HYDROTHERMAL SYNTHESIS OF CARBON QUANTUM DOT FOR PHOTOCATALYTIC APPLICATION

PROJECT SUBMITTED TO

MAHATMA GANDHI UNIVERSITY, KOTTAYAM

IN PARTIAL FULFILLMENT OF THE REQUIREMENT OF THE AWARD OF DEGREE OF

MASTER OF SCIENCE IN PHYSICS

BY

SUJI SARA PAUL

Reg. No: AM23PHY013

Year of Study: 2023 – 2025

UNDER THE GUIDANCE OF

DR. SUSAN MATHEW

ASSISTANT PROFESSOR

DEPARTMENT OF PHYSICS

ST. TERESA'S COLLEGE (AUTONOMOUS)

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CERTIFICATE

This is to certify that the project work entitled **"Hydrothermal Synthesis of Carbon Quantum Dot for Photocatalytic Application"** submitted for the partial fulfillment of the requirements for the award of the Degree of Master of Science in Physics of Mahatma Gandhi University is the work done by **SUJI SARA PAUL** (AM23PHY013) during the period of study (2023-2025) under the guidance of Dr. Susan Mathew (Asst. Professor) in the Department of Physics, **ST. TERESA'S COLLEGE.**

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I, Suji Sara Paul, final year M.Sc. Physics student of the Department of Physics and Centre for Research, St. Teresa's College (Autonomous), Ernakulam, do hereby declare that this project entitled "**Hydrothermal Synthesis of Carbon Quantum Dot for Photocatalytic Application**" is an original work done under the guidance of **Dr. Susan Mathew**, Asst Professor, Department. Of Physics, St. Teresa's College (Autonomous), Ernakulam in partial fulfillment for the award of the degree of Master of Physics. I further declare that this project is not partially or wholly submitted for any other purpose and the data included in this project is collected from various sources and are true to the best of my knowledge.

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Hydrothermal Synthesis of Carbon Quantum Dot for Photocatalytic Application

ABSTRACT

Hydrothermal synthesis has been widely employed for the fabrication of carbon quantum dots (CQDs). The average sizes of CQDs are typically controlled by adjusting precursor concentrations, processing temperatures, and reaction times. In this study, CQDs were synthesized using different filling volumes (30% and 50%) of sucrose solution in a hydrothermal reactor, while keeping all other experimental parameters constant.

Specifically, nitrogen-doped carbon dots (NCQDs) synthesized with a 50% filling volume were studied in detail. Their optical properties were analyzed using UV-Visible spectroscopy, and photoluminescence (PL) confirmed the successful formation of CQDs, offering insights into their electronic structure and energy levels. A comparative study between undoped CQDs and nitrogen-doped CQDs was also conducted.

The antioxidant activity of NCQDs, evaluated using the DPPH free radical method, demonstrated a scavenging activity of 80.84%, indicating significant antioxidant potential and the ability to neutralize free radicals. Furthermore, the solar photocatalytic activity of NCQDs synthesized with a 50% filling volume, tested at two concentrations, confirmed their long-term stability and suitability for applications such as pollutant degradation and water purification.

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CHAPTER 1

1.1 GENERAL INTRODUCTION

Nanoscience is the study of structures and materials on the scale of nanometers (one billionth of a meter). It focuses on understanding and manipulating matter at the atomic, molecular, and supramolecular levels. The field emerged from advances in physics, chemistry, biology, and materials science, allowing scientists to explore how materials behave differently at the nanoscale.

Nanotechnology studies and builds materials and devices on the nanometer scale (one-billionth of a meter). At this level, normal materials show unusual physical and chemical properties. Scientists and engineers use these special behaviors to create innovations in medicine, electronics, energy, and more.

Nanomaterials—materials engineered at the nanoscale—have gained significant attention due to their potential to revolutionize various sectors. Some key advantages include, improved Strength and durability for instance, Carbon nanotubes and graphene are far stronger than steel but much lighter, making them ideal for aerospace, automotive, and construction industries. Materials in the nanometer scale exhibit unique properties such as increased strength, lighter weight, enhanced reactivity, improved electrical conductivity that are not seen in their bulk counterparts. These novel characteristics open up a wide range of possibilities across various scientific and industrial domains.

Nanomaterials increase the efficiency of photovoltaic cells and batteries Nanotechnology improves the storage capacity and charging speed of batteries.

Medical Applications include targeted drug delivery directly to cancer cells, reducing side effects. Also, in diagnostics, Nano sensors offer high sensitivity for early disease detection.

Environmental Benefits include Water purification. Nanomaterials like Nano-silver and Nano-filters help remove pollutants and pathogens from water. Catalysts at the nanoscale improve air and water purification systems.

In the field of Electronics and Computing, Nanotechnology enables faster, smaller, and more energy-efficient devices, critical for the development of next-gen electronics and quantum computing.

Nano-fertilizers and Nano-pesticides improve crop yield and reduce environmental damage.

In the current era of technological transformation and environmental challenges, nanoscience and nanotechnology offer promising solutions for sustainable development, healthcare innovation, clean energy, and smarter electronics—making them key drivers of future progress.

1.2 CARBON QUANTUM DOT

Carbon Quantum Dots (CQDs) represent a novel and versatile class of zero-dimensional carbon-based nanomaterials, typically less than 10 nanometers in diameter. These quasi-spherical nanoparticles possess a unique combination of quantum confinement effects and abundant surface functional groups, which together impart exceptional photoluminescent, electronic, and chemical properties. Unlike traditional semiconductor quantum dots (CdSe or PbS), CQDs are predominantly composed of carbon, making them inherently more biocompatible, environmentally benign, and chemically stable—ideal for a wide range of applications from biomedicine to optoelectronics.

The emergence of CQDs stems from the growing need for safer, sustainable nanomaterials that do not involve toxic heavy metals. They can be synthesized from a vast array of carbon-rich precursors—including organic acids, carbohydrates, biomass, and even waste materials—using cost-effective and scalable techniques such as hydrothermal treatment, microwave irradiation, pyrolysis, or electrochemical oxidation. The simplicity and tunability of these methods allow precise control over the size, crystallinity, surface passivation, and functionalization of CQDs.

One of the most intriguing features of CQDs is their tunable photoluminescence, which is strongly dependent on particle size, surface defects, and doping. Their emission wavelengths can span across the visible spectrum and beyond, and their fluorescence is generally stable under a range of environmental conditions. Furthermore, heteroatom doping (e.g., with nitrogen, sulfur, or phosphorus) can significantly alter the electronic structure of CQDs, enhancing their quantum yield, shifting emission wavelengths, and introducing new catalytic or sensing functionalities.

Recent advances in CQD research have broadened their applicability to include diverse fields such as bioimaging, drug delivery, solar energy conversion, environmental monitoring, and photocatalytic pollutant degradation. Their excellent water dispersibility, ease of surface modification, and intrinsic fluorescence make them ideal candidates for bio applications, while their photochemical activity and stability enable promising roles in energy and environmental technologies.

In light of these advantages, carbon quantum dots are rapidly evolving from a scientific curiosity to a platform material with profound implications across nanoscience and technology. Ongoing research is focused not only on understanding their fundamental photo-physics but also on engineering their properties for targeted, real-world applications.

Carbon Quantum Dots (CQDs) are characterized using techniques such as UV-Visible spectroscopy, photoluminescence (PL) analysis, and antioxidant activity assays to understand their optical and functional properties. UV-Visible spectroscopy reveals characteristic absorption peaks due to π–π^* and n–π^* transitions, indicating the presence of conjugated carbon structures and surface functional groups. PL spectroscopy confirms the quantum nature of CQDs, showcasing excitation-dependent emission related to surface states and electronic transitions. Antioxidant activity, commonly evaluated using the DPPH method, demonstrates the ability of CQDs—especially nitrogen-doped ones—to scavenge free radicals, reflecting their potential in biomedical and environmental applications.

1.2.1 Structural Specification of Carbon Quantum Dots (CQDs)

The structure of Carbon Quantum Dots (CQDs) is central to their remarkable optical, electronic, and chemical properties. At the nanoscale, CQDs exhibit a hybrid structure composed of a carbon-rich core and a chemically active surface, both of which can be precisely tuned during synthesis.

I. Core Structure

The core of a CQD is typically composed of sp^2-hybridized carbon atoms arranged in graphitic domains interspersed with sp^3-hybridized regions. This hybrid nature results in a semi-crystalline or amorphous structure depending on the synthesis method and precursor used.

In crystalline CQDs, high-resolution transmission electron microscopy (HRTEM) often reveals lattice fringes with interplanar spacings around corresponding to the planes of graphitic carbon.

Amorphous CQDs, on the other hand, lack distinct lattice fringes and exhibit more disordered carbon arrangements, often with a higher density of defects and edge sites.

II. Quantum Confinement

Due to their ultra-small size (<10 nm), CQDs exhibit quantum confinement effects, where the motion of charge carriers (electrons and holes) is restricted in all three spatial dimensions. This confinement leads to discrete energy levels and size-dependent band gaps, which significantly influence the photoluminescence and absorption behavior of CQDs.

III. Surface Structure and Functional Groups

The surface of CQDs plays a dominant role in determining their solubility, chemical reactivity, and fluorescence characteristics. It typically contains a variety of oxygen-, nitrogen-, or sulfur-containing functional groups, such as Hydroxyl (-OH) Carboxyl (COOH), Carbonyl (C=O), Amine ($-NH_2$) and Sulfonate ($-SO_3H$).

These groups are introduced either naturally from the carbon precursor during synthesis or via post-synthesis functionalization. The surface chemistry governs the biocompatibility, and interaction with other molecules, making CQDs highly versatile.

IV. Surface Defects and States

The presence of surface defects—including vacancies, edge states, and heteroatom dopants—creates energy traps that are responsible for the excitation-dependent photoluminescence of CQDs. These trap states, often located between the π and π^* bands of the carbon core, act as emissive centers, and their density and distribution can be controlled via doping or passivation.

V. Heteroatom Doping

Doping the CQD structure with elements like nitrogen, sulfur, phosphorus, or boron can significantly enhance their electronic properties. For instance, Nitrogen doping introduces lone-pair electrons and modifies the electron density, improving conductivity and enhancing fluorescence. Doping also reduces the bandgap and introduces additional active sites, which is particularly useful in catalysis and sensing applications.

VI. Shell/Core-Shell Structures

In some cases, CQDs are designed as core-shell structures where a passivating shell (organic or inorganic) is applied to enhance quantum yield, improve stability, or alter surface charge. This structural modification helps suppress non-radiative recombination pathways and improves photostability.

Structural Features of CQDs

FEATURES	DETAILS
Core Material	sp^2/sp^3 hybridized carbon, graphitic or amorphous
Size	Typically, <10 nm
Crystallinity	Mostly Amorphous
Surface Functional Groups	–OH, –COOH, $–NH_2$, C=O,
Surface Properties	Hydrophilic, reactive, tunable
Defects/States	Surface traps responsible for photoluminescence
Doping Elements	N, S, P, B (enhance conductivity and emission)

Table 1.1 structural features of CQDs

1.2.2 Properties of Carbon Quantum Dots (CQDs)

I. Optical Properties

i. Photoluminescence (PL):

One of the most remarkable properties of CQDs is their strong and tunable photoluminescence. CQDs emit light upon excitation, and this emission is often excitation-dependent, meaning the emission wavelength changes based on the excitation wavelength. This behavior arises from Quantum confinement effects due to small size, surface states, defects and edge functional groups and heteroatom doping .PL makes CQDs suitable for bioimaging, sensors, and light-emitting devices.

ii. UV-Visible Absorption:

CQDs show characteristic absorption in the UV-visible range. Common peaks include; 230–280 nm due to π–π* transitions in aromatic sp^2 domains. A broad absorption around 300–400 nm related to n–π* transitions of surface functional groups (e.g., –COOH, –OH). These features confirm the presence of conjugated π systems and functional groups.

II. Electrical and Electronic Properties

CQDs possess semiconducting behavior due to their quantum-confined structure and surface modifications. Their bandgap is tunable based on particle size, surface functionalization and doping with elements like N, S, or P.

This makes them useful in photovoltaics, transistors, and supercapacitors. Doped CQDs show improved conductivity and charge transfer efficiency, enhancing their performance in electrochemical sensors and catalysts.

III. Chemical Properties

i. Surface Functionality:

CQDs are rich in functional groups such as –OH, –COOH, $–NH_2$, and –CHO, either from the precursor or introduced intentionally. These groups enhance water dispersibility and allow for bioconjugation and functionalization. It also Facilitate metal ion sensing and catalysis.

ii. Redox Activity:

CQDs can participate in electron transfer processes, making them suitable for photocatalytic degradation of pollutants, energy storage systems and oxidation-reduction sensors.

IV. Biological Properties

i. Biocompatibility:

Unlike traditional quantum dots (e.g., CdSe), CQDs are made from carbon—a naturally abundant, non-toxic element. Their surface can be tailored to reduce immunogenicity or enhance compatibility with biological systems.

ii. Antioxidant Activity:

CQDs can scavenge free radicals, especially when doped with nitrogen or sulfur. Evaluated using assays like DPPH (2,2-diphenyl-1-picrylhydrazyl) CQDs show high radical scavenging ability due to presence of electron-rich sites and surface oxygen/nitrogen groups.

This makes them potential candidates for therapeutics and bioprotective coatings.

V. Photocatalytic Properties

CQDs exhibit promising photocatalytic activity under UV or visible light due to efficient electron-hole separation, light-harvesting ability across a wide spectrum and ability to transfer

electrons to reactive species (e.g., O_2, H_2O). The applications include Photodegradation of dyes and pollutants, water splitting and CO_2 reduction. Nitrogen or sulfur doping enhances charge separation and extends light absorption.

