea of exploiting their radiative transition through the effective role of surface traps. In most of the situations, the excitation dependence of CNPs could be controlled through managing the emissive trapping states introduced by surface groups such as C−O, C=O, O=C−OH, etc., with various energy levels. But, if all the surface states of CNPs are passivated, the emission is supposed to occur only through radiative transition of sp\textsuperscript{2} carbon (most probably π to π* transition), finally resulting in an excitation-independent photoluminescence. Many authors have often used nitrogen-containing organic compounds specially those having short chains, as effective passivating agents in this case.\textsuperscript{[30,31]} Hence, amino group could be an effective means to achieve the excitation-independent behavior of CNPs by surface passivation. Most importantly, we have further demonstrated that such new CNP-PANI composites can be applicable as a selective PL sensing probe, through the quenching of emission in presence of Fe\textsuperscript{3+} ions in the dispersion, with a detection limit as low as \(1.2 \times 10^{-9}\text{ m}\). Moreover, we have embedded CNPs into a conducting polymer which can be proved further as an appropriate solid-state architecture to be applied as phosphors for white light-emitting devices. Also, here we have used cooking oven produced waste carbon as the source of CNPs which can be a great replacement for the expensive and unsustainable source materials thus stepping toward the green nanotechnology.

\section{2. Results and Discussions}

\subsection{2.1. Surface and Chemical Structure Analyses}

Detailed information about the chemical composition of as-synthesized CNP-incorporated PANI samples has been explored using tapping mode phase imaging atomic force microscopy (AFM) (PI-AFM) technique by applying sample bias voltage. PI-AFM is a sensitive nanoscale probing method to detect the phase shift of cantilever oscillation and its proximal interaction with sample surface, associated with stiffness, viscoelasticity, and chemical composition of the material.\textsuperscript{[32]} Here, we have applied surface voltage during phase imaging of sample so that it can impart enhancement of the image contrast with effect of localized electrostatic field. Figure 1a shows the PI of heterogeneous regions in phase-separated CNP-incorporated PANI composite. Circular spots with average size of 40 nm can be ascribed to CNPs within polymer matrix. Observed topographical features of the corresponding area (Figure 1b) do not show any kind of structural effects, which corroborates that PI-AFM is the result of a localized variation of different chemical compositional effects. Such PI is quite effective to determine the surface modification of polymer materials containing nanoparticles. Figure S1a,b (Supporting Information) is representative field emission scanning electron microscopy (FESEM) images of carbon nanoparticles (as directly obtained from the waste carbon product of cooking oven) and the typical CNP-incorporated PANI samples, respectively.

The X-ray photoelectron spectroscopy (XPS) results indicate that a typical CNP-PANI sample is mainly composed of carbon, nitrogen, and oxygen (see Figure S3, Supporting Information). In order to speculate on the influence of incorporated CNPs on PANI, C1s and N1s core levels are further quantitatively deconvoluted which is shown in Figure 2a. The high-resolution spectrum of C1s exhibits four main peaks, centered at about 284.3 (C=C or C−H), 285.0 (C≡N), 286.7 (C=N+ or C−O), and 288.6 (C=O) eV.\textsuperscript{[31–35]} The typical XPS N1s core-level spectra for CNP-PANI sample are shown in Figure 2a. The relatively broad peak suggests the existence of different component peaks. Thus, the high-resolution peak of N1s is deconvoluted and reasonably fitted with four Gaussian–Lorentzian peaks having binding energy values of \(=398.1, 399.2, 400.7, \text{and } 402.2\text{ eV}\). The peak with the lowest binding energy (398.1 eV) is due to imine-like (C=N) structure, and the peak centered at 399.2 eV is attributed to amine-like nitrogen atoms (−NH−).\textsuperscript{[31,36]} The peak centered at 400.7 is attributed to cationic nitrogen atoms on the polymer backbone and the highest binding energy peak (402.2 eV) is due to the protonated amine units.\textsuperscript{[31,36]} The XPS data were compared to a pure PANI sample as well as to samples of varying amount of CNPs (not shown here). No systematic changes in C1s and N1s could be detected, which is an indication that CNPs are embedded in PANI and do not reside on the surface, confirming the AFM measurement. Fourier transformed infrared (FTIR) and Raman spectroscopy
were used to analyze the chemical structure of as-prepared samples. A FTIR spectrum of typical CNP-PANI sample with different synthesis time duration is depicted in Figure 2b. As expected, some typical characteristic absorption bands of PANI were observed in the spectra. For instance, 1560–1558 and 1488–1456 cm\(^{-1}\) (due to stretching vibration of C–C in quinoid (Q) and benzenoid (B) rings, respectively), 1305–1285 cm\(^{-1}\) (attributed to \(\pi\)-electron delocalization induced in polymer by protonation of doping process), 1251–1233 cm\(^{-1}\) (associated with C-N stretching of the secondary aromatic amine), 1152–1110 cm\(^{-1}\) (due to aromatic C-H in-plane bending), as well as 820–814 cm\(^{-1}\) (related to out-of-plane deformation of C-H in the 1,4-disubstituted benzene ring) were observed.\(^{[37]}\)

