SYNTHESIS OF BIOMOLECULE DERIVED CARBON DOTS

M.Sc. Thesis

by

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DISCIPLINE OF CHEMISTRY

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A THESIS

Submitted in partial fulfillment of the

requirements for the award of the degree

of

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INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **SYNTHESIS OF BIOMOLECULES DERIVED CARBON DOTS** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DISCIPLINE OF CHEMISTRY, INDIAN INSTITUTE OF TECHNOLOGY INDORE**, is an authentic record of my own work carried out during the time period **JULY 2020** to **JUNE 2021** under the supervision of **Dr. Tridib K. Sarma,** Associate professor, Discipline of Chemistry, Indian Institute of Technology Indore.

The matter presented in the thesis has not been submitted by me for the award of any other degree of this or any other institute.

Ayushi Srivastava

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Dr. Tridib K. Sarma

Ayushi Srivastava has successfully given her M.Sc. Oral Examination held on 08.06.2021

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09/06/2021

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Date: 11.06.2021

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Ayushi Srivastava

M.Sc. 2^{nd} Year

Dedicated to

My Family, Friends and teachers

ABSTRACT

In recent years, luminescent carbon dots have gained widespread attention because of their small size, low cost and relatively strong fluorescence properties. These carbon quantum dots are widely used in various potential, biomedical, physical, electronic and optical applications; such as light emitting diodes, chemical sensors, solar cells, bioimaging and electrocatalysis etc. Carbon quantum dots can be synthesized by multiple methods such as hydrothermal method, microwave pyrolysis, arc discharge method and electrochemical synthesis. In this report different properties, preparation methods and applications of CDs will be summarized.

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NOMENCLATURE

Nm	Nanometer
mL	Milliliter
Mg	Milligram
G	Gram
M	Molar

ACRONYMS

NaOH	Sodium Hydroxide
aq.	Aqueous
Rt	Room temperature
Min	Minute
UV-Vis	Ultra violet- Visible
GL	Glucose
Adeno	Adenosine
Cy	Cytidine
PL	Photoluminescence
CDs	Carbon dots