VI. Thermal and Chemical Stability

CQDs are highly thermally stable and chemically inert under a wide range of conditions, which is crucial for applications in harsh chemical environments, high-temperature processes and long-term biomedical implants or sensor.

VII. Solubility and Dispersibility

Due to surface functional groups, CQDs are highly soluble in water and polar solvents. Their colloidal stability ensures uniform distribution in solutions, ease of processing into films or composites and high reproducibility in applications like drug delivery and printing.

VIII. The bandgap and optoelectronic properties of CQDs

The bandgap is the energy difference between the valence band (where electrons are normally) and the conduction band (where electrons move freely). In CQDs, this bandgap determines how they interact with light.

CQDs exhibit a size-dependent bandgap due to the quantum confinement effect—as their size decreases (typically below 10 nm), the bandgap increases.
Smaller CQDs means Larger bandgap, Emission at shorter wavelengths (blue/UV).
Larger CQDs means Smaller bandgap, Emission at longer wavelengths (red/infrared). This tunability is key for customizing optical responses.

The bandgap of CQDs usually ranges from 2.0 eV to 6.0 eV, depending on factors like size, surface passivation, functional groups, and synthesis method.

They exhibit strong photoluminescence, broad absorption, and good electrical conductivity—making them ideal for next-generation optoelectronic devices.

The combination of optical tunability and electrical activity is what makes CQDs stand out in flexible electronics, lighting, solar energy, and biosensing.

IX. High Surface-to-Volume Ratio

A high surface-to-volume ratio means more atoms or functional groups are exposed on the surface, increasing the material's interaction with its environment which leads to enhanced

chemical reactivity, better surface functionalization (for sensors or drug loading) and improved performance in catalysis, sensing, and energy storage.

CQDs' properties to their real-world applications

CQD PROPERTY	APPLICATION	EXPLANATION
Photoluminescence (PL)	Bioimaging, Fluorescent probes, LEDs	Tunable and bright fluorescence allows labeling of cells, tissues, and devices.
Biocompatibility	Drug delivery, Biosensors, Medical diagnostics	Safe for use in biological environments with minimal toxicity
Aqueous Solubility	Biomedical imaging, Environmental sensing	High water solubility improves dispersibility and interaction with bio-systems
Electrical Conductivity	Electrochemical sensors, Supercapacitors, Batteries	Conductive properties enhance charge transfer in electronic applications
Surface Functionalization	Targeted drug delivery, Biosensors, Antimicrobial agent	Modifiable surfaces allow specific interactions with target molecules or cells
Chemical Stability	Chemical sensors, Catalysis	Stable in harsh chemical environments; ensures long-term functionality.
Photostability	Long-term bioimaging, Photodetectors	Resists degradation under prolonged light exposure

Table 1.2 CQDs' properties to their real-world applications

1.2.3 EXPERIMENTAL TECHNIQUES

Different synthesis methods are used to prepare Carbon Quantum Dots (CQDs). These methods are broadly categorized into "Top-down" and "Bottom-up" approaches, depending on whether the material is broken down from bulk or built up from smaller molecules.

- Top-Down Methods
- Bottom-Up Methods

I. Top-Down Methods

i. Laser ablation

Laser ablation is a top-down physical method used to synthesize CQDs by vaporizing a carbon source (typically a graphite target) using high-energy laser pulses. The laser breaks down the bulk carbon material into nanoscale carbon clusters, which then form carbon quantum dots in the presence of a surrounding liquid or gas medium. A solid carbon target (usually graphite or carbon powder) is placed in a chamber filled with a liquid medium such as distilled water, ethanol, or acetone.

A pulsed or continuous laser (commonly Nd:YAG laser) is focused onto the target surface. The intense laser beam causes localized heating and vaporization of the carbon target.

The high-temperature plasma plume formed cools rapidly in the liquid, leading to the nucleation of carbon nanodots. The ablated carbon clusters aggregate and react with the surrounding medium, forming carbon quantum dots with surface functional groups (like –OH, –COOH). The colloidal solution is collected and subjected to centrifugation, filtration, or dialysis to remove large particles or unreacted debris. Its advantages include high purity CQDs with fewer chemical impurities. It allows synthesis in a controlled environment. Size and shape can be tuned by adjusting laser parameters. Suitable for surface modification by changing the surrounding medium.

ii. Arc Discharge Method

The arc discharge method is a top-down physical technique that involves generating an electric arc between two graphite electrodes under controlled conditions to break down bulk carbon into nanostructures, including carbon quantum dots (CQDs). This method was originally developed for synthesizing carbon nanotubes and fullerenes but has also been adapted for CQDs. Two graphite electrodes are placed a short distance apart inside a chamber filled with

inert gas (e.g., argon or helium) or sometimes a liquid medium. A direct current (DC) voltage is applied across the electrodes, initiating an electric arc between them.

The arc produces extremely high temperatures (~4000–6000°C) at the anode surface, causing sublimation of graphite into plasma-phase carbon atoms. These carbon atoms condense and nucleate into various nanostructures, including CQDs.

The resulting CQDs are collected from the soot deposited on the chamber walls or in the liquid medium. The product is further purified using filtration, centrifugation, or dialysis to isolate CQDs.

Its advantages include, high-purity, crystalline CQDs,can generate multiple carbon nanostructures (including CNTs, fullerenes).Simple concept; no need for complex precursors or reagents.

iii. Electrochemical Oxidation

Electrochemical oxidation is a top-down method that involves breaking down bulk carbon materials like graphite or carbon fiber into carbon quantum dots by applying an electrical potential in an electrolytic cell. This method is considered relatively simple, low-cost, and environmentally friendly, offering tunable control over the size and surface chemistry of the resulting CQDs. Electrochemical Cell setup consist of two electrodes which are immersed in an electrolyte solution (commonly KOH, NaOH, or H_2SO_4). Graphite rods or carbon paper are typically used as the anode and cathode.

A DC voltage or current is applied. The carbon from the anode oxidizes, releasing carbon ions and fragments into the electrolyte. These fragments undergo further oxidation and passivation to form CQDs, often functionalized with groups like –COOH, –OH, and –C=O. The solution turns brown or yellowish due to CQD formation. The CQDs are purified using centrifugation, filtration, and dialysis to remove unreacted materials and impurities.

Its advantages include simple equipment (basic electrochemical cell). Mild synthesis conditions (ambient temperature and pressure).Tunable properties by adjusting voltage, time, and electrolyte. It produces functionalized CQDs without post-modification. It is used renewable carbon sources.

iv. Ultrasonic Treatment (Sonication)

Ultrasonic treatment, also known as sonication, is a top-down physical method that utilizes high-frequency ultrasound waves (20 kHz – 1 MHz) to break down bulk carbon materials (such as graphite, carbon soot, or biochar) into nanoscale carbon quantum dots. The method works through acoustic cavitation — the formation, growth, and implosive collapse of microscopic bubbles in a liquid, which generates intense local temperature and pressure.

Preparation of Carbon Dispersion: The carbon precursor (e.g., graphite powder, activated carbon, or soot) is dispersed in a solvent like water, ethanol, or acidic/basic solutions. The dispersion is subjected to ultrasound waves using a probe sonicator or ultrasonic bath.

Ultrasound induces cavitation bubbles that collapse violently, producing localized hotspots (~5000 K) and shock waves that fragment the carbon.

The mechanical forces break down larger carbon particles into smaller, luminescent CQDs. Surface groups may also form due to oxidation from the solvent or additives. The resulting solution is centrifuged or filtered to remove larger particles. Dialysis or ultrafiltration is used to isolate the monodispersed CQDs.

Advantages include, simple and low-cost setup, Works at ambient conditions (no high temperature or pressure). Eco-friendly, especially when water is the solvent. It can be used with various carbon sources including biomass.

II. Bottom-Up Methods

i. Hydrothermal/Solvothermal Synthesis

Hydrothermal synthesis is a bottom-up chemical approach used widely for producing carbon quantum dots from organic precursors under high temperature and pressure in a sealed vessel (typically a Teflon-lined autoclave). This method allows carbonization and passivation of organic molecules into well-dispersed, luminescent CQDs with functionalized surfaces.

Selection of Precursor: Organic precursors rich in carbon, nitrogen, and oxygen are used, such as: Citric acid, Glucose, Urea, Plant extracts, Waste biomass.

The precursor is dissolved in water or an organic solvent, and the solution is transferred to a Teflon-lined stainless-steel autoclave.

The autoclave is sealed and heated to 150–250°C for several hours (typically 4–12 hours). Under these conditions, hydrothermal carbonization occurs, forming nanometer-sized carbon cores and introducing oxygen-containing functional groups.

The solution is cooled to room temperature. The resulting brown/yellow CQD solution is filtered, centrifuged, and dialyzed to remove larger particles and unreacted residues.

Its advantages include, simple and scalable method, uses green, renewable, and low-cost carbon sources. Produces CQDs with tunable fluorescence properties. In-situ surface functionalization (e.g., –OH, –COOH, –NH_2). Environmentally friendly when using biomass/waste materials.

ii. Microwave-Assisted Synthesis

Microwave-assisted synthesis is a bottom-up technique that uses microwave radiation to rapidly heat a carbon-rich precursor, promoting carbonization and passivation in a short time. This method is known for its fast reaction rates, uniform heating, and energy efficiency, making it a popular route for producing luminescent CQDs.

Precursor Selection is the first step, Organic, carbon-rich precursors are used, such as: Citric acid, Glucose, Amino acids, Biomass or plant extracts Urea (for N-doping).

The precursor is dissolved in water or other suitable solvent and placed in a microwave-compatible container (usually a glass vial or Teflon container). The solution is subjected to microwave heating (typically 600–900 W) for a few minutes. The reaction proceeds via rapid heating, often reaching high temperatures (150–250°C) within minutes.

The mixture is allowed to cool naturally or under running water. The CQDs are then purified by centrifugation, filtration, and dialysis to remove larger particles and by-products.

Advantages include, rapid and uniform heating → short synthesis time. Energy-efficient and eco-friendly. It is a simple setup: uses a domestic or lab microwave. High yield and fluorescence tunability. Easy to scale up for mass production.

iii. Thermal Pyrolysis Synthesis

Thermal pyrolysis is a bottom-up synthesis method that involves the thermal decomposition of carbon-rich organic materials at high temperatures in the absence of oxygen. This method leads to the carbonization of the precursor, producing CQDs with luminescent properties. It is a simple, scalable, and cost-effective technique.

Precursor Selection, Common carbon-rich precursors include: Citric acid, Glucose, Amino acids (like glycine), Carbohydrates, Biomass or agricultural waste.

The precursor is placed in a crucible or glass beaker. It is heated directly on a hotplate or in a furnace at high temperature (200–400°C) for a certain duration (usually 30–120 minutes). As temperature increases, the precursor melts, dehydrates, and carbonizes, forming dark-colored carbonaceous materials with nanoscale structures.

The carbonized product is dissolved in water or an alkaline solution. Sonication or stirring is used to disperse the CQDs. The solution is filtered, centrifuged, and often dialyzed to purify and isolate the CQDs.

Advantages include simple and inexpensive equipment. There is no special atmosphere needed in many cases. It produces functionalized CQDs with good optical properties. It uses green or biomass-derived precursors.

iv. Carbonization in Furnace.

Carbonization in a furnace is a bottom-up thermal method where organic precursors are subjected to controlled heating at high temperatures in a furnace, leading to the decomposition of the precursor and the formation of carbon quantum dots. This technique promotes dehydration, polymerization, and aromatization, resulting in the carbonization of the material into nanoscale CQDs.

Precursor Preparation include Organic carbon-rich precursors are selected, such as: Citric acid, Glucose, Urea (for N-doped CQDs), Biomass (like orange peels, sugarcane bagasse, etc.). These may be dried or slightly pre-treated before carbonization.

The precursor is placed in a ceramic or quartz crucible. It is introduced into a muffle furnace or tube furnace. Temperature is gradually increased to 300–600°C, typically under an inert atmosphere (e.g., nitrogen or argon) to prevent oxidation.

At elevated temperatures, the organic material undergoes pyrolytic decomposition. It loses water and volatile gases, and undergoes aromatization, forming carbon nuclei that coalesce into CQDs.

After the carbonization is complete, the product is cooled to room temperature. It is then dispersed in water or an alkaline solution, sonicated to break aggregates, and filtered/centrifuged to collect CQDs.

