Nitrogen and Phosphorus Co-Doped Carbon Dots for Selective Detection of Nitro Explosives

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ABSTRACT: In this work, a highly selective and sensitive method has been developed for the detection of trinitrophenol (TNP), which is a dangerous explosive. For this purpose, N and P co-doped carbon dots (NP-Cdots) have been used. Synthesis of N and P co-doped carbon dots has been carried out by a simple and quick method. X-ray photoelectron spectroscopy analysis was carried out to detect the doping of N and P. These carbon dots are insoluble in water (inNP-Cdots). These carbon dots were functionalized by treating them with conc. HNO₃ so that they become water-soluble (wsNP-Cdots). These dots were characterized by different analytical techniques such as IR, UV−vis, and fluorescence spectroscopy. The as-prepared wsNP-Cdots have good fluorescence properties. The average diameter of wsNP-Cdots is found to be 5.7 nm with an interlayer spacing (d-spacing) of 0.16 nm. The as-prepared wsNP-Cdots are highly sensitive and selective toward TNP, as observed using a fluorescence quenching technique. The quenching constant for TNP is found to be very high (8.06 × 10⁴ M⁻¹), which indicates its high quenching ability. The limit of detection is found to be 23 μM.

1. INTRODUCTION

Nitro aromatic compounds are widely used in present-day military explosives.¹,² These nitro containing compounds have widespread applications in military explosives over the last 100 years.³ Commonly used nitroexplosive ingredients are 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), and 2,4,6-trinitrophenol (TNP).⁴,⁵ TNT is the most demonstrative nitro aromatic compound,⁶ while DNT is volatile and soluble and used as an intermediate for the synthesis of TNT.⁷⁸ TNP has extraordinary explosive power, and it is used in a variety of different industries such as fireworks, matches, dyes, leather, and glass. It is widely recognized as a toxic pollutant, and it also possess mutagenic properties as it transforms into picramic acid (2-amino-4,6-dinitrophenol).⁹¹⁰ They are also used in industrial explosives and often found in a land which is unexploded.¹¹ They can be soaked into land water and then mix and pollute the sea.¹²¹³ These contaminations may lead to adverse effects on humans, such as anemia; liver function disabilities; and discoloration of hair, skin, and nails, and so forth.¹⁴¹⁵ Therefore, the detection of these explosives has become the most challenging duty in daily life as it concerns with homeland safety, forensic research, and military applications.¹⁶

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and phosphorous doping in carbon nanomaterials is carried out. Therefore, easy and quick synthesis of N- and P-doped carbon nanomaterials is a key requirement. Many reports have reported N doping to carbon nanotubes, graphene, and carbon nanoparticles. However, different defects were observed in N-doped C-dots such as frail resistance to the metal ion interface and low-stable decentrality in water. To overcome this defects, P is frequently used to dope in N-doped C-dots. In few reports, phosphoric acid has been used with aliphatic amine/NH\textsubscript{3}·H\textsubscript{2}O for the doping of P and N in C-dots. In another case, the use of 1,2 diethylenediamine has been reported as an N-dopant, whereas phosphoric acid was used as a P-dopant. Later, the N and P dual doped C-dots were used to detect Cr(VI) and Fe\textsuperscript{3+} ions under low concentration and for drug delivery. Hence, easy and quick synthesis of N- and P-doped carbon nanomaterials is important.

Herein, we report the easy and quick method for the synthesis of N and P co-doped NP-Cdots. Dextrose is used as a carbon source, liq. NH\textsubscript{3} is used as N source, and P\textsubscript{2}O\textsubscript{5} is used as the source of P. As-prepared NP-Cdots are insoluble in water; however, after treatment with conc. HNO\textsubscript{3}, they become water soluble. wsNP-Cdots have good fluorescence properties, and they have high selectivity toward nitro explosives, TNP. In order to define an ideal sensor, several parameters such as high selectivity, water solubility, reasonable sensitivity, and low toxicity need to be fulfilled. The proposed sensor has high selectivity, reasonable sensitivity, water solubility, and low toxicity.

