Green Synthesis of Copper-doped Carbon Dots from Ziziphus mauritiana leaves

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Abstract— **The carbon dots display adjustable physicochemical attributes and visual qualities. They have garnered significant notice due to their environmentally sustainable strategy. The carbon dots exhibit tunable physicochemical characteristics and optical properties. They have gained considerable attention because of environmentally friendly approach. In this study, we described a simple biogenic procedure for synthesizing Cu-doped carbon dots (Cu-CDs) using $CuCl_2 \cdot 2H_2O$ and dried Ber (Ziziphus mauritiana) leaves as a renewable, nitrogen-rich carbon precursor. The synthesis uses the leaf's inherent biomolecules to aid in copper ion chelation and consistent doping during carbonization. Photoluminescence, UV-visible spectra, Fourier-transform infrared spectroscopy (FT-IR), Energy-dispersive X-ray Spectroscopy (EDX), Dynamic Light Scattering (DLS), and Field Emission Scanning Electron Microscopy (FESEM) were used to analyze the manufactured CDs. Characterization revealed the synthesis of amorphous, quasi-spherical nanoparticles with oxygen-rich surface functional groups and effective copper inclusion. The Cu-CDs exhibited robust excitation-dependent photoluminescence, generating bright blue fluorescence (maximum emission at 450 nm) under 360 nm excitation, with doping considerably increasing the quantum yield. This study emphasizes the potential of Ziziphus mauritiana biomass for eco-friendly nanomaterial manufacturing by demonstrating how copper doping tailors the photophysical and catalytic properties of CDs, making them promising for environmental sensing and bioanalytical applications.**

Index Terms—**Carbon dots, Copper, Ziziphus mauritiana leaves**

I. INTRODUCTION

The paradigm of modern material sciences is increasingly being driven by the dual demands of exceptional performance and environmental sustainability. Due to their remarkable photoluminescence (PL), excellent water solubility, low cytotoxicity, and tunable surface chemistry, carbon dots (CDs) a zero-dimensional category of quasi-spherical carbon nanomaterials typically measuring less than 10 nm have emerged as a crucial platform in this domain (1, 2). Since their unexpected discovery in 2004, CDs have demonstrated revolutionary potential in a variety of applications, including bioimaging (3), chemical sensing (4), photocatalysis (5), drug delivery (6), and light-emitting diodes (7). Poor absorption in the visible spectrum, a lack of catalytic active sites, and moderate photoluminescence quantum yields (PLQYs) limit the performance of pristine CDs, making them less useful for advanced technological tasks (8). Hetero-atom doping is an effective and versatile way for creating CDs with improved and unique properties. Foreign atoms, like metals, nitrogen (N), sulfur (S), or phosphorus (P), can be added to the carbonaceous matrix to alter its optical, electrical, and chemical properties.

This can introduce defect sites, change the electronic density, and create new surface states (9, 10). Transition metals are particularly promising among different dopants. In particular, copper provides a special blend of redox activity, affordability, natural abundance, and inherent catalytic and optical qualities (11). Therefore, copper-doped carbon dots (Cu-CDs) are a synergistic hybrid material in which copper ions (Cu^{+}/Cu^{2+}) that can be incorporated in the matrix, coordinated on the surface, or both functionally complement the benign carbon core. Better charge separation and transfer (12), increased peroxidase-like enzyme mimicking activity (13), redshifted and intensified PL emission (14), and the introduction of magnetic or phosphorescent properties (15) are all possible outcomes of this doping. The resultant materials perform better in applications such photocatalytic degradation of pollutants, antibacterial agents, and electrochemical sensing (16, 17).

Despite these encouraging characteristics, the traditional production of metal-doped CDs often uses toxic solvents or energy-intensive procedures (such as pyrolysis or arc-discharge) and non-renewable, petroleum-derived precursors (such as urea or citric acid) (18, 19). These procedures go against to the global trend toward green and sustainable manufacturing. As a result, the area is undergoing a clear shift towards "green synthesis," which is consistent with the fundamental ideas of green chemistry expressed (20). This strategy focuses on using water as the main solvent, renewable biomass (such as fruit peels, agricultural residues, and plant extracts) as carbon sources, and mild reaction conditions (such as hydrothermal/ solvothermal treatment, microwave irradiation) to reduce energy consumption and environmental impact (21, 22). Beyond straightforward precursor substitution, the ideology includes waste prevention, atom economy, and the circular economy's key idea of producing high-value materials from low-value waste streams (23). Green synthesis has a deeply functional justification in addition to an ecological one. Heteroatoms (N, O, S, P, etc.), proteins, carbohydrates, and polyphenols are naturally abundant in natural biomass precursors and function as self-doping and passivating agents (24, 25). These elements promote uniform doping and inhibit the formation of large, distinct metal oxide nanoparticles during carbonization by facilitating the in-situ formation of heteroatom-doped CDs and providing an abundance of oxygenated functional groups (–COOH, –OH, C=O) that can efficiently chelate and stabilize metal ions like Cu^{2+} (26, 27). Biomass's inherent complexity may result in the creation of co-doped systems, such as N, S co-doped CDs, where the combination of metal and non-metal dopants can enhance material properties even further (28, 29).The doping process in green synthesis is frequently a coordinated event where the metal ion interacts with the biomass's breaking down molecular fragments, resulting in its encapsulation within the developing carbon core or firm coordination on the surface, according to recent mechanistic studies [30,32]