Thus, FTIR spectra display essentially the same absorptive characteristics as that of pristine PANI.\(^{[38,39]}\) But, there is slight red shifting in peak positions with different reaction time durations which may be attributed to the incorporation of CNPs. The quinoid/benzenoid (Q/B) ratio when calculated from FTIR spectra for a particular sample is observed to decrease with increasing time duration of polymerization, that is, with preceding functionalization of CNPs within the polymer. Also, the Q/B ratio as determined by FTIR has smaller values for the sample prepared using higher CNP concentrations (Figure S4, Supporting Information) signifying the presence of more reduced emeraldine segments in these functionalized materials. This can be attributed to strong interactions existing between CNPs and PANI in which the functionalized CNPs reduce PANI through charge transfer.

**Figure 3** shows the Raman spectra of a typical CNP-PANI sample (CP, for time T1–T4) excited by 532 nm laser line in air ambient environment. In the spectra, two very intense but broad and diffused peaks can be seen as main characteristics. So, they are deconvoluted into the fitted ones to obtain a relevant idea about constituent elements, that is, CNPs and PANI. The vibrational bands at \(\approx\)1356 and 1564 cm\(^{-1}\) are the so-called D and G bands of carbon for disorder-induced feature (usually due to the presence of amorphous disordered carbon structure of CNPs) and stretching mode of C–C bonds, respectively.\(^{[40]}\) Here, the intensity ratio of D and G-band (\(I_D/I_G\)) is found to have decreasing value due to decrease in the relative intensity of D-band with increasing polymerization and CNP incorporation. It indicates that the effective defects are decreasing which is also further supported by PL results showing narrow-sharp peak with increasing time for a particular sample. On the other hand, the conventional Raman spectra of PANI have bands situated at the regions: 1165–1520 cm\(^{-1}\) (different C–N stretching modes—amines, imines, polarons, bipolarons) and 1570–1650 cm\(^{-1}\) (quinoid or benzenoid rings C–C stretching modes).\(^{[41,42]}\) In the present spectral decomposition, the contributory peaks
from PANI are at around 1180, 1456–1470, and 1612–1649 cm\(^{-1}\) (some peaks cannot be even decomposed for PANI due to the immense effect of CNPs in D and G-band positions, therefore neglected for analysis). Relative intensity of the band at around 1180 cm\(^{-1}\) has been increased with increasing polymerization time (T1–T4), verifying the predominance of polaronic carriers from benzenoid rings. The band at 1470 cm\(^{-1}\) has decreasing intensity with time and shifts toward lower wavenumber region down to 1456 cm\(^{-1}\). This can be attributed to C=\(\equiv\)N stretching of the quinoid and the shifting is due to incorporation and attachment of CNPs within PANI. The peak around 1612–1649 cm\(^{-1}\) is due to C=C stretching effects from quinoid and benzenoid rings but difficult to separate for verifying their individual contribution. This subpeak (as shown in Figure 3a–d) becomes very broad (FWHM value increases from 83.0 to 387.0) with increasing polymerization time and subsequently has also its center shifted from 1612 to 1649 cm\(^{-1}\) for corresponding samples CP-T1 to CP-T4. Such kind of increase in FWHM is already reported by Salvatierra et al.\(^{[42]}\) and is in the benzenoid part of the peak. Hence in this work here, the particular Raman peak broadening with increasing time from T1 to T4 indicates the formation of PANI enriched with more benzenoid units, when the amount of CNPs in the nanocomposites is higher. It also further gives the reason behind enhanced PL performance. Therefore, both Raman and FTIR indicate the functionalization of CNPs by PANI to form CNP-PANI where the amino group has played a key role for surface passivation, thus generating enhanced

Figure 2. Analytical spectra of XPS and FTIR. a) Selective high-resolution XPS spectra of C1s and N1s. b) Analytical FTIR spectra of sample series of CP for different reaction time T1, T2, T3, and T4 (1.5, 2, 2.5, and 3 h, respectively). The dotted lines in the figure indicate the blue shift of some peaks which can be associated with reaction time of CNP-PANI.

