SYNTHESIS AND CHARACTERIZATION OF FLUORESCENT CARBON QUANTUM DOTS AND THEIR MULTIFUNCTIONAL APPLICATIONS

Thesis submitted in partial fulfillment for the award of the degree of

Doctor of Philosophy

By

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It is certified that the work contained in the thesis titled ***"Synthesis and Characterization of Fluorescent Carbon Quantum Dots and Their Multifunctional Applications"*** by ***"Pradeep Kumar Yadav"*** has been carried out under my supervision and this work has not been submitted elsewhere for a degree.

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I, ***"Pradeep Kumar Yadav"***, certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of ***"Prof. Syed Hadi Hasan"*** from ***"July 2017" to "July 2022"***, at the ***"Department of Chemistry"***, Indian Institute of Technology (BHU), 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. I further declare that I have not wilfully copied any other's work, paragraphs, text, data, results, *etc.*, reported in journals, books, magazines, reports dissertations, theses, *etc.*, or available at websites and have not included them in this thesis and have not cited as my own work.

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It is certified that the above statement made by the student is correct to the best of my knowledge.

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Dedicated to My Beloved

PARENTS

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Pradeep Kumar Yadav

List of Schemes

AA	Ascorbic acid
AgNPs	Silver nanoparticles
A. lakoocha	*Artocarpus lakoocha*
A. indica	*Azadirachta indica*
F. benghalensis	*Ficus benghalensis*
AuNPs	Gold nanoparticles
c	Concentration absorbing molecule in $mol.m^{-3}$
Carbon dots-oxaliplatin	(CD-Oxa)
CIE	Commission Internationale de l'Éclairage
CeONPs	Cerium oxide nanoparticles
CNTs	Carbon nanotubes
CDs	Carbon dots
CQDs	Carbon quantum dots
N-CQDs	Neem-Carbon Quantum dots
G-CQDs	Green-Carbon Quantum Dots
B-CQDs	Boron doped-CQDs
P-CQDs	Phosphorous doped-CQDs
S-CQDs	Sulfur doped Carbon Quantum Dots
N,S-CQDs	Nitrogen sulfur co-doped CQDs
N,P-CQDs	Nitrogen and Phosphorous co-doped CQDs
d	Interplanar spacing
DSSCs	Dye-sensitized solar cells
DMSO	Dimethyl sulphoxide
EDAX	Energy-dispersive X-ray spectroscopy
et al.	Co-authors
FT-IR	Fourier transform infrared spectroscopy
FL	Fluorescence
GB-CDs	Green-Blue Carbon Dots
GSH	Glutathione
H_2O_2	Hydrogen peroxide

HRP	Horseradish peroxidase
I_t	Emission intensity decay
I_0	Intensity of the incident radiation
IV	Instrumental variables
ITO	Indium doped Tin oxide
ISC	Intersystem crossing
IFE	Inner filter effect
IONPs	Iron oxide nanoparticles
I_t	Intensity of the transmitted radiation
Ksv	Stern-volmer constant
K_m	Michaelis–Menten constant
LED's	Light emitting diodes
LOD	Limit of detection
MA	Methyl alcohol
MONPs	Metal oxide nanoparticles
MRI	Magnetic resonance imaging
MTT	3-(4, 5-dimethylthiazol-2-yl)-2, 5-diphenyl-tetrazolium bromide
NaAc	Sodium acetate buffer
NMNPs	Noble metal nanoparticles
oxTMB	Oxidized TMB
PBS	Phosphate buffer saline
PdNPs	Palladium nanoparticles
PdNPs	Palladium nanoparticles
PGMs	Platinum group metals
PBS	Phosphate buffer saline
PVD	Physical vapor deposition
PVA	Polyvinyl alcohol
PEI	Polyethyleneimine
ppb	Parts per billion
QY	Quantum yield

QS	Quinine sulfate
R^2	Correlation coefficient
RBCs	Red blood cells
RSD	Relative standard deviation
SAED	Selected area diffraction pattern
SBD	Schottky Barrier Diodes
SH-SY5Y	Neuroblastoma cells
t	Time (min)
Tyr	Tyrosine
TPA	Terephthalic acid
TTDDA	Trioxa-tridecanediamine
TEM	Transmission electron microscopy
TiO_2	Titaniumoxide
TiONPs	Titanium dioxide nanoparticles
TMB	Tetramethylbenzidine
UV-vis	Ultra-violet visible
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction spectroscopy
µL	Microlitre
mL	Millilitre
ε	Molar absorption coefficient
θ	Angle (degree)
λ	Wavelength

