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Synthesis of Organic Material-Derived Carbon Quantum Dots: Nitrogen Doping and Fluorescence Modulation for Metal Ion Sensing

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Abstract. Nitrogen-doped carbon quantum dots (N-CDs) were synthesized from Terung Dayak (Solanum ferox) using a microwave-assisted method. This study investigated their optical properties and fluorescence modulation in the presence of metal ions. The synthesis involved citric acid as the carbon precursor and urea as the nitrogen dopant, leading to well-dispersed N-CDs with enhanced fluorescence characteristics. UV-Vis and fluorescence spectroscopy confirmed the successful incorporation of nitrogen, which resulted in a redshifted emission peak and improved fluorescence intensity compared to undoped CDs. The band gap analysis using Tauc plots indicated an increase in energy gap upon nitrogen doping, suggesting modifications in the electronic structure. Furthermore, fluorescence response experiments demonstrated that the presence of Pb^{2+} ions significantly enhanced the emission intensity, indicating potential applications in metal ion sensing. The results highlight the influence of nitrogen doping on the optical properties of carbon quantum dots and their promising use in fluorescence-based sensing applications.

Keywords : Carbon quantum dots, nitrogen doping, fluoroscence, micro-wave-assisted

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Introduction

The A subclass of carbon-based nanomaterials, carbon quantum dots or carbon dots (CDs), has gained significant attention due to their unique optical properties, chemical abbilities, biocampability, and low toxicity[1], [2], [3]. Unlike conventional quantum dots, CDs exhibit tuneable photoluminiscence, strong fluoroscence, and excellent solubility in aqueous media, making them suitable for broad applications, such as bioimaging, optoelectronics, catalysis, and sensing[4], [5], [6], [7]. Their fluoroscence properties arise from quantum confinment effect and the surfaces state modification, which can be fine-tuned through synthesis strategies to enhance the performances of the CDs for spesific application [8]. The versality of CDs in material science has driven extensive research into optimixing their synthesis, surface modification, and functionalization for targeted applications.

In recent decades, green synthesis of CDs from natural resources has emerged as sustainable approach to produce a nanomaterial based on carbon. There are two methods to synthesis carbon dots, top-down and bottom-up methods [9], [10]. The top-down approach is methods involve breaking down larger carbonaceousd materials, such as graphite, carbon nanotube, or graphene oxide, into nanoscale CDs using some techniques such as laser ablation, electrochemical oxidation, or arc discharge [11], [12]. However, these techniques need special equiment. In contrast, bottom-up approach to synthesis CDs involve assembly from small organic molecule or biomass-derived precusor through chemical reaction, like pyrolysis, hidrothermal, or microwave-assisted synthesis (MAS). The bottom-up method is particularly attractive due to its ability to control the surface chemistry of CQDs, leading to enhanced optical properties and tunable fluorescence behavior[13], [14]. Furthermore, this method can be done without special equipment. Recent advancements in bottom-up synthesis have focused on utilizing green and sustainable precussors to develop enviromentally friendly CDs.

While the choice of synthesis method—whether top-down or bottom-up—significantly influences the structural and optical properties of CDs, further modifications, such as heteroatom doping, offer an additional strategy to enhance their fluorescence efficiency, electronic structure, and sensing capabilities[15]. Doping CDs with heteroatoms such as nitrogen (N) is an effective strategy to modulate their electronic structure and enhance fluorescence efficiency[16]. The use of nitrogen-rich precursors, such as urea, during CQD synthesis enables the incorporation of amine or pyrrolic functional groups, which significantly alter the optical and electronic properties of the resulting nanomaterials. Despite the potential advantages of N-doped CDs, further exploration is needed to understand the influence of nitrogen doping on fluorescence behavior, particularly in the presence of metal ions.