Chapter 1

Introduction

In recent years, carbon dots with below 10 nm size are considered as a new member to the family of fluorescent carbon-based nanomaterials. Carbon quantum dots (CQDs)/carbon dots (CDs) are widely used as metal-based quantum dots alternatives because of their good biocompatibility, excellent fluorescent properties, tuneable photoluminescence, low cost, low toxicity, high stability, small sizes and high quantum yield; which provides wide spectrum of applications in the field of science such as potential applications, biomedical applications, application in anticounterfeiting and in optical electronic devices like sensors.[1-10] Fluorescent carbon nano particles were first reported accidentally in 2004 when researchers purified CNTs (single-walled).[11] Again, using laser ablation method, nanoscale CDs were synthesised for the first time in 2006 by Sun and co-workers but the QY was very low (about 10%).[12] In 2013, using hydrothermal method and ethylenediamine and citric acid as precursors, Yang’s group synthesised carbon dots with polymer like structures and properties and this time the quantum yield was up to 80% which was the highest value of quantum yield of carbon dots.[13] Thereafter, many researchers developed lots of strategies and technologies for achieving high performance carbon dots. As of now, according to different properties and mechanism of formation, carbon dots are mainly classified into three categories; Carbonized polymer dots, Graphene carbon dots and Carbon quantum dots. Third category of CDs are widely known nowadays because of their strong fluorescence characteristics and small size with zero dimensions. In the field of energy, nowadays carbon quantum dots are playing a very important role because of their wide potential applications. In recent days, carbon quantum dots are employed as photo/electro catalysts, CD based light emitting diodes (CLEDS), rechargeable batteries, supercapacitors, fuel cells and solar cells because of their high electron mobility, some unique optical properties, low cost and environmental friendliness. As photocatalysts carbon dots are used for pollutants degradation, carbon di oxide reduction, water splitting and a few chemical reactions in solar energy conversion. For enhancing catalytic activity and improving durability, carbon dots are combined with some metals, metal-based semiconductors or other carbon materials. For enhancing carbon dots electrocatalytic properties, researchers use heteroatom doping. -OH, -COOH, -NH2 etc. these are some of the abundant functional groups which act as active coordination site on the surface of carbon dots with transition metal ions. During electrocatalytic process, heteroatom (N, O, S, P etc.) doped carbon quantum dots increase the electrocatalytic performances by promoting favourable charge transfer. In recent times, researchers are widely using heteroatom doping for carbon nano particles for improvement of their electronic and luminescent optical properties. [7,14] Nowadays CDs are often used as photosensitizers in the process of waste-water treatment and water splitting. Due to low cost, environment friendliness and adjustable PL colours, carbon dots are considered as a good replacement of toxic metal-based semiconductor quantum dots in light emitting diodes. [15] Carbon dots play important roles in solar cells which include separation of photogenerated electron-hole pair facilitation, improvement in device environmental stability and light absorption range broadening. Carbon dots can improve cell efficiency and dramatically increase stability over high temp and humidity and can convert the harmful UV lights into visible lights. [16] CDs are used for improvement in electrochemical performance of supercapacitors and for that CDs are hybridized with polymers, other carbon materials or metal oxides which enhances their practical applications. [17] In these days, rechargeable batteries are known for their effectiveness in energy storage technologies. Via surface engineering, carbon dots create an excellent interface for intercalation between electrolytes and electrodes which provides more stability, more active sites and thus increases transfer and diffusion which improves electrochemical properties. [18] In this report, we shall introduce the physical and chemical properties, potential applications and synthetic methods of preparation such as microwave synthesis, laser ablation, hydrothermal synthesis, combustion oxidation, arc discharge method and thermal decomposition of the luminescent carbon quantum dots. Due to the simple set up and uniformity in outcome particle size with high quantum yield, hydrothermal method is one of the most commonly used method for carbon quantum dot synthesis whereas microwave pyrolysis is known as a well-established, simple and environmental-friendly preparation method of carbon dots rich in oxygen group, due to the commercialization and rapid synthesis. Laser ablation method is used to synthesize carbon dots with fluorescence properties, good water solubility and narrow size distribution. Limitations of this method are high cost and complicated operations. Large particle size of some carbon dots limits the arc discharge method of synthesis. [19,20,21]

Chapter2

EXPERIMENTAL SECTION

2.1 MATERIALS AND METHODS: D-Glucose, adenosine, cytidine and sodium hydroxide all chemicals and precursors were purchased from Sigma-Aldrich. In experiments, ultrapure water was used to dissolve all the precursors for solution preparation. Glucose and both N-CDs were synthesised by a one-step hydrothermal method in laboratory.

2.2 SYNTHESIS OF CARBON DOTS:

2.2.1 SYNTHESIS OF GLUCOSE CDs- Glucose CDs were prepared by a one-step hydrothermal method. 0.075 g D-GL was weighed and then dissolved in water (10 mL). pH (=10) was maintained using 1M NaOH solution. The obtained solution was then transferred into a cleaned Teflon lined autoclave and kept for heating in an oven for 6 hrs at temperature 140°C. After completion of heating, the solution was kept for cooling at rt and then centrifuged for 30 min at 10000 rpm and after that, centrifuged solution was dialysed for 24 hours.

