



Tomas Bata University in Zlín

Centre of Polymer Systems

Doctoral Thesis Summary

Preparation and characterization of carbon dots for versatile applications

**Příprava a charakterizace mnohostranně aplikovatelných
uhlíkových teček**

Author: R. Blessy Pricilla, M.Sc., Ph.D.

Degree program: Nanotechnology and advanced materials

Degree course: Nanotechnology and Advanced Materials

Supervisor: prof. Ivo Kuřitka, Ph.D. *et* Ph.D.

Consultant: Mgr. David Škoda, Ph.D.

External Examiners: prof. RNDr. František Krčma, Ph.D.
doc. Ing. Marián Lehocký, Ph.D.

Zlín, February 2024

© R Blessy Pricilla

Published by **Tomas Bata University in Zlín** in the Edition **Doctoral Thesis Summary**.

The publication was issued in the year 2024

Key words in Czech: *Uhlíkové tečky, vysoký výtěžek, multifunkční, protipadělatelský, LED, sensor, antibakteriální, šifrování informace*

Key words: *Carbon dots, high yield, multifunctional, anticounterfeit, LED, sensor, antibacterial, information encryption decryption*

Full text of the doctoral thesis is available in the Library of TBU in Zlín.

ISBN 978-80-7678-241-9

DEDICATION

This Ph.D. thesis is dedicated to my Family (Rajendran, Ruby, Lillian and Ebenezer, Premalatha, Joy), husband (John Wesley Ebenezer), Best friend (A. Stephena Elsie) and my supervisors and colleagues working in CPS.

ABSTRACT

Every material science research is enriched by the addition of carbon-based materials. Carbon dots are a new type of luminescent nanoparticles that belong to the carbon family and are currently gaining popularity. They have attracted broad research interests because of their excellent physiochemical properties and characteristics like low-cost synthesis, novel optical properties, nontoxicity, biocompatibility, etc. Due to their multi-functionality, they are widely used in various applications such as sensing, catalysis, bioimaging, security, anti-counterfeiting, and optoelectronics. Since it is a recently explored material, its challenges related to product yield, optical efficiency, and functionalization remain problematic and open to research.

In this thesis work, various carbon dots have been obtained by exploring multiple precursor categories: Proteins, Biomass, and organic. The precursors used are non-toxic and free of rare earth elements and metals, making the prepared carbon dots environmentally friendly and independent from problematic sources. Different synthesis methods, such as microwave, hydrothermal, and heating, were utilized to obtain a reasonably high yield. These methods are low-cost and straightforward to manipulate. We targeted diverse applications for all our carbon dots, thus making them a multifunctional nanomaterial. Examples of the various applications demonstrated for the carbon dots include anticounterfeit, LEDs, sensing, antibacterial, information encryption decryption, etc.

Keywords: *Carbon dots, high yield, multifunctional, anticounterfeit, LED, sensor, antibacterial, information encryption decryption*

ABSTRAKT

Uhlíkové materiály pronikly do všech oblastí materiálově-vědného výzkumu. Uhlíkové tečky jsou nový typ luminiscenčních nanočástic patřící mezi uhlíkové materiály a jejich popularita stále vzrůstá. Přitahují široký zájem výzkumníků díky svým vynikajícím fyzikálněchemickým vlastnostem a dalším charakteristikám, jako jsou nízké náklady na syntézu, nové optické vlastnosti, netoxičnost, biokompatibilita apod. Díky své multifunkcionalitě jsou široce využívány v různých aplikacích, jako je sensorika, katalýza, biologické zobrazování, bezpečnostní a protipadělatelské aplikace a optoelektronika. Jelikož je to teprve nedlouhou dobu zkoumaný materiál, výzvy spojené s výtěžností syntézy, optickou účinností a funkcionalizací zůstávají problémem, a jsou stále otevřeny dalšímu zkoumání.

V této disertační práci byly připraveny různé uhlíkové tečky při zkoumání několika kategorií výchozích surovin: bílkovin, biomasy, a organických látek. Tyto látky jsou netoxické a obejdou se bez prvků vzácných zemin a kovů, což činí připravované uhlíkové tečky příznivými pro životní prostředí a nezávislými na obtížně dostupných zdrojích. Byly využity různé metody syntézy jako jsou mikrovlnná syntéza, hydrotermální syntéza i prostý ohřev, aby bylo dosaženo dostatečně vysokých výtěžků. Záměrem bylo najít různé aplikace pro všechny připravené uhlíkové tečky, abychom vskutku dosáhli multifunkčního nanomateriálu. Příklady, které to demonstrují zahrnují protipadělatelské aplikace, LED, sensoriku, antibakteriální účinek, šifrování informace apod.

Klíčová slova: Uhlíkové tečky, vysoký výtěžek, multifunkční, protipadělatelský, LED, sensor, antibakteriální, šifrování informace

(This page has been intentionally left blank.)

ACKNOWLEDGMENTS

First, I would like to thank my Almighty Father, Jesus Christ and the Holy Spirit for blessing me with wisdom, knowledge and understanding to complete my research work successfully. Without his grace, this research would not have been possible.

I want to convey my heartfelt gratitude to my doctoral supervisor, **Prof. Ivo Kuritka**, for his continuous support and guidance throughout my doctoral study. His valuable inputs in my research works have helped me better understand my research and produce successful results. I also appreciate my co-supervisor, **David Skoda**, for guiding me in my experimental work. His insights were very thought-provoking, which resulted in the enrichment of my work. My special thanks to **Pavel Urbanek** for being a continuous source of inspiration and support. His support with my experiments and their analysis helped me present my work productively. I would like to thank **Michal Urbanek** for helping me to obtain good microscopic images. I would also like to thank **Pavol Suly** for his assistance in helping me achieve good outcomes when using my material for a specific application. I am immensely grateful to all my other colleagues who helped me conduct my experiments and bring successful results. With their consent and cooperation, this thesis was finished on time.

I want to express my sincere appreciation to Tomas Bata University in Zlin, which awarded me financial support through a **Ph.D. scholarship** and an **IGA project** fund. The financial support financed my living and academic expenses like travelling to conferences abroad and paying for publications.

Furthermore, I would also like to acknowledge **Prof. Aharon Gedanken**, Bar Ilan University, Israel, for allowing me to research on carbon dots and their applications in his laboratory. I sincerely thank **Dr. Maruthapandi Moorthy** for teaching and guiding me into new research areas in carbon dots.

Finally, I am indebted to my many friends and colleagues in the **Centre of Polymer Systems**, who stood with me in all my ups and downs. I am incredibly thankful to my husband, **John Wesley E.**, and my best friend, **A. Stephena Elsie**, for their continuous love and understanding. This academic journey would not have reached its goal without their support.

TABLE OF CONTENTS

ABSTRACT	4
ABSTRAKT	5
1. INTRODUCTION	11
2. BACKGROUND	12
2.1 Precursors for Synthesis.....	12
2.2 Synthesis	14
2.3 Structure	15
2.4 Photoluminescence Mechanisms	16
2.4.1 Quantum Confinement Model.....	16
2.4.2 Surface state effect	17
2.4.3 Molecular state effect	17
2.5 Phosphorescence of carbon dots	18
2.5.1 Phosphorescence Activation in CDs	19
3. MOTIVATION.....	22
4. AIM OF THE DOCTORAL THESIS	23
5. EXPERIMENTAL SECTION	24
5.1 Experimental for casein based CDs	24
5.1.1 Materials required, Instrumentation and Characterization.....	24
5.1.2 Preparation of Carbon nanodots derived from casein	25
5.1.3 Preparation of SEBS/CND nanocomposite film	25
5.1.4 Preparation of CND ink.....	26
5.1.5 Preparation of CND-LEDs	26
5.1.6 Detection of Fe ³⁺ ions.....	26
5.1.7 Real water sample analysis.....	27
5.2 Experimental for of carbon dots derived from <i>Syzygium cumini</i> L. (SCL) seed extract	27
5.2.1 Materials Required, Instrumentation and Characterization	27
5.2.2 Preparation of Carbon dots derived from <i>Syzygium cumini</i> L.	28
5.2.3 Antibacterial activity of CDs.....	28
5.2.4 Antibacterial activity of CDs on fabric	29

5.3	Experimental for carbon dots derived from 1,10 Phenanthroline.....	29
5.3.1	Materials Required, Instrumentation and Characterization.....	29
5.3.2	Preparation for control experiments	30
5.3.3	Preparation of RTP CDs derived from 1,10 Phenanthroline.....	31
5.3.4	Preparation of RTP CDs as security inks	31
5.3.5	Preparation of RTP CDs as LED phosphor material.....	31
6.	Summary of the research objectives	32
7.	Conclusions and Summary of the research works.....	33
8.	Contribution to Science and Practice.....	36
9.	Future prospects	38
	REFERENCES	39
	LIST OF SCHEMES.....	44
	LIST OF ABBREVIATIONS AND SYMBOLS	46
	CURRICULUM VITAE.....	48
	LIST OF PUBLICATIONS AND PROJECTS	49

(This page has been intentionally left blank.)

1. INTRODUCTION

Nanotechnology is a field of science and technology that deals with manipulating atoms and molecules at a scale less than 100 nm. The idea behind this started with a talk given by Richard Feynman in 1959 on the topic “There is plenty of room at the bottom.” Since then, this multidisciplinary field has undergone broad research to discover its application in different technology fields. The advantages of nanotechnology are based on the ability to alter material structures at extremely small scales to obtain specified features. As we go from the bulk to the nano size of a material, there is an enormous change in the physical and chemical properties. The large surface-to-volume ratio at the nanoscale greatly benefits these nanosystems.

In nanotechnology, the synthesis of nanomaterials plays a huge role in obtaining the required properties of a material. Two basic approaches are followed for synthesizing nanomaterials to get the desired features: top-down and bottom-up. The top-down approach involves breaking down bulk material into nano-sized structures or particles. Some of the different top-down approaches include lithography, arc discharge, and laser ablation methods. One of this approach's main disadvantages is its imperfection of the surface structure. On the other hand, the bottom-up approach involves the building up a material atom by atom, molecule by molecule, and cluster by cluster. Examples of bottom-up synthesis methods include sol-gel, microwave, and chemical co-precipitation. Compared to the top-down approach, bottom-up approaches are more efficient because of better structure formation. These approaches can potentially create less waste and are more economical.

Among the nanomaterials being examined and studied, carbon dots (CDs) have become a hot research topic due to their excellent properties. These dots open up many new opportunities for science and industry today. Researchers are developing customized CDs to meet the various needs of industries like nanomedicine, electronics, food, batteries, textiles, sensors, etc. Different approaches are being studied to synthesize these CDs with sufficient product yield and excellent properties. However, since it is a recently developed material, the quest still prevails due to its challenges like product yield and optical efficiency. In this doctoral thesis, we report the synthesis, characterization and applications of different CDs synthesized via different precursors and methods. Precursors such as proteins, biomass and organics are used for the synthesis. The synthesis methods involved are simple, low cost and productive. The diversity of the

synthesized carbon dots is shown through various applications like anticounterfeit, sensing, phosphor for Light Emitting Diodes (LEDs), antibacterial, information encryption decryption, security, etc. The novel CDs' unique functional and optical properties make them a universal material for multiple applications.