2. EXPERIMENTAL SECTION

2.1. Chemicals and Instrumentation. TNT and RDX were donated by HEMRL Pune, India. Other nitro derivatives were purchased from Sigma-Aldrich. Nitrate and acetate salts of different metal ions were purchased from SD fine chemicals. Distilled water was used throughout the experiment. The PerkinElmer FT-IR spectrometer was used to record the IR spectra of inNP-Cdots and wsNP-Cdots in the range of 4000–400 cm\textsuperscript{-1}. For the absorption spectra of TNP, a UV-2450 PC Shimadzu UV–Vis spectrophotometer was used. X-ray photoelectron spectroscopy (XPS) measurements were carried out on AXIS Supra, Kratos Analytical, UK. For transmission electron microscopy (TEM) analysis, Philips TEM CM 200 was used with operating voltages ranging between 20 and 200 kV, while for high-resolution TEM (HRTEM), field emission gun-transmission electron microscope 300 kV, Tecnai G2, F30 with accelerating potential 300 kV was used. All fluorescence studies were carried out using an RF-5301PC Shimadzu Spectrofluorophotometer at 298 K. Merck silica gel 60 F254 thin layer chromatography (TLC) plates were used for the live application of wsNP-Cdots. Fluorescence decay was recorded by a Delta Flex time-correlated single-photon counting technique using 350 nm excitation light with full-width half maximum of instrument response function 77 ps. A photomultiplier hybrid (PMT-hybrid) was used as a detector to monitor the emitting photons through a monochromator. All the fluorescence decay collected at an emission polarizer were set at a magic angle (54.7°) to avoid the effect of rational relaxation of the molecule on the observed decay. Emission decays were fit by IRF (Instrument Response Function) which is collected by the ludox solution. Decay spectra fitted by using Ez time software through an iterative deconvolution method

\[ I(t) = I_0 \sum a_i e^{-t/\tau_i} \]

where \( I_0 \) and \( I(t) \) are the photoluminescence intensity at \( t = 0 \) and \( t = t \), respectively, \( \tau \) is the lifetime, and \( a_i \) is the amplitude of the \( i \)th component.
2.2. Synthesis of inNP-Cdots. In a typical synthesis, 3 mL of saturated solution of dextrose in aq. NH₃ was added dropwise to 1 g of P₂O₅. The reaction is highly exothermic, and a black mass is obtained. Further addition of water subsidizes the reaction. Then, the reaction mixture is centrifuged to collect inNP-Cdots. It is then washed with distilled water for several times and dried in an oven.

2.3. Synthesis of wsNP-Cdots. wsNP-Cdots were synthesized using a previously reported method. In a typical synthesis, to 500 mg of inNP-Cdots, 100 mL 40% conc. HNO₃ solution was added. The resultant mixture was then refluxed for 6 h. After that nitric acid solution was decanted off. The residue obtained was centrifuged and dried on a water bath. The black mass was again redissolved in water and kept on a water bath (100 °C) till dryness. The same procedure was carried out till the traces of nitric acid get removed. The final black mass was dried and used for further analysis. A graphical illustration is shown in Scheme 1.

2.4. Detection of TNP. The detection of TNP was carried out at room temperature using a fluorescence quenching technique. For the detection of TNP, first, a stock solution of wsNP-Cdots was prepared by adding 5 mg of wsNP-Cdots to 100 mL of distilled water. Then, 10 μL of TNP (1 × 10⁻² M) solution was added to the 2 mL stock solution, and the emission intensity at 340 nm was observed. A constant volume of TNP (10 μL) was added gradually to the same solution to examine further quenching of wsNP-Cdots. For comparison, 10 μL of other nitro explosives (1 × 10⁻² M) and metal ions (1 × 10⁻² M) were added to the 2 mL stock solution of wsNP-Cdots, and the emission intensity at 340 nm was checked.

3. RESULT AND DISCUSSION

3.1. IR Spectroscopy. To check the surface functionalization of the prepared wsNP-Cdots, IR spectroscopy was used. The IR spectra of inNP-Cdots and wsNP-Cdots are shown in Figure 1. In the inNP-Cdots spectrum, the peak at 1608 cm⁻¹ corresponds to the C=C stretching frequency and the peak around 3000 cm⁻¹ corresponds to O–H stretching. In inNP-Cdots and wsNP-Cdots, the peak observed at 1703 cm⁻¹ corresponds to the C=O stretching frequency but having different intensity. The increase in the intensity of peak at 1703 and 3000 cm⁻¹ relative to inNP-Cdots clearly indicates the presence of carboxylic and hydroxy groups on the surface of wsNP-Cdots, leading to the formation of defects on the surface. Because of these surface defects, the wsNP-Cdots become water soluble. The peaks observed at 1436 and 879 cm⁻¹ could be attributed to C–P and P–O–C bonds.