Among the various strategies to enhance the optical properties of CDs, nitrogen doping has emerged as an effective approach to improve fluorescence efficiency and quantum yield [17], [18]. This surface modification not only alters the electronic structure of CDs but also plays a crucial role in their interactions with external species, including metal ions, which can further modulate their fluorescence behavior. The interaction of CDs with metal ions plays a crucial role in determining their fluorescence properties, making them valuable as fluorescent probes for metal ion sensing. Metal ions can influence the fluorescence behavior of CDs through various mechanisms, including fluorescence quenching (turn-off), fluorescence enhancement (turn-on), or wavelength shifts[19], [20], [21], [22]. The selective fluorescence response of CDs to specific metal ions is primarily dictated by the surface functional groups present on CDs, which facilitate interactions with metal ions through coordination or electrostatic attraction. The development of CDs with enhanced metal ion selectivity and sensitivity remains a key research focus for applications in environmental monitoring, biomedical diagnostics, and chemical sensing. Therefore, in this study, we investigate the synthesis of N-doped CDs from Terung Dayak (Solanum ferox) as precursors using a microwave-assisted approach and evaluate their optical properties, fluorescence behavior, and the influence of metal ion in fluoroscence ability. Our findings contribute to the growing a knowledge on nitrogen-doped carbon dots and their potential applications in fluorescence-based sensing technologies.

Experimental

Materials and intruments. The materials used in this study include dayak eggplant (Solanum ferox), urea, citric acid, lead(II) nitrate, nickel(II) sulfate, cobalt(II) nitrate, zinc(II) sulfate, iron(III) chloride. The equipment used included a sonicator, a home oven with Electrolux EMM20K22B brand, UV-Vis Marco single beam, Shimadzu RF60000 spectrofluorometer..

Synthesis of CDs. Carbon dots (CDs) were synthesized using a modified version of Rajamanikandan's method. In this process, 10 mL of Dayak terung juice was placed in a microwave-safe Teflon container and mixed with 1 g of citric acid. The mixture was homogenized using a sonicator for 3 minutes before being subjected to microwave irradiation at 800 W for 3 minutes. The resulting brownish liquid was purified by centrifugation at 4000 rpm, followed by filtration through a 0.2 µm membrane filter.To prepare nitrogen-doped CDs (N-CDs), the same procedure was followed with the addition of 1 g of urea. The synthesized CDs were subsequently characterized for their optical properties using UV-Vis spectroscopy and fluorescence spectroscopy.

Fluoroscence Response of Carbon Dots in the Presence of Metal Ions. Stock solution (10 ppm) of Pb^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, and Fe^{3+} were prepared by dissolving lead(II) nitrate, nickel(II) sulfate, cobalt(II) nitrate, zinc(II) sulfate, iron(III) chloride in deionized water. The solution were stirred until dissolution was complete. A 10 ppm solution of CDs was prepared in deionized water. To ecvaluate the fluoroscence response to metal ion, an equal volume of the CDs soolution was mixed with each ion solution separately. The fluoroscence intensity of the resulting mixtures was recorded using fluoroscence spectrophotometer awith an excitation wavelength 370 nm.

Result and Discussion

The CDs and nitrogen-doped CDs (CDNs) were synthesized using a one-pot microwave-assisted method with Terung Dayak fruit juice as the carbon source. The rapid heating provided by the microwave irradiation not only promotes efficient carbonization but also facilitates the incorporation of nitrogen by adding an appropriate dopant (e.g., urea). This method results in carbon nanomaterials with uniform particle size and well-defined surface functionalities, which are critical to their optical behavior.Following synthesis, the optical properties of both CDs and CDNs were characterized using UV-Vis and fluorescence spectroscopy. The introduction of nitrogen into the carbon framework significantly alters the electronic structure, as evidenced by enhanced fluorescence intensity and a shift in the absorption peaks. The improved optical properties of CDNs are attributed to the formation of new emissive states and better surface passivation, which reduce nonradiative decay pathways.