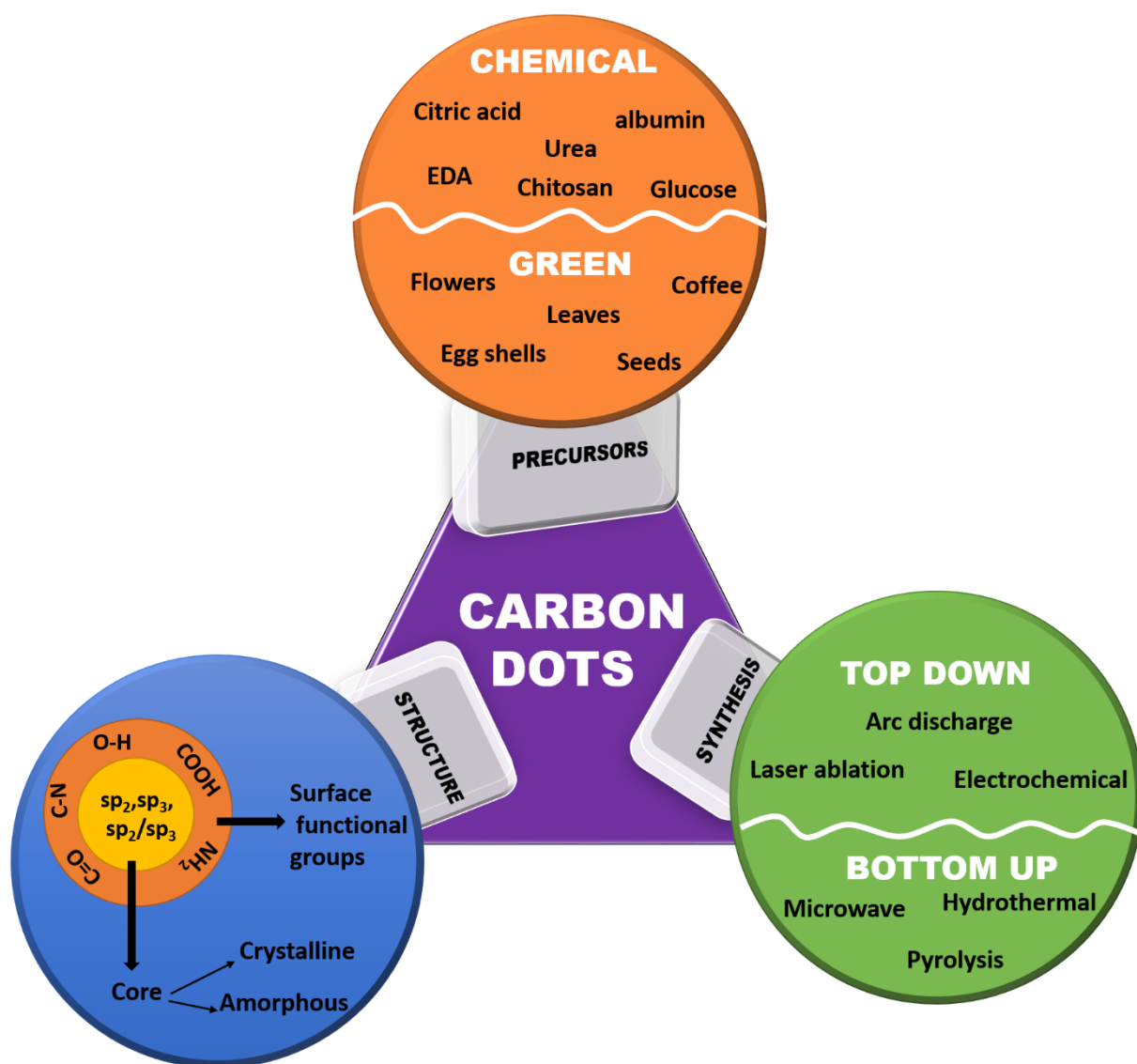
2. BACKGROUND

CDs are nanoparticles with dimensions less than 10nm, belonging to the carbon family. Xu and his colleagues discovered them in 2004 during the purification of single-walled carbon nanotubes [1]. These dots are primarily composed of elements C, H, O, and N [2]. The CDs comprise sp^2/sp^3 hybridized carbon in the core and with surface functional groups. Their structure depends on the precursor and the synthesis conditions. They have been explored massively in the last few years because of their tremendous properties like bright fluorescence, biocompatibility [3], low cost and easy synthesis. Among their different properties, their optical properties are given much attention because of their widespread applications in the field of light emitting diodes [4], anticounterfeit technology [5], bioimaging [6] and optoelectronics [7]. An overview of the various precursors and synthesis approaches used to obtain CDs is in Scheme 1.

2.1 Precursors for Synthesis

The two primary precursor sources used to synthesize carbon dots are chemical and green.

One of the main reasons chemical precursors are used is because of their ability to give high product yield and optical efficiency. Among the chemical precursors, the two sub-categories are acidic and non-acidic precursors [8]. Some of the acidic precursors used in synthesizing CDs include citric acid, boric acid, ascorbic acid, phthalic acid, tartaric acid, succinic acid, etc. Citric acid precursor combined with ethylenediamine yields one of the most excellent fluorescence quantum yields, at 85.69%[9]. Also, amino acids have several advantages of being a precursor because of their non toxic, biocompatible and eco-friendly characteristics. The different types of functional groups available with amino acids greatly enhance CDs chemical and optical properties. Non-acidic precursors include graphite oxide, poly(ethylene glycol), glucose, bovine serum albumin, chitosan, etc. Non- acidic precursors also provide remarkable properties, thus proving their potential compared to acidic precursors. Due to their unique properties, they are effectively used in versatile applications[10].



Scheme 1. Schematic representation of precursors, synthesis approaches, and structure of CDs (Own courtesy).

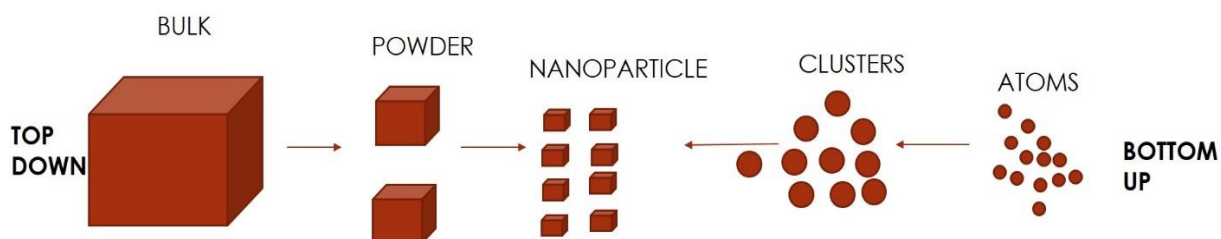
Research is progressing towards green sources due to their simple, low-cost, and large-scale production of high-quality carbon dots. Some of the green sources include fruits, seeds, leaves, vegetables, waste products etc. The different chemical groups in the raw materials provide exciting properties to the synthesized carbon dots. Acidic fruits like lemon and citrus sinensis are rich in glucose, fructose, and ascorbic acid, and their peels are rich in proteins and fibers. As a result, the carbon dots have higher fluorescence characteristics. Seeds having excellent anti-inflammatory, antioxidant, and antimicrobial properties have been used as precursors of carbon dots to eradicate various microorganisms. Leaves also serve as excellent precursor material. Recently, the carbon dots obtained from *Calotropis procera* leaves gave a quantum yield of 71.95% [11].

Surface functionalization alters the CDs surface with functional molecules or polymers, while doping adds atomic impurities into C-dots to change their electronic structure. Using compounds like urea, thiourea, and ethylenediamine to introduce heteroatoms like nitrogen and sulphur also increases the luminescence of the CDs. Heteroatoms can be used to modify the electronic bandgap. The sp^2 -conjugation is disrupted by a small number of heteroatoms, which causes the band gap to increase. On the contrary, a high concentration of heteroatoms can also lead to a decrease in the band gap [12].

In our thesis work, a protein called “Casein” was used as a precursor in the first study. Casein is a readily available milk protein. It has both hydrophobic and hydrophilic domains. They contain large quantities of calcium and calcium phosphate. It is rich in essential amino acids. The second study used *Syzygium cumini L.* (SCL) as a biomass precursor. SCL is a natural seed belonging to the tropical and subtropical family of Myrtaceae, generally known as Indian blackberry or Jamun. They have high contents of phenolic acids and flavonoids [13]. Due to their low cost, non-toxic properties and healing potential, they are frequently used in biological applications. In the third work, 1, 10 phenanthroline, an organic precursor, was used to synthesize phosphorescent CDs. Its aromatic structure, with the presence of a suitable hetero atom, is fundamental in obtaining appropriate inter system conversion, thus attaining phosphorescent characteristics.

2.2 Synthesis

Controllable preparation of CDs is critical to scientific study and application development, which can be realized through careful choice of synthetic methods. The CDs can be synthesized using both top down and bottom up approaches [14-16]. Some of the examples include Laser ablation [17], Electrochemical synthesis [18], arc discharge [19], Microwave [20], and hydrothermal [21]. Scheme 2 represents a schematic representation of the top down and bottom up approaches to obtaining carbon nanoparticles.



Scheme 2. Schematic representation of top down and bottom up approaches

Even though CDs are synthesized using both Top-down and Bottom-up methods, Bottom-up methods are generally chosen because of their simplicity, low cost, controlled surface functionalization, and ability to control particle shape and size.

2.3 Structure

The structure of CDs is composed of core and surface functional groups. Depending upon the synthesis, the core can be either crystalline or amorphous, and the surface groups can host different polar and nonpolar groups. CDs with crystalline cores tend to have a graphitic structure mostly. In such a structure, the core is composed of sp^2 hybridized carbon stacked on each other. The crystallinity of the core is analyzed through different techniques like X-ray diffraction, Raman spectroscopy, and high-resolution Transmission microscopy. On the other hand, amorphous carbon dots [22] contain a mixture of sp^2 and sp^3 hybridized carbon with different proportions without any lengthy periodicity in the core. Apart from the core structure, the CDs have similar features, whether crystalline or amorphous.

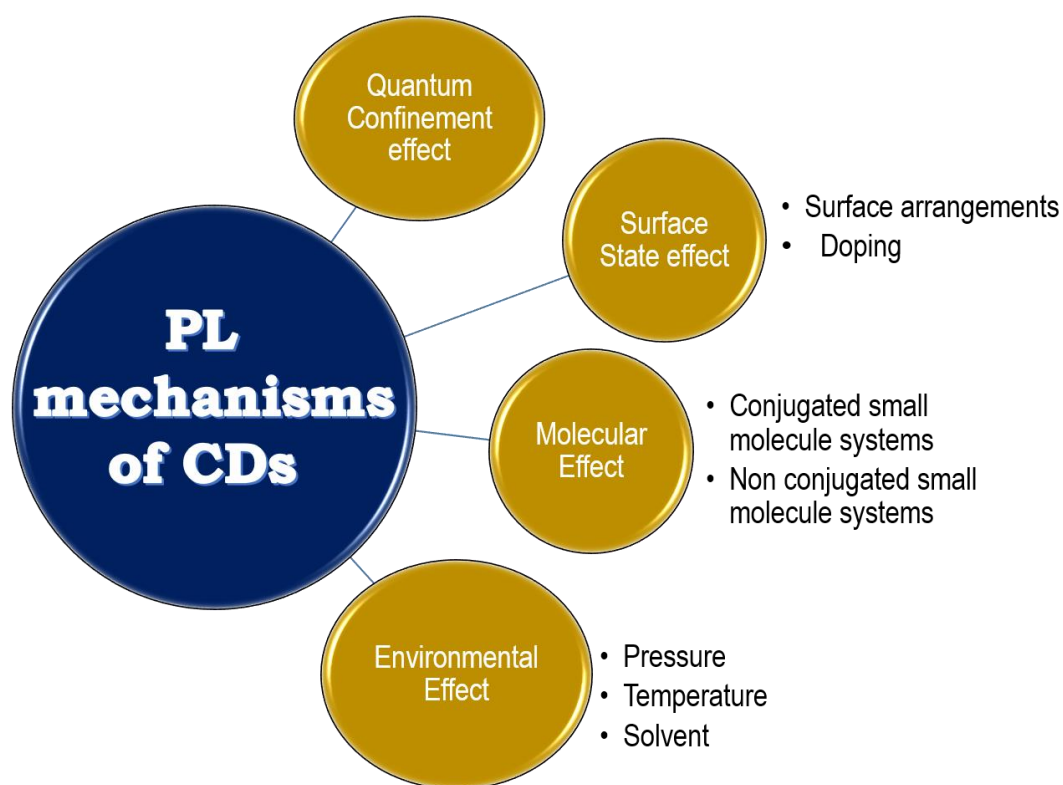
The surface of the CDs possesses different functional groups, which can be easily analyzed through Fourier Transform Infrared spectroscopy (FTIR) or X-ray photoelectron spectroscopy. Some CDs have high oxygen content due to the oxidation of core/surface groups. The surface might contain groups that are hydrophilic, hydrophobic, or amphiphilic. One of the essential aspects of the synthesis of CDs is proper surface passivation. The surface passivation plays a crucial role in providing bright luminescence. Dangling bonds, non-radiative states, radicals, and other defects can be found on a bare C-dot surface. Because of these defect sites, C-dots are vulnerable to external contamination, resulting in poor photostability and low quantum yields [23].