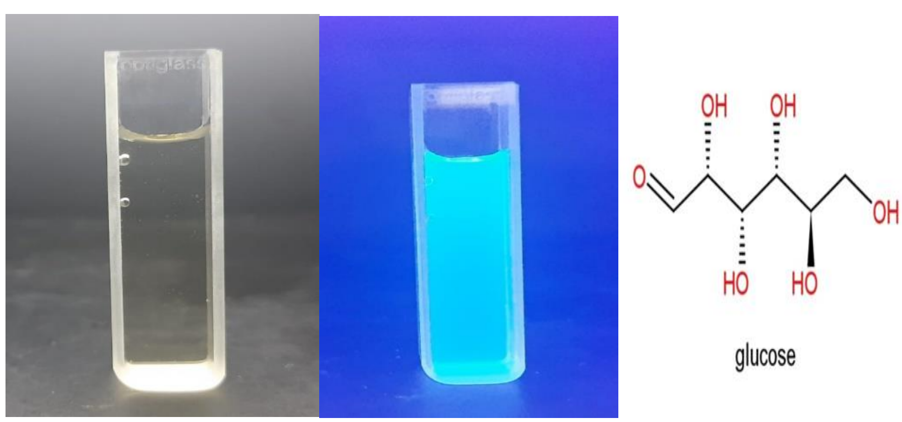
2.2.2 SYNTHESIS OF ADENOSINE CDs- N-doped adenosine CDs were synthesized by a one-step hydrothermal method. 0.0134 g of Adeno was weighed and then dissolved in ultrapure water (10 mL). The obtained solution was transferred into a cleaned Teflon lined autoclave and kept for heating in an oven for 9 hrs at temperature 200°C. After heating, the solution was kept for cooling at rt and centrifuged for 10 min at 10000 rpm. The brownish-yellow solution was obtained by removing the deposit in the centrifuge.

2.2.3 SYNTHESIS OF CYTIDINE CDs- N-doped cytidine CDs were synthesized by a one-step hydrothermal method. 0.0122 g of Cytidine was weighed and then dissolved in ultrapure water (10 mL). The obtained solution was then transferred into a cleaned Teflon lined autoclave and kept for heating in an oven for 9 hours at 200°C temperature. After that, the solution was kept for cooling at rt and then centrifuged for 10 min at 10000 rpm.

Two types of N-carbon dots were synthesized by one step hydrothermal method using Cytidine and adenosine as precursors.

1

2



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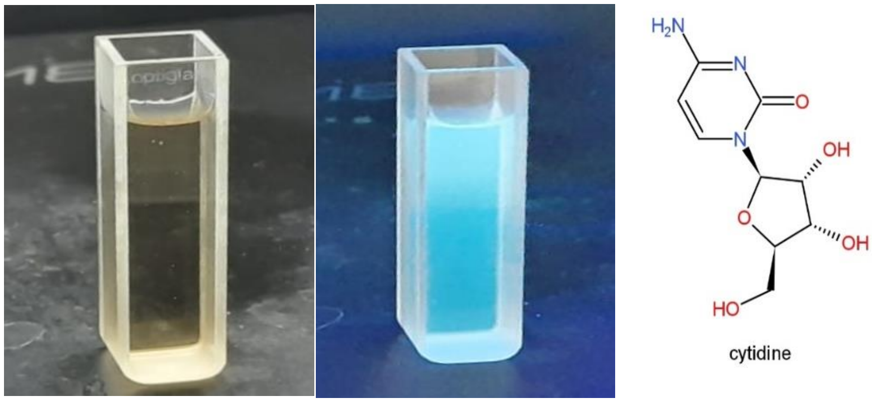

Figure: 1 Photographs and fluorescence photographs of 1) adenosine, 2) glucose and 3) cytidine CDs

Chapter 3

RESULTS AND DISCUSSION

3.1 CHARACTERIZATION OF SYNTHESIZED CDs:

All three CDs were synthesized by a one-step hydrothermal synthesis. Carbon dots are well known for their self-quenching effect also known as concentration quenching. When concentration becomes large, the decrease of fluorescence intensity is observed which leads to a red shift in fluorescence spectrum.

Fluorescence and UV Vis spectra, both were investigated for all the synthesized carbon dots using fluorescence spectrophotometer and UV-spectrophotometer. For the CDs, intense blue fluorescent lights were observed when we kept them in the UV chamber which can also be seen from the photographs 1b, 2b and 3b of the diluted carbon dot solutions. Photographs were taken with a smartphone.