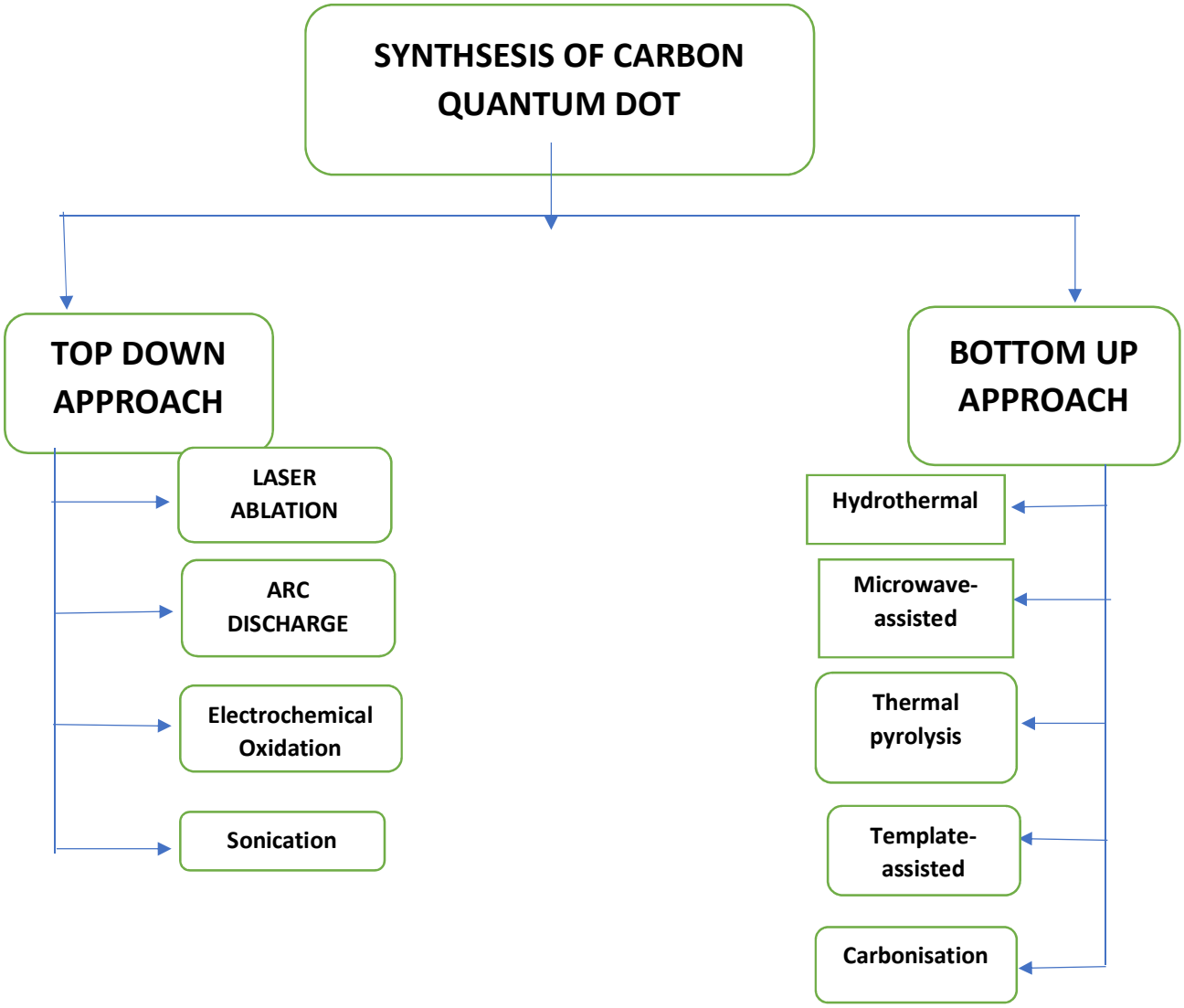
Its Advantages are, it can be used for mass production, produces stable, crystalline or amorphous CQDs, ideal for biomass or waste-to-nanomaterial conversion, allows fine-tuning of particle properties via temperature/time control.

v. Template-Assisted Synthesis

Template-assisted synthesis is a bottom-up method used to control the size, shape, and structure of CQDs by using templates or scaffolds that direct the growth of carbon nanostructures. This technique is especially useful when uniform morphology and narrow size distribution of CQDs are desired. The templates act as a physical constraint, regulating the spatial distribution of the carbon precursors during the carbonization process.

Choose a hard or soft template depending on the desired CQD features. Precursor materials like glucose, citric acid, or biomass extracts are infiltrated into the template's pores or domains. The system is heated under controlled conditions (e.g., 250–500°C) in an inert atmosphere (N_2 or Ar) to convert the precursors into carbon nanostructures. Hard templates are removed via chemical etching (e.g., HF or NaOH to dissolve silica). Soft templates can be removed by washing with solvents or thermal degradation. The resulting CQDs are filtered, dialyzed, and centrifuged to isolate monodispersed carbon quantum dots.

Advantages are, it enables precise size and shape control of CQDs, produces highly uniform and monodisperse particles and can design functionalized CQDs by modifying templates or precursors. It is useful for tailoring optical and electronic properties.


SYNTHSESIS OF CARBON QUANTUM DOT
TOP DOWN APPROACH
LASER ABLATION
ARC DISCHARGE
Electrochemical Oxidation
Sonication
BOTTOM UP APPROACH
Hydrothermal
Microwave-assisted
Thermal pyrolysis
Template-assisted
Carbonisation

Comparison Table of Methods

Method	Approach	Advantages	Limitations
Laser Ablation	Top-down	High purity, crystalline CQDs	Expensive equipment, low yield
Arc Discharge	Top-down	High temp control, good crystallinity	Complex, hazardous gases
Electrochemical Oxidation	Top-down	Easy setup, tunable	Harsh chemicals, lower control
Sonication	Top-down	Simple, low-cost	Low yield, poor uniformity
Hydrothermal	Bottom-up	Eco-friendly, high-quality CQDs	Long reaction times
Microwave-assisted	Bottom-up	Fast, energy-efficient	Overheating risk
Thermal pyrolysis	Bottom-up	Simple, no solvent	Broad size distribution
Template-assisted	Bottom-up	Controlled morphology	Expensive, multi-step

Table 1.3 Comparison Table of Methods

1.2.4. Nitrogen Doped Carbon Quantum Dot

Nitrogen-Doped Carbon Quantum Dots (N-CQDs) are an advanced form of carbon quantum dots in which nitrogen atoms are intentionally introduced into the carbon matrix. This process, known as doping, significantly enhances the physical, chemical, optical, and electronic properties of the CQDs.

Nitrogen is considered one of the most effective dopants for carbon-based nanomaterials because it has a similar atomic size to carbon and offers additional lone-pair electrons, which improve the charge distribution and electronic structure of CQDs.

I. Enhancement Through Nitrogen Doping

By introducing nitrogen atoms into the CQD structure, several important properties are improved:

i. Photoluminescence (PL):

N-doping increases the number of defect sites and surface functional groups, which act as light-emitting centers. This leads to brighter and more stable fluorescence compared to undoped CQDs, and often increases the quantum yield significantly.

ii. Electronic Properties:

The presence of nitrogen atoms alters the electronic distribution in the carbon network. This results in better electron transport, improved conductivity, and reduced bandgap, making N-CQDs more efficient for electronic and optoelectronic applications.

iii. Chemical Reactivity and Functionalization:

Nitrogen introduces active sites (such as amine groups), which increase the surface reactivity of CQDs. This makes N-CQDs more suitable for drug delivery, biosensing, and chemical detection, since they can easily bind to other molecules.

iv. Photostability and Environmental Stability:

N-CQDs are more resistant to photobleaching and stable under various pH and temperature conditions. This makes them reliable for long-term applications like bioimaging and environmental sensing.

Nitrogen-doped CQDs offer a remarkable upgrade over undoped CQDs, especially in terms of fluorescence, conductivity, and surface functionality. These enhancements make N-CQDs a powerful tool in next-generation technologies spanning healthcare, energy, electronics, and environmental protection.

II. Morphological Changes in Nitrogen-Doped CQDs

i. Size and Shape.

Size Reduction: N-doping often results in smaller particle sizes compared to undoped CQDs. This is due to enhanced nucleation during synthesis, promoted by nitrogen-rich precursors.

Shape: N-CQDs generally retain a quasi-spherical shape, but may show a more uniform and finer morphology due to better control over growth kinetics.

Smooth Surface: Surface becomes smoother and more homogeneous because nitrogen aids in passivating surface defects.

ii. Structural Changes in N-CQDs

Nitrogen doping can promote a more graphitized (ordered) carbon structure, depending on the synthesis method**.**

iii. Functional Groups and Surface Chemistry

N-CQDs have increased numbers of amine ($–NH_2$), pyridinic-N, pyrrolic-N, or graphitic-N groups. These nitrogen species integrate into the carbon lattice in different ways:

Pyridinic-N: Substitutes a carbon atom at the edge, donating one electron to the π system.

Pyrrolic-N: Adds to a five-membered ring, contributing two electrons.

Graphitic-N: Replaces carbon within the graphene plane, enhancing conductivity.

Impact of Structural and Morphological Changes

Aspect	Effect of N Doping
Surface Reactivity	Increases due to more nitrogen-containing functional groups
Optical Properties	Enhanced photoluminescence, tunable emission wavelengths due to surface defects
Electrical Conductivity	Improves due to electron-donating nitrogen groups, especially graphitic-N
Quantum Yield	Higher fluorescence efficiency due to surface passivation
Stability	Increased chemical and photostability

Table 1.4 Impact of Structural and Morphological Changes in NCQDs

N-doping leads to smaller, more uniform, spherical particles with smoother surfaces. It Introduces different nitrogen configurations into the carbon lattice, increasing functional sites, crystallinity, and electron mobility. These changes are not just cosmetic—they directly enhance the performance of N-CQDs in applications like biosensing, optoelectronics, catalysis, and energy storage.

1.2.5. Application of Nitrogen Doped CQD

I. Antioxidant Activity of Nitrogen-Doped CQDs

Nitrogen-doped carbon quantum dots exhibit strong antioxidant properties, primarily due to their surface chemistry, electronic structure, and high reactivity. This makes them highly effective in neutralizing reactive oxygen species (ROS) and scavenging free radicals, which is crucial in preventing oxidative stress in biological systems.

Mechanism of Antioxidant Action includes,

- Free Radical Scavenging: N-CQDs can donate electrons or hydrogen atoms to free radicals (like DPPH•, •OH, or $O_2^{\bullet -}$), converting them into stable, non-reactive species. This is due to the presence of electron-rich nitrogen groups (e.g., amine,) and surface –OH and –COOH groups that interact with ROS.
- Redox Activity: The sp^2 carbon core combined with nitrogen functionalities enhances redox behavior, enabling N-CQDs to act as electron donors or acceptors depending on the environment.
- Surface Functional Groups: Pyridinic-N and graphitic-N help in enhancing the electron transfer ability. Hydrophilic groups increase water solubility, ensuring efficient dispersion in biological systems for antioxidant action.

Common assays used to measure antioxidant activity of N-CQDs include:
DPPH Radical Scavenging Assay it measures ability to reduce the purple DPPH radical to a yellow-colored compound.

N-CQDs exhibit excellent antioxidant activity due to nitrogen-induced electon-rich surfaces and enhanced redox capabilities. Their biocompatibility, water solubility, and non-toxic nature make them ideal for biomedical and environmental uses. These dots serve as efficient free radical scavengers, protecting cells, materials, or solutions from oxidative damage.

Antioxidant N-CQDs can protect cells from oxidative stress, making them ideal for therapeutics, drug delivery systems, and tissue engineering can be used in formulations to protect skin from oxidative damage caused by pollution or UV light. It is used as additives or sensors to monitor and preserve antioxidant levels in food and crops. Scavenging of free radicals helps reduce oxidative damage in ecosystems.

II. Photocatalytic Activity of Nitrogen-Doped CQDs (N-CQDs)

Photocatalysis is a process where a material absorbs light and uses the energy to drive chemical reactions — often to degrade pollutants, generate hydrogen, or reduce CO_2. N-CQDs serve as excellent photocatalysts or photocatalyst enhancers due to their unique optical and electronic properties enhanced by nitrogen doping.

Mechanism of Photocatalysis in N-CQDs include,

- Light Absorption & Excitation: Under UV or visible light, N-CQDs absorb photons, and electrons (e^-) are excited from the valence band to the conduction band, leaving behind holes (h^+).
- Charge Separation: Nitrogen doping introduces surface defects and mid-gap states, which help trap electrons or holes, improving charge separation and reducing recombination losses.
- Reactive Species Formation: The separated electrons and holes react with water (H_2O) and oxygen (O_2) in the environment to produce reactive oxygen species (ROS):

  $e^- + O_2 \rightarrow \bullet O_2^-$ (superoxide radical)
  $h^+ + H_2O \rightarrow \bullet OH$ (hydroxyl radical)
- Degradation or Conversion: These ROS then attack organic pollutants (like dyes or pharmaceuticals) or assist in processes like hydrogen evolution (H_2 production) or CO_2 reduction.

N atoms introduce active sites and enhance the electron-donating capacity-doping reduces the bandgap, enabling absorption of visible light, not just UV facilitates better charge mobility, making the photocatalytic process more efficient. Advantages of N-CQDs in Photocatalysis include, Visible light activity due to reduced bandgap, non-toxic and eco-friendly, High stability under light exposure, Easily tunable surface and optical properties and Excellent dispersibility in aqueous systems.

Nitrogen-doped carbon quantum dots are efficient, sustainable photocatalysts that can harness light energy to drive useful chemical reactions. Their activity is boosted by nitrogen doping, which enhances light absorption, improves charge separation, and facilitates ROS generation. These properties make N-CQDs highly attractive for environmental remediation, renewable energy production, and green chemistry.

III. Photothermal Applications of Nitrogen-Doped Carbon Quantum Dots

Photothermal therapy (PTT) involves the conversion of light (especially near-infrared or NIR light) into heat, which is then used for therapeutic or functional purposes, such as cancer treatment, antibacterial activity, or material processing. N-CQDs are gaining attention as efficient photothermal agents because of their tunable optical properties and excellent biocompatibility.

Nitrogen doping enhances the electronic and structural properties of CQDs, making them better absorbers of NIR light, ideal for deep tissue penetration. More efficient at converting light into heat due to localized electron excitation and surface defects. It is biocompatible and non-toxic, suitable for in vivo use. It is easily dispersible in water, which is crucial for biomedical applications.

Mechanism of Photothermal Conversion include,

- Light Absorption: N-CQDs absorb NIR or visible light, exciting electrons to higher energy states.
- Non-radiative Relaxation: Instead of emitting light (like fluorescence), the excited electrons release energy as heat via non-radiative relaxation.
- Localized Heating: This leads to a localized increase in temperature, which can be harnessed for applications like killing cancer cells or bacteria.