When it comes to the CDs electronic structure, the CDs π states can be ascribed to aromatic sp^2 hybridized atoms in the core. It has been reported that as the number of aromatic carbons increases, the energy difference between π -states decreases, similar to π -conjugation in organic compounds. Functional groups containing electron lone pairs, such as carbonyls, amines, amides, and thiols, are accountable for CDs n-states. If lone pair-carrying functional groups are coupled to aromatic sp^2 -hybridized carbons, electron transfers from the functional groups' n-states to the aromatic carbons' π^* -states can occur. Orbital overlap and the functional groups' electron withdrawing/donating abilities also affect the

interaction between the π and n states of carbon dots. The use of hetero atoms can only affect the electronic structure if they can interact with the sp^2 network [12].

2.4 Photoluminescence Mechanisms

Even though the exact Photoluminescence (PL) mechanism for the emission characteristics of carbon dots has not yet been concluded, many different kinds of PL mechanisms are speculated [24]. The following Scheme 3 represents the various of PL mechanism models. Amongst them, the standard PL mechanism models used to explain the emission features of CDs include the Quantum confinement effect, surface state effect, and molecular state effect. Sometimes due to the inefficiency of the individual models, two or more models are combined together to explain the PL mechanism of the carbon dots.



Scheme 3. Schematic representation of the various PL mechanism models responsible for the photoluminescence of CDs (Own courtesy)

2.4.1 Quantum Confinement Model

This kind of mechanism comes into effect in the case of defect-free and impurity-free dots. When a photon is absorbed, the electron gets excited to the conduction band, leaving a hole in the valence band. The recombination as a follow-up leads

to an emission known as fluorescence. This intrinsic bandgap fluorescence is entirely governed by Quantum confinement effects, where the exciton confinement effect helps understand the size dependence and spectral homogeneity due to particle size distribution. This model's noteworthy features are narrow PL emission band and excitation-independent emission. For dots with well-defined crystalline cores, PL strongly depends on the size [25]. An increase in the size of the particles leads to a red-shifted emission and leads to the narrowing of the bandgap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital. The size of the dots can be effectively controlled by synthesis techniques, surface modification, and purification methods [26].

2.4.2 Surface state effect

In many instances, quantum confinement is not observed because of surface defects and traps due to the presence of various surface functional groups and hetero atoms. In such a scenario, the photoexcited electron/hole is trapped by the surface defects or traps, followed by recombination, leading to nonradiative transitions or radiative transitions of lower energy. Variations in the surface arrangements of CDs could modify their electron energy levels or light-emitting locations and could even trigger emission in CDs that were previously non-luminous. Generally, this PL mechanism comprises two mechanisms from different sources: the core with its intrinsic quantization effects and the particle surface. These are controlled by the surface functional groups and defects. The hybridization of the carbon backbone and the attached chemical groups plays a huge role in determining the electronic level of the dots [27]. A typical feature of this PL behaviour is their excitation-dependent emission. A generalized explanation for the redshift observed under this mechanism is given to the increased surface oxidation [28]. Controlling the surface functional groups and attaining efficient doping in the system aids in regulating CDs luminescence characteristics. The surface configurations and hetero atom doping with nitrogen, fluorine, sulphur, etc., significantly affect the electronic structure of the CDs, thereby affecting their luminescence.

2.4.3 Molecular state effect

Small molecules that exist independently of the carbon core but are physiochemically adsorbed to the CDs surface may also be the source of PL emission. The molecular state model is based on the presence of fluorescent molecular species, either free or attached to the CDs structure. They are present

as a significant contributor towards the CDs luminescence. These states are mostly obtained from bottom-up synthesis methods, as small molecules tend to react immediately to form fluorophore molecules [24]. This kind of PL emission provides a very broad emission band due to the superimposition of several emissions. This typical mechanism is suppressed when there is a quenching by the surface emitter groups like the heavy atoms. Non-conjugated molecular systems play a vital role in determining the chemical structure of fluorophores and their luminescent center can exist without the presence of CDs. However, conjugated small molecules do not always exhibit molecular luminescence. The conjugation effect might apply to some of such molecules.

Apart from these standard models some of the other environmental factors playing a vital role in influencing the luminescence of CDs include solvent [29] temperature [30] and pressure [31].

In some cases, a single PL mechanism cannot explain the complete working photoluminescence mechanism of the CDs. Hence, more than one mechanism is interconnected to fully explain the luminescence [32]. Some of the different combinations include, the carbon core and surface state effect [33], conjugation effect and surface functional groups [34] and conjugation effect and defects [35]. The work by Krysmann and the team suggest that only a high temperature can lead to the formation of a carbogenic core, resulting in a PL due to the presence of both molecular fluorophores and the carbogenic core [36]. Without a carbogenic core, the observed PL is derived solely from surface states that serve as PL emitter centers.

Based on all the above mechanisms, it can be seen that the PL behaviour strongly depends on the synthetic methods and their conditions, surface functionalization or passivation, and the presence of the small molecules, which are either already present or are found as the byproducts of the reactions.

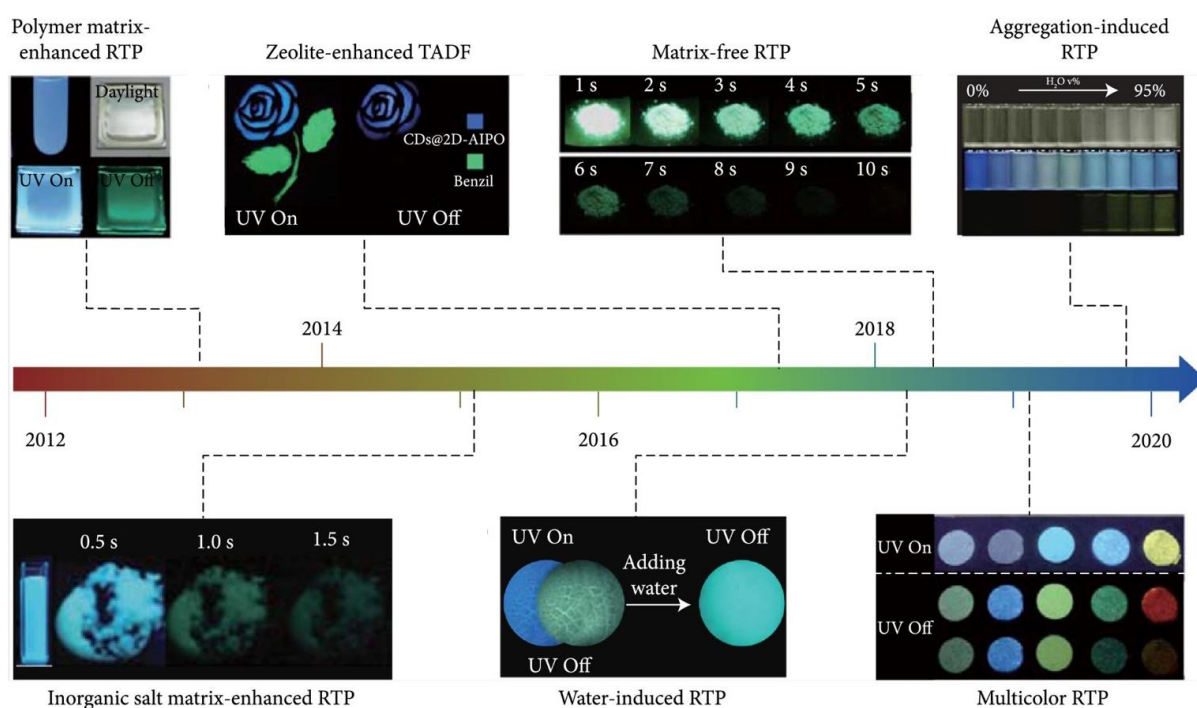
2.5 Phosphorescence of carbon dots

Phosphorescence is a phenomenon in which electrons relax from the singlet state to the triplet state and then slowly return to the ground state following an appropriate light source stimulation. There are different types of phosphorescent materials available, like rare earth metals [37] and organic materials [38]. However, they suffer disadvantages like expensive raw materials, complex synthesis, difficult purification, etc. Phosphorescent carbon dots [39] have captured recent attention due to their simple preparation, low cost, small size, and excellent optical properties. However, it is essential to obtain good stabilization

strategies to protect the triplet species of the CDs, as their phosphorescence is quenched fast by external factors like oxygen and water. Here are some activation strategies for obtaining effective phosphorescence in carbon dots and their composites

2.5.1 Phosphorescence Activation in CDs

The phosphorescence of CDs is achieved by obtaining enhanced spin-orbit coupling and efficient intersystem crossing. Precursors and synthetic methods play a huge role in stabilizing the excited triplet species and thereby attaining good phosphorescence [40]. Scheme 4 shows the various milestones achieved in the development of phosphorescent CDs over the years.



Scheme 4. Schematic representation of the selective milestones in the development of afterglow CDs in the last decade (adopted from [40] under CC BY 4.0).

Some of the methods used to activate phosphorescence are as follows:

Hydrogen Bonding activation

In this approach, Hydrogen Bonding plays a vital role in achieving phosphorescence. The excited triplet species are stabilized due to the formation of hydrogen bonds between the surface functional groups and the matrices. Due to the fixation effect, the nonradiative relaxation of the luminescent centers is reduced, and phosphorescence is attained. In a work by Li and the team, room

temperature phosphorescence of CDs was achieved using CDs and cyanuric acid. They utilized water molecules to construct hydrogen-bonded networks between CDs and cyanuric acid particles. The hydrogen-bonded network greatly enhanced the phosphorescence characteristics [41].

Molten salt activation

Molten salts undergo a phase transformation from solid to liquid at high temperatures. It is possible to easily regulate the carbonization temperatures of precursors by carefully selecting a combination of widely available salts that will strictly control the melting temperature of molten salts. Feng and team obtained room temperature CDs using neutral red, KNO_3 , MgCl_2 , and KH_2PO_4 as starting materials. The Mg metal ion accelerated the intersystem crossing, and the insoluble salt shell was used to suppress the non-radiative transition. The aggregated salt shell improved the structural rigidity and increased the phosphorescence lifetime [42].

Covalent Bond activation

Due to its strong bond strength, this activation outweighs the other two. Hydrogen bonding interactions can be the first step toward creating covalent bonding between matrices and CDs. The hydrogen bonds can then be converted into covalent bonding at high temperatures or by extending the reaction time. In 2018, Tian and their team developed CDs and embedded them in a PVA matrix through thermal annealing at 200°C . The establishment of chemical bonding between the two components stabilized the triplet species and enabled the material to be phosphorescent [43].

Zeolite Encapsulation activation

Zeolites are well-defined structures with uniform pores. Zeolites are tiny, crystalline solids made of aluminosilicates or aluminophosphates with homogeneous porosity and clearly defined shapes. As host matrices for encapsulating, they are appealing for encapsulation and activation of phosphorescence. In 2022, Zhong and team synthesized CDs@zeolite composite with multicolor fluorescence and phosphorescence. They impregnated the CDs into the RHO zeolite through in situ hydrothermal synthesis and calcined it. Using this method, a strong host-guest interaction was achieved. Temperature-controlled calcination provides a distinct pore architecture, exceptional stability of the zeolite matrix, surface oxidation level, and carbon core size of confined CDs. The resulting composites were stable, and intense phosphorescence was observed in solid and aqueous solutions [44].