The current thesis work signifies the synthesis of fluorescent carbon quantum dots from various economical viable precursors for the sensing of metal ions and biosensor. Carbon quantum dots (CQDs) have excellent properties such as good water solubility, easy surface functionalization, low-cytotoxicity and strong fluorescence emission. CQDs are regarded as zero-dimensional (0D) materials and their size ranges from 1 and 10 nm. CQDs are also named as carbon dots (CDs) and carbon nanoparticles (CNPs). Because of their high surface energy and large surface area, CQDs could be utilized for catalysis, schottky barrier diode, optronic devices, drug delivery, bioimaging and in sensing applications. To improve the functionality and optical properties of CQDs, a large number of efforts have been made in the preparation using various techniques like chemical oxidation, arc discharge, laser ablation, electrochemical oxidation, microwave irradiation, and hydrothermal method. The electrochemical oxidation and chemical oxidation method require very strong acids while arc discharge and laser ablation require sophisticated and expensive instruments, The Microwave irradiation method provids an easy path for the synthesis of CQDs within a few minutes; though one of the major limitations of this method is its uncontrollable reaction conditions. Therefore, the hydrothermal method is highly demanded because of its rapidity, simplicity, controlled reaction conditions, cost-effectiveness and one-step process. Various organic precursors like citric acid, tartaric acid, ascorbic acid, glucose, sucrose, glycerol, and glycol have been utilized for the synthesis of CQDs. For surface passivation, different organic polymeric moieties, like polyethylene glycol, polyethyleneimine, 4,7,10-trioxa-1,13-tridecanediamine etc have been commonly utilized. Addition to this, various natural organic precursors such as orange juice, green grass, soybean, milk, pomelo peel, plant leaves, potato, cocoon silk soy milk, etc have been utilized for the synthesis of CQDs. Although, the synthesis of CQDs with high QY is still a challenge.

Chapter 1 Describes the complete literature survey related to economical and green routes for synthesizing fluorescent CQDs. Present chapter illustrates the various types of nanomaterials and their synthesis approaches in brief. The history and an overview of CQDs have also been examined in the current chapter. This chapter also gives in details about the properties and applications of CQDs, objective and scope of the present thesis work.

Chapter 2 Provides detail regarding the experimental procedure, materials and methods used in the preparation, characterization and applications of CQDs. A variety of applications of CQDs like sensing of metal ions, ascorbic acid, cell cytotoxicity, bioimaging, and schottky barrier diodes have also been included in this article.

Chapter 3 In this chapter, an eco-friendly and zero-cost technique has been established for the preparation of CQDs by one-pot hydrothermal treatment of leaf extracts of Neem (*Azadirachta indica*). The QY of as-prepared Neem-carbon quantum dots (N-CQDs) was obtained to be 27.2 %. N-CQDs exhibited peroxidase-mimetic enzyme activity towards the oxidation of peroxidase substrate 3,3',5,5' tetramethylbenzidine (TMB) in the presence of hydrogen peroxide (H_2O_2). In addition, the kinetic of peroxidase-like catalytic activity follows the Michaelis-Menten and ping-pong pathway. Further, the H_2O_2 concentration-dependent oxidation of TMB motivated for the colorimetric detection of H_2O_2 in a linear range from 0.1 to 0.5 mmol/L with a limit of detection (LOD) of 0.035 mmol/L. Besides this, the oxidized blue color TMB (ox-TMB) were reduced in native TMB with ascorbic acid (AA) selectively without causing any interference of other reducing agents. The linearity for the detection of AA was lying between 5-40 μM with LOD up to 1.773 μM. Finally, we have used the practical feasibility for the detection of AA in real samples such as common fresh fruits.

Chapter 4 Herein, a facile**,** green and eco-friendly approach has been applied for the synthesis of fluorescent green-blue carbon dots (GB-CDs) through the one-pot hydrothermal treatment of *Artocarpus lakoocha* seeds for the first time and entirely characterized via a variety of instrumental techniques such as fluorescent spectroscopy, Transmission Electron Microscope (TEM), X-Ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and Fourier Transform Infra-Red spectroscopy (FT-IR) analysis. The as-prepared GB-CDs exhibited high fluorescent quantum yields (QY) up to 38.5 % and high photostability based on which GB-CDs were successfully applied as a sensitive nanoprobe for the detection of Fe^{3+} ion which showed linearity from 2 to 6 μM with a limit of detection (LOD) of 0.6 μM. The sensing of Fe^{3+} was further investigated in the bona fide sample like river water and human blood serum. In addition, to explore the potential application, MTT assay was carried out on SH-SY5Y neuroblastoma cells. The results showed negligible cytotoxicity and high cell viability, revealing that as-prepared GB-CDs could be utilized as fluorescent probe in living cells.

Chapter 5 In this chapter, a facile and straightforward approach has been designed to prepare fluorescent green carbon quantum dots (G-CQDs) from the latex of Ficus *benghalensis* as a carbon source and polyethyleneimine as a nitrogen source. Various instrumental techniques such as TEM, XRD, FT-IR and XPS were employed to characterize G-CQDs**.** Interestingly; as-prepared CQDs exhibited green fluorescence with 41.2 % quantum yield and showed excitation-dependent emission. The G-CQDs were applied as a fluorescent probe for the selective and sensitive Tyrosine (Tyr) detection with a detection limit of 0.13 µM. Further, to explain the quenching mechanism, a fluorescence lifetime experiment was performed. In addition to this, the detection of Tyr was performed in the milk sample. Based on semiconducting properties, the synthesized G-CQDs were effectively applied to fabricate a Schottky barrier diode on Indium doped tin oxide (ITO) substrate. On the whole, the work is a novel illustration of the demanding optoelectronic device application of G-CQDs.