Nitrogen-doped CQDs are next-generation photothermal materials, offering an ideal blend of light absorption, heat generation, and biological safety. Their applications in cancer treatment, antibacterial therapy, and controlled drug delivery are paving the way for non-invasive and targeted biomedical technologies.

IV. Biomedical Applications of N-CQDs

Nitrogen-doped carbon quantum dots (N-CQDs) have gained immense attention in biomedical science due to their excellent biocompatibility, non-toxic nature, strong photoluminescence, and versatile surface chemistry. Nitrogen doping further enhances their optical and electronic properties, making them ideal for a range of diagnostic and therapeutic applications.

Bioimaging (Fluorescent Imaging): N-CQDs emit strong, tunable fluorescence under UV or visible light. It is used for cellular imaging, tumor tracking, and in vivo imaging. It has high photostability and low cytotoxicity make them safer alternatives to traditional dyes or quantum dots containing heavy metals (like CdSe).

Biosensing: N-CQDs change their fluorescence in the presence of specific biomolecules, ions, or pH changes. It includes Glucose sensing and detection of metal ions (like Fe^{3+}, Hg^{2+}) and DNA/protein interaction studies.

Drug Delivery: N-CQDs can be loaded or conjugated with drugs and directed toward specific cells or tissues. Its application includes, targeted delivery of anticancer drugs, antibiotics, or gene therapy agents.

Antimicrobial and Antibiofilm Agents: Under light exposure, N-CQDs generate reactive oxygen species (ROS) or heat to kill bacteria. Its application includes, wound dressings, surgical instruments, or coatings for implants.

V. Applications of N-CQDs in Forensic Science

Nitrogen-doped carbon quantum dots (N-CQDs) are emerging as innovative tools in forensic science due to their unique optical, chemical, and surface properties. Their small size, strong fluorescence, and ability to interact with biomolecules make them excellent candidates for forensic applications that require sensitive detection, visualization, and trace evidence analysis.

Latent Fingerprint Detection: N-CQDs bind to sweat residues or oils left behind in fingerprints. Under UV or visible light, they fluoresce brightly, revealing clear fingerprint patterns. Its advantages include, high sensitivity even on complex or multi-colored surfaces. It is non-destructive and non-toxic. It can work under ambient or UV light, no need for chemical developers.

Detection of Biological Fluids (e.g., Blood, Saliva, Urine): -CQDs can selectively bind to components like proteins, DNA, or enzymes found in bodily fluids. Fluorescence changes signal the presence and location of biological traces on crime scenes. It is Useful for trace detection on fabrics or hard-to-see surfaces. It enables fluorescent tagging for later lab analysis.

DNA Sensing and Analysis: N-CQDs are used in label-free DNA detection, useful for forensic genotyping. They can intercalate with DNA or attach via electrostatic interactions, altering fluorescence signals. It can be used for Quantifying DNA, monitoring DNA hybridization, detecting DNA damage or degradation.

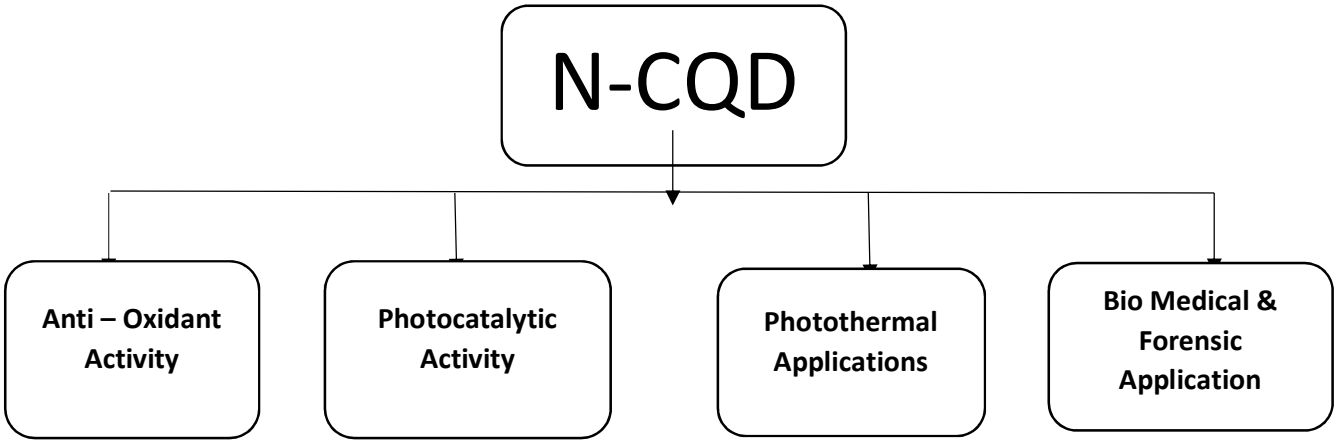
Explosive and Drug Residue Detection: N-CQDs can be engineered to fluoresce in the presence of explosives (e.g., TNT, RDX) or illicit drugs. Surface functionalization with selective

receptors allows for rapid field testing. Its advantages include On-site, portable detection, Visual confirmation through fluorescence "on/off" behavior.

Ink and Document Analysis: N-CQDs can be used to detect forgery or ink tampering by interacting with certain dyes and solvents. It can highlight invisible writing or alterations under UV light. It may serve in authenticity verification of documents, currency, or stamps.

Their ability to fluoresce under UV, interact with trace biomolecules, and be tailored for specific targets makes them highly effective in both the field and the lab.

Applications of N-CQDs



1.3 LITERATURE SURVEY

Key Literature Sources and Findings:

1. Zhu et al., 2013 — Chemical Communications, "Facile synthesis of carbon dots with tunable photoluminescence properties": Described a hydrothermal route using citric acid as a precursor. Demonstrated tunable emission by adjusting synthesis time and PH. Highlighted low cytotoxicity and potential in bioimaging.

2. Baker & Baker, 2010 — Angewandte Chemie,
   Pioneering work showing hydrothermal treatment of glucose yields fluorescent CQDs. Emission depends on size and surface states. Suggested hydrothermal methods can produce CQDs with controlled oxidation levels.

3. Shen et al., 2012 — Nanoscale

   Used biomass waste (banana peels) under hydrothermal treatment. Proved green synthesis route, emphasizing sustainable material use. Resultant CQDs showed high quantum yield and excitation-dependent emission.

4. Wang et al., 2015 — Journal of Materials Chemistry B

   Developed nitrogen-doped CQDs via hydrothermal treatment of urea and citric acid. Demonstrated enhanced fluorescence due to N-doping and improved quantum yield. Applications in biosensing and imaging were explored.

5. Xu et al., 2016 — Sensors and Actuators B

   Synthesized CQDs via hydrothermal carbonization of orange juice.

   Used for fluorescence-based heavy metal sensing (Fe^{3+}, Hg^{2+}). Low-cost and highly effective, especially for environmental applications.

Common Precursors and Conditions

Carbon Source	Nitrogen Source (if doped)	Temperature	Time
Citric acid	Urea or ethylenediamine	200 °C	3 hours
Glucose/fructose	Ammonia solution	180 °C	6 hours
Biomass (peels, pulp)	glycine	160°C	4 hours
sucrose	glycine	180 °C	3 hours

Table1.5 Common Precursors and Conditions

1.4. MOTIVATION AND OBJECTIVES

In recent years, carbon quantum dots (CQDs) have emerged as a cutting-edge class of carbon-based nanomaterials due to their exceptional photoluminescence, chemical stability, water solubility, low toxicity, and excellent biocompatibility. These properties make CQDs highly promising for a variety of applications in bioimaging, drug delivery, environmental monitoring, photovoltaics, and optoelectronics.

The motivation behind this project stems from the growing need to develop sustainable nanomaterials using green chemistry principles, while simultaneously achieving high quantum

yield, tunable fluorescence, and desired surface functionalities. Hydrothermal synthesis not only meets these goals but also allows for doping with heteroatoms (e.g., nitrogen), which further enhances the optical and electronic properties of CQDs.

This project focuses on the hydrothermal synthesis of CQDs — a green, low-cost, and scalable method that uses water as a solvent and allows the conversion of various carbon-rich precursors (e.g., citric acid, glucose, biomass) into fluorescent CQDs under high temperature and pressure. The process enables easy surface functionalization and heteroatom doping (e.g., with nitrogen), thereby enhancing their fluorescence quantum yield and tailoring their physicochemical properties for specific applications.

The study aims to synthesize, optimize, and characterize CQDs using hydrothermal techniques. Characterization techniques such as UV-Vis, photoluminescence spectroscopy will be employed to evaluate the structural and optical properties of the synthesized CQDs. Furthermore, the project seeks to explore how synthesis parameters (like temperature, time, and doping agents) influence the material's performance and investigate their potential use in biosensing, imaging, and environmental applications.

By adopting eco-friendly approaches and sustainable materials, this research aligns with modern goals of green nanotechnology and opens up new avenues for affordable and efficient carbon-based nanomaterials in scientific and industrial applications.

PART 2

1.5. CHARACTERIZATION TECHNIQUES

In nanoscience and nanotechnology, materials exhibit unique physical, chemical, optical, and mechanical properties due to their nanoscale dimensions (typically 1–100 nm). These properties often differ significantly from their bulk counterparts. To understand, optimize, and utilize these materials effectively, it is essential to characterize their size, structure, composition, surface chemistry, morphology, and performance.

Characterization techniques provide insights to size and shape of nanoparticles, crystallinity and phase structure, elemental composition optical and electronic behavior, surface properties and functional groups. It also determines nanoparticle size and distribution and examine surface

morphology and texture. It helps in understanding chemical bonding and composition. It also evaluates optical and electrical properties and confirm purity, crystallinity, and phase.
Transmission Electron Microscopy (TEM) is widely used to determine the size, shape, and morphology of nanomaterials at atomic or near-atomic resolution, offering direct visual confirmation of nanoscale structures. Scanning Electron Microscopy (SEM) complements TEM by providing detailed images of surface topography and particle distribution.
To investigate the crystalline or amorphous nature of materials, X-ray Diffraction (XRD) is employed, which reveals structural phases and lattice arrangements. Chemical composition and surface functional groups are commonly analyzed using Fourier Transform Infrared Spectroscopy (FTIR), which identifies vibrational modes of chemical bonds, while X-ray Photoelectron Spectroscopy (XPS) offers elemental and bonding state information at the surface level.

Optical properties, including light absorption and emission, are studied through UV-Visible (UV-Vis) and Photoluminescence (PL) spectroscopy, which help in evaluating the quantum confinement effect and band gap energies crucial for optoelectronic applications. Additionally, Atomic Force Microscopy (AFM) provides three-dimensional surface mapping at the nanoscale, useful for determining the surface roughness and topographical features.
Together, these techniques form a comprehensive tool kit to characterize CQDs and other nanomaterials, ensuring precise control over their synthesis, structure, and performance.

In this section, different characterization technique used in our work are uv -visible spectroscopy, photoluminescence spectroscopy, DPPH free radical scavenging activity.

1.5.1 UV- Visible Spectroscopy

UV-Visible spectroscopy is an analytical technique used to measure the absorption of ultraviolet (200–400 nm) and visible light (400–800 nm) by a substance. It provides critical information about a material's electronic structure, particularly the optical band gap, and is extensively used in nanomaterial research to assess light absorption behavior, quantum effects, and conjugation in molecules.

UV-Vis spectroscopy is based on the Beer-Lambert Law, which relates the absorption of light to the properties of the material through which the light passes.

Beer-Lambert Law: The Beer-Lambert Law states that the absorbance of light by a substance is directly proportional to the concentration of the absorbing species and the path length through which the light passes.

$$A = \varepsilon \times c \times l$$

A = Absorbance (no units)

ε = Molar absorptivity (L mol^{-1} cm^{-1})

c = Concentration of the solution (mol L^{-1})

l = Path length of the cuvette (cm)

When a material is exposed to UV or visible light, electrons in its atoms or molecules absorb photons and are promoted from a lower energy state (ground state) to a higher energy state (excited state). The wavelength and intensity of the absorbed light provide valuable information about electronic transitions like,

$\pi \rightarrow \pi^*$ (pi to pi-star) transitions (common in conjugated systems),

$n \rightarrow \pi^*$ (non-bonding to pi-star) transitions (often seen in carbonyl or nitrogen-containing groups).

A light source (typically a deuterium lamp for UV and a tungsten lamp for visible) emits a broad spectrum of light. The beam passes through a monochromator, which selects a specific wavelength. The selected light passes through the sample solution in a quartz cuvette.The detector measures the transmitted light, and the spectrophotometer calculates the absorbance.

UV-Vis spectroscopy is a powerful, non-destructive tool used to characterize optical properties of nanomaterials such as Carbon Quantum Dots (CQDs). It reveals,

- Absorption Peak: CQDs typically show strong absorption in the UV region (~200–400 nm) due to $\pi \rightarrow \pi^*$ transitions of C=C bonds and $n \rightarrow \pi^*$ transitions from C=O or N-containing groups.
- Band Gap Estimation: Using Tauc plots, the optical band gap of CQDs can be estimated from the absorbance data, which is critical for understanding their semiconducting behavior.

- Quantum Confinement Effect: A blue shift in the absorption edge (shift toward shorter wavelengths) is often observed in smaller CQDs due to the quantum size effect, confirming size-dependent properties.
- Doping and Surface Modification: The appearance or shift in absorption bands can also indicate successful doping (e.g., with nitrogen, sulfur) or functional group changes.

Tauc Plot – Principle and Band Gap Determination

Tauc plot is used to determine the optical band gap (Eg) of semiconducting materials like Carbon Quantum Dots (CQDs) using UV-Vis absorption data.