Self protective activation

This approach is like a one step synthesis of CDs with phosphorescence characteristics inbuilt during the synthesis. In 2021, Su and the team developed N-CDs with blue and green room temperature phosphorescence emissions. They used Polyethylenimine as the carbon source and the cross-linking agent, and phosphoric acid was used to speed up the formation of the carbon core. These carbon dots were effectively used in the detection of promethazine. It was found that the electron transfer from CDs to promethazine increased the phosphorescence lifetime, leading to promethazine detection [45].

3. MOTIVATION

As a researcher, your goal is to revolutionize the industry by creating a material that is not only easily attainable and low-cost but also has excellent properties with multiple, versatile applications. By achieving this objective, you can make a significant impact on the world by providing a solution that meets the needs of a variety of industries and reduces environmental pollution that arises due to the synthesis of different types of materials for different purposes. Additionally, choosing an environmentally friendly production method that is scalable is crucial. By doing so, we not only contribute towards a safer and cleaner environment, but we also set ourselves up for sustainable growth and success.

Considering all these factors, we fixed our direction towards working with carbon dots, the new rising star. These newly discovered nanolights in the carbon family have taken the world by storm due to their wonderful and unique properties. Unlike non-carbon dots, which have been linked to toxicity and environmental problems, carbon dots provide superior advantages. The carbon dots can be synthesized using various resources available in the homeland and with simple methods, thus minimizing the use of expensive raw materials. The emergence of these novel multifunctional fluorophores has revolutionized the field of nanotechnology, taking it to unprecedented heights of improvement. These remarkable compounds possess many benefits, including aqueous solubility, biocompatibility, non-toxicity, high sensitivity, exceptional electron-donating and accepting capabilities, and high optical efficiency. As a result, they have become a sustainable and environmentally friendly alternative to traditional materials, paving the way for a brighter and greener future of technological advancement. Nevertheless, the synthesis methods for preparing CDs are still at the laboratory level, and productive efficiency remains a big challenge.

This doctoral thesis aims to create a novel type of multifunctional carbon dots. By utilizing affordable, non-toxic, and easily accessible precursors, we can create multifunctional carbon dots that can potentially transform a wide range of fields. A particular focus has been given to developing synthesis methods that can produce these carbon dots on a larger scale, and we have conducted extensive research to understand their properties. Our findings have shown that the carbon dots developed in this work are highly effective and provide exceptional functionalities that make them ideal for use in different fields. With the development of these innovative carbon dots, we are excited to contribute to a brighter and more sustainable future.

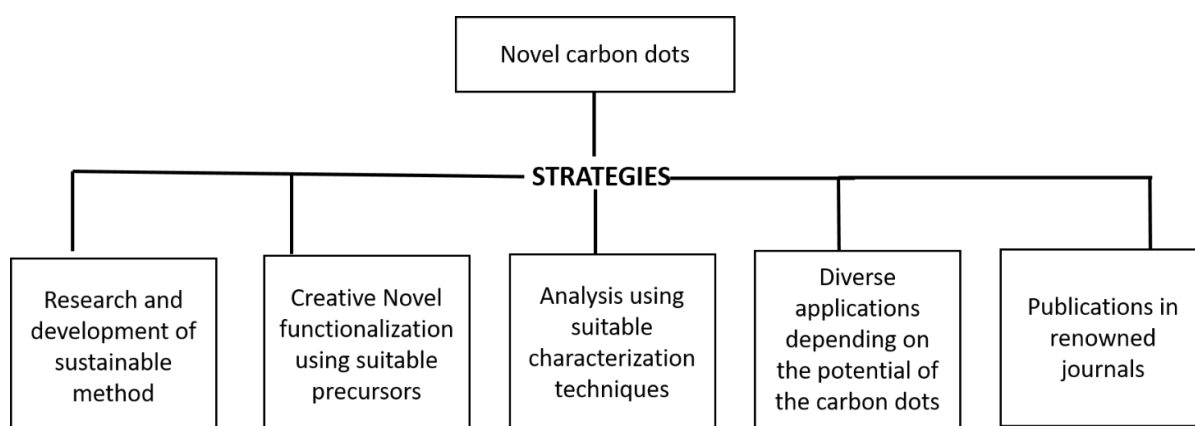
4. AIM OF THE DOCTORAL THESIS

This dissertation aims to create a novel type of multifunctional carbon dots utilizing available and abundant source materials with simple and effective production methods. Fluorescence and phosphorescence shall be the main functionality of the prepared CDs, which is to be studied, and from which the various applicability demonstrations are expected. Besides that, other functionalities, such as antimicrobial activity, will be investigated according to the newly discovered characteristics of the prepared materials.

The doctoral thesis was accomplished with well-designed objectives. The different objectives of the doctoral thesis work are summarized below.

1. Source selection – The source material should be green and sustainable. Proteins, Biomass and organic precursors shall be explored.
2. The choice of the method – A quick and controllable method of synthesis should be used. The method should help with fast and scalable production.
3. Characterization – Morphology – TEM; structure – XRD, FTIR, XPS; electronic properties – PL and UV-Vis. Analysis of their structure and properties and luminescence mechanism shall be achieved.
4. The application potential of the prepared CDs will be explored in different fields such as anticounterfeit, sensing, phosphor for LEDs, antibacterial, security etc.
5. Publication in renowned journals

The following Scheme 5 indicates a summary of the research objectives of this doctoral work.



Scheme 5. Scheme indicating the research goals for the doctoral work

5. EXPERIMENTAL SECTION

This Chapter explains about the instruments and the methods used for the different types of CDs synthesized.

5.1 Experimental for casein based CDs

5.1.1 Materials required, Instrumentation and Characterization

Polyvinylpyrrolidone (PVP) and styrene-ethylene-butylene-styrene (SEBS) are bought from Sigma Aldrich. MPC 85 Micellar Casein was obtained from a local dealer in the Czech Republic. Deionized water was used for the preparation purpose. The Polyethylene terephthalate (PET) substrates used for printing were acquired from Novacentrix, Texas. Metal ion salts such as $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, NaNO_3 , KNO_3 , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were bought from sigma Aldrich. The various solvents, such as ethylene glycol and isopropanol, were purchased from PENTA, Czech Republic. The deionized water used for all experiments had a conductivity of $1 \mu\text{S}/\text{cm}$ and a pH of 6.3. All the chemicals and reagents were utilized without any additional purification [BP1].

The size of Carbon nanodots was estimated using a Transmission Electron Microscope (TEM). The JEOL JEM 2100, TEM was performed at 300 kV (LaB₆ cathode, point resolution 2.3 Å equipped with OLYMPUS SYS TENGRA camera (2048 × 2048 pixels)). Image J Software was used to determine the particle size. The particles were dissolved in water, coated on a TEM grid, and dried overnight. The next day, the grid was used for imaging. An X-ray powder diffractometer (Rigaku Miniflex 600) was used to obtain the X-ray diffraction pattern, which was achieved using CoK α radiation ($\lambda = 1.7903 \text{ \AA}$) at a beam voltage of 40 kV and a beam current of 100 mA. The absorption studies were performed on Perkin- Elmer Lambda 1050, UV-Vis spectrophotometer. The emission studies were performed at room temperature on photoluminescence (PL) spectrophotometer FLS920 and Edinburgh Instruments (Xe lamp with a double monochromator used for excitation). 5 mg of the freeze-dried carbon nanodots sample was dissolved in 5 ml water for both UV and PL experiments. To execute the studies, 1 mL of this solution was obtained and made up to 3 mL. Both detector sensitivity and excitation source intensity were adjusted in the obtained spectra. The Fourier Transform Infrared (FTIR) spectra analysis was resolved on Thermo Scientific Nicolet 6700 spectrometer by applying the ATR method with the diamond crystal ($4000\text{--}400 \text{ cm}^{-1}$, resolution 2 cm^{-1} , 64 scans). The Dimatix

Materials Printer (FUJIFILM DMP-2800 series) was used to print with the CND ink. The thermogravimetric analysis was accomplished on a Setaram LabSys Evo with a TG/DSC sensor in an air atmosphere (Heating ramp 5°C min⁻¹, up to 1000 °C). The contact angle studies were done on the SEE System (Advex Instruments, Czech Republic). The total optical transmission of the samples was measured using a spectrometer Lovibond RT850i (Tintometer Limited) along with the ASTM D 1003[BP1].

5.1.2 Preparation of Carbon nanodots derived from casein

Casein, a sustainable carbon source, and PVP, an efficient stabilizer, are used to synthesize highly efficient individual carbon nanodots (CND). In a beaker, 20 ml of ethylene glycol was added to 0.1 g of casein for the synthesis. Ethylene glycol is used as a solvent as well as a reducing agent. The solution was ultrasonicated for 60 minutes to obtain a good dispersion. In a separate beaker, 0.2 g of PVP was dissolved in 20 ml of ethylene glycol using ultrasonication for 10 minutes. Both solutions were mixed, poured into a Teflon-lined container, and placed in the microwave reactor. The microwave-assisted reaction was performed at 200 °C for 30 minutes with 100 % (600 W) power. The brown colour solution obtained after synthesis is filtered using a 0.22 µm membrane filter. Using a dialysis bag (3.5 KD), the filtered solution is dialyzed for two days to remove all the undesired particles. Lastly, the dialyzed solution is freeze-dried for two days to obtain the required product. The product yield is calculated using the following equation (5.1) below [46].

$$PY = \frac{m_{\text{CND}}}{m_{\text{CA}} + m_{\text{PVP}}} * 100\% \quad (5.1)$$

Where m_{CND} indicates the mass of the CND obtained after lyophilization, m_{CA} indicates the mass of casein, and m_{PVP} indicates the mass of PVP. The product yield attained utilizing this formula was found to be 25% [BP1].

5.1.3 Preparation of SEBS/CND nanocomposite film

SEBS/CND nanocomposite film preparation was carried out by preparing 20 wt % of SEBS solution and 0.25 wt % (C1), 0.5 wt % (C2), and 1wt % (C3) CND solution in chloroform. The two solutions were mixed in a 2:1 volume ratio and stirred for approximately 60 minutes. Once mixed sufficiently, the solution is

slowly poured onto a petri dish and covered to allow the film to dry slowly overnight [BP1].

To determine the hydrophobic or hydrophilic nature of the film, water contact angle (WCA) studies were performed. For the study, five measurements were carried out on the same film substrate at different places, using 5 μL of water for each droplet. Deionized water, having a conductivity of about 0.09 $\mu\text{S}/\text{cm}$, was used to perform the analysis. Typically, the substrate is claimed to be hydrophilic if the contact angle is less than 90° . However, if the contact angle is more than 90° , the substrate is claimed to be hydrophobic [BP1].

5.1.4 Preparation of CND ink

The luminescent CND ink was prepared by blending the CND solution with ethylene glycol. The mixture contains 1 wt % of CND in water and ethylene glycol in a 2:1 volume ratio. The presence of ethylene glycol increases the viscosity of the ink. The ink is dispersed adequately in a sonicator for 10 minutes. The prepared CND ink is then loaded into the cartridge of the Dimatix Materials Printer and kept in the cartridge holder. The printer head nozzles and PET substrate were maintained at 30°C and 40°C , respectively [BP1].

5.1.5 Preparation of CND-LEDs

To obtain the proper dispersion of CND into the SEBS polymer solution, 1 ml of 20 wt % of CND in chloroform was added drop by drop for an hour in 2 ml of 22 wt % SEBS solution in chloroform. After adding CND, the solution was allowed to be stirred for another hour. This mixture was then poured onto a petri dish slowly and covered to allow the film to dry overnight. The obtained uniform CND/SEBS nanocomposite film with a minimum thickness of about 3 mm was mounted as a flat layer on the LED device with a wavelength of 365 nm. The luminescence spectra of the device were recorded separately [BP1].

5.1.6 Detection of Fe^{3+} ions

To investigate the efficiency of CND as a sensor probe, 500 μM of all the metal ions were prepared and mixed with the standard CND solution. To prepare the standard CND solution, 5 mg CND was mixed in 5 ml of water and diluted to obtain an absorbance value of 0.1 (0.25 ml CND sol in 2750 ml water). The CND and the metal ion salts were mixed to a 1:1 ratio, and the fluorescence response was recorded at an excitation wavelength of 370 nm.