Figure 3. Raman spectra of CNP-PANI. Fitted Raman bands of sample series of CP for different reaction times T1, T2, T3, and T4. The red line indicates the fitted total profile adjustment where black dots have displayed the experimental data. Dotted blue lines are fitted for D and G bands of amorphous CNPs incorporated in PANI. The peak ratio of \(I_D/I_G\) decreases with the polymerization time (T1 to T4). Solid blue lines are fitted for three peak regions from PANI.
photoluminescence properties of CNPs and PANI qualitatively and quantitatively.

### 2.2. Optical Behavior of CNP-PANI

To investigate the optical properties of as-prepared CNP-PANI samples, UV–vis absorbance and PL spectra of the CNP-PANI dispersions were analyzed. Figure 4a shows several characteristic absorption peaks of CNP-PANI composites. The absorption bands, observed at 230 and 268 nm can be assigned to $\pi-\pi^*$ (aromatic $sp^2$ domains) and $n-\pi^*$ (broken symmetry transition from C=O) transitions in functionalized CNPs.\(^{[43,44]}\)

Other absorption around 368 nm corresponds to $\pi-\pi^*$ benzenoid transition within PANI.\(^{[40,45]}\) Besides, the connected chemical groups between CNPs and PANI may contribute to the absorption region band starting from 320 to 560 nm, which can arise from $\pi-\pi$ interaction. Absorption at 368 and 460 nm can be attributed to a transition from $\sigma$ and $\pi$ orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). A circumstantial study of PL emission has been performed upon using this energy band as excitation.

CNP-PANI nanocomposites in the present study have exhibited excitation-independent triple-band emission which is an excellent outcome to utilize the waste carbon product for further optoelectronic applications at the same time making the process economic and green. A dynamic study of PL characteristics has been performed for the assorted series of composites for different amounts of carbon nanoparticles functionalized within polyaniline (CP and h-CP series) associating with different reaction times (T1–T4). The particular of samples with their notation have been given in the Experimental Section. Figure 4b represents triple-band PL emission spectra for the sample series of CP for different functionalization time when excited at 280 nm. The strong emission peak at 360 nm ($I_{P1}$) may be attributed to benzenoid $\pi-\pi^*$ transition in the polymer backbone due to the well-matched absorption band information obtained earlier during the UV–vis study (i.e., the peak at 368 nm corresponding to benzenoid $\pi-\pi^*$ transition of PANI component).\(^{[46]}\) The other peak at \(\approx 466\) nm ($I_{P2}$) is due...
to synergic effect between the two, CNPs and PANI for their conjugation. Another peak at ≈596 nm (I_P3) can be assigned as a luminescence effect from functionalized CNPs. Emission at 530–570 nm has been previously reported for NH₂-functionalized carbon materials.[17] In the present work, a further red-shift in PL emission for CNP-PANI should have originated from the change of electronic structure by formation of functionalized CNP-PANI. However initially, for time T1 we have noticed a low intense broad emission peak originating from 400 to 750 nm, may be a combined effect of peak I_P2 and I_P1. The result can be attributed to a weak interaction between CNPs and PANI in the elementary form of reaction. Also, a tiny peak around 350 nm has been originated due to PANI. But, with increasing polymerization time the three peaks come out and get intensified. This observation implies that the strong triple-band emission state exists in CNP-PANI hybrid systems, unlike most previously reported PL of carbon particles.[47,48] The comparative PL emission for these three consecutive wavelengths has been influenced by the reaction time between CNPs and PANI. The phenomenon can be due to the development of an oxidation-resistant reaction through the introduction of CNPs in aniline monomer during polymerization. This can be correlated with the results of Q/B ring ratio, determined from FTIR analysis. Decreasing nature in Q/B signifies the presence of more reduced emeraldine segments in CNP-PANI composite, can be ascribed to strong π-π interaction between CNPs and PANI. Consequently, CNPs interact with polymeric chains where the incorporated carbon nanoparticles reduce the PANI through charge transfer, increasing strongly with reaction time. As a result, with time (from T1 to T4) CNPs incorporated within PANI lead to an influential effect on PL emissions for I_P2 and I_P3. The contributing effect of PL emission due to functionalized form of CNPs can be analyzed from the integrated peak ratio of I_P2/I_P1 and I_P3/I_P1, where I_P1 is the PL emission from PANI itself. Interestingly, the ratios (I_P2/I_P1 and I_P3/I_P1) rise from T1 to T4 indicating strong π-π interaction within the composite. Peak intensities were recorded as maximum values for the sample CP-T4. All these features are well distinguished from other previously reported CNPs.[17] The optical performance relates to the change of chemical structure or local environment of CNPs that have occurred here due to the functionalization of common oven produced carbon material into polyaniline matrix.