A Tauc plot is a graphical method used to estimate the optical band gap of semiconductors from their UV-Vis absorption spectra. It is based on the relationship between the absorption coefficient (α) and the photon energy (hν) near the absorption edge.

Tauc Relation**: $(\alpha h\nu)^n = A(h\nu - Eg)$**

α = Absorption coefficient

hν = Photon energy (in electron volts, eV)

A = Constant

Eg = Optical band gap (eV)

n = Type of electronic transition:

n=1/2 for direct allowed transitions (common in CQDs)

n= 2 for direct allowed transitions (common in CQDs)

Band gap estimation is critical for optoelectronic applications, bioimaging, solar cells, and photocatalysis. Due to quantum confinement, CQDs show size-dependent band gaps, making this analysis essential.

1.5.2 Photoluminescence (PL)

Photoluminescence (PL) is the emission of light (photons) from a material after it absorbs photons (light energy). It is a non-destructive optical technique that helps in understanding the electronic structure, energy levels, and defects of a material, particularly semiconductors and quantum dots**.**

The fundamental principle is based on photo-excitation and radiative recombination:

- Excitation: When a material is irradiated with light (usually UV), electrons absorb energy and are promoted from the valence band to the conduction band or from the ground state to an excited state.
- Relaxation: After reaching the excited state, electrons lose some energy non-radiatively (via vibration or heat).
- Emission (PL): Electrons then recombine with holes, releasing energy in the form of visible or near-infrared light—this is photoluminescence.

In photoluminescence (PL) spectroscopy, a sample is first exposed to a beam of high-energy light, usually in the ultraviolet (UV) or visible range. This light excites electrons in the material, promoting them from their ground state (usually the valence band) to a higher energy state (typically the conduction band). Once excited, the electrons do not remain in the higher energy state for long. They lose some energy through non-radiative processes such as vibrational relaxation or interactions with the surrounding matrix.

Eventually, the electrons fall back down to their original energy level or to an intermediate level, and in doing so, they release the excess energy in the form of light—this emitted light is the photoluminescence. The emitted light is collected and analyzed by a spectrometer, which records the intensity of the light across different wavelengths, resulting in a PL spectrum. This spectrum reveals key information about the electronic structure, band gap, and surface defects of the material.

In the case of Carbon Quantum Dots (CQDs), this technique is especially useful because their emission properties vary with size, doping, and surface functionalization, making PL spectroscopy a powerful tool for their optical and structural characterization.

The position of the PL peak may shift depending on the material's particle size, defects, or dopants, allowing researchers to infer structural or surface changes.

Additionally, excitation-dependent PL behavior, particularly in Carbon Quantum Dots (CQDs), reveals the presence of multiple emissive sites and varying energy states, which is key for applications in bioimaging and sensing.

Carbon Quantum Dots (CQDs) exhibit strong and tunable photoluminescence, making them highly attractive for applications in optoelectronics, sensing, and bioimaging. Their photoluminescence originates mainly from two factors: the quantum confinement effect and surface state emissions. Due to their extremely small size (typically less than 10 nm), CQDs show size-dependent electronic properties, where smaller dots emit higher-energy (blue) light and larger ones emit lower-energy (red) light.

Additionally, the presence of various surface functional groups and defect sites contributes to multiple emission pathways, leading to excitation-dependent fluorescence—a distinctive property of CQDs. This means that the emission color can be tuned simply by changing the excitation wavelength.

Furthermore, doping CQDs with elements such as nitrogen can enhance their photoluminescence intensity and modify the emission characteristics by altering the electronic structure and introducing new emissive states. These unique and versatile PL behaviors make CQDs ideal for multicolor imaging, fluorescent labeling, and energy-related applications.

It is widely used to determine the optical band gap of materials, which is essential for designing devices like LEDs, solar cells, and photodetectors. PL spectroscopy also plays a critical role in identifying defects and impurities in materials, since non-radiative recombination centers often quench or alter PL signals.

In addition, PL spectroscopy is employed in chemical sensing, where changes in fluorescence intensity or wavelength indicate the presence of specific ions or molecules. Its non-destructive nature, high sensitivity, and capability for real-time monitoring make PL spectroscopy a powerful and versatile analytical tool.

Photoluminescence (PL) spectroscopy offers several notable advantages that make it a valuable tool in materials science, nanotechnology, and optoelectronic research.

One of its biggest strengths is that it is a non-destructive technique, allowing researchers to analyze delicate or expensive samples without altering or damaging them. It is also highly sensitive, capable of detecting even trace levels of luminescent materials or subtle changes in composition and structure.

Additionally, it is well-suited for a wide variety of sample types, including solids, liquids, films, and nanostructures.

For materials like Carbon Quantum Dots (CQDs), PL spectroscopy is especially advantageous due to its ability to track size-dependent emission, surface functionality, and doping effects, all of which are crucial for tuning their performance in various applications. Its versatility and effectiveness across disciplines make it a go-to technique for both fundamental research and applied sciences.

1.5.3. DPPH Free Radical Scavenging Analysis.

DPPH stands for 2,2-diphenyl-1-picrylhydrazyl, a stable free radical with a deep violet color in solution. It is widely used in antioxidant assays to evaluate the free radical scavenging ability of natural products, nanomaterials (like NCQDs), and plant extracts due to its stability and easily detectable color change**.**

The DPPH assay is based on the reduction of the DPPH radical in the presence of a hydrogen-donating antioxidant (i.e., a free radical scavenger). When DPPH encounters a molecule capable of donating a hydrogen atom (like an antioxidant), it accepts the hydrogen, becoming a non-radical (reduced) form, which causes a color change from deep violet to pale yellow.The change in absorbance is measured spectrophotometrically at a wavelength of around 517 nm.

DPPH·+AH→DPPH-H+A·

DPPH• = stable free radical

AH = antioxidant (e.g., NCQDs)

DPPH-H = reduced form of DPPH (yellow)

A• = oxidized form of antioxidant

The assay simulates the oxidative stress environment in biological systems where antioxidants neutralize harmful free radicals. By observing how effectively a compound reduces DPPH radicals, it gives insight into its potential antioxidant activity, which is key in pharmaceutical, nutritional, and cosmetic research.

For nanomaterials like NCQDs (Nitrogen-doped Carbon Quantum Dots), the presence of nitrogen and oxygen-containing groups enhances their ability to donate electrons or hydrogen, making them efficient free radical scavengers.

To perform the DPPH free radical scavenging assay, a solution of DPPH, typically prepared in methanol or ethanol, is first prepared and kept in the dark to prevent premature degradation. The sample under investigation, such as nitrogen-doped carbon quantum dots (NCQDs), is then added to the DPPH solution in varying concentrations.

The mixture is gently shaken and incubated in the dark at room temperature for about 30 minutes to allow the reaction to occur. During this period, if the sample has antioxidant properties, it will donate electrons or hydrogen atoms to the DPPH radicals, reducing them and causing a visible color change from deep violet to yellow.

After incubation, the absorbance of each mixture is measured using a UV-Vis spectrophotometer at 517 nm. A control sample containing only DPPH without the antioxidant is also measured for reference.

The percentage of DPPH radical scavenging is then calculated by comparing the absorbance of the control and the sample. This procedure helps quantify the antioxidant activity of the test material in a simple, reliable, and reproducible manner.

To Calculate the percentage inhibition,

$$\% \text{ Inhibition} = \frac{(A_0 - A_s) \times 100}{A_0}$$

A_0 = absorbance of DPPH solution (control)

A_s = absorbance with sample

A higher % inhibition indicates stronger antioxidant activity. A gradual decrease in absorbance at 517 nm confirms the radical scavenging behavior of the tested material.

The DPPH assay is particularly useful for evaluating the antioxidant potential of Nitrogen-doped Carbon Quantum Dots (NCQDs) due to its simplicity, sensitivity, and effectiveness in detecting free radical scavenging activity.

NCQDs are known to possess various surface functional groups, such as hydroxyl, carboxyl, and amine groups, which play a significant role in electron or hydrogen donation. These properties enhance their ability to neutralize reactive free radicals, mimicking the antioxidant behavior required in biological systems.

The DPPH assay provides a quick and direct way to assess this capability by measuring how efficiently the NCQDs reduce the stable DPPH radical.

Furthermore, nitrogen doping in CQDs often introduces additional active sites and alters the electronic structure, leading to improved antioxidant performance.

Evaluating NCQDs with the DPPH method helps confirm their potential application in biomedical fields, such as drug delivery, wound healing, and disease prevention, where oxidative stress mitigation is crucial.

CHAPTER 2
SYNTHESIS AND CHARACTERISATION

2.1. HYDROTHERMAL SYNTHESIS OF CQDs VARYING FILLING VOLUME.

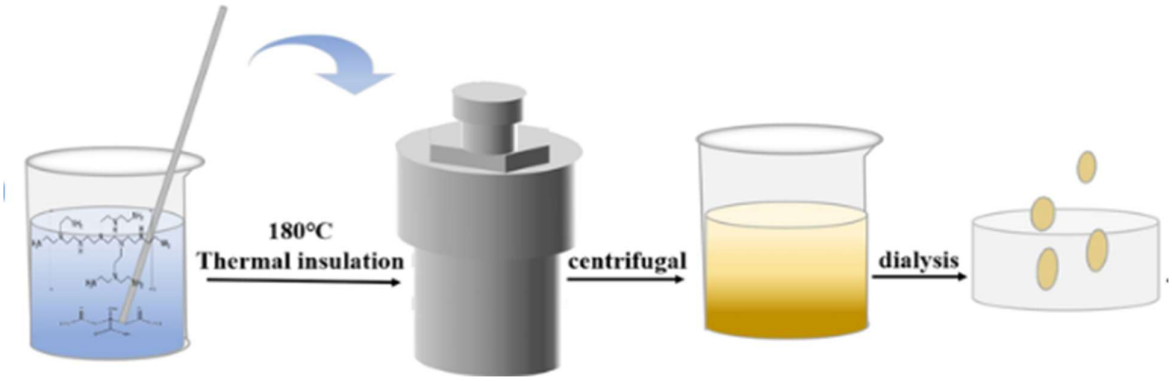
Sucrose ($C_{12}H_{22}O_{11}$) dissolved in deionized water (DI) with 2 wt% has been used for all hydrothermal syntheses of the CQDs. To investigate the influence of precursor filling volumes on the size distributions of CQDs, the precursor was placed into a Teflon lined stainless steel autoclave (volume = 500 ml) with a different filling volume (30%,40%,50%of the total capacity).

The hydrothermal reactor was then annealed in a hot air furnace (Binder) at 180 °C for 3 hours and gradually cooled to a room temperature.

A change in the color from dark to light brown is observed in the hydrothermal solutions synthesized with the filling volumes from 30% to 50% under the ambient light. The sample is then centrifuged and filtered.

Because the CQDs are synthesized with the same sucrose concentration, hydrothermal autoclave, and temperature profile, the differences in the CQD sizes are strongly influenced by the filling volumes or the heterogeneous surface between the precursor and reactor.

In this respect, experimental parameters for a large-scale fabrication of the CQDs should not only be considered the precursor concentrations, processing temperatures, and reaction times, but also included the heterogeneous interfaces.

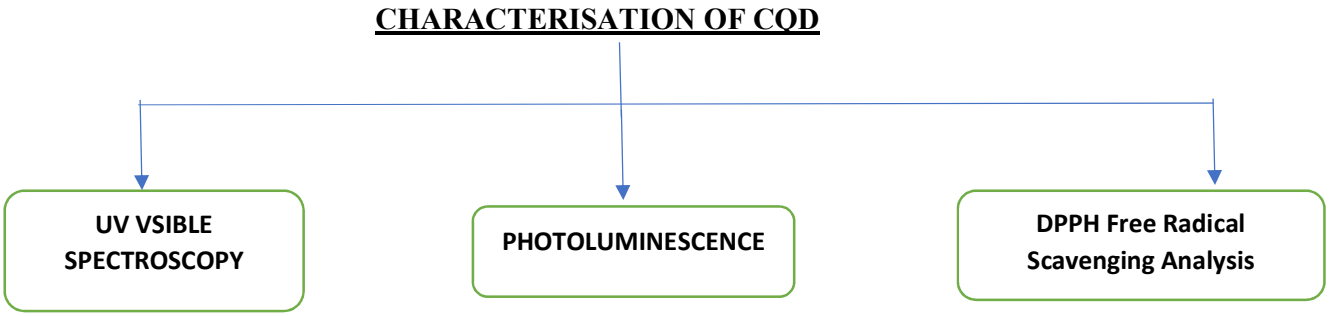


2.2. SYNTHESIS OF NITROGEN DOPED CARBON QUANTUM DOT

Sucrose ($C_{12}H_{22}O_{11}$) dissolved in deionized water (DI) with 2 wt% has been used for all hydrothermal syntheses of the CQDs along with Glycine ($C_2\,H_5\,NO_2$). Sample of filling volume 50% filling volume is synthesized.

The hydrothermal reactor was then annealed in a hot air furnace (Binder) at 180 °C for 3 hours and gradually cooled to a room temperature. A change in the color from dark to light brown is observed in the hydrothermal solutions synthesized with the filling volumes 50% under the ambient light. The sample is then centrifuged and filtered.

2.3. CHARACTERISATION



I. UV VISIBLE SPECTROSCOPY

The absorption spectra of samples are obtained using the UV Visible Spectrophotometer – JASCO (V-670 PC). It measures the absorption of light in the UV (200–400 nm) and visible (400–700 nm) regions, providing insights into band gapenergy, optical transitions, and material purity In this study, UV-Vis spectroscopy was utilized to analyse CQD of different filling volume (40 %, 50% ,N doped CQD of 50% filing volume) by evaluating their optical characteristics.