The UV and fluorescence spectra are avaliable in figure 1. The fluorescence spectra of carbon dots (CD) and nitrogen-doped carbon dots (CDN) exhibit notable differences. CDN demonstrates significantly higher fluorescence intensity compared to CD, with a redshifted emission peak. This shift suggests that nitrogen doping alters the electronic structure, introducing new energy levels or defect states that enhance emission efficiency. The increased fluorescence intensity in CDN can be attributed to enhanced surface passivation, where nitrogen doping introduces additional functional

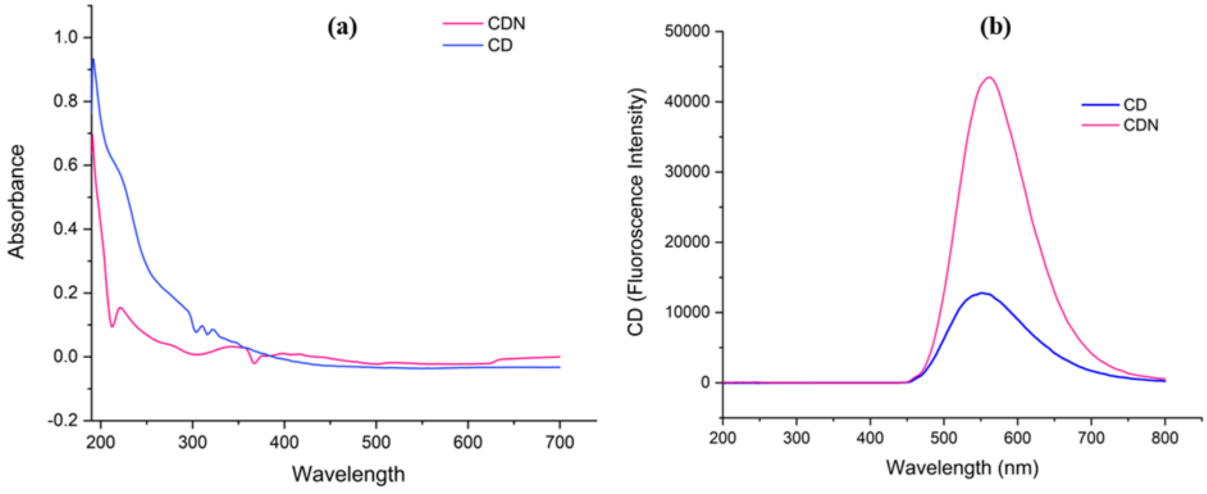

Figure 1. UV Vis Spectra (a) and fluoroscence spectra (b) of CD and CDN

groups that reduce non-radiative recombination. Furthermore, nitrogen doping creates new emissive energy states that facilitate radiative recombination and improve quantum yield by enhancing electron-hole recombination efficiency.

The UV-Vis absorption spectra reveal additional distinctions. CD exhibits strong absorption in the UV range, particularly below 300 nm, primarily due to π-π* transitions in aromatic C=C bonds. In contrast, CDN shows a slightly lower absorption intensity, with additional features appearing around 200–250 nm, likely due to n-π* transitions introduced by nitrogen doping. Moreover, the absorption tail in the visible region is slightly extended for CDN, indicating a reduced energy gap, which correlates with the observed redshift in fluorescence. The electronic transitions in carbon dots involve both π-π* and n-π* transitions. The π-π* transitions, which are observed in both CD and CDN, correspond to sp^2 hybridized carbon domains and are primarily responsible for absorption in the UV region. However, in CDN, n-π* transitions become more prominent due to the presence of nitrogen, involving lone pairs on heteroatoms interacting with the π-conjugated system. This interaction leads to redshifted absorption and emission, further supporting the observed spectral differences.