The UV-vis absorption spectra of synthesized glucose CDs is shown in Figure 2. Absorption peaks at 280 nm indicates the n-π* transitions of C=O bonds. This peak cannot be seen in the spectra of D-glucose solution. With increase in hydrothermal duration, an increased absorbance of the C=O peak was observed.

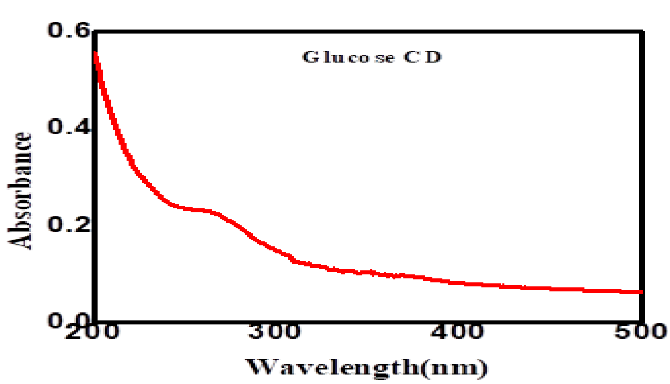

Figure:2 Absorption spectra of glucose CDs

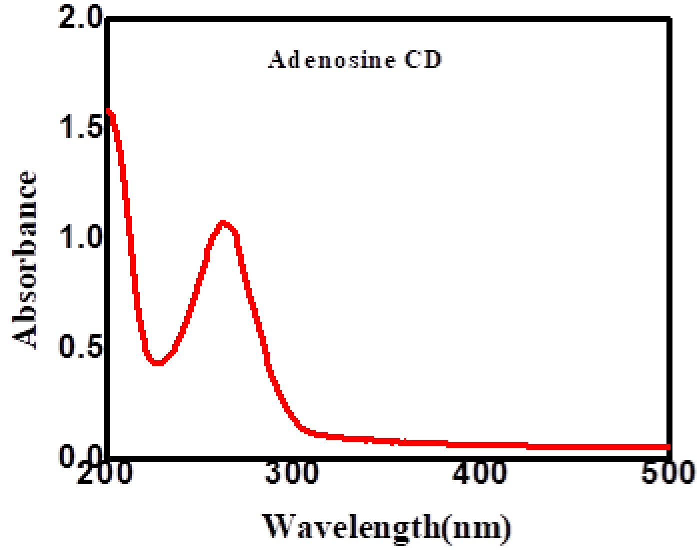

Figure:3 Absorption spectra of adenosine CDs

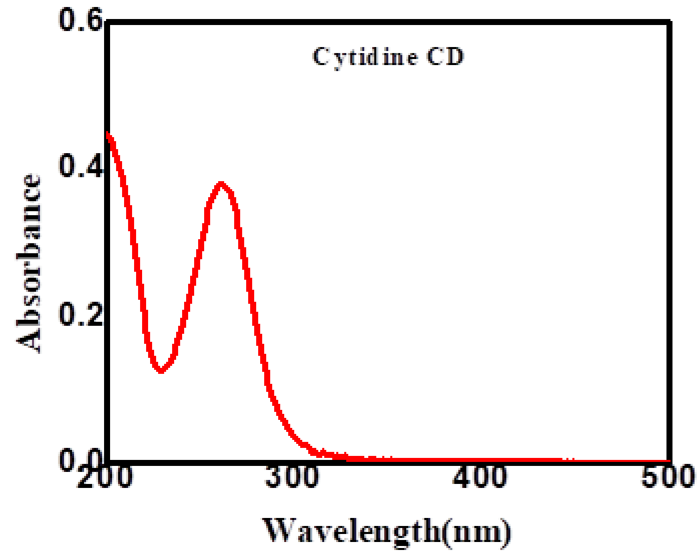

Figure:4 Absorption spectra of cytidine CDs

The UV-vis spectra of adenosine and cytidine CDs are shown in figure: 3 and 4 respectively. The slight shift in peaks of both the CDs were observed from their original substrates with peaks near 260 nm which suggested the conversion of those precursors into carbon dots. The spectra show a broad peak around 260-290 nm range for both carbon dots which indicate the typical n-π* C=O transition or absorption of an aromatic π system.