The effectiveness and creativity in this field are supported by recent research. For example, green-synthesized CDs derived from waste Ocimum sanctum leaves (32), banana peel (33), and waste pomelo peel (34) have shown exceptional sensing capabilities. Studies on metal doping have demonstrated the successful green manufacture of CDs doped with zinc (35), manganese (36), and cerium (37) for a variety of uses. In particular, recent studies have produced Cu-CDs for sensing, catalysis, and bioimaging using precursors such as Moringa oleifera leaves (38), sweet pepper (39), and Phyllanthus emblica fruit (40). These studies confirm the viability of the green approach, but they also draw attention to persistent difficulties, such as regulating the exact oxidation state of copper (Cu^{+} vs. Cu^{2+}) (41), attaining uniform doping distribution to guarantee batch-to-batch reproducibility (42), and completely clarifying the structure-property relationship in these intricate, biomass-derived systems (43). Additionally, although applications are investigated, there is frequently a lack of a systematic comparison study assessing the improvement directly related to copper doping within a green synthesis framework, from optical characteristics to catalytic efficacy.

This study analyzes an environmentally friendly one-pot hydrothermal synthesis of copper-doped carbon dots using Ziziphus mauritiana leaves as a sustainable source of heteroatoms and carbon. Physico-chemical characterization (using EDX, FT-IR and UV-Vis) confirms successful doping, determine copper chemical state, and analyze structural features.

II. EXPERIMENTAL SECTION

2.1. Materials and Characterization

Copper salts were purchased from Sigma Aldrich (~ 99 % purity) and used directly without further purification. The Ziziphus mauritiana leaves were collected from Rajasthan, India. Then these leaves dried and converted into small pieces with cutting. Then cutting leaves were washed from distilled water to remove extra impurities. All other reagents were of analytical grade and utilized without further purification. All of the samples and solutions were prepared with distilled water. PerkinElmer spectrophotometer was used to record Fourier transform infrared (FTIR) spectra. The absorbance of synthesized carbon dots has been explored by UV-Vis spectrophotometer (Shimadzu UV-2600). The elemental composition was carried by energy dispersive X-ray spectroscopy (EDX) on a JEOL JSM -7600F system. Horiba FluoroMax-4 spectrometer was employed for examine the fluorescence properties of synthesized material.

2.2. Synthesis of Cu-doped CDs

Ziziphus mauritiana leaves were hydrothermally treated in a single step using $CuCl_2•2H_2O$ as a reaction precursor to create the Cu-CDs as illustrated in Figure 1. In short, 2 mg of $CuCl_2•2H_2O$ were dissolved in 30 ml of distilled water after some dried Ziziphus mauritiana leaves were crushed and subjected to bath sonication for five minutes. After the resulting mixture was put into a 50 ml stainless steel autoclave with Teflon, the reaction system was sealed and heated to 180 °C for three hours. Centrifuging was employed to collect the products once the obtained solution had naturally cooled to room temperature. The resulting Cu-CDs solution was then purified.

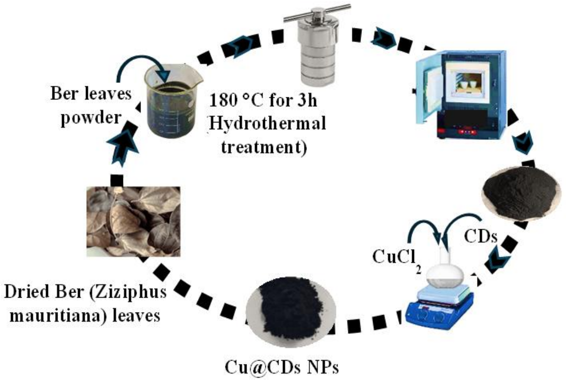

Figure 1. Schematic illustration showing the synthesis of Cu@CDs nanoparticles

III. RESULTS AND DISCUSSION

Characterization of Cu-CDs.