The above study has gradually revealed how we have achieved interesting PL properties from the CNP-PANI composites which had no such distinguished and sharp features for its individual components whether it is CNPs or PANI (just broad hump-like spectra as shown in Figure S5, Supporting Information). Additionally, we have studied more details in the variation of PL emission correlated with the change in CNPs concentration within PANI. Figure 4c,d shows PL emission spectra for lower concentration of CNPs (named with l-CP) and higher concentration of CNPs (named with h-CP), respectively. Though for higher CNP concentration (than that in CP series samples) there is no pronounced change in the pattern of emission, but for lower CNP concentration we have noticed some anomalous features (compatible with the previously discussed reasons). For example, the PL emission spectrum for sample l-CP-T1 (with low CNP concentration and initial stage of functionalization) exhibits a strong peak of I_P1 at 364 nm with a weak shoulder of I_P2 unlike other CNP-PANI samples. The initial hump of second PL emission peak (I_P2) can be attributed to weak synergic effect between the two, CNPs and PANI for their conjugation. The low intense blunt peak at ≈596 nm (I_P3) can also be understood as a feeble luminescence effect from the weakly functionalized CNPs. Further, the integrated peak area ratio of I_P2/I_P1 and I_P3/I_P1 are getting higher with increasing reaction time, which is justifiable by the previous analysis due to the presence of lower CNP concentration and lower functionalization effect therefore. More explicitly, the integrated areas of as discussed peak ratio ((I_P2/I_P1 and I_P3/I_P1) for all the series samples (l-CP, CP, and h-CP) for functionalization time T2, T3, and T4 have been illustrated in Figure 4e. According to this analytical data, it is clear that the luminescence effect from CNP-PANI composite is progressive for sample series of CP and it effectively shows promising results for CP-T4, comparable with all others photoluminescence effects.

In accordance with the absorption spectra of CNP-PANI composites, we measured PL excitation-emission (PLE) maps within the UV-visible range. Figure 5 shows a consecutive series of PLE maps of samples CP-T1, CP-T2, CP-T3, and CP-T4. An acute arena of PL emission centered at 596 nm (I_P1) clearly reveals in all the PLE maps which is the effect of surface passivation on the optical properties of functionalized CNPs within PANI. All the consecutive PLE maps have been followed by the formation of metamorphosis in arena of I_P1. The shape of the PL arena has been changed from circular to elliptical with increasing interaction between CNPs and PANI. These observed features of metamorphosis in PL arena are the results of narrower and sharper emission of I_P1 with increasing T-value. Decrease in peak broadening is because of increase in surface passivation with ongoing functionalization time duration, causing less defect states. It can also be noticed that the most intense point of the arena (reddish part of the PLE map) is shifted toward exposition to higher excitation wavelength from T1 to T4. In detail, the demonstration of PL emission at 596 nm when the excitation wavelength is changed from 420 to 560 nm has been shown in the Supporting Information. Figure S6 (Supporting Information) shows how the emission peak at 596 nm first increases for increasing excitation wavelength and reaches a maximum at PLE of 540 nm and then starts to decrease with further increase in excitation wavelength, while the peak position remains unchanged. Generally, the PL reported for carbon dots are highly excitation-dependent originating from inhomogeneous dot size effect and or surface defects. However, in the present case, PL of CNPs is thoroughly showing excitation-independent behavior which is considered to be related to the surface passivation effect because of using NH₂-group-rich aniline as the starting monomer. During the in situ polymerization process to form PANI while simultaneously functionalizing CNPs, it is the surface amino groups that passivate the traps on surface of CNPs and lead to a single transition mode. In addition, another interesting observation in PLE maps has been noticed for all the CNP-PANI composites at the elementary reaction condition (i.e., T1 state). PLE maps of l-CP-T1 and h-CP-T1 have been given in Figure S7 (Supporting Information). An anomalous behavior of emission has been noticed for l-CP-T1 where the I_P1 displays more intense
emission comparable with $I_{P3}$, indicating less functionalization effect of CNPs with PANI.