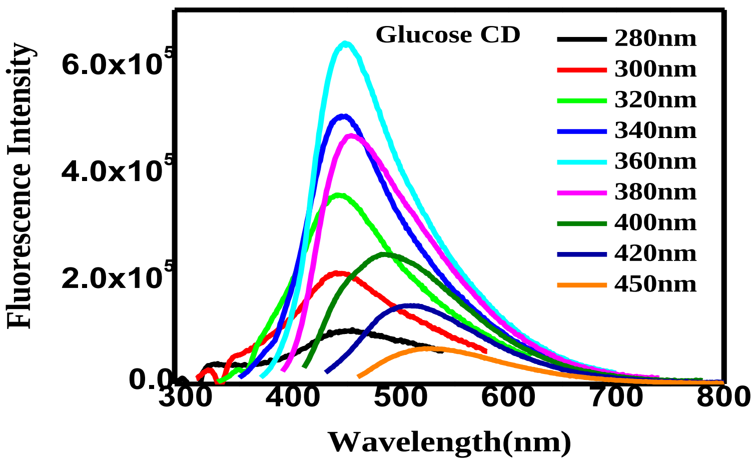

Figure:5 Fluorescence spectra of glucose carbon dots

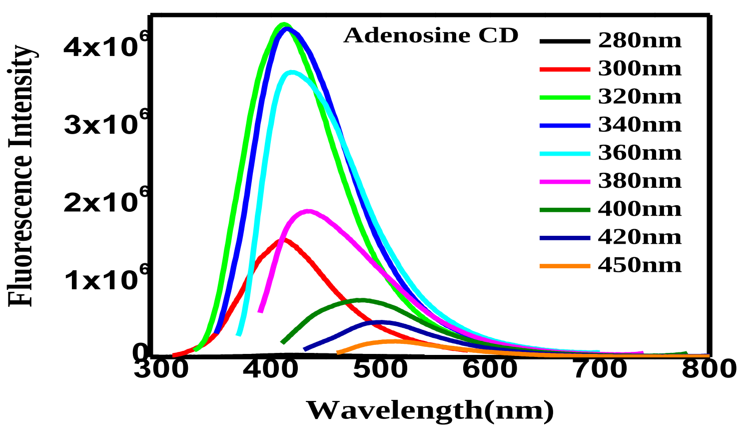

Figure:6 Fluorescence spectra of adenosine carbon dots

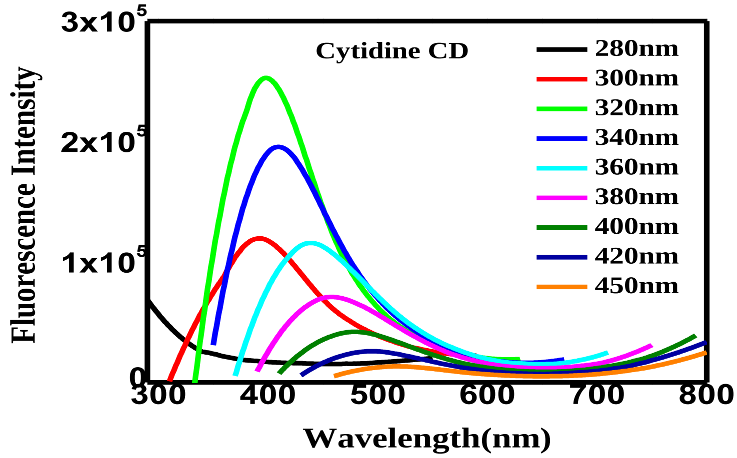

Figure:7 Fluorescence spectra of cytidine carbon dots

To understand the optical properties and applications of CDs, PL Studies were carried out. To further know the photoluminescence properties, the photoluminescence excitation and emission spectra of prepared CDs with different wavelengths were observed. Excitation dependent fluorescence can be seen under 300-400 nm range with intervals of 10 nm.