Specifically, it was employed to determine the optical band gap through Tauc's plot. Band gap energies were calculated from the absorption edge, yielding critical insights into the nanoparticles suitability for potential optoelectronic applications.

i. 40 % CQD

40% CQD is synthesized and its absorption peak analysed using uv visisble spectroscopy technique showed an absorption peak at 268.03nm , pairs). suggests that the material strongly absorbs photons of that energy.This absorption can happen because it matches a band-to-band electronic transition (typical in semiconductors and insulators) and it could also match a defect level transition if there are impurity states. It could also hint at excitonic absorption (bound electron-hole). A strong absorption peak at 268 nm usually means ,The material absorbs UV light efficiently.The electronic transition happening is between the valence band and conduction band, or from defect states.

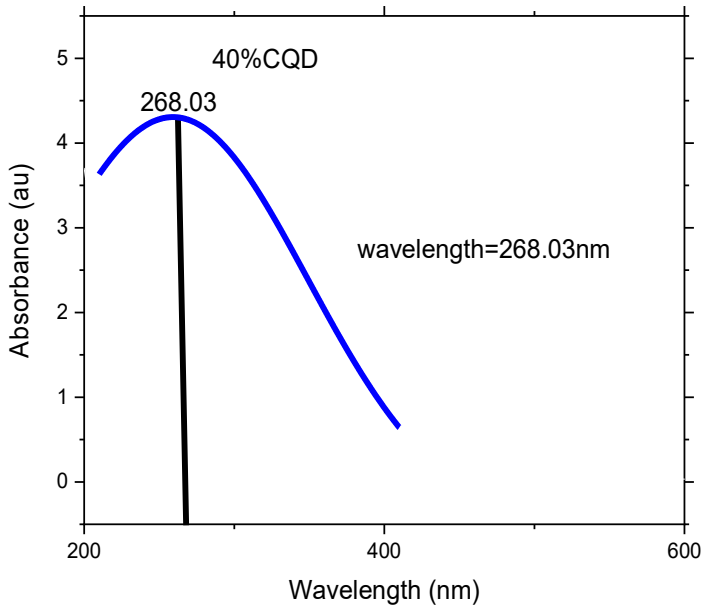


Fig 2.3.1 a: (i) UV absorption spectra

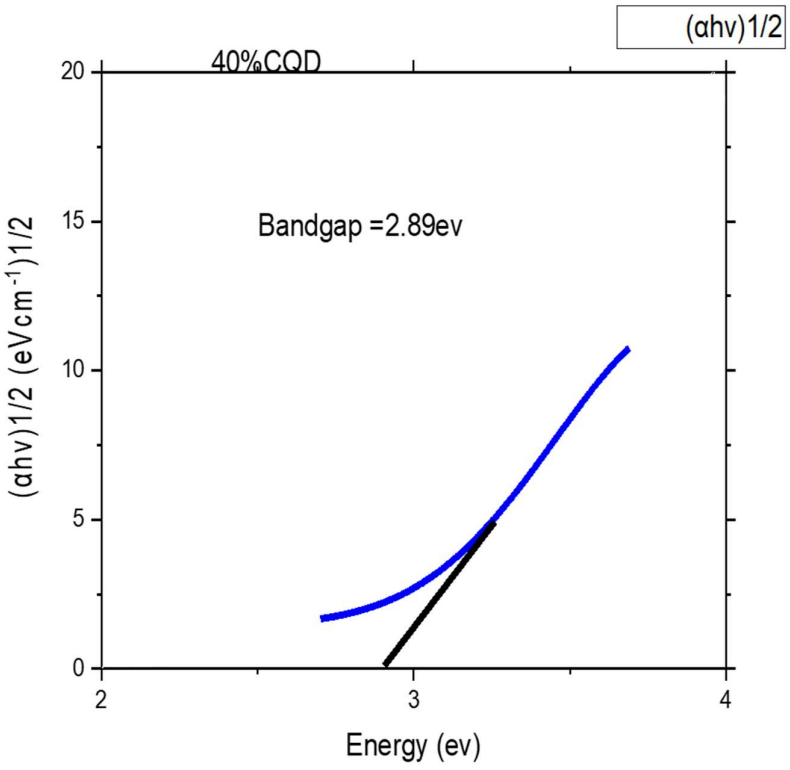


Fig2.3.1 b: (ii) Tauc plot of 40 % CQD

A 2.89 eV band gap suggests that they absorb in the UV and possibly emit (fluoresce) in the blue region (around 430–450 nm).These CQDs could show strong blue fluorescence under UV light (~365 nmThe band gap refers to the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in the CQDs. A band gap of 2.89 eV means that these dots can efficiently absorb ultraviolet (UV) light around 429 nm and are likely to emit bright blue fluorescence when excited, making them highly useful in bioimaging and optical applications.

The small size of CQDs, typically less than 10 nm, leads to quantum confinement, where the motion of electrons and holes is restricted within a tiny volume. This confinement increases the energy required for electronic transitions, hence widening the band gap compared to bulk materials.). Due to their strong UV absorption, high photostability, tunable fluorescence, and low toxicity, CQDs with a band gap around 2.89 eV are highly desirable for applications in fluorescence sensing, bio-labeling, light-emitting devices, and photocatalysis.

ii. 50 % CQD

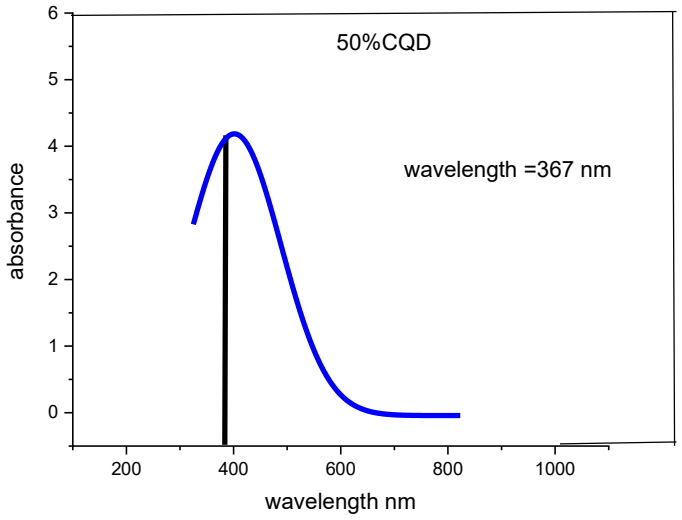


Fig 2.3.1 c : (i) UV absorption spectra

367 nm lies in the UV region of the electromagnetic spectrum. This is within the range where many CQDs tend to absorb light, and it's more aligned with typical quantum dot behavior.The

absorption at 367 nm suggests that these CQDs are absorbing ultraviolet (UV) light, which can excite the electrons in the carbon-based nanomaterial to a higher energy state.

After absorbing light at 367 nm, CQDs typically re-emit the absorbed energy as fluorescence at a longer wavelength (lower energy).This re-emission usually occurs in the visible range, with fluorescence typically observed between 400 nm to 700 nm. The exact emission wavelength depends on the size, surface functionalization, and composition of the CQDs.

The absorption peak at 367 nm typically arises from the π-π transition* (π to the excited π* state) of the carbon core or surface states of the quantum dot. In simpler terms, when CQDs absorb light at 367 nm, electrons in the valence band get excited to higher energy levels (conduction band or excited states), and this transition is associated with the specific absorption peak.

The 367 nm absorption peak for Carbon Quantum Dots is likely associated with the electronic transitions of electrons in the quantum dots, driven by quantum confinement effects, surface functionalization, and possible defects. The UV absorption at this wavelength is typical for smaller CQDs or those with specific surface modifications, and it represents the energy required to excite the electrons from the valence band to a higher excited state. After absorbing at this wavelength, CQDs usually re-emit light at a longer wavelength, which corresponds to their fluorescence.

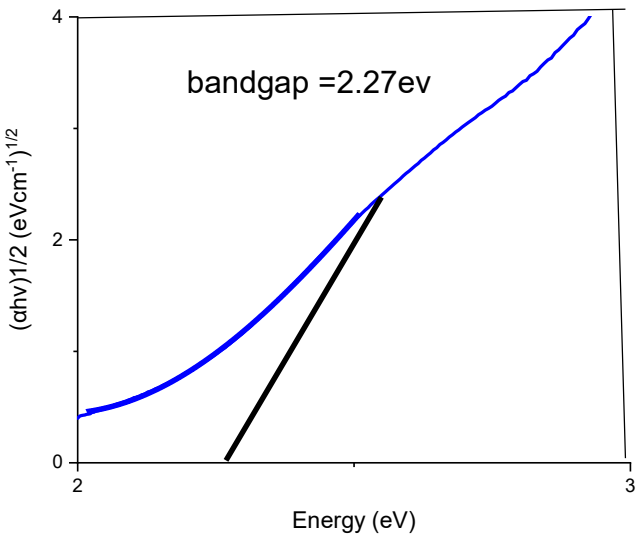


Fig 2.3.1 d : (ii) Tauc plot of 50 % CQD

A bandgap of 2.27 eV for Carbon Quantum Dots (CQDs) or any semiconductor material implies specific electronic properties. A bandgap of 2.27 eV is relatively moderate, and it corresponds to the energy required to promote an electron from the valence band to the conduction band. This energy difference dictates the optical properties (like absorption and emission spectra) and the electronic conductivity of the material.

After absorbing light at or near this wavelength , the CQDs would typically emit fluorescence at a longer wavelength (lower energy). The emission would depend on the size, surface chemistry, and doping of the CQDs, but typically this would be in the green to yellow range of the visible spectrum, as CQDs tend to exhibit a Stokes shift (emission at longer wavelengths than the excitation).

iii. NITROGEN DOPED CQD (50 % FILLING VOLUME

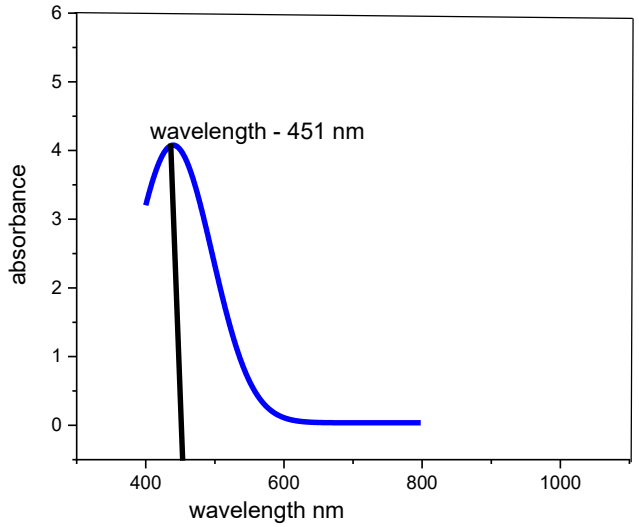


Fig 2.3.1 e : (i) UV absorption spectra

A material that absorbs light at 451 nm would have a bandgap around 2.3eV. This is in the blue region of the visible spectrum, meaning that the material can absorb blue light effectively.

After absorbing light at 451 nm, the material would typically re-emit fluorescence at a longer wavelength (lower energy). The emission wavelength would likely be in the green or yellow region of the visible spectrum, depending on the specific material and its properties.

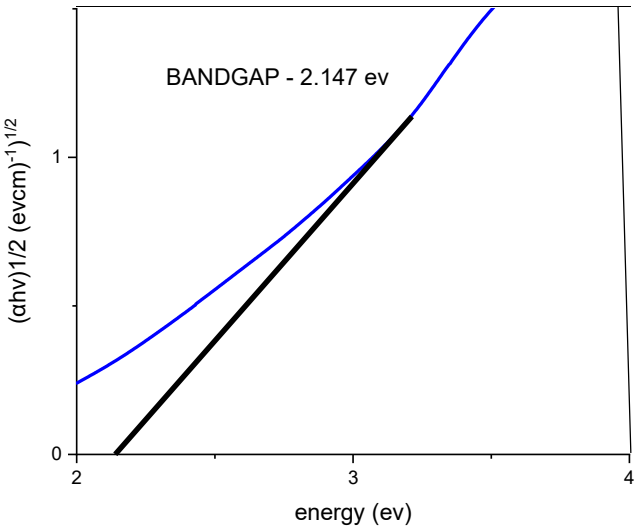


Fig 2.3.1 f : (ii) Tauc plot of N doped 50 % CQD

A 2.147 eV bandgap for nitrogen-doped carbon quantum dots (N-CQDs) suggests specific electronic and optical properties that are a result of both the quantum dot size and the nitrogen doping. A 2.147 eV bandgap corresponds roughly to a wavelength of about 496 nm (very close to blue-green light).

N-CQDs with a 2.147 eV bandgap will absorb light at blue wavelengths and possibly emit fluorescence at a slightly longer wavelength, often in the green part of the spectrum.

$\pi \rightarrow \pi^*$ transition: This happens in the carbon core (sp^2 domains). Electrons in a π-bond (delocalized electrons in carbon-carbon double bonds) get excited to a π^* antibonding orbital. This is the main reason for a strong UV absorption peak .

$n \rightarrow \pi^*$ transition (important due to nitrogen): non-bonding electrons, such as lone pairs from nitrogen (e.g., from amine or amide groups). These lone pair electrons jump into a π^* antibonding orbital. This causes another absorption peak, often at a slightly longer wavelength.