As-synthesized CNP-PANI samples were also found to be strongly luminescent on a substrate (deposited as thin films). As shown in Figure 6, the fluorescence image of a typical CNP-PANI sample obtained by confocal microscopy exhibits a bright and intense luminescence effect from the material (excitation wavelength: 488 nm). However, it should be cautioned that the observed brightness variation might also be subject to effects from some measurement issues, such as some luminescent centers being slightly out of the focal plane.

2.3. Concentration-Dependent PL

Furthermore, Figure 7a shows a clear correlation of $I_{P2}/I_{P1}$ and $I_{P3}/I_{P1}$ with the concentration of a typical sample series of CP-T4, dispersed in the solution. Each time sample concentration was decreased to half of the previous one. The exponential decreasing factor of the integrated peak ration of $I_{P2}/I_{P1}$ and $I_{P3}/I_{P1}$ indicates that these changes in the dispersion of the CP-T4 can have large effects on the number of reabsorption events a photon undergoes. It can be because of photon reabsorption\(^{[49,50]}\) at the lower wavelength emission (PL emission at $\approx 360$ nm) which is most strongly affected by concentration of CNP-PANI in the solution, over the total detected emissions.

For the range of concentrations investigated, it shows a purely monotonic trend with the peak rations.

Again, we have investigated the PL emission around at 596 nm with excitation of 500 nm. The PL intensity is completely dependent on the sample concentration. Initially, PL intensity increases with decreasing factor of sample concentration in the solution. But further decrease of sample concentration, PL intensity decreases again. The phenomenon can be
2.4. PL Probing for Ion Sensing

Recently, photoluminescent carbon dot-based nanosensors are being extensively developed for practical field applications.\textsuperscript{[52,53]} So, here we have tried to explore the feasibility of using as-prepared CNP-PANI as a PL sensing platform and found that it can be actually used as an effective PL probe for the detection of Fe\textsuperscript{3+} ion. It is well-known that Fe\textsuperscript{3+} ions are indispensible for a large number of living systems and act as a key material for many important biochemical processes like oxygen uptake, oxygen metabolism, and electron transfer. So, detection of such metal ions is considered to be highly desirable. Here in Figure 8a, the PL intensity of as-synthesized CNP-PANI (optimized one, i.e., CP-T4; excitation wavelength: 500 nm) at 596 nm was observed to decrease gradually with increasing Fe\textsuperscript{3+} ion concentration, indicating that Fe\textsuperscript{3+} can effectively quench the photoluminescence of CNP-PANI.