5.1.7 Real water sample analysis

For the real water analysis, 500 μL of tap water was taken, mixed with CND and Fe^{3+} solutions, and made up to 4 ml. The solution was spiked with two different concentrations. After the spiking, their respective PL response was recorded. The recovery rate was calculated using the following equation:

$$R(\%) = \left[\frac{C_1 - C_2}{C_3} \right] * 100 \quad (5.2)$$

Where C_3 is the spiked concentration, C_2 is the concentration of Fe^{3+} ions present inside the water samples before the addition of Fe^{3+} ions, and C_1 is the concentration of Fe^{3+} ions in the water sample after the spiking of the known concentration of Fe^{3+} ions.

5.2 Experimental for of carbon dots derived from *Syzygium cumini* L. (SCL) seed extract

5.2.1 Materials Required, Instrumentation and Characterization

SCL seeds were obtained from Tamil Nadu, India. They were crushed using a mixer to get their powder. Ultrapure water from Alfa (Haverhill, MA, USA) was used to synthesize CDs. The gram-positive and gram-negative bacteria, namely *Escherichia coli* (ATCC 25,922), *Staphylococcus aureus* (ATCC 29,213), *Staphylococcus epidermidis* (ATCC 12,228), and *Klebsiella pneumoniae* (ATCC 700,603), were obtained from Dr. Banin's Lab, The Mina and Everard Goodman Faculty of Life Science, Bar Ilan University, Israel. To check the antibacterial properties of the CDs on textiles, a commercial 100 % cotton fabric was used [BP2].

The image of the particle size of CDs was captured in the transmission electron microscope with the model number TEM-JEOL-2100 (Peabody, MA, USA). A few drops of the dialyzed CDs solution were dropped on the copper grid and dried overnight at 60 °C. The absorbance studies were conducted on the UV–visible spectrophotometer-type Varian Cary 100 Bio Spectrophotometer. A Varian Cary Eclipse fluorescence spectrophotometer was used to attain the emission studies. Fourier transform infrared (FTIR) spectra ranging from 500 to 4000 cm^{-1} were collected from a Tensor 27 spectrometer (Bruker, Germany). The surface charge was analyzed on Malvern Zetasizer Nano-ZS (Malvern, UK). X-ray

photoelectron spectroscopy was conducted on an XPS, Nexsa spectrometer (England). The binding energies for all elements were set by the C1s peak at 285 eV. The reactive oxygen species (ROS) generation of CDs was recorded on a Bruker X-band spectrometer (121 EPR 100d) with DMPO (5,5-dimethyl-1-pyrroline-Noxide) as a spin trap. The CDs solution (40 μ L) was taken and mixed with 10 μ L of DMPO (0.01 M) for electron paramagnetic resonance (EPR) measurement. The blank was measured using deionized water without CDs [BP2].

5.2.2 Preparation of Carbon dots derived from *Syzygium cumini* L.

Initially, dried SCL was taken and ground nicely using a mixer. From the obtained powder, 1 g of SCL was taken in 60 ml of water. This mixture was stirred at around 90 °C for 60 minutes at 650 rpm. After 60 minutes, the solution was centrifuged at 9000 rpm to remove the larger particles. Next, the supernatant was taken, put in a Teflon container, and kept for hydrothermal reaction. The reaction was allowed to run for 8 hours at 200 °C. After cooling, a dark brown solution was obtained. Subsequently, the solution was filtered using a 0.22 μ M filter. The filtered solution was dialyzed for 24 hours. Finally, the dialyzed solution was again filtered using a 0.22 μ M filter and stored in the fridge for further characterization and applications [BP2].

5.2.3 Antibacterial activity of CDs

The four bacteria, namely *Escherichia coli* (EC), *Staphylococcus aureus* (SA), *Staphylococcus epidermidis* (SE), and *Klebsiella pneumonia* (KP), were grown overnight with agitation at 120 rpm in lysogeny broth (LB) at 37 °C. The emerging bacterial concentration was analyzed by taking absorbance at 595 nm (OD⁵⁹⁵). Based on the values obtained, the bacterial concentration was adjusted to 10⁵.

For the antibacterial studies with CDs, 500 μ L of CDs and 500 μ L of 10⁵ bacterial solutions were mixed and incubated at various intervals with constant shaking at 120 rpm. The control consisted of only bacterial solution and water. To observe the time-dependent activity of the CDs, three time intervals of 0 hrs, 12 hrs, and 24hrs were selected. After each time interval, an appropriate amount of the incubated sample was taken and plated in a 96-well plate, and up to 7 dilutions were performed. After dilution, 5 μ L of each dilution was taken and plated on an agar plate and incubated at 37 °C along with the control. A similar procedure was carried out for various concentrations of the CDs for 24 hours. The well known

colony forming unit (CFU) method was used to calculate the rate of bacterial growth observed in the agar plate [BP2].

5.2.4 Antibacterial activity of CDs on fabric

To observe the antibacterial effect of CDs on textiles, the probe ultrasonication method was used for coating. Commercial 100 % cotton cloth with dimensions 1 cm*1 cm was taken and put in 20 ml of CDs solution and sonicated. The sonication was performed for 1 hour with an amplitude of 30 %. After 1 hr, the cloth was dried in an oven at 70 °C overnight. The dried cloth was then used for antibacterial studies for the four bacteria [BP2].

The procedure is similar to that of the CDs solution. For the antibacterial experiment with fabric, the fabric was incubated with 1 ml of bacteria overnight at 37 °C with constant shaking at 120 rpm. After 24 hours, an appropriate amount is taken and diluted in a 96-well plate with up to 7 dilutions. From each dilution, 5 µL is taken and plated on an agar plate and incubated overnight at 37 °C. The CFU method was utilized to observe the bacterial growth [BP2].

5.3 Experimental for carbon dots derived from 1,10 Phenanthroline

5.3.1 Materials Required, Instrumentation and Characterization

1,10 phenanthroline and Boric acid were acquired from Sigma Aldrich. The UV LED diodes were purchased from Roithner Lasertechnik, Austria. No additional purification was performed before using any of the chemicals. The water utilized had a pH of 6.3 and a conductivity of 0.09 µS/cm.

The particle size of the Room temperature phosphorescence (RTP) CDs was carried out on the TEM model, JEOL JEM 2100 microscope, operated at 300 kV (LaB6 cathode, point resolution 2.3 Å equipped with OLYMPUS SYS TENGRA camera (2048 × 2048 pixels)). The RTP CDs were dissolved in water and then applied to the TEM grid in small amounts for the analysis. The grid was allowed to dry overnight, and the next day, the grid analysis was obtained. The particle size was analyzed using ImageJ software. Powder XRD diffraction patterns were obtained on an X-ray powder diffractometer (Rigaku Miniflex 600) using CoK α radiation ($\lambda = 1.7903 \text{ \AA}$), operated at a beam voltage of 40 kV and a beam current of 100 mA. The XRD pattern was analyzed by converting CoK α radiation to CuK α radiation ($\lambda = 1.54 \text{ \AA}$) using PowDLL Converter. The functional groups were studied using Thermo Scientific Nicolet 6700 Fourier Transform Infrared

(FTIR) spectrophotometer using the ATR method with the diamond crystal (4000–400 cm^{-1} , resolution 2 cm^{-1} , 64 scans). PL measurements were conducted on photoluminescence (PL) spectrophotometer FLS920, Edinburgh Instruments (Xe lamp with a double monochromator used for excitation in continuous-wave regime at room temperature). The phosphorescence studies were obtained on a self-designed experimental setup. A laboratory UV lamp (UVLMS-38, Analytik Jena US) operated in the 302 nm mode was utilized as a light source. The emitted light from the RTP CDs was collected from an optical guide. An Avantes AvaSpec 2048 spectrometer (Avantes B.V., The Netherlands) was employed as a detector. The luminance of the self standing self matrix RTP CDs films was collected using Chromameter CS 160 (Konica Minolta, Japan). The DRUV/Vis measurement was obtained on a UV–Vis spectrometer Avantes Avaspec 2048 with an integration sphere with a 50 mm diameter and an integration time of detector 1000 ms. The Kubelka Munk function was used to convert the reflectance data. Elemental analysis was carried out using two methods – ICP and CHNS. Boron content was ascertained by ICP-OES spectroscopy performed on an iCAP PRO XPS Duo spectrometer (Thermo Scientific) with the use of a boron spectral line at wavelength 249.773 nm. The experimental parameters were set as follows: radial view, 12 mm height, RF power 1050 W, nebulizer gas flow 0.55 l min^{-1} . The CHNS analysis was collected from Flash 2000 CHNS/O+MAS200R (Thermo Scientific). Two samples were collected from various batches of the CDs. A sample of two to three milligrams was used, and each analysis was carried out three times.

5.3.2 Preparation for control experiments

Control experiments comparing the individual precursor components and the precursor mixture were carried out to examine the efficacy of the photoluminescence spectra of RTP CDs as compared to the precursors. To conduct the experiment, for the first set, 1.5 g of Boric acid (BA) and 5 mg of phenanthroline were mixed in a mortar and pestle and thoroughly ground. For the second set, the same precursors were used in the subsequent control, combined with a small amount of water to create a paste, and dried in a vacuum oven. For the third set, a drop of water was added to each of the above mixtures. The PL response of these three sets was studied.

5.3.3 Preparation of RTP CDs derived from 1,10 Phenanthroline

The synthesis of Room temperature phosphorescence carbon dots (RTP CDs) was obtained using a simple heating approach. Typically, 3 g of boric acid and 10 mg of 1,10 phenanthroline were mixed with 40 mL water in a beaker. 1, 10 phenanthroline was used as a carbon precursor, and boric acid was used to attain a self matrix. The beaker was covered with foil to prevent fast evaporation of water. The beaker was heated in an oven for 5 hrs at 200 °C. Next, the mixture was allowed to cool overnight. The following day, a glassy product was obtained. The product was broken down to powder with a mortar and pestle for other characterizations and applications. The product yield was calculated using the same equation as (5.1), which is as follows:

$$PY = \frac{m_{\text{RTP CDs}}}{m_{\text{BA}} + m_{1,10 \text{ Phen}}} * 100 \% \quad (5.3)$$

Where m_{CDs} indicates the mass of the RTP CDs obtained after the synthesis, m_{BA} indicates the mass of Boric acid, and $m_{1,10 \text{ Phen}}$ indicates the mass 1,10 Phenanthroline. The product yield attained utilizing this formula was found to be 57%.

5.3.4 Preparation of RTP CDs as security inks

To demonstrate data encryption decryption, the RTP CDs were dispersed in water with a 50 mg/mL concentration. For fake ink, salicylic acid in ethanol was used. The desired pattern was printed and cut into the desired shape. The correct information was painted with RTP CDs, and the wrong information was painted with fake ink.

5.3.5 Preparation of RTP CDs as LED phosphor material

RTP CDs were made into pellets to demonstrate the use of RTP CDs as LED phosphor materials. Briefly, 80 g of RTP CDs were compressed and formed into a pellet. The pellets obtained were 0.44 mm thick. The pellet was placed on top of 310 nm and 340 nm LEDs, and their respective electroluminescence was recorded and studied.