II. PHOTOLUMINESCENCE PROPERTIES

Photoluminescence property of carbon quantum dots of different filling volume and nitrogen doped CQD is analyzed at the excitation peak of 240 nm ,260nm, 270nm for 40%, 50 % and N-CQD of 50% respectively.

i. 40% CQD

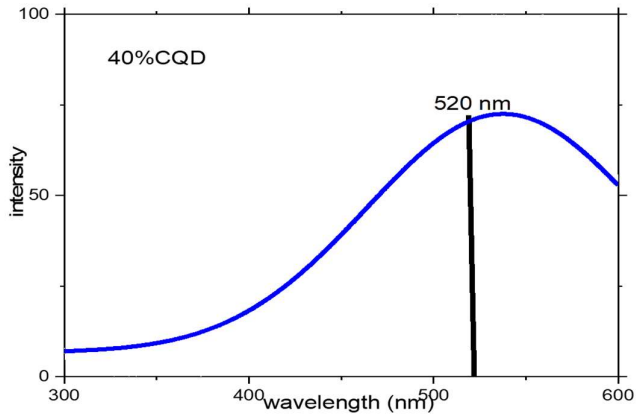


Fig 2.3.2 a : PL emission spectra for 40% CQD sample of excitation wavelength 240nm

Excitation at 240 nm gives photoluminescence (PL) emission at 520 nm. 240 nm is deep UV light. It has high energy — around 5.17 eV. When the CQDs absorb this high-energy UV light, electrons get excited from low energy levels (like valence band) to very high-energy states (conduction band or even above it).

After excitation, the electron relaxes non-radiatively (loses some energy internally — vibrations, phonons). Then, it recombines radiatively (emits light) at a lower energy.520 nm corresponds to green light (~2.38 eV energy).

Mostly $\pi \rightarrow \pi^*$ transitions between carbon-carbon double bonds (C=C). Very weak $n \rightarrow \pi^*$ transitions (only from oxygen-related groups,

ii. 50 % CQD

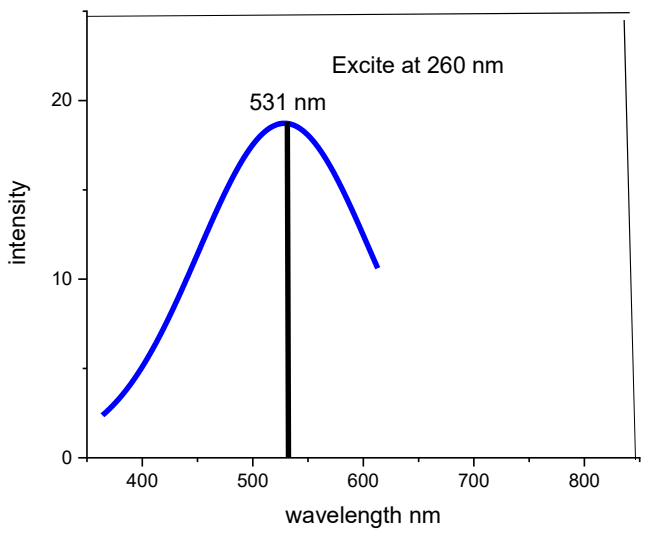


Fig 2.3.2 b : PL emission spectra for 50% CQD sample of excitation wavelength 260nm

In carbon quantum dots (CQDs), the photoluminescence at 530 nm is primarily due to surface state-mediated transitions rather than direct band-to-band recombination. When CQDs absorb high-energy photons (often in the UV range), electrons are excited from the valence band (π orbital) to the conduction band (π* orbital). The transition responsible for this photoluminescence is mainly a surface trap-to-ground state transition, rather than a direct π → π* bandgap transition.

The core of carbon quantum dots is made of conjugated sp^2 domains (small clusters of carbon atoms with double bonds — like mini-graphene patches). When UV light shines on CQDs, it promotes electrons from π (valence-like band) to π* (conduction-like band).This is called a direct π → π* excitation.

iii. NITROGEN DOPED CQD OF 50% FILLING VOLUME

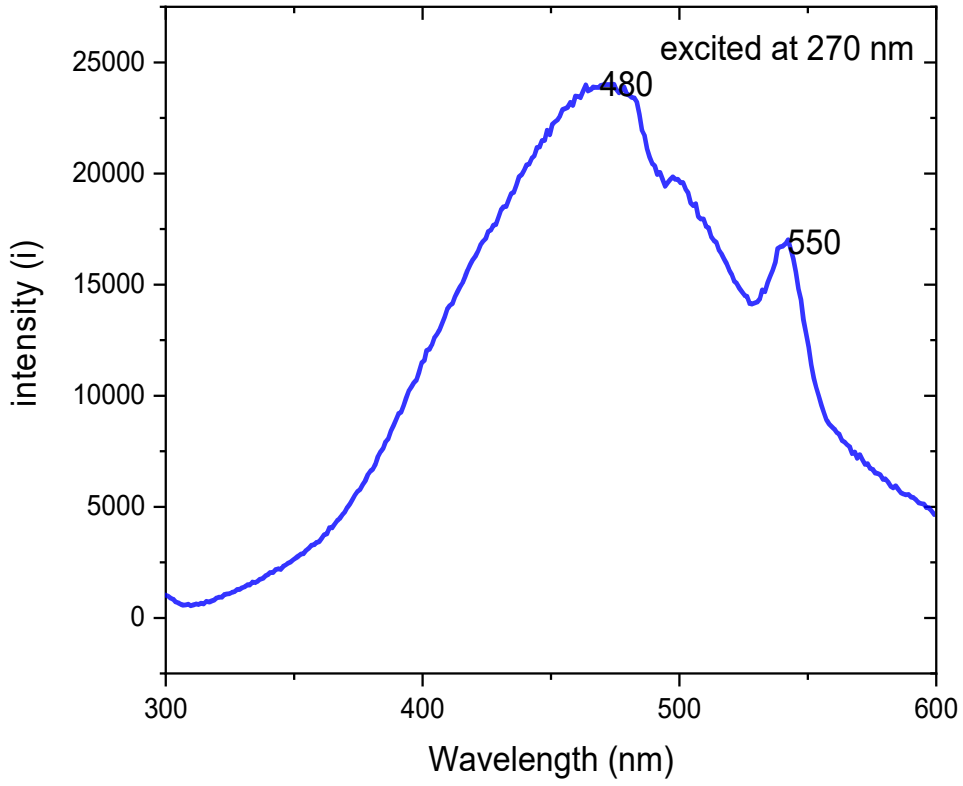


Fig 2.3.2 c : PL emission spectra for 50% N- CQD sample of excitation wavelength 270nm

N-doped carbon quantum dots (N-CQDs) show photoluminescence (PL) at 480 nm. 480 nm is in the blue-green region of visible light. In nitrogen-doped CQDs, nitrogen atoms are introduced into the carbon network (as -NH_2, pyridinic N, pyrrolic N, etc.).

This modifies the electronic structure in two major ways: Creates new mid-gap states (trap states) and Narrows or adjusts the effective bandgap.

Electrons absorb energy and move from the valence band (π orbitals) to the conduction band (π* orbitals). Instead of immediately recombining, electrons often fall into nitrogen-related defect states (which are *inside* the bandgap). From these intermediate states, they recombine radiatively, emitting photons.

The electron is recombining through nitrogen-doped trap states. The energy gap between the trap state and the ground state is about 2.58 eV, matching the 480 nm emission.

N-doped CQDs, when you see PL at 550 nm, it suggests radiative recombination is happening at a lower energy than for smaller CQDs (which usually emit in the blue-green range).

III. DPPH free radical scavenging activity

A mixture of 1.5 mL sample (nitrogen doped CQD) and 1.5 mL 0.2 mM ethanolic DPPH(2,2-Diphenyl-1-picrylhydrazyl.) solution was vortexed and incubated in darkness for 30 minutes. The absorbance was measured at 517 nm with ethanol as the blank and DPPH solution without the sample as the control. The sample with lower absorbance expresses a more significant free radical scavenging activity (RSA).

RESULT

$$\text{Percentage of scavenging activity} = \frac{\text{Absorbance of control} - \text{Absorbance of sample}}{\text{Absorbance of control}} \times 100$$

Absorbance of control (DPPH) = 2.0049

Absorbance of sample 1a = 0.3889

Absorbance of sample 1 b = 0.3791

Average absorbance = (0.3889+0.3791) /2 = 0.768/2 = 0.384

$$\text{Percentage of scavenging activity} = \frac{2.0049 - 0.384}{2.0049} \times 100$$

$$= 0.8084 \times 100$$

Percentage of scavenging activity = **80.84 %**

80% scavenging activity indicates that the N-CQDs are capable of neutralizing 80% of the DPPH free radicals in the solution. In simpler terms, 80% of the DPPH radicals were reduced or deactivated by the N-CQDs, showing that these quantum dots possess significant antioxidant properties.

An 80% scavenging rate is quite high and suggests that N-CQDs exhibit good antioxidant potential. The presence of nitrogen doping likely plays a role in enhancing their ability to trap

free radicals due to the formation of nitrogen-related functional groups that can interact with radicals.

An 80% scavenging activity in the DPPH test shows that N-doped carbon quantum dots are highly effective in neutralizing free radicals, suggesting their potential as strong antioxidants in various fields like medicine, food preservation, and cosmetics.

2.4. PROFILE OF N-CQD

Nitrogen-doped Carbon Quantum Dots (N-CQDs) are a class of carbon-based nanomaterials that have quantum dot properties combined with the inclusion of nitrogen atoms into the carbon network. These quantum dots are typically less than 10 nm in size, making them nanoscale materials with unique optical, electronic, and chemical properties**.**

Synthesis Technique include hydrothermal/solvothermal synthesis: Using nitrogen-containing precursor with Glycine ($C_2\ H_5\ NO_2$) to heat the mixture in a sealed environment, resulting in the formation of N-CQDs.

Nitrogen doping: Nitrogen atoms are incorporated into the CQD structure, creating various types of nitrogen species.

Amine (-NH_2) and Amide (-$CONH_2$) groups: Nitrogen-containing functional groups on the surface. These nitrogen species introduce defect states, modifying the electronic properties of the CQDs, which in turn impacts their optical and electronic behavior.

Photoluminescence (PL): N-CQDs can exhibit strong fluorescence when excited by UV or visible light. The emission wavelength can be tuned by altering the size of the CQDs, the type of nitrogen doping, and the surface functionalization. Emission peaks typically range from 450 nm to 550 nm, with blue, green, or yellow fluorescence depending on the doping and surface modification.

Bandgap: N-doping narrows the bandgap of the carbon quantum dots. The electronic states associated with nitrogen doping lower the energy levels in the conduction band and may introduce mid-gap states, which affect the electron transfer processes.

Antioxidant Activity DPPH Scavenging, N-CQDs have shown significant antioxidant activity in the DPPH radical scavenging assay, with scavenging efficiency often around 80% or higher.

This suggests that N-CQDs can efficiently neutralize free radicals, which is crucial for applications in biomedical and environmental fields.

N-CQD shows Photocatalysis. N-CQDs can be used for solar energy conversion and environmental degradation of pollutants due to their semiconductor properties.

Nitrogen-doped Carbon Quantum Dots (N-CQDs) are a versatile class of carbon-based nanomaterials with unique optical, electronic, and antioxidant properties. Their fluorescent emission, antioxidant activity, and biocompatibility make them useful in a variety of applications, from bioimaging and drug delivery to environmental sensing and energy storage. The incorporation of nitrogen introduces defect states that significantly modify the properties of the quantum dots, enhancing their functionality in these areas.

2.5. COMPARATIVE STUDY ON CQD AND N-CQD

Property	CQDs (Pristine Carbon Quantum Dots)	N-CQDs (Nitrogen-Doped Carbon Quantum Dots)
Bandgap	Typically **2.5–5.5 eV**	**Lower (2.0–4.0 eV)** due to mid-gap states
Photoluminescence (PL) Peak	Usually in the **blue region (350–500 nm)**	Redshifted to **green-yellow (480–550 nm)**
Optical Absorption	Strong absorption in UV (≈ 300–400 nm)	Extends to visible range (≈ 400–600 nm)
Electron Transfer Efficiency	Moderate	**Higher** due to additional nitrogen-related donor states
Photocatalytic Activity	Limited to UV-light-driven reactions	**Enhanced visible-light activity** due to bandgap reduction

Table 2.1 Comparative Study on CQD and N-CQD

2.6. SUMMARY

In this study carbon quantum dot are synthesized in hydrothermal method by mixing sucrose and deionized water appropriately to produce 2 wt %. The mixture is then placed in a hydrothermal reactor unit at a temperature of 180 °C for 3 hours.

Nitrogen doped CQDs are prepared by mixing glycine to the same mixture of sucrose and deionized water.

The sample is prepared by varying the filling volume and keeping all other parameters constant.

Sample of filling volume 40% and 50 % is synthesized along with nitrogen doping

Characterization technique such as UV visible spectroscopy, photoluminescence and DPPH scavenging activity is done.

CHAPTER 3
PHOTOCATALYTIC ACTIVITY OF NITROGEN DOPED CARBON QUANTUM DOT ON DYE POLLUTANT.

Nowadays, water resources are being tainted by organic dyes, harmful chemicals, plastics etc. due to large scale industrialization and urbanization of human society. The removal of such hazardous waste is highly necessary to make the water potable. Traditional water purification is not suitable for removing organic dyes since they are very stable against temperature, light etc. Photocatalysis, the process of accelerating photoreaction in the presence of a catalysts is an excellent method to remove the dangerous pollutants.

This chapter analyses the solar photocatalytic activity of Nitrogen doped carbon quantum dot on Methylene Blue (MB) dye solution. It is found that the sample show remarkable photocatalytic degradation efficiency.