This quenching can be simply attributed to nonradiative electron-transfer process generated due to adsorption of Fe\textsuperscript{3+} ion on the surface of material that involves partial transfer for an electron in the excited state to the d orbital of Fe\textsuperscript{3+}. To get insight into the quenching mechanism, corresponding data were analyzed by the familiar Stern–Volmer equation. The full concentration range (0–60 × 10\textsuperscript{-6} m) plot as presented in Figure 8b is not rigorously following the conventional linear Stern–Volmer equation inferring that both dynamic and static quenching processes occur in the above-mentioned analytical system. Other two types of CNP-PANI samples (h-CP-T4 and l-CP-T4) have also responded (Figure S8, Supporting Information) in this sensing experiment but the quenching effect is much lower than that of CP-T4 (see inset of Figure 8b). A PL emission titration experiment was also performed for CP-T4 for evaluating the quantitative detection capability of this system at a signal-to-noise ratio of 3. The limit of detection (LOD) of Fe\textsuperscript{3+} is estimated to be about 12 × 10\textsuperscript{-9} m based on three times standard deviation rule (LOD = 3δ/slope) from the linear fit of Stern–Volmer equation in the range of 0–160 × 10\textsuperscript{-9} m (the correlation coefficient $R^2$ is 0.99, Figure S9, Supporting Information). The result is significantly lower compared to the previous results.\textsuperscript{[54,55]} So, the material is highly sensitive toward detecting Fe\textsuperscript{3+} ions. In addition, to evaluate the detection ability of this system for other various biologically and environmentally relevant metal ions, we investigated the PL quenching effect for ions including Na\textsuperscript{+}, K\textsuperscript{+}, Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Mn\textsuperscript{2+}, Fe\textsuperscript{3+}, Ag\textsuperscript{+}, Cu\textsuperscript{2+}, Co\textsuperscript{2+}, Zn\textsuperscript{2+}, and Pb\textsuperscript{2+}. The response of the assay was tested for these different ions at a concentration of 10 × 10\textsuperscript{-6} M under the same conditions as those used with Fe\textsuperscript{3+} (Figure S10, Supporting Information). Remarkably, no significant PL quenching effect was observed for adding the other metal ions (some showed minimal quenching effect such that the influence is almost negligible) except Cu\textsuperscript{2+} ions. The Cu\textsuperscript{2+} ions showed dramatic decrease in the PL intensity; herein the quenching can be ascribed to the fact that Cu\textsuperscript{2+} is a paramagnetic ion with unfilled d shell and hence can result in quench of the PL intensity via electron or energy transfer. Though Cu\textsuperscript{2+} showed a relatively strong quenching effect (Figure S11, Supporting Information) but, while tested for titration experiment for comparing the detection ability with that of Fe\textsuperscript{3+} under same conditions, the results demonstrated for Fe\textsuperscript{3+} ions are far better.
atom of the amino groups on CNP-PANI surface enables this composite material as a promising nanosensing platform for Fe$^{3+}$ ions with high efficiency and selectivity criteria. Even if Cu$^{2+}$ at high concentration interferes with Fe$^{3+}$ detection, the issue can be circumvented by using ethylenediaminetetraacetic acid (EDTA) as a strong chelating agent of Cu$^{2+}$ ions, indicating also the ability of transforming our system toward the Fe$^{3+}$ selectivity.

In summary, incorporation of carbon nanoparticles within polyaniline has been proven to be an effective strategy for producing fluorescent CNPs. Moreover, no further chemical modification is needed before using cooking oven produced trash carbon materials; thus, it incorporates green nanotechnology for efficient reduction of waste products and offers the advantages of an economic and less toxic procedure for application. Such CNP-PANI nanocomposites exhibit excitation-wave-length-independent photoluminescent behavior with luminescence intensity progressively increasing as the CNPs content increased; the optimal condition was also achieved where photoluminescence reached its maximum. The CNP-PANI nanocomposites exhibit broad PL spectra covering most of the visible range but with three distinct intense peaks, thus opening up the possibility of using these materials as luminophores in white light LEDs and multicolor patterning systems. As-synthesized CNP-PANI has been further tested as a sensing platform for metal ions which provided data in support of its highly sensitive detection ability for Fe$^{3+}$ and Cu$^{2+}$ ions. Our present study is important because it provides a simple, low-cost route toward incorporating carbon nanoparticles within a polymer to get CNP-PANI that can be used further for sensing and other optoelectronics devices.

3. Experimental Section

**Reagents and Materials:** CNPs used in the present work were simply the waste carbon product collected from cooking oven (the morphology of the waste carbon comprised of CNPs is discussed later in the Results and Discussions). Aniline monomer (Aldrich) was distilled under vacuum prior to use. Ammonium persulfate (APS; 99.99%, Aldrich) and all other reagents like hydrochloric acid (HCl; 35%, Alfa Aesar) and ethylenediaminetetraacetic acid (EDTA) as a strong chelating agent of Cu$^{2+}$ and other optoelectronics devices.