6. SUMMARY OF THE RESEARCH OBJECTIVES

This thesis work aims at the preparation of different types of carbon dots with high optical and functional characteristics for diverse applications. Here is a point-wise summary of the achieved research goals

- A successful selection of novel, sustainable, renewable and economical precursors was performed. The three types of precursors involved in the study are Casein, *Syzygium cumini L.*, and 1, 10 phenanthroline. Casein is a sustainable, readily available milk protein rich in amino acids. *Syzygium cumini L.* seed is a renewable biomass precursor. They are low-cost, nontoxic, and rich in phenolic acids and flavonoids. 1, 10 Phenanthroline is a hetero atom containing an economical organic precursor with an aromatic structure. It serves as an excellent precursor for phosphorescence applications.
- After the selection of suitable precursors, three different methods were selected to synthesize CDs. The methods used include microwave reactor-assisted, hydrothermal, and simple heating methods. In all these methods, CDs were synthesized at 200°C but at different time intervals. All these methods produced suitable, appropriate and relatively scalable production of CDs. The methods abided by the green chemistry principles, including using less hazardous chemicals, locally available and abundant renewable feedstock, safe solvents for synthesis and inherently safer chemistry for accident prevention.
- The different types of carbon dots obtained via the different methods were characterized using various characterization techniques, including TEM, FTIR, UV-VIS, PL, XPS, ICP, Elemental, TGA, etc. Their morphology, structure, functional and optical characteristics were studied in detail. Specific attention has been paid to the comprehension of the optical properties of CDs. Their optical working mechanism was deeply analyzed and elucidated.
- The excellent functional and optical properties of the CDs enabled them to be utilized for multiple applications. The various applications of CDs explored include anticounterfeit, metal ion sensing, fluorescent markers, LED phosphor, information encryption decryption and antibacterial. This indicates that the synthesized CDs can be used for multiple applications.
- Publication in renowned journals of RSC and Springer was achieved. Furthermore, publication in Wiley is opted as the next publication target.

7. CONCLUSIONS AND SUMMARY OF THE RESEARCH WORKS

A brief summary of the research work carried out has been given below:

The first chapter, entitled: SYNTHESIS OF CARBON DOTS FROM CASEIN MICELLES AND THE ORIGIN OF THEIR LUMINESCENCE

In this research work, CND was developed using a simple microwave-assisted approach. This method produced a product yield of 25% with respect to the initial precursor concentration. The high yield corresponds to almost quantitative pyrolysis of the initial material directly to the quantum dots, which is a distinct feature of the discovered synthesis and can be explained by the proper choice of the initial casein source having a hierarchically organized structure. Hence, the CND was obtained as a result of casein disintegration into submicelles, followed by the formation of individual casein coils corresponding to the size of the CND. Partial carbonization of the casein coils resulted in the formation of CND. These CND showed blue fluorescence when excited at 365nm and demonstrated the typical excitation wavelength dependent PL emission spectrum. A new PL mechanism explanation, “competitive model,” was introduced to explain the unique blue shift followed by a red shift in the PL spectra and the portion of UV luminescence independent of the excitation wavelength. The defects and disorders in the CNDs were explained with the help of the Urbach and WAT region tailing deep into the band gap in the absorption spectrum. Polymer composites with SEBS were obtained with good photostability, optical transmittance, and mechanical properties. CND was produced in the form of ink to be utilized in the anticounterfeit market for polymer ink with appreciable thermal stability. The polymer nanocomposite SEBS/CND film was demonstrated for its application as an anticounterfeit film for packaging and security applications. The remarkable transparency of this polymeric nanocomposite makes it a highly promising material for a wide range of applications in diverse fields such as information technology, defence, transportation, and environmental protection. Its exceptional qualities offer unparalleled advantages that significantly enhance performance and efficiency, making it a valuable asset in various industries. The study proposes CND as a potential phosphor material for LEDs, using a unique experimental setup that reduces UV transmission and avoids self-absorption, thus improving efficiency. The CND was also employed for effectively sensing Fe^{3+} ions in an aqueous environment. Hence, the above-obtained results help to conclude that the

synthesized CND can be used as a universal material for multipurpose applications.

The core of this work was published with the title “*Unravelling the highly efficient synthesis of individual carbon nanodots from casein micelles and the origin of their competitive constant-blue-red wavelength shift luminescence mechanism for versatile applications*” (Authorship contribution: R Blessy Pricilla: Investigation, writing, reviewing, and editing.)

The second chapter, entitled: BIOMASS-DERIVED CARBON DOTS AS A POTENTIAL ANTIMICROBIAL AGENT

This research reports the syntheses of CDs using *Syzygium cumini L.*, a renewable biomass precursor. The hydrothermal method, a green preparation approach, was used to obtain the CDs. The synthesis was done at 200 °C for 8 hours, followed by dialysis and freeze-drying. Various characterization techniques like TEM, SEM, FTIR, UV-Vis, and PL were used to study and analyze the structural, functional, and optical properties of CDs. The obtained CDs were spherical in shape, with an average size of 6.3 nm. They exhibited excitation wavelength-dependent PL emission spectrum due to the surface state PL mechanism. A blue fluorescence was achieved when the CDs were excited. The antibacterial properties of the synthesized CDs were tested against four pathogens involving two gram-positive and two gram-negative bacteria. The CDs were found to be effective against *Staphylococcus aureus* and *S. epidermidis* within 12 h and *Escherichia coli* and *Klebsiella pneumonia* within 24 h at 500 µg/mL. The potential of carbon dots was also tested in textiles. The carbon dots were embedded into a 100% commercial cotton textile using an ultrasonication probe for 1 hour. The CDs-coated cotton textile also showed potential antibacterial effects against all the tested gram-positive and gram-negative bacteria. Even though the exact mechanism is unclear, the expected mechanism of work against the eradication of the bacteria by the CDs has been explained.

This work was published with the title “*Biomass-derived Carbon dots and their coated surface as a potential antimicrobial agent*”. (Authorship contribution: R Blessy Pricilla: Investigation, writing, and editing.)

The third chapter, entitled: SELF MATRIX CARBON DOTS WITH ULTRALONG ROOM TEMPERATURE PHOSPHORESCENCE LIFETIME

This research work describes the synthesis of room temperature phosphorescence carbon dots using 1, 10 phenanthroline, an organic precursor. Boric acid was used to obtain a rigid matrix environment for the CDs to produce phosphorescence. A simple heating method was used to obtain the RTP CDs. A high product yield of 57% of the initial source compound mass is attained using this method. The efficiency of the synthesis is due to the simplicity of the method used. The mass loss is almost only the dehydration of boric acid to the blend of pyroboric acid and boron trioxide matrix, whereas the chemical transformation of the organic material is a minor contribution. The self matrix RTP CDs exhibit excellent fluorescence and phosphorescence emission. Blue fluorescence is obtained when excited at 302nm. However, phosphorescence is obtained when the excitation source is removed. The unique phosphorescence characteristics are attained due to various factors such as efficient spin-orbit coupling, intersystem crossing, covalent bonding, etc. The rigid matrix provided by boric acid stabilizes the triplet species, thereby reducing nonradiative decay. The self matrix RTP CDs possess excitation wavelength-independent PL spectra, possibly due to the presence of a simple core structure and uniform surface states. The effect of temperature and precursor ratio concentration on the phosphorescence lifetime was also studied. It was revealed that increased precursor concentration and temperature reduced the phosphorescence lifetime. The RTP CDs produced ~22 s naked eye phosphorescence with a 2.4 s average lifetime. These values of phosphorescence lifetime make the RTP CDs a highly competitive material in self matrix RTP CDs. The various applications of RTP CDs demonstrated in this work include anticounterfeit, information encryption decryption, LED Phosphor, and water sensitivity. The above results and applications of RTP CDs validate their use as an economical, sustainable, and ubiquitous material for diverse purposes in multiple fields.

This work will be published with the title *“Exploring the Ultralong Lifetime of Self Matrix 1,10 Phenanthroline and Boron-based Room Temperature Phosphorescence Carbon Dots for Multiple Applications.”* (Authorship contribution: R Blessy Pricilla: Investigation, writing, reviewing, and editing.)

8. CONTRIBUTION TO SCIENCE AND PRACTICE

The doctoral thesis, encompassing three pivotal chapters, contributes to the field of material science, mainly focusing on the synthesis, properties and applications of carbon dots (CDs). This research underscores the potential of CDs in various domains and illustrates the integration of scientific inquiry and practical utility.

The fundamental objective of this dissertation was to obtain new carbon dot materials from economic and sustainable resources. This was accomplished as the precursors used in this work fulfilled these requirements. The methods of synthesis involved in this work are also green, ensuring the environment's safety. The methods gave appreciable product yields, opening a pathway to reach the market from the lab scale production. Synthesized carbon dots are an incredibly versatile and valuable resource with applications in electronics, sensing, biology, security, and more. By using CDs, we can reduce the environmental impact caused by synthesizing multiple materials for different needs. Adopting the use of CDs can significantly contribute towards a healthier planet for the future age to come.

The work on synthesis and applications of casein-derived CND delineates a novel method for synthesizing carbon nanodots (CND) from casein micelles, employing a microwave-assisted approach. The key scientific contribution here lies in the high yield and efficient conversion process, showcasing an almost quantitative transformation from casein to quantum dots. This advancement not only adds a new dimension to the understanding of material synthesis but also paves the way for more sustainable and efficient production methods in nanotechnology.

The synthesized CNDs have practically demonstrated immense potential in many possible application fields. Their utility in creating polymer composites with improved photostability, optical transmittance, and mechanical properties opens new avenues in material engineering. Furthermore, the application of CNDs in anti-counterfeit films and as a potential phosphor material for LEDs exemplifies their practical relevance, particularly in fields like information technology and environmental protection.

The work on biomass-derived CDs as antimicrobial agents shifts the focus to the antimicrobial potential of CDs synthesized from *Syzygium cumini* L., a renewable

biomass. The scientific contribution here lies in exploring CDs' structural, functional, and optical properties obtained from an unconventional source but mainly in discovering their efficacy against various bacterial pathogens. This research enriches our understanding of the antimicrobial properties of nanomaterials and opens up new research pathways in finding other than nano-silver and similar demanding material solutions.

From a practical standpoint, integrating these CDs into textiles to confer antibacterial properties represents a significant leap in hygiene and consumer products. Such application potentially enhances the value of everyday materials and contributes to public health by offering a novel method to combat bacterial infections.

The work on phosphorescence CDs with extended lifetimes presents a successful approach to synthesizing self matrix room-temperature phosphorescence carbon dots (RTP CDs). The scientific significance of this work lies in the extended phosphorescence lifetime achieved through a simple heating method, advancing our understanding of luminescent materials.

The practical implications of this research are far-reaching. These self matrix RTP CDs have demonstrated potential in diverse applications such as anti-counterfeit measures, information encryption, and LED phosphors. Moreover, their sensitivity to moisture can be further studied to obtain a stimuli-responsive-based application. This versatility showcases the economic and sustainable attributes of the prepared CDs and their adaptability across various industries.

In summary, the research presented in this doctoral thesis significantly contributes to both science and practice. Scientifically, it expands our understanding of carbon dots, their synthesis, and their properties. Practically, it translates these scientific insights into tangible application potential demonstrations across multiple industries, ranging from healthcare to information technology. This thesis exemplifies the symbiotic relationship between scientific research and practical application.

9. FUTURE PROSPECTS

Even though the results achieved are reasonable, there is always room to improve performance. With the ever-changing research trends and future directions, it is imperative to set clear goals for the future of carbon dots. By identifying the following goals, we can continue our work towards obtaining the carbon dots with higher efficiency for different applications:

- Development and scale-up of methods giving high product yield, showing an open gateway for industrial applications.
- Discovering precursors adhering to sustainability and green chemistry metrics, thus enabling the achievement of atom economy, carbon economy, and energy efficacy.
- Development of Carbon dots with specific hetero atom doping to obtain higher optical quantum yield and tailored luminescence properties.
- Creative functionalization with suitable organic moieties is expected to increase the optical quantum efficiency, thereby giving high-effulgent Carbon dots.
- Successful nanocomposite preparation will help us to attain new standards of efficient materials.
- Discovering other multiple applications of the Carbon dots and their composites in different fields.