(i) FTIR spectra

The FTIR spectra of the pristine carbon dots (CDs) and Cu-doped carbon dots (Cu-CDs) exhibit several characteristic absorption bands, indicating the presence of surface functional groups. As shown in figure 2, a broad band around 3200–3500 cm^{-1} is attributed to the stretching vibrations of O–H and N–H groups, suggesting abundant hydroxyl and amine functionalities on the surface of the CDs. The peak near 2920–2850 cm^{-1} corresponds to C–H stretching vibrations of aliphatic groups. The band at 1650-1700 cm^{-1} corresponds to the C=O stretching of carbonyl or amide groups, indicating oxidized surface states. Absorption near 1550-1600 cm^{-1} indicates C=C stretching of aromatic or graphitic domains. Peaks were observed in the area of C-N and C-O stretching vibrations at 1200-1400 cm^{-1} indicate the presence of functional groups with heteroatoms. [44]. Cu-CDs show minor shifts and intensity changes in carbonyl and hydroxyl areas compared to pristine CDs, indicating coordination interactions between Cu ions and oxygen or nitrogen-containing surface groups. Additionally, the appearance or enhancement of bands in the 500–700 cm^{-1} region can be attributed to Cu–O or Cu–N vibrations, supporting the successful incorporation of copper species onto the carbon dot surface. Overall, the FT-IR results confirm that metal coordination occurs mainly through the surface functional groups without significantly altering the carbonaceous core structure.

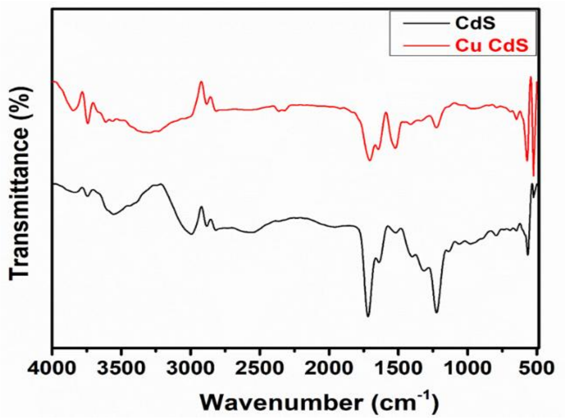

Figure 2. FT-IR spectra of CdS and Cu-doped CdS.

(ii) UV-Visible absorption spectra

The UV–visible absorption spectra of the pristine carbon dots (CDs) and Cu-doped carbon dots (Cu-CDs) show a strong absorption band in the UV region around 250–280 nm, which can be attributed to the π–π^* transitions of the aromatic C=C bonds present in the graphitic carbon core. A weaker and broader shoulder extending into the 300–350 nm region is associated with n–π^* transitions of surface functional groups such as C=O or C–N, indicating the presence of oxygen- and nitrogen-containing moieties on the dot surface as shown in figure 3.

Cu-CDs exhibit a minor shift in intensity and band broadening as compared to immaculate CDs. This pattern indicates an interaction between copper species and surface functional groups, potentially altering the surface states and energy levels of carbon dots. The absence of a visible plasmonic band suggests that copper is not present as metallic nanoparticles, but rather coordinated with surface functional groups or incorporated into the carbon framework [45]. Overall, the spectra show that the basic carbon dot structure remains following Cu insertion, with modest modifications due to metal-ligand interactions.

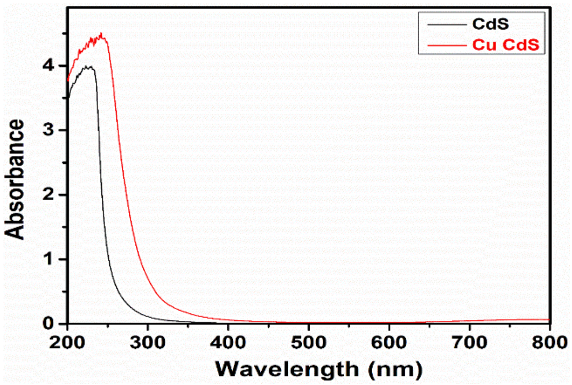

Figure 3. UV-Vi's spectra of CdS and Cu-doped CdS.

(iii) Fluorescence & Edx

The emission spectrum of pristine carbon dots (CDs, black line) and copper doped carbon dots (Cu-CDs, red line), when excited at 320 nm, shows a peak around 423 nm. This represents the blue emission of carbon dots, as can be seen from Figure 4. Compared to the pristine CDs, the Cu-CDs exhibit a slight decrease in emission intensity while maintaining a similar peak position. This reduction in fluorescence intensity indicates that the incorporation of Cu species introduces additional non-radiative pathways, likely through metal–ligand interactions with surface functional groups. Such interactions can facilitate electron or energy transfer processes, leading to partial fluorescence quenching.