3.2. Morphological Studies. The morphology of NP-Cdots was investigated by TEM and HRTEM microscopy. TEM images of inNP-Cdots are shown in Figure 2a,b. The presence of particles in the cluster form can be seen in the image. However, a close observation reveals the formation of somewhat spherical particles. The HRTEM images of wsNP-Cdots are shown in Figure 2c,d. Distinct uniform spherical particles of wsNP-Cdots can be seen in these images. The average size of wsNP-Cdots is found to be 5.7 nm. The maximum number of wsNP-Cdots ranges between 5 and 7 nm in size. The HRTEM image of such wsNP-Cdots shows the presence of layers, and the interlayer spacing (d-spacing) is found to be 0.16 nm (Figure 2d) which is characteristics of such materials.

3.3. XPS Analysis. XPS is an important tool to detect the presence of elements present in a material. Figure 3 shows the XPS spectrum of the inNP-Cdots. The presence of four elements, namely, C, O, N, and P in the material is observed, which confirms the doping of N and P in the Cdots. High-resolution peak fitting of C₁s (Figure 3b) shows that three prominent peaks corresponds to three binding states. The peak at 283.6 eV corresponds to C≡C, and the peak at 285.2 eV corresponds to C–OH binding states. The peak at 284.7 eV is attributed to C–C/C≡P, which confirms the bonding between C and P. In O₁s, high-resolution spectrum (Figure 3c), binding states observed at 530.5, 530.7, and 531.9 eV are ascribed to O=C–O, O=O, and P–O respectively. Figure 3d shows high-resolution peak fitting of N₁s revealing three prominent peaks viz. 393.3, 398.7, and 401.1 eV. The peak at 393.3 eV corresponds to pyrrolidine like N and peak 398.7 eV corresponds to pyridinic like N, which confirms the two different states of N. The peak at 401.1 eV corresponds to graphitic N. Two different peaks observed in the XPS spectrum at 130.1

Figure 1. IR spectra of inNP-Cdots (black) and wsNP-Cdots (red).

Figure 2. TEM and HRTEM images of inNP-Cdots and wsNP-Cdots. (a,b) TEM images of inNP-Cdots showing a spherical morphology. (c) HRTEM image of wsNP-Cdots with a spherical morphology and (d) HRTEM image showing the interlayers with an interplanar distance in wsNP-Cdots.
and 190.5 eV can be attributed to P2P (Figure 3e) and P2S (Figure 3f), respectively. High-resolution peak fitting of P2P shows two prominent peaks at 131.1 and 133.9 eV, which corresponds to P2p3/2 and P−C, respectively, while P2S shows only one prominent peak at 190.5 eV.46

3.4. Fluorescence Spectroscopy. In the detection of any analyte, optical properties play a very important role. When excited at different wavelengths wsNP-Cdots emit light at different wavelengths with different intensity. wsNP-Cdots has a wide range of fluorescence excitation wavelengths. When excited at 280−540 nm with an increment of 20 nm, it shows photoluminescence at every wavelength (Figure 4). High fluorescence emission intensity is observed when excited at a wavelength of 380 nm. The fluorescence observed in these particles is due to the extensive surface derivatization through carboxylic and hydroxy groups. When inNP-Cdots treated with conc. HNO3, defects were formed on the surface of inNP-Cdots which leads to their solubilization in water. The high density of carboxylic groups on the surface of wsNP-Cdots leads to quantum confinement and surface passivation. Because of this wsNP-Cdots has a wide range of fluorescence through the visible area (280−540 nm).52−54 The other possible mechanism for such luminescence is radiative combination of excitations.52−54