REFERENCES

Author's articles

[BP1] **R. Blessy Pricilla**, David Skoda, Pavel Urbanek, Michal Urbanek, Pavol Suly, Eva Domincova Bergerova and Ivo Kuritka, Unravelling the highly efficient synthesis of individual carbon nanodots from casein micelles and the origin of their competitive constant-bluered wavelength shift luminescence mechanism for versatile applications, *RSC Adv.*, 2022,12, 16277-16290. <https://doi.org/10.1039/D2RA01911F>

[BP2] **R. Blessy Pricilla**, Moorthy Maruthapandi, Arulappan Durairaj, Ivo Kuritka, John H.T.Luong, Aharon Gedanken, Biomass-derived Carbon dots and their coated surface as a potential antimicrobial agent, *Biomass Conv. Bioref.* (2023). <https://doi.org/10.1007/s13399-023-03968-6>

Other references

[1] XU, Xiaoyou, RAY, Robert, GU, Yunlong, PLOEHN, Harry J., GEARHEART, Latha, RAKER, Kyle and SCRIVENS, Walter A. Electrophoretic Analysis and Purification of Fluorescent Single-Walled Carbon Nanotube Fragments. *Journal of the American Chemical Society*, vol. 126, (2004) no. 40, pp. 12736-12737. ISSN 0002-7863.

[2] SCIORTINO, Alice, CANNIZZO, Andrea and MESSINA, Fabrizio. Carbon Nanodots: A Review—From the Current Understanding of the Fundamental Photophysics to the Full Control of the Optical Response. *C*, vol. 4, (2018) no. 4, pp. 67. ISSN 2311-5629.

[3] QU, S. N., WANG, X. Y., LU, Q. P., LIU, X. Y. and WANG, L. J. A Biocompatible Fluorescent Ink Based on Water-Soluble Luminescent Carbon Nanodots. *Angewandte Chemie-International Edition*, vol. 51, (2012) no. 49, pp. 12215-12218. ISSN 1433-7851.

[4] ZHENG, Jing-xia, LIU, Xing-hua, YANG, Yong-zhen, LIU, Xu-guang and XU, Bing-she. Rapid and green synthesis of fluorescent carbon dots from starch for white light-emitting diodes. *New Carbon Materials*, vol. 33, (2018) no. 3, pp. 276-288. ISSN 2097-1605.

[5] GUO, Jiazhuang, LI, He, LING, Luting, LI, Ge, CHENG, Rui, LU, Xuan, XIE, An-Quan, LI, Qing, WANG, Cai-Feng and CHEN, Su. Green Synthesis of Carbon Dots toward Anti-Counterfeiting. *ACS Sustainable Chemistry & Engineering*, vol. 8, (2020) no. 3, pp. 1566-1572. ISSN 2168-0485.

- [6] LU, Wenjing, GONG, Xiaojuan, YANG, Zhenhua, ZHANG, Yuexia, HU, Qin, SHUANG, Shaomin, DONG, Chuan and CHOI, Martin M. F. High-quality water-soluble luminescent carbon dots for multicolor patterning, sensors, and bioimaging. *RSC Advances*, vol. 5, (2015) no. 22, pp. 16972-16979. ISSN 2046-2069.
- [7] STEPANIDENKO, Evgeniia A., USHAKOVA, Elena V., FEDOROV, Anatoly V. and ROGACH, Andrey L. Applications of Carbon Dots in Optoelectronics. *Nanomaterials*, vol. 11, (2021) no. 2, pp. 364. ISSN 2079-4991.
- [8] OMAR, Nur A., FEN, Yap W., IRMAWATI, Ramli, HASHIM, Hazwani S., RAMDZAN, Nur S. and FAUZI, Nurul I. A Review on Carbon Dots: Synthesis, Characterization and Its Application in Optical Sensor for Environmental Monitoring. Online. *Nanomaterials*, 2022, vol. 12, no. 14. ISSN 2079-4991.
- [9] ARAB, Solmaz, MASOUM, Saeed and SEYED HOSSEINI, Elahe. Engineering the Synthesis of Luminescent Carbon Dots With Ultra High-Quantum Yield Using Experimental Design Approach in Order to Develop Sensing Applications. *IEEE Sensors Journal*, vol. 20, (2020), pp. 1705-1711. ISSN 1558-1748.
- [10] MOHAMMADI, Susan, MOHAMMADI, Somayeh and SALIMI, Abdollah. A 3D hydrogel based on chitosan and carbon dots for sensitive fluorescence detection of microRNA-21 in breast cancer cells. *Talanta*, vol. 224, (2021), pp. 121895. ISSN 0039-9140.
- [11] GHOSH, Subhadeep, GUL, Anam Rana, PARK, Chan Yeong, XU, Ping, BAEK, Seung Hoon, BHAMORE, Jigna R., KIM, Min Woo, LEE, Min, KAILASA, Suresh Kumar and PARK, Tae Jung. Green synthesis of carbon dots from *Calotropis procera* leaves for trace level identification of isoprothiolane. *Microchemical Journal*, vol. 167, (2021), pp. 106272. ISSN 0026-265X.
- [12] MARGRAF, Johannes T., STRAUSS, Volker, GULDI, Dirk M. and CLARK, Timothy. The Electronic Structure of Amorphous Carbon Nanodots. *The Journal of Physical Chemistry B*, vol. 119, (2015) no. 24, pp. 7258-7265. ISSN 1520-6106.
- [13] KADIYALA, Nalinee Kanth, MANDAL, Badal Kumar, RANJAN, Shivendu and DASGUPTA, Nandita. Bioinspired gold nanoparticles decorated reduced graphene oxide nanocomposite using *Syzygium cumini* seed extract: Evaluation of its biological applications. *Materials Science and Engineering: C*, vol. 93, (2018), pp. 191-205. ISSN 0928-4931.
- [14] KUMAR, Pawan, DUA, Shweta, KAUR, Ravinder, KUMAR, Mahesh and BHATT, Geeta. A review on advancements in carbon quantum dots and their

application in photovoltaics. *RSC Advances*, vol. 12, (2022) no. 8, pp. 4714-4759. ISSN 2046-2069.

[15] MANSURIYA, Bhargav D. and ALTINTAS, Zeynep. Carbon Dots: Classification, Properties, Synthesis, Characterization, and Applications in Health Care—An Updated Review (2018–2021). Online. *Nanomaterials*, 2021, vol. 11, no. 10. ISSN 2079-4991.

[16] SHARMA, Anirudh and DAS, Joydeep. Small molecules derived carbon dots: synthesis and applications in sensing, catalysis, imaging, and biomedicine. *Journal of Nanobiotechnology*, vol. 17, (2019) no. 1, pp. 92. ISSN 1477-3155.

[17] REYES, Delfino, CAMACHO, Marco, CAMACHO, Miguel, MAYORGA, Miguel, WEATHERS, Duncan, SALAMO, Greg, WANG, Zhiming and NEOGI, Arup. Laser Ablated Carbon Nanodots for Light Emission. *Nanoscale Research Letters*, vol. 11, (2016) no. 1, pp. 424. ISSN 1556-276X.

[18] WANG, Chen- I., WU, Wei-Cheng, PERIASAMY, Arun Prakash and CHANG, Huan-Tsung. Electrochemical synthesis of photoluminescent carbon nanodots from glycine for highly sensitive detection of hemoglobin. *Green Chemistry*, vol. 16, (2014) no. 5, pp. 2509-2514. ISSN 1463-9262.

[19] CHAO-MUJICA, F. J., GARCIA-HERNÁNDEZ, L., CAMACHO-LÓPEZ, S., CAMACHO-LÓPEZ, M., CAMACHO-LÓPEZ, M. A., REYES CONTRERAS, D., PÉREZ-RODRÍGUEZ, A., PEÑA-CARAVACA, J. P., PÁEZ-RODRÍGUEZ, A., DARIAS-GONZALEZ, J. G., HERNANDEZ-TABARES, L., ARIAS DE FUENTES, O., PROKHOROV, E., TORRES-FIGUEREDO, N., REGUERA, E. and DESDIN-GARCÍA, L. F. Carbon quantum dots by submerged arc discharge in water: Synthesis, characterization, and mechanism of formation. *Journal of Applied Physics*, vol. 129, (2021) no. 16, pp. ISSN 0021-8979.

[20] WANG, Q., LIU, X., ZHANG, L. and LV, Y. Microwave-assisted synthesis of carbon nanodots through an eggshell membrane and their fluorescent application. *Analyst*, vol. 137, (2012) no. 22, pp. 5392-5397. ISSN 0003-2654.

[21] AMJAD, Mishal, IQBAL, Maheen, FAISAL, Amir, JUNJUA, Arshad Mahmood, HUSSAIN, Irshad, HUSSAIN, Syed Zajif, GHRAMH, Hamed A., KHAN, Khalid Ali and JANJUA, Hussnain Ahmed. Hydrothermal synthesis of carbon nanodots from bovine gelatin and PHM3 microalgae strain for anticancer and bioimaging applications. *Nanoscale Advances*, vol. 1, (2019) no. 8, pp. 2924-2936. ISSN 2516-0230.

[22] SIDDIQUE, Abu Bakar, PRAMANICK, Ashit Kumar, CHATTERJEE, Subrata and RAY, Mallar. Amorphous Carbon Dots and their Remarkable Ability

to Detect 2,4,6-Trinitrophenol. *Scientific Reports*, vol. 8, (2018) no. 1, pp. 9770. ISSN 2045-2322.

[23] PARK, Y., YOO, J., LIM, B., KWON, W. and RHEE, S. W. Improving the functionality of carbon nanodots: doping and surface functionalization. *Journal of Materials Chemistry A*, vol. 4, (2016) no. 30, pp. 11582-11603. ISSN 2050-7488.

[24] AI, Lin, YANG, Yisen, WANG, Boyang, CHANG, Junbiao, TANG, Zhiyong, YANG, Bai and LU, Siyu. Insights into photoluminescence mechanisms of carbon dots: advances and perspectives. *Science Bulletin*, vol. 66, (2021) no. 8, pp. 839-856. ISSN 2095-9273.

[25] CAYUELA, A., SORIANO, M. L., CARRILLO-CARRIÓN, C. and VALCÁRCEL, M. Semiconductor and carbon-based fluorescent nanodots: the need for consistency. *Chemical Communications*, vol. 52, (2016) no. 7, pp. 1311-1326. ISSN 1359-7345.

[26] YAO, Bowen, HUANG, Hui, LIU, Yang and KANG, Zhenhui. Carbon Dots: A Small Conundrum. *Trends in Chemistry*, vol. 1, (2019) no. 2, pp. 235-246. ISSN 2589-5974.

[27] ZHU, Shoujun, SONG, Yubin, ZHAO, Xiaohuan, SHAO, Jieren, ZHANG, Junhu and YANG, Bai. The photoluminescence mechanism in carbon dots (graphene quantum dots, carbon nanodots, and polymer dots): current state and future perspective. *Nano Research*, vol. 8, (2015) no. 2, pp. 355-381. ISSN 1998-0000.

[28] CARBONARO, Carlo Maria, CORPINO, Riccardo, SALIS, Marcello, MOCCI, Francesca, THAKKAR, Swapneel Vijay, OLLA, Chiara and RICCI, Pier Carlo. On the Emission Properties of Carbon Dots: Reviewing Data and Discussing Models. *C*, vol. 5, (2019) no. 4, pp. 60. ISSN 2311-5629.

[29] STEPANIDENKO, Evgeniia A., AREFINA, Irina A., KHAVLYUK, Pavel D., DUBAVIK, Aliaksei, BOGDANOV, Kirill V., BONDARENKO, Daniil P., CHEREVKOV, Sergei A., KUNDELEV, Evgeny V., FEDOROV, Anatoly V., BARANOV, Alexander V., MASLOV, Vladimir G., USHAKOVA, Elena V. and ROGACH, Andrey L. Influence of the solvent environment on luminescent centers within carbon dots. *Nanoscale*, vol. 12, (2020) no. 2, pp. 602-609. ISSN 2040-3364.

[30] ZHANG, Hao, YOU, Jiajian, WANG, Jiahui, DONG, Xuezhe, GUAN, Ruifang and CAO, Duxia. Highly luminescent carbon dots as temperature sensors and “off-on” sensing of Hg²⁺ and biothiols. *Dyes and Pigments*, vol. 173, (2020), pp. 107950. ISSN 0143-7208.