The FESEM image of the Cu-doped carbon dots reveals a thin, wrinkled and layered nanosheet-like morphology. Figure 5 (a, b) illustrates a uniform distribution of carbon, oxygen, and copper throughout the material according to the relevant EDX elemental mapping.

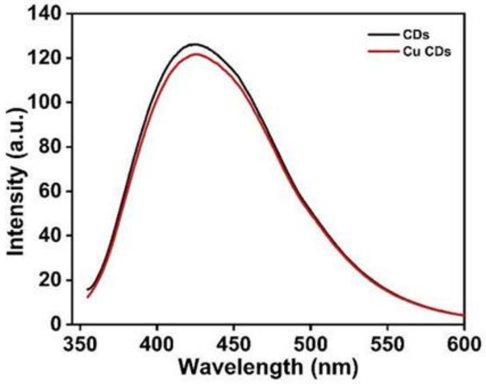

Figure 4. PL emission spectra of CdS and Cu-doped CdS.

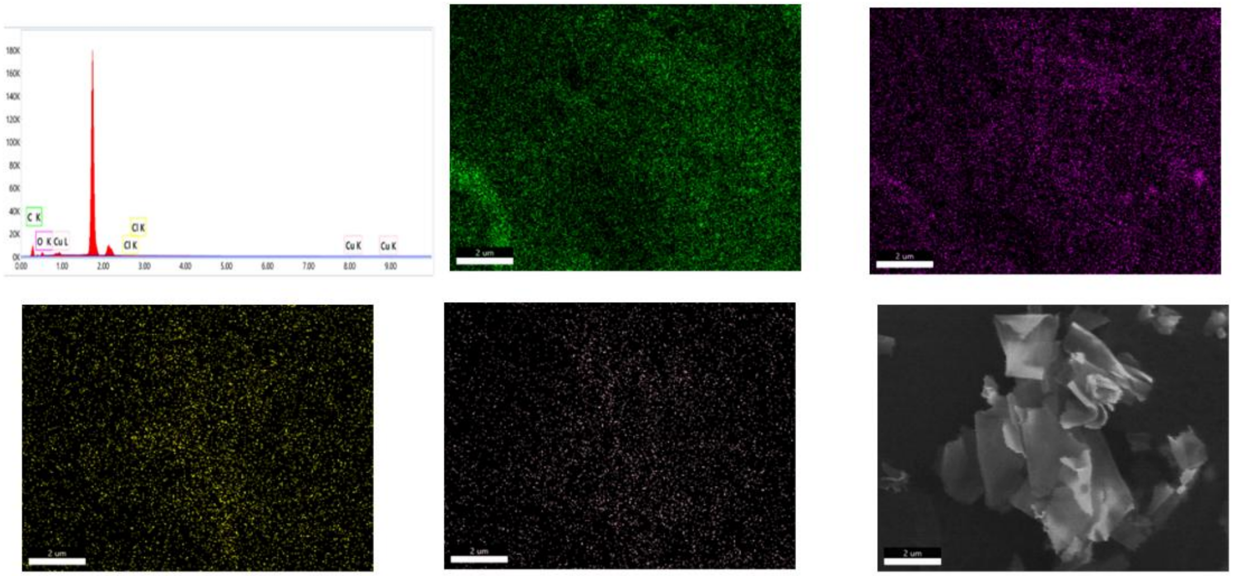

Figure 5. a) EDX mapping and b) FESEM image of Cu-doped Cd

IV. CONCLUSION

The synthesis of copper doped carbon dots (Cu-CDs) was achieved using one-pot hydrothermal synthesis. The aqueous extract of leaves from Ziziphus mauritiana plant and $CuCl_2•2H_2O$ were used as carbon precursor and copper precursors, respectively. This technique employs green and renewable biomass waste products as well as water in a cost-effective and sustainable process consistent with green chemistry. The successful doping of copper was confirmed through various analysis. The FT-IR analysis revealed the presence of functional groups of oxygen and nitrogen compounds that help in Copper (II) coordination due to the presence of vibrational Cu-O and Cu-N bonds. EDX analysis confirmed the presence of carbon, oxygen, and copper. With very slight spectrum shifts that indicate electronic interactions during doping, optical analysis revealed that the Cu-CDs maintained the distinctive absorption characteristics of undoped carbon dots. The Cu-CDs show blue emission centered at about 423 nm, according to fluorescence spectroscopy. The introduction of metal-induced non-radiative relaxation pathways is responsible for the partial quenching of this fluorescence that was seen after doping. In conclusion, it has been shown that Ziziphus mauritiana leaves are an efficient and sustainable precursor for the production of Cu-doped carbon dots with good metal incorporation. These Cu-CDs consequent optical and structural characteristics make them attractive options for use in industries like sensing and catalysis.

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