3.5. Detection of TNP. Solution-based fluorescence quenching experiments were carried out for the detection of TNP in aqueous medium. Figure 5a shows the fluorescence spectra of wsNP-Cdots and TNP−wsNP-Cdots under the same experimental conditions, and Figure 5b exhibits the corresponding Stern−Volmer (SV) plot. When excited at 340 nm wsNP-Cdots gives a strong emission at 452 nm. When TNP (1 × 10−2 M) was added to the solution of wsNP-Cdots (0.05 mg/mL), the quenching of fluorescence occurs (Figure 5a). Even after quenching of the wsNP-Cdots, there is no change in emission wavelength. Sequential fluorescence quenching titrations were carried out by constant addition of nitro explosives. Fast and high quenching occurs during the quenching titrations.

By adding 10 μL solution of TNP (1 × 10−2 M) to the wsNP-Cdots (0.05 mg/mL) solution, 69.56% quenching occurs (Figure 6), which is very high compared to other nitro explosives and metal ions. Great selectivity observed for TNP among other nitro explosives, namely, TNT, RDX, 2,6-DNT, DMDNB, nitromethane, and metal ions such as Zn2+, Ni2+, Co2+, Cu2+, Pb2+, Cd2+, Na+, Ba2+, and Fe2+ (1 × 10−2 M) (Figure 6).

Furthermore, the fluorescence quenching efficiency of TNP was determined by using the SV plot. The SV plot of I0/I versus concentration of the analyte is shown in Figure 7. It is plotted for titrations in the range of 100−300 μM. The SV plot is linear and gives 0.9861 correlation coefficient (R2). The quenching constant and sensitivity were calculated by using

![Figure 3. (a) Full scan XPS spectrum of inNP-Cdots along with high-resolution XPS spectra of (b) C 1s, (c) O 1s, (d) N 1s, (e) P 2p, and (f) P 2S.](image)

![Figure 4. Fluorescence emission spectra of wsNP-Cdots at excitation in the range of 280−540 nm with an increment of 20 nm. Inset—solution of wsNP-Cdots in water in the absence and presence of UV light.](image)
eqn \( I_0/I = 1 + K_{SV}[\text{TNP}] \), where \( I_0 \) and \( I \) are the fluorescence intensities of wsNP-Cdots before and after the addition of TNP, \( K_{SV} \) is quenching constant, and \([\text{TNP}]\) is molar concentration of TNP. Using this equation, the quenching constant has been estimated to be \( 8.06 \times 10^4 \) M\(^{-1}\). The calculated quenching constant is very high which indicates the quenching ability of wsNP-Cdots toward TNP is very good.\(^{55}\)

The detection limit (LOD) is calculated by the formula, LOD = \( 3\sigma/k \), where \( \sigma \) is the standard deviation of blank sample and \( k \) is slope of the SV plot. Using this equation, the LOD is found to be 23 \( \mu \)M.

To examine the interference study, it is better to check the quenching response of wsNP-Cdots toward TNP in the presence of other nitro explosives and metal ions. Figure 8 shows the sequential quenching intensity of TNP in the presence of other analytes. After the addition of other analytes (10 \( \mu \)L, 1 \( \times \) \( 10^{-2} \) M) to the solution of wsNP-Cdots (2 mL, 0.05 mg/mL), there is no such quenching in the fluorescence intensity, but after the addition of TNP (10 \( \mu \)L, 1 \( \times \) \( 10^{-2} \) M) to the same solution, quenching is initiated. The stepwise reduction in fluorescence intensity clearly indicates the high sensitivity of the wsNP-Cdots toward TNP even in the presence of other nitro explosives and metal ions.

To recognize the selectivity and quenching mechanism of wsNP-Cdots toward TNP, different mechanisms such as photoinduced electron transfer and Förster resonance energy transfer (FRET) was considered. As the SV plot is nonlinear (Figure 5b), it is indicated that the mechanism is through FRET, not by photoinduced electron transfer.\(^{56}\) The resonance energy transfer only occurs when the absorbance band of the analyte and emission band of the fluorophore has an effective overlap, and both the analyte and fluorophore are adjacent.\(^{57}\)

The resonance energy transfer plays an effective role in
fluorescence quenching along with the improvement in sensitivity. From Figure 9a, it is clearly seen that there is overlap between the both spectrums (emission band of the fluorophore and absorbance band of the analyte). The quenching mechanism is explained in Figure 9b. Upon excitation, wsNP-Cdots gives fluorescence but in the presence of the TNP, it transfers the fluorescence resonance energy to TNP. TNP absorbs it, and quenching in fluorescence occurs.