The Tauc plot is a widely used method for determining the optical band gap of semiconductors and nanomaterials, including carbon dots (CDs). This method is based on the Tauc relation, which describes the relationship between the absorption coefficient () and photon energy () using the equation 1.

$$(\alpha h\nu)^n = A(h\nu - E_g) \qquad (1)$$

Where A is a constant, Eg is the optical band gap, and n depends on the type of electronic transition. The exponent n in Tauc plot is an important parameter that provides insight into crystallinity and electronic band. In some case, n = 2, it indicates a dirrect allowed transistion that typically founf in material with well-defined crystalline structure. But in this experiment, the exponent is due to indirect allowed transition, which commonly associated with amorphous or polycristalline materials. In these materials, the band structure is less well-defined, requiring phonon interaction to facilitates electronic transition. Commonly, carbon dots exhibit indirect transition due to structural disordser and the presence of defect states.

The Tauc plot of CD and CDN are available in figure 2. The provided Tauc plot compares the optical band gaps of pristine carbon dots (CD) and nitrogen-doped carbon dots (CDN). The results indicate that the band gap of CD is 5.77 eV, whereas the band gap of CDN is 6.09 eV. The increase in the band gap of CDN compared to CD suggests that nitrogen doping significantly influences the electronic structure of the material. Several factors could contribute to this change. One primary reason is the quantum confinement effect, where the introduction of nitrogen alters the size of conjugated carbon domains, effectively increasing the band gap. Additionally, nitrogen doping modifies the electronic density of states, potentially shifting both the conduction and valence bands. The presence of nitrogen atoms can create new electronic states, affecting charge carrier distribution and electronic transitions, thereby leading to a wider band gap.

The observed increase in the band gap has several implications for the optical properties of the material. A higher band gap in CDN means that the material absorbs light at higher photon energies (shorter wavelengths). This property is particularly significant in applications that require materials with strong UV absorption and tunable fluorescence emission, such as in optoelectronic devices, biosensing, and photocatalysis. Moreover, the shift in band gap suggests that nitrogen doping can be used as a strategy to fine-tune the optical and electronic properties of carbon dots, making them more suitable for specific technological applications.

The optical properties of CDN upon interaction with metal ions can be explained based on their electronic structure, surface chemistry, and the role

