

Synthesis of Low Dimensional Carbon Nanostructures for Sensing, Bio-imaging and Optoelectronic Devices



Thesis submitted in partial fulfillment for the

Award of Degree

Doctor of Philosophy

By

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***Dedicated
To
My Family***

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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
QD	Quantum Dot
CQD	Carbon Quantum Dot
Chl- CQD	Chlorophyll Doped 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/ \emptyset	Quantum Yield
ZnO	Zinc Oxide
M Ω .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
VOLET	Vertical Organic Light Emitting Transistor
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
(F0/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
T50	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 garnered the scientific community's attention and have emerged as novel valuable materials. Carbon, one of the most plentiful substances on earth, and its allotropes such as fullerenes, carbon nanotubes, and graphene and carbon quantum dots have been proposed in the past two decades for energy generation, sensing, bio-imaging, and drug delivery due to their exceptional qualities and ease of production. Carbon quantum dots (CQDs) are recognized as zero-dimensional materials (diameters as small as 10 nm) with enhanced optical and electronic properties such as intense fluorescence, high electron mobility, bio-compatibility and high stability. Since their accidental discovery in 2004 during the purification of single-wall nanotubes, CQDs have been intensively explored and applied in numerous fields during the past two decades. Compared to semiconductor quantum dots, CQDs are predominantly composed of a carbonous core, making them biocompatible and non-toxic. They can be employed as biomarkers, metal sensors, optical sensors, light-harvesting material, fluorescent ink, anti-cancer agents, and possible drug delivery agents because of the inexpensive precursor material. Multiple studies have demonstrated that CQDs can be produced at high temperatures and pressure from various starting materials while retaining similar photo-physical properties. It would be advantageous to investigate further the optical and electronic properties of CQDs. Their sizes and shapes have been well examined regarding the morphology of CQDs. Although the study of nanostructured carbon materials has witnessed a rapid expansion and remains an active research topic, fundamental understandings of the growth mechanisms and essential elements responsible for synthesizing CQDs are still lacking. Carbon-based nanomaterials are currently regarded as a milestone in nanotechnology because they expedite scientific advancement and have numerous industrial uses. This thesis

discusses various strategies for synthesizing and incorporating carbon nanomaterials into sensing, bio-imaging, and optoelectronic systems. The synthesis methods of carbon quantum dots have been examined in depth using various spectroscopic and microscopic techniques. CQDs have been synthesized utilizing different plant leaves as precursors and water and ethanol as solvents at varying 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 230°C. We have functionalized CQDs with chlorophyll utilizing chlorophyll-rich banana 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, chlorophyll-rich CQDs were evaluated for their anti-cancer potential in cervical cell lines. We have also shown that CQDs can be used to detect ammonia gas and lead in drinking water. This thesis also discusses the application of carbon nanomaterials such as CQDs and carbon nanotubes to optoelectronic devices. We have exhibited CQDs as an electron transport layer in OLED for the first time. Due to its large specific surface area, high electron mobility, plentiful surface defects, and active sites, a thin film of CQDs has been produced by spin coating to form an electron transport layer in OLED. We have fabricated thin layers of carbon nanotube-doped green polymer as the emissive layer in OLED and OLET to improve these devices' performance. Doping SWNT increased luminosity and decreased threshold voltage. In addition, we have fabricated a VOLET by putting a capacitor on the top of an OLED. This extraordinary device has two functions: it generates light as an OLED and switches current as a transistor. Using

the gate electrode, it is simple to adjust the current and luminosity of VOLET. This device will operate at low voltage due to its vertical integration, providing a solution for display applications. This work will provide crucial information regarding the characteristics of carbon nanostructures, enabling researchers to move forward and explore the untapped potential of CQDs, improve present research, and develop new applications for this unique class of nanomaterials.