To confirm the FRET mechanism, we measured the fluorescence lifetime of wsNP-Cdots in the presence and absence of TNP. Figure 10 displays fluorescence decay profiles of wsNP-Cdots with various concentrations of TNP.

3.6. Real Time Detection. For a practical use of any application, a method has to be easy and one should be able to carry out it anywhere. Taking this into consideration, we have prepared wsNP-Cdots (0.05 mg/mL)-coated TLC plates. The as-prepared TLC plates show good fluorescence under UV lights. The individual TLC plates were half-dipped in the aqueous solution of analytes (1 × 10^{-2} M), and the fluorescence quenching for each analyte was observed. The TLC plate dipped in TNP shows high quenching while other TLC plates show no quenching (Figure 11). This observation clearly indicates the use of wsNP-Cdots for selective and real-time detection of TNP.

4. CONCLUSIONS

In conclusion, N and P co-doped NP-Cdots were quickly and easily synthesized. As-prepared inNP-Cdots are water insoluble and after treatment with conc. HNO₃, they become water soluble (wsNP-Cdots). The wsNP-Cdots are having very low particle size and show the characteristic interlayer spacing of carbon materials. The wsNP-Cdots show good fluorescence properties, and they are highly selective and sensitive (23 μM) toward nitro explosive TNP. Easy real-time use of wsNP-Cdots-coated TLC plates for the detection of TNP is also possible.

Table 1. Fluorescence Lifetimes of wsNP-Cdots in the Presence of TNP

| amount of TNP added (μL) | a₁ | a₂ | a₃ | τ₁ (ns) | τ₂ (ns) | τ₃ (ns) | τav (ns) |
|--------------------------|----|----|----|---------|---------|---------|----------|
| 0                        | 0.34 | 1.91 | 0.12 | 7.68 | 0.54 | 0.24 | 1.7 |
| 5                        | 0.34 | 1.94 | 0.11 | 7.75 | 0.55 | 0.26 | 1.65 |
| 10                       | 0.34 | 1.92 | 0.12 | 7.68 | 0.54 | 0.25 | 1.71 |
| 20                       | 0.35 | 1.91 | 0.12 | 7.46 | 0.53 | 0.27 | 1.7 |
| 30                       | 0.35 | 1.87 | 0.12 | 7.33 | 0.53 | 0.25 | 1.67 |
| 40                       | 0.36 | 1.88 | 0.13 | 7.22 | 0.51 | 0.28 | 1.76 |
| 50                       | 0.36 | 1.83 | 0.14 | 6.90 | 0.52 | 0.28 | 1.76 |
| 60                       | 0.37 | 1.77 | 0.47 | 0.28 | 0.16 | 6.68 | 1.79 |
| 70                       | 0.46 | 0.28 | 0.39 | 1.77 | 0.15 | 6.74 | 1.83 |

Where a₁ + a₂ + a₃ = 1 and τav = a₁τ₁ + a₂τ₂ + a₃τ₃.

To confirm the FRET mechanism, we measured the fluorescence lifetime of wsNP-Cdots in the presence and absence of TNP. Figure 10 displays fluorescence decay profiles of wsNP-Cdots with various concentrations of TNP.

Figure 9. (a) Emission spectrum of wsNP-Cdots and absorption spectrum of TNP shows high extent of overlap and (b) fluorescence quenching mechanism of wsNP-Cdots in the presence of TNP.

Figure 10. Fluorescence lifetime decay profiles wsNP-Cdots with various concentrations of TNP.

Figure 11. Real-time detection of TNP along with other analytes (1 × 10^{-2} M) using wsNP-Cdots (0.05 mg/mL)-coated TLC plates (a) for blank and (b–r) for water, Zn+2, Ni+2, Co+2, Cu+2, Pb+2, Cd+2, Na+, Ba+2, Fe+2, TNP, RDX, 2,6 DNT, 2,4 DNT, DMDNB, nitromethane, and TNT, respectively.
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