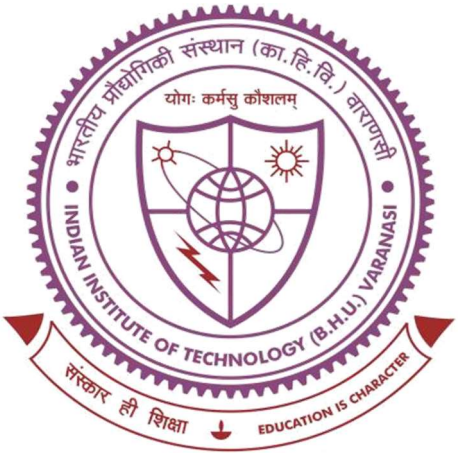
BIOGENIC SYNTHESIS OF NANOSTRUCTURES FOR SENSING, OPTOELECTRONICS, AND THERAPEUTICS



Thesis submitted in partial fulfillment for the Award of Degree

Doctor of Philosophy

By

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CERTIFICATE

It is certified that the work contained in the thesis titled **"Biogenic Synthesis of Nanostructures for Sensing, Optoelectronics, and Therapeutics"** by **"Ravi Pratap"** (Roll No. **18171009**), in partial fulfilment of the requirement for the award of degree of **Doctor of Philosophy** at **Indian Institute of Technology (B.H.U), Varanasi** is a record of her own work carried out under my supervision and guidance, and this work has not been submitted elsewhere for a degree.

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I, Ravi Pratap (Roll No. 18171009), certify that the work embodied in this thesis is my own bona fide work and carried out by me under the supervision of **Dr. Avanish Singh Parmar** from **25th July 2018** to **21st November 2023** at the **Department of Physics**, Indian Institute of Technology, Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis.

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Dedicated

To

My Grand Mother

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List of Abbreviations and Symbols

D	Dimensional
CVD	Chemical Vapour Deposition
AFM	Atomic Force Microscopy
TEM	Transmission Electron Microscopy
SEM	Scanning Electron Microscopy
HRTEM	High Resolution Transmission Electron Microscopy
XRD	X-ray diffraction
ITO	Indium Tin Oxide
FLG	Few-layered Graphene
nm	Nanometre
m^2/g	Meter Square Per Gram
GO	Graphene Oxide
OH	Hydroxide
-O-	Epoxide
FRET	Förster Resonance Energy Transfer
CQD	Carbon Quantum Dot
PL	Photoluminescence
λ	Wavelength
UV	Ultraviolet
CdTe	Cadmium Telluride
ZnSe	Zinc Selenide
PbS	Lead Sulphate
CL	Chemiluminescence
ECL	Electrochemical Luminescence
UCPL	Up-conversion Photoluminescence
PET	Photoinduced Electron Transfer
CNT	Carbon Nanotube
SWCNT	Single Walled Carbon Nanotube
MWCNT	Multi walled Carbon Nanotube
HOMO	Highest Occupied Molecular Orbital

LUMO	Lowest Unoccupied Molecular Orbital
NIR	Near Infra-red
AIEE	Aggregation Induced Emission Enhancement
AIEQ	Aggregation Induced Emission Quenching
SQE	Static Quenching Effect
DQE	Dynamic Quenching Effect
ET	Energy Transfer
CND	Carbon Nano Dot
GQD	Graphene Quantum Dot
PD	Polymeric Dot
PEG	Poly Ethylene Glycol
QY/ Ø	Quantum Yield
ZnO	Zinc Oxide
MΩ.cm	Mega Ohm. Centimeter
DMSO	Dimethyl sulfoxide
HCl	Hydrochloric Acid
NaCl	Sodium Chloride
$CaCl_2$	Calcium Chloride
$CdSO_4$	Cadmium Sulfate
$ZnCl_2$	Zinc Chloride
$Ag(NO_3)$	Silver Nitrate
$Pb(NO_3)_2$	Lead Nitrate
$SnCl_2$	Stannous Chloride
kV/eV	Kilo Volts/Electron Volts
PL	Photoluminescence
I/*A*/ η	Intensity/Absorbance/Refractive Index
R	Reference
DPPH	2,2-diphenyl-1-picrylhydrazyl
MTT	3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide
µg/L	Micro Gram per Litre
A	Absorbance
-CN	Cyano

-COOH	Carboxylic
nM	Nano Molar
pM	Pico Molar
AuNP	Gold Nanoparticle
AgNP	Silver Nanoparticle
FTIR	Fourier Transform Infrared Spectroscopy
EPA	Environmental Protection Agency
NCCS	National Centre for Cell Science, Pune
DMEM	Dulbecco's Modified Eagle Medium
MEM	Minimum Essential Medium
IC50	Half Maximal Inhibitory Concentration
ROS	Reactive Oxygen Species
RFI	Relative Fluorescence Intensity
DAPI	4′,6-diamidino-2-phenylindole
ETL	Electron Transport Layer
HTL	Hole Transport layer
EL	Emissive Layer
LED	Light-emitting Diode
OLED	Organic Light Emitting Diode
OLET	Organic Light Emitting Transistor
BNQDs	Boron nitride quantum dots
OSC	organic solar cells
DLS	Dynamic Light Scattering
XPS	X-ray Photoelectron Spectroscopy
SAED	Selected Area Electron Diffraction
(C=O), C-O	Carboxyl, Carbonyl
C-H, C=C	Carbon Bonds
τ_{avg}	Average Photoluminescence Lifetime
(F_0/F)	Relative Fluorescence Response
K_{sv}	Stern–Volmer Quenching Constant
C	Concentration of the Quencher
LOD	Limit of Detection
LSPR	Localized Surface Plasmon Resonance