3.1. INTRODUCTION

Water pollution is the main predicament faced by the world today, causing serious health issues and diseases to mankind. Water pollution is caused by the contamination of water bodies due to increasing urbanization and industrialization. Since water is a universal solvent, chemicals and other microorganisms that flow into the same easily get dissolved, thereby causing pollution.

Effluences from chemical and textile industries which is extremely poisonous due to the presence of dyes, chemicals and other hazardous metal ions are the main causes of water contamination and cannot be removed by traditional methods of purification such as boiling, filtering, winnowing through cloth etc. Photocatalysis is an effective technique to remove dye waste from the polluted water.

Carbon quantum dots (CQDs) have garnered significant attention over the past decade due to their unique optical, chemical, and electronic properties, especially their strong and tunable photoluminescence, excellent aqueous solubility, chemical inertness, and biocompatibility.

Among various strategies to enhance the intrinsic properties of CQDs, heteroatom doping, particularly with nitrogen, has proven highly effective. Nitrogen doping introduces additional active sites, modulates the electronic structure, and improves the conductivity of CQDs, resulting in enhanced charge separation and transfer capabilities. These modifications are

critically important in the context of photocatalysis, where efficient generation and migration of charge carriers are essential for high catalytic activity.

Photocatalysis relies on the absorption of light to generate electron–hole pairs, which can participate in subsequent redox reactions.

Traditional photocatalysts often suffer from limitations such as rapid recombination of charge carriers, limited visible-light absorption, and low stability. N-CQDs offer solutions to these issues. Their high surface area-to-volume ratio facilitates the rapid transfer of charge carriers, while the introduction of nitrogen atoms into the sp^2-carbon network increases the density of localized electronic states, narrows the bandgap, and enhances visible light absorption.

Furthermore, the nitrogen functionalities (such as pyrrolic-N, pyridinic-N, and graphitic-N) act as active centers, promoting the separation of photogenerated electrons and holes and enabling more efficient catalytic cycles.

In addition to acting as standalone photocatalysts, N-CQDs are also widely utilized as cocatalysts when integrated with other semiconductor materials (e.g., TiO_2, ZnO, g-C_3N_4). In such composites, N-CQDs can serve as electron reservoirs or sensitizers, extending the photo response into the visible region and significantly improving photocatalytic efficiency through synergistic charge transfer mechanisms.

Moreover, their ability to undergo up conversion photoluminescence allows them to convert low-energy photons into higher-energy ones, further boosting the photocatalytic performance under sunlight.

Applications of N-CQDs-based photocatalytic systems span various fields, including the degradation of organic pollutants, hydrogen generation through water splitting, CO_2 photoreduction into value-added fuels, and antibacterial activities. Their facile and green synthesis routes, combined with tunable surface chemistry and environmental friendliness, position N-CQDs as highly versatile and sustainable materials for next-generation photocatalytic technologies.

Thus, understanding and optimizing the photocatalytic mechanisms of N-CQDs, including their band structure engineering, charge carrier dynamics, and surface functionalization, is essential for advancing their practical applications in environmental and energy-related fields.

In this work, the solar photodegradation activities of Nitrogen doped carbon quantum dot on methylene blue (MB) dye have been investigated in detail.

3.2. EXPERIMENTAL

The dye which is commonly used in industrial applications Methylene Blue (MB) found to cause water contamination and serious environmental issues, have been selected to analyze the photocatalytic performance of the prepared samples. For the analysis, dye solutions were prepared for the concentration of 100 ppm. The sample is then analyzed in two concentrations, 2ml sample in 10ml dye solution and 4ml sample in 10 ml dye solution.

The samples were added and stirred for one hour in the dark to reach equilibrium absorption condition. The solution was then exposed to sunlight and solutions were collected at regular intervals of time in dark bottles. The intensity of absorption peaks of dyes at different time intervals were determined by UV-visible absorption spectrum for the analysis of dye degradation efficiency of the samples. The catalytic activity of samples in the above dyes at dark was also studied and no significant degradation was observed.

3.3 PHOTOCATALYTIC ACTIVITY OF THE SAMPLE ON DYE

3.3.1 4ml Sample Per 10ml Dye Solution

Methylene Blue ($C_{16}H_{18}N_3SCl$) is a cationic dye used in textile industry for a variety of purposes. Effluents from such industries can cause eye burn which may be responsible for permanent injury to the eyes of human as well as aquatic animals. It can also cause irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea. Methylene blue also causes irritation to the skin when there is a direct contact.

MB has got an absorption peak at 665nm. The time dependent degradation nature of MB on Nitrogen doped carbon quantum dot under sunlight irradiation is shown in the Figure 3.1

UV-visible absorption peak observed at 663nm gets flattened and almost a complete decolorization of MB solutions occurred on solar exposure.

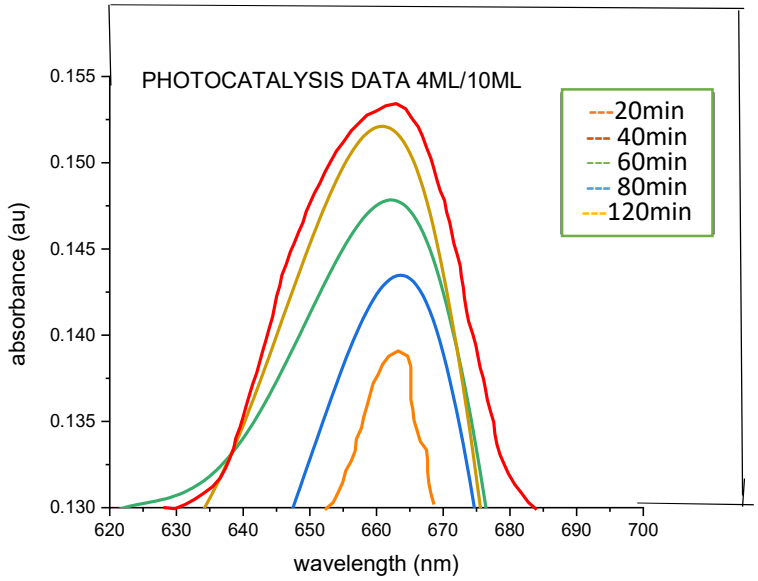


Fig 3.1 The variation of absorption of MB dye solution with wavelength for 4 ml of Nitrogen doped carbon quantum dot

$$The\ dye\ degradation\ efficiency\ at\ any\ time\ t\ \eta = \frac{Co - Ct}{Co} \times 100$$

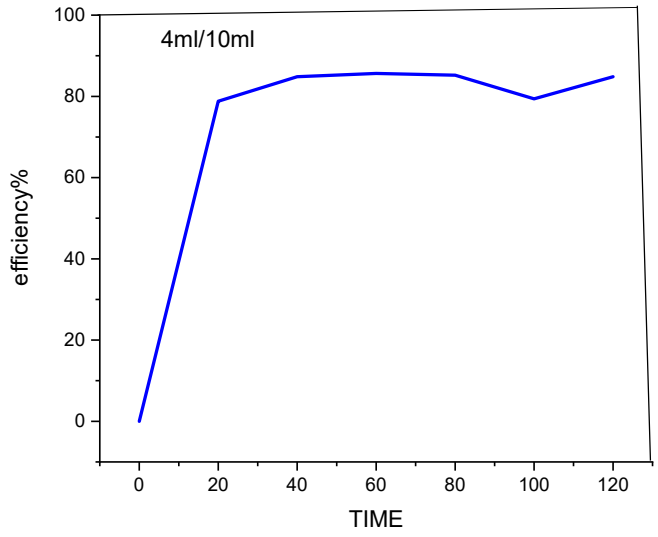


Fig 3.2 depict efficiency (%) of the photocatalytic activity of the prepared sample in MB.

In order to check the reusability of the samples, the photocatalytic activity of N-CQD on MB has been investigated repeatedly. The sample showed 85% efficiency for MB within 80 minutes. This confirms the photo stability of the composite which agrees with many scientific journals.

3.3.2. 2ml Sample Per 10ml Dye Solution

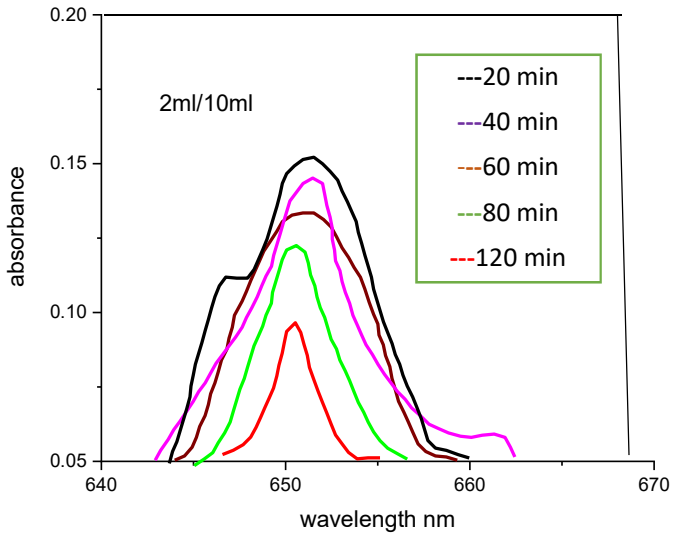


Fig 3.3 The variation of absorption of MB dye solution with wavelength for 2ml of Nitrogen doped carbon quantum dot

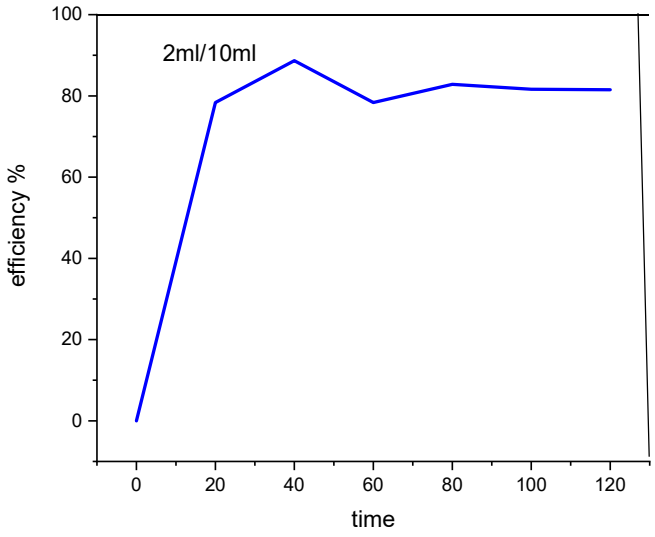


Fig 3.4 The efficiency of photocatalytic activity in 2ml /10ml dye solution

The photocatalytic activity of N-CQD on MB has been investigated repeatedly. The sample showed 82 % efficiency for MB within 80 minutes.

SAMPLE	TIME (MIN)	EFFICIENCY (%)
2ML/10ML	80 MIN	82%
4ML/10ML	80 MIN	85%

Table 3.1 shows the conclusion of efficiency

The improved photocatalytic efficiency observed with 4 mL of photocatalyst in 10 mL of dye solution, compared to 2 mL, can be attributed to the increased availability of active sites for the photocatalytic reaction. A higher volume of catalyst introduces more surface area, which enhances the interaction between the dye molecules and the photocatalyst. This leads to the generation of more reactive oxygen species, such as hydroxyl radicals and superoxide ions, which are crucial for the degradation process.

Additionally, with more catalyst present, there is greater absorption of light, resulting in increased excitation of electrons and improved charge separation efficiency. This accelerates the photocatalytic breakdown of the dye.

However, it is important to note that while increasing the catalyst volume up to a certain point improves efficiency, excessive loading can lead to light scattering, reduced light penetration, and particle agglomeration, which may eventually decrease photocatalytic performance. Therefore, 4 mL may represent a more optimal catalyst-to-dye ratio compared to 2 mL in this context.

3.4. CONCLUSION

In summary, carbon quantum dots (CQDs) and nitrogen-doped carbon quantum dots (N-CQDs) were successfully synthesized via a simple and eco-friendly hydrothermal method. The incorporation of nitrogen atoms effectively enhanced the electronic and surface properties of the CQDs, leading to improved functional performance.

The synthesized N-CQDs exhibited excellent antioxidant activity, attributed to the presence of surface functional groups and nitrogen-induced electron-donating characteristics. Additionally, their strong light absorption, high surface area, and photostability enabled their effective application as photocatalysts for the degradation of organic pollutants.

These results demonstrate that N-CQDs synthesized through hydrothermal routes are promising multifunctional nanomaterials for environmental remediation and biomedical applications, owing to their synergistic antioxidant and photocatalytic properties.

3.5. FUTURESCOPE

The successful hydrothermal synthesis of nitrogen-doped carbon quantum dots (N-CQDs) offers promising opportunities for further development in both environmental and biomedical fields. Future research can focus on optimizing the doping process to enhance their photocatalytic and antioxidant performance. By adjusting parameters such as the type and number of dopants, synthesis temperature, and reaction time, the properties of N-CQDs can be fine-tuned for specific applications.

In photocatalysis, expanding studies to include a wider range of pollutants and operating under natural sunlight conditions could make N-CQDs more practical for real-world environmental remediation. Combining them with other materials like metal oxides or semiconductors may improve their stability and charge separation efficiency, leading to more effective and long-lasting photocatalysts.

On the biomedical side, the strong antioxidant activity of N-CQDs suggests potential use in healthcare, particularly for treating oxidative stress-related conditions. However, further biological testing, including toxicity and biocompatibility studies, is essential before clinical applications can be considered.

Lastly, exploring eco-friendly, large-scale production methods using natural or waste-derived carbon sources could make these materials more sustainable and affordable. With continued research, N-CQDs could play a significant role in addressing challenges in water purification, pollution control, and biomedical technology

3.6. REFERENCE

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