- [31] JIANG, Lei, DING, Haizhen, LU, Siyu, GENG, Ting, XIAO, Guanjun, ZOU, Bo and BI, Hong. Photoactivated Fluorescence Enhancement in F,N-Doped Carbon Dots with Piezochromic Behavior. *Angewandte Chemie International Edition*, vol. 59, (2020) no. 25, pp. 9986-9991. ISSN 1433-7851.
- [32] ZHU, Panpan, TAN, Kejun, CHEN, Qian, XIONG, Jie and GAO, Lixia. Origins of Efficient Multiemission Luminescence in Carbon Dots. *Chemistry of Materials*, vol. 31, (2019) no. 13, pp. 4732-4742. ISSN 0897-4756.
- [33] YU, Jingjing, LIU, Chang, YUAN, Kang, LU, Zunming, CHENG, Yahui, LI, Lanlan, ZHANG, Xinghua, JIN, Peng, MENG, Fanbin and LIU, Hui. Luminescence Mechanism of Carbon Dots by Tailoring Functional Groups for Sensing Fe³⁺ Ions. Online. *Nanomaterials*, 2018, vol. 8, no. 4. ISSN 2079-4991.
- [34] LIU, Cui, BAO, Lei, YANG, Mengli, ZHANG, Song, ZHOU, Miaomiao, TANG, Bo, WANG, Baoshan, LIU, Yufei, ZHANG, Zhi-Ling, ZHANG, Bing and PANG, Dai-Wen. Surface Sensitive Photoluminescence of Carbon Nanodots: Coupling between the Carbonyl Group and π -Electron System. *The Journal of Physical Chemistry Letters*, vol. 10, (2019) no. 13, pp. 3621-3629. ISSN 1948-7185.
- [35] GAN, Zhixing, WU, Xinglong and HAO, Yanling. The mechanism of blue photoluminescence from carbon nanodots. *CrystEngComm*, vol. 16, (2014) no. 23, pp. 4981-4986. ISSN 1466-8033.
- [36] KRYSMANN, Marta J., KELARAKIS, Antonios, DALLAS, Panagiotis and GIANNELIS, Emmanuel P. Formation Mechanism of Carbogenic Nanoparticles with Dual Photoluminescence Emission. *Journal of the American Chemical Society*, vol. 134, (2012) no. 2, pp. 747-750. ISSN 0002-7863.
- [37] GUPTA, Isha, SINGH, Sitender, BHAGWAN, Shri and SINGH, Devender. Rare earth (RE) doped phosphors and their emerging applications: A review. *Ceramics International*, vol. 47, (2021) no. 14, pp. 19282-19303. ISSN 0272-8842.
- [38] LIU, Yang, ZHAN, Ge, LIU, Zhi-Wei, BIAN, Zu-Qiang and HUANG, Chun-Hui. Room-temperature phosphorescence from purely organic materials. *Chinese Chemical Letters*, vol. 27, (2016) no. 8, pp. 1231-1240. ISSN 1001-8417.
- [39] ZUO, Kun, LIU, Weifeng, LIU, Xiaojing and LIU, Xuguang. Phosphorescence of Carbon Dot: The Intrinsic Mechanism and Recent Progress. *Carbon Trends*, vol. 12, (2023), pp. 100278. ISSN 2667-0569.
- [40] PENG, Chenxi, CHEN, Xue, CHEN, Meiling, LU, Shenci, WANG, Yu, WU, Suli, LIU, Xiaowang and HUANG, Wei. Afterglow Carbon Dots: From

Fundamentals to Applications. *Research*, vol. 2021, (2021), pp. 1-27. ISSN 2639-5274.

[41] LI, Qijun, ZHOU, Ming, YANG, Mingyang, YANG, Qingfeng, ZHANG, Zhixun and SHI, Jing. Induction of long-lived room temperature phosphorescence of carbon dots by water in hydrogen-bonded matrices. *Nature Communications*, vol. 9, (2018) no. 1, pp. 734. ISSN 2041-1723.

[42] FENG, Qi, XIE, Zhigang and ZHENG, Min. Room temperature phosphorescent carbon dots for latent fingerprints detection and in vivo phosphorescence bioimaging. *Sensors and Actuators B: Chemical*, vol. 351, (2022), pp. 130976. ISSN 0925-4005.

[43] TIAN, Zhen, LI, Di, USHAKOVA, Elena V., MASLOV, Vladimir G., ZHOU, Ding, JING, Pengtao, SHEN, Dezhen, QU, Songnan and ROGACH, Andrey L. Multilevel Data Encryption Using Thermal-Treatment Controlled Room Temperature Phosphorescence of Carbon Dot/Polyvinylalcohol Composites. *Advanced Science*, vol. 5, (2018) no. 9, pp. 1800795. ISSN 2198-3844.

[44] ZONG, Siyu, WANG, Bolun, YIN, Xin, MA, Wenyan, ZHANG, Jiani and LI, Jiyang. Calcination-controlled fabrication of carbon dots@zeolite composites with multicolor fluorescence and phosphorescence. *Nano Research*, vol. 15, (2022) no. 10, pp. 9454-9460. ISSN 1998-0000.

[45] SU, Qian and YANG, Xiaoming. Promoting Room Temperature Phosphorescence through Electron Transfer from Carbon Dots to Promethazine. *ACS Applied Materials & Interfaces*, vol. 13, (2021) no. 34, pp. 41238-41248. ISSN 1944-8244.

[46] XIE, Y., ZHENG, J., WANG, Y., WANG, J., YANG, Y., LIU, X. and CHEN, Y. One-step hydrothermal synthesis of fluorescence carbon quantum dots with high product yield and quantum yield. *Nanotechnology*, vol. 30, (2019) no. 8, pp. 085406. ISSN 0957-4484.

LIST OF SCHEMES

Scheme 1. Schematic representation of precursors, synthesis approaches, and structure of CDs (Own courtesy).....	13
Scheme 2. Schematic representation of top down and bottom up approaches .	14
Scheme 3. Schematic representation of the various PL mechanism models responsible for the photoluminescence of CDs (Own courtesy).....	16

Scheme 4. Schematic representation of the selective milestones in the development of afterglow CDs in the last decade (adopted from [58] under CC BY 4.0).....	19
Scheme 5. Scheme indicating the research goals for the doctoral work	23
Scheme 6. Schematic representation of the formation of CND from Casein micelles (Own courtesy).	Chyba! Záložka není definována.
Scheme 7. (a) Schematic representation of the synthesis of carbon dots and their antibacterial application (b) Schematic representation of the textile coated carbon dots and their antibacterial application [BP2](Own courtesy).	Chyba! Záložka není definována.
Scheme 8. Scheme illustrating the production of RTP Carbon dots	Chyba! Záložka není definována.
Scheme 9. Scheme representing the phosphorescence and fluorescence mechanism of self matrix RTP CDs (Own courtesy).	Chyba! Záložka není definována.

LIST OF ABBREVIATIONS AND SYMBOLS

BA	Boric acid
CDs	Carbon dots
CND	Carbon Nanodots
CQD	Carbon Quantum Dots
EC	<i>Escherichia coli</i>
EG	Ethylene glycol
FTIR	Fourier Transform Infrared
h ν	Photon energy
KP	<i>Klebsiella pneumonia</i>
LUMO	Lowest unoccupied molecular orbital
m_{BA}	mass of the boric acid
m_{CA}	mass of the casein
m_{CND}	mass of the carbon nanodots
m_{PVP}	mass of the PVP
m_{PVP}	mass of the 1, 10 phenanthroline
m_{RTPCDs}	mass of the room temperature phosphorescence carbon dots
PET	Polyethylene terephthalate
PL	Photoluminescence
PVP	Polyvinylpyrrolidone
RTP	Room Temperature Phosphorescence
SA	<i>Staphylococcus aureus</i>
SCL	<i>Syzygium cumini L.</i>
SE	<i>Staphylococcus epidermidis</i>
SEBS	Styrene-ethylene-butylene-styrene
TEM	Transmission Electron Microscope
UV-Vis	Ultraviolet visible
WAT	Weak absorption tail
WCA	Water contact angle
XPS	X-ray photoelectron spectroscopy

α	Absorbance
CB ₁	Conduction Band 1
CB ₂	Conduction Band 2
T ₁	Tauc region 1
T ₂	Tauc region 2
MS	Molecular state
U	Urbach energy
Eg ₁	Energy gap 1
Eg ₂	Energy gap 2

CURRICULUM VITAE

Name	R. Blessy Pricilla
Date of birth	26/10/1995
Place of birth	Tamil Nadu, India
Permanent address	IUAC, Sumeru-1, Aruna asaf ali marg, New Delhi- 110067, India
Affiliation	Centre of Polymer Systems, Tomas Bata University in Zlín, třída Tomáše Bati 5678, 760 01, Zlín, Czech Republic
Email	pricilla@utb.cz
Education	2019- to date Center of Polymer Systems, Tomas Bata University in Zlin , Czech Republic Ph.D. studies in Nanotechnology and advanced Materials 2013-2018 M.Sc Nanoscience and Technology Karunya Institute of Science and Technology Coimbatore, India

INTERNSHIP ABROAD

Three month internship in **Bar Illan University, Israel** on the topic “*Synthesis and coating of Carbon Dots on Textiles for antibacterial applications*” under the guidance of Professor **Aharon Gedanken**

Languages known: English, Tamil, Hindi

LIST OF PUBLICATIONS AND PROJECTS

1. **R. Blessy Pricilla**, Moorthy Maruthapandi, Arulappan Durairaj, Ivo Kuritka, John H.T.Luong, Aharon Gedanken, Biomass-derived Carbon dots and their coated surface as a potential antimicrobial agent, Biomass Conv. Bioref. (2023). <https://doi.org/10.1007/s13399-023-03968-6>
2. **R. Blessy Pricilla**, David Skoda, Pavel Urbanek, Michal Urbanek, Pavol Suly, Eva Domincova Bergerova and Ivo Kuritka, Unravelling the highly efficient synthesis of individual carbon nanodots from casein micelles and the origin of their competitive constant-bluered wavelength shift luminescence mechanism for versatile applications, RSC Adv., 2022,12, 16277-16290. <https://doi.org/10.1039/D2RA01911F>
3. **R. Blessy Pricilla**, Pavel Urbanek, Jakub Sevcik, David Skoda, Jan Antos, Lukas Munster, and Ivo Kuritka, Exploring the Ultralong Lifetime of Self Matrix 1,10 Phenanthroline and Boron-based Room Temperature Phosphorescence Carbon Dots for Multiple Applications- **(To be submitted to advanced optical materials-wiley)**

CONFERENCES ATTENDED

- Proceedings 12th International Conference on Nanomaterials - Research & Application, Brno, Czech Republic.-2020
R. Blessy Pricilla; David Skoda; Pavel Urbanek; Michal Urbanek and Ivo Kuritka; Facile microwave –assisted synthesis of casein derived carbon nanodots: DOI : <https://doi.org/10.37904/nanocon.2020.3681>
- 33rd International Conference on Diamond and Carbon Materials, Palau de Congressos de Palma, Mallorca, Spain -2023
Poster Presentation on the Topic “Casein based carbon nanodots as the sensor probe for selective detection of Fe³⁺ ions in aqueous environment”

PROJECTS

IGA/CPS/2020/003 - "Preparation and characterization of nanoparticles for advanced applications", member of the team.

IGA/CPS/2021/002 - "Preparation and characterization of nanocomposite systems", member of the team.

RP/CPS/2020/006 - "Smart nanomaterials: from basics to application", member of the team.

IGA/CPS/2022/002- "Preparation and characterization of advanced nanocomposite systems", member of the team.

IGA/CPS/2023/006- "Preparation and characterization of advanced nanocomposite systems", member of the team.

RP/CPS/2022/007- Safe and sustainable-by design advanced material systems and technologies- member of the team.

R. Blessy Pricilla, M.Sc., Ph.D.

Preparation and characterization of carbon dots for versatile applications

Příprava a charakterizace mnohostranně aplikovatelných uhlíkových teček

Doctoral Thesis Summary

Tomas Bata University in Zlin

Nam. T.G. Masaryka 555, 760 01, Zlin

Edition: published electronically

Typesetting by: R. Blessy Pricilla

This publication has not undergone any proofreading or editorial review

Publication year: 2024

First Edition

ISBN 978-80-7678-241-9