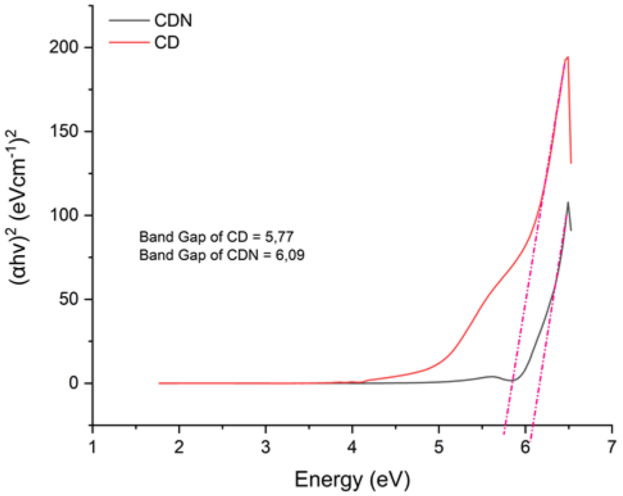

Figure 2. Tauc Plot of CD and CDN based on UV data

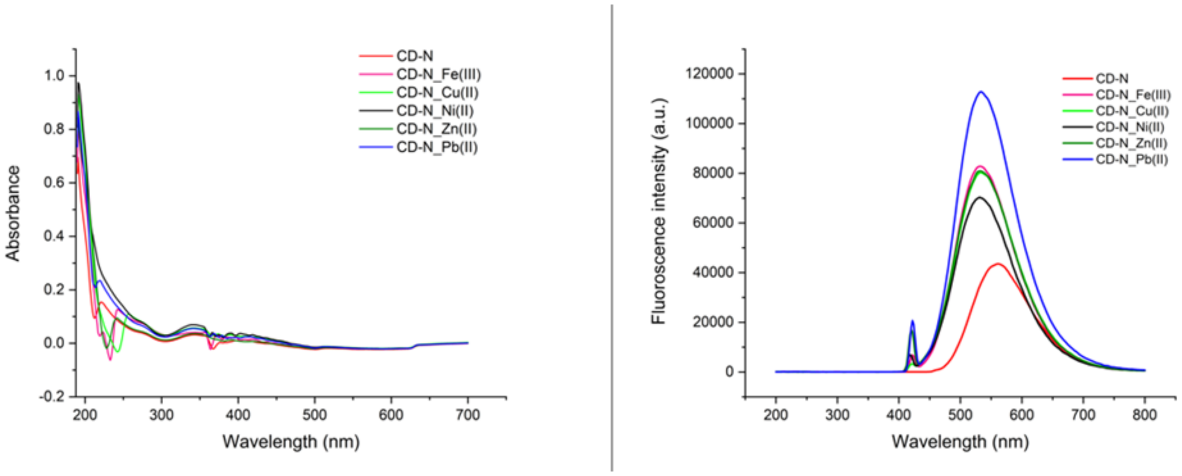

Figure 3. UV Spectra and Fluoroscence Spectra of CDN in interaction with metal ion

of metal coordination in modifying their fluorescence behavior. The UV and fluoroscence spectra of CDN with influence of metal ion are available in figure 3. In the UV absorbance spectrum, the strong absorption bands in the UV region (below 300 nm) correspond to π-π* transitions from the aromatic carbon core and n-π* transitions from functional groups like hydroxyl, carboxyl, or nitrogen-based moieties. The slight variations in absorption upon metal ion addition indicate interactions between the metal ions and CDN, which can modify electronic transitions and alter charge transfer dynamics.

The fluorescence properties of CDN are significantly affected by metal ion coordination. The undoped-metal CDN exhibits strong fluorescence due to the radiative recombination of excitons within the conjugated carbon network. When metal ions are introduced, they can either quench or enhance fluorescence, depending on their electronic properties and interaction with surface functional groups of CDN. In this study, all metal ion can enhaced the fluoroscence ability of CDN. Pb(II) ion induces a significant enhancement in fluorescence intensity. This enhancement can be attributed to several factors. The fluorescence enhancement mechanism of CDN for Pb^{2+} detection is primarily attributed to the inhibition of photo-induced electron transfer (PET) when Pb^{2+} interacts with functional groups on the CDN surface. PET is a common quenching mechanism in fluorescent nanomaterials, where the excited-state electrons of CDN transfer to electron-deficient groups, leading to non-radiative recombination and decreased fluorescence intensity. In the absence of Pb^{2+}, surface defects and functional groups such as hydroxyl, carboxyl, or amine groups may act as electron traps, promoting PET and thereby reducing fluorescence efficiency.

Overall, the observed fluorescence modulation is governed by the interplay between metal ion coordination, electron transfer mechanisms, and surface state modifications. The fluorescence enhancement caused by Pb(II) ion suggests potential applications in bioimaging or fluorescence-based detection systems for lead ions. Understanding these interactions at a deeper level can aid in designing carbon dot-based probes for selective metal ion detection and fluorescence-based applications.

Conclusion

This study successfully synthesized nitrogen-doped carbon quantum dots (N-CDs) from Solanum ferox using a rapid and eco-friendly microwave-assisted method. The incorporation of nitrogen significantly enhanced the optical properties, as evidenced by increased fluorescence intensity, red-shifted emission, and modifications in the electronic structure. Tauc plot analysis revealed an increased band gap in N-CDs, further supporting the structural and electronic modifications induced by nitrogen doping. The fluorescence response experiments demonstrated a selective enhancement in fluorescence intensity upon interaction with Pb^{2+} ions, suggesting the potential of N-CDs for applications in metal ion sensing. These findings contribute to the ongoing exploration of green-synthesized carbon dots as functional nanomaterials for environmental monitoring and bioanalytical applications. Future research should focus on further optimizing synthesis conditions and exploring additional applications of N-CDs in biosensing and optoelectronics.

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