ECQD/WCQDs	Ethanol-based and Water-based Carbon Quantum Dots
SPB	Surface Plasmon Band
WHO	World Health Organization
ppb	parts per billion
DI	Deionized Water
DW	Dry weight
T_{50}	Half Life
MD	Molecular Dynamics
PEDOT: PSS	Poly3,4ethylenedioxythiophene: polystyrenesulfonate
PFO	Polyfluorene
PSBF	Polyspirobifluorene
ODA	Octadecylamine
LDH	Lactate Dehydrogenase
DCB	Dichlorobenzene

Preface

Carbon nanomaterials have gradually attracted the attention of the scientific community and emerged as new valuable materials. Carbon, one of the most abundant substances on Earth, and its allotropes such as fullerenes, carbon nanotubes, graphene and carbon quantum dots have been proposed for energy generation, sensing, bio-imaging and drug delivery in the past two decades due to their extraordinary properties and ease of fabrication. Carbon quantum dots (CQDs) are considered zero-dimensional materials (with a diameter as small as 10 nm) with enhanced optical and electronic properties such as intense fluorescence, high electron mobility, biocompatibility and high stability. Since their accidental discovery in 2004 during the purification of single-walled nanotubes, CQDs have been intensively researched over the last two decades and used in numerous fields. Compared to semiconductor quantum dots, CQDs consist mainly of a carbonaceous core, which makes them biocompatible and non-toxic. They can be used as biomarkers, metal sensors, optical sensors, light-harvesting material, fluorescent ink, anti-cancer agents and, due to the low-cost precursor material, also as potential drug carriers. Several studies have shown that CQDs can be produced at high temperature and high pressure from different precursor materials while maintaining similar photophysical properties. It would be beneficial to further investigate the optical and electronic properties of CQDs. The morphology of CQDs has been well studied in terms of their size and shape. Although the study of nanostructured carbon materials has experienced rapid development and remains an active research topic, there is still a lack of fundamental understanding of the growth mechanisms and the essential elements responsible for the synthesis of CQDs. Carbon-based nanomaterials are currently considered a milestone in nanotechnology as they drive scientific progress and have numerous industrial applications. In this work, different strategies for the synthesis and use of carbon nanomaterials in sensing, bio-imaging and optoelectronic systems are discussed. The synthesis methods for carbon quantum dots have been studied in detail using various

spectroscopic and microscopic techniques. For the synthesis of CQDs, different plant leaves were used as starting materials and water and ethanol as solvents at different temperatures depending on the application.

This thesis also investigates the applications of CQDs in sensing and bio-imaging. We demonstrate that the optical and morphological properties of CQDs can be tuned by varying the hydrothermal synthesis temperature from 120°C to 220°C. We have functionalized CQDs with chlorophyll utilizing chlorophyll-rich Plumeria leaves in ethanol as a carbon source because chlorophyll dissolves easily in ethanol which is less hazardous than other organic solvents. CQDs synthesized at 160°C can be used as a dual probe sensor for the selective detection of Hg^{+} ions and As^{3+} ions with lower detection limits. In another study, gold nanoparticles (GNP) were synthesized with Tulsi and Vinca extracts exhibiting different shapes and sizes with enhanced crystallinity. The T+V gold nanoformulation exhibited superior cytotoxicity against breast cancer cells (4T1) in vitro and showed remarkable tumor regression in a mouse model. The anti-cancer potential was attributed to the release of anti-cancer metabolites and alterations in antioxidant metabolic pathways, as evidenced by the modulation of glutathione family enzymes and oxidative stress markers. The T+V gold nanoformulation exhibited negligible toxicity in normal cells and\ organs, highlighting its potential as an effective and safe therapeutic agent. In a separate study, fluorescent functionalized carbon quantum dots (CQDs) were synthesized by a hydrothermal method using Plumeria plant leaves and Tb 3+ ions as a surface passivator. The doped CQDs exhibited excitation-dependent photoluminescence with strong peaks attributed to Tb3+ doping. In combination with a UV chip, the CQDs exhibited efficient white light emission, making them promising candidates for white light emitting diodes (WLEDs). The resulting WLEDs had the desired color coordinates, color temperatures and a high color rendering index (CRI). Finally, boron nitride quantum dots (BNQDs) were synthesized from boron nitrate

nano powder through a hydrothermal process. The BNQDs exhibited excellent sensing behavior towards p-nitrophenol (PNP) with a low detection limit of about 7.91 pM. Time-resolved photoluminescence studies confirmed the high selectivity and sensitivity of the BNQDs for PNP sensing. The cost-effective and environmentally friendly synthesis approach presented in this study contributes to the development of nanomaterial-based sensing technologies with potential applications in environmental monitoring. Overall, our versatile approach in the synthesis and characterization of nanomaterials demonstrates their versatility for sensing and therapeutic applications and highlights their potential impact on various scientific and technological fields.