**Preparation of CNP-PANI:** Waste carbon products were used here without any further chemical modification or purification. The preparatory strategy was both green and economic. The polymerization was done in 1:1 (v/v) ethanol-water media. Ethanol here helped to disperse the CNPs within precursor during reaction and also slow down the polymerization process to some extent. The CNPs were introduced into the polymer following a typical chemical oxidative polymerization of aniline at 0 °C (ice bath) in presence of APS as oxidant and HCl as dopant. Aniline was added to 20 mL of ethanol-water solution and cooled at 0 °C. Some amount of CNPs (for different samples preparation, 1.1, 2.2, and 4.4 mg) was dispersed in 10 mL of ethanol-water mixture (to ensure stable dispersion it was mildly stirred for 1 h on a magnetic stirrer with 430 rpm speed) and then APS and HCl (both used with the same number of moles as the number of moles of aniline monomer) were added to it. After that, this mixture was kept for cooling at 0 °C for few minutes and then was dropwise added to the precooled monomer solution with 10 s shaking. The polymerization was allowed to continue unagitated for 1.5 h or more (for other samples with time.
variations, e.g., 2, 2.5, and 3 h). The dark green precipitate was collected after filtration and several times washing with DI water and methanol and was finally dried in a vacuum oven at 60 °C for 24 h. Either powders or films were obtained depending on the nature of characterization requirements. The optimized sample was obtained by using 2.2 mg of CNPs; hence the following nomenclature is used: CP for the series of the optimized ones with different time durations like T1 (1.5 h), T2 (2 h), T3 (2.5 h), T4 (3 h); J-CP and H-CP for lower and higher concentrations of CNPs (i.e., 1.1 and 4.4 mg), respectively.

Characterizations: The measurement of phase imaging under bias voltage has been performed by AFM (Asylum MFP-3D) in tapping mode using high-resolution conducting probe. Morphological studies and composition analysis were carried out by FESEM-FIB (Carl Zeiss Auriga Crossbeam microscope) equipped with an EDX (OXFORD) analyser. The samples were further characterized by FTIR spectroscopy and UV-vis–NIR spectroscopy (Shimadzu, UV-3101PC). FTIR spectra for the samples were acquired using an attenuated total reflectance (ATR) sampling accessory (Smart iTR) equipped with a single-bounce diamond crystal on a Thermo Nicolet 6700 Spectrometer (used in the absorbance mode at 50 scans with a resolution of 4 cm⁻¹ for frequency range 400–4000 cm⁻¹). XPS was performed on a KRATOS Analytical AMICUS instrument equipped with an achromatic Al Kα X-ray source (1486.6 eV). For a typical analysis, the source was operated at voltage of 10 kV and current of 10 mA. The survey spectra were acquired using a step of 1 eV, whereas 0.1 eV was employed for acquiring narrow scan regions. The pressure in analysis chamber was less than 5 × 10⁻⁶ Pa. The deconvolution of peaks was done with fitting by a Gaussian–Lorentzian ratio of 0.5 and a constant FWHM of 1.9 eV. The binding energy of all samples was corrected for eventual charging by shifting the convoluted peak intensity of C1s to 284.6 eV. The Raman measurements energy of all samples was corrected for eventual charging by shifting the convoluted peak intensity of C1s to 284.6 eV. The Raman measurements with the excitation laser line of 532 nm were performed using a WITEC Confocal Raman system in air ambient environment. The diamond crystal on a Thermo Nicolet 6700 Spectrometer (used in the analyser. The samples were further characterized by FTIR spectroscopy and composition analysis were carried out by FESEM-FIB (Carl Zeiss).

Detection of ions: The detection of Fe³⁺ ions was performed in PBS (10 × 10⁻³ M, pH 7.1) buffer solution. In a typical run, CNP-PANI sample dispersion (loading 10 µg mL⁻¹) was added into 3 mL of PBS buffer in a spectrophotometer quartz cuvette, followed by addition of different concentrations of Fe³⁺ ions. The PL spectra were recorded after reaction for 15 min. To investigate the selectivity of Fe³⁺ ions and possible interference of other cations, following salts were used: NaCl, KCl, CaCl₂, CdCl₂, MgCl₂, MnCl₂, FeCl₃, AgNO₃, CuCl₂, ZnCl₂, H₂O, CoCl₂, FeSO₄, and ZnCl₂, and tested with the sample stock solution (10 × 10⁻³ M) in buffer in a similar way. All the experiments were performed at room temperature.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
carbon nanoparticles, functionalization, ion sensing, photoluminescence, polyaniline


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