For glucose carbon dots an excitation peak was observed as shown in **Figure-8.** When excitation wavelength increases from 340 to 390 nm, a shift in emission peak to a longer wavelength can also be seen which is 498 nm from 451 nm. 360 nm was the optimum wavelength under which the maximum photoluminescence intensity was reached.

For adenosine and cytidine carbon dots, excitation peaks were observed at 330 nm wavelength. The emission peaks were observed at 410 nm wavelength, as shown in **Figure-9 and 10.**

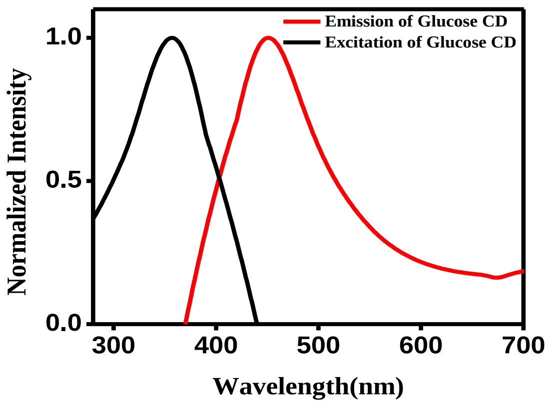

Figure: 8 Photoluminescence spectra of Glucose CDs,

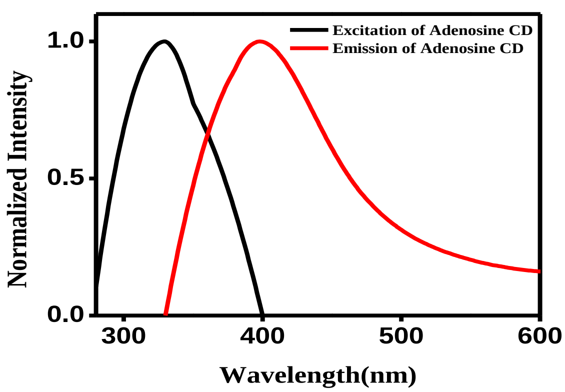

Figure:9 Photoluminescence spectra of adenosine CDs

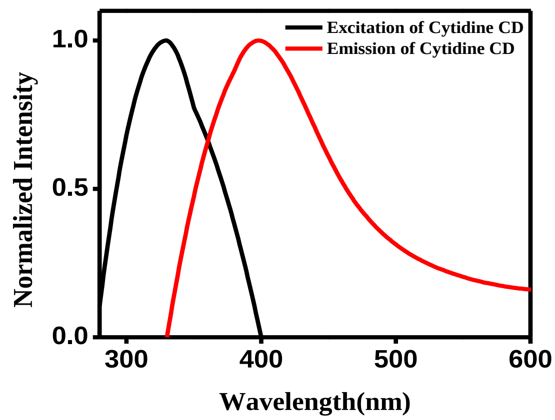

Figure:10 Photoluminescence spectra of cytidine CDs

3.2 Stability study of synthesized N-doped CDs:

Both the prepared N-doped carbon dots show great stability. To determine the photostability, the CDs were kept under the exposure of UV-light for 60 minutes. Under 365 nm, slight changes in fluorescence were observed which suggested that N-doped CDs exhibit good photostability. N-doped carbon dots are stable for 90 days if we kept them at 4°C. In high concentration media, N-doped CDs are quite stable. Change in pH can affect the fluorescence of N-doped carbon dots.

Chapter: 4
CONCLUSION

We prepared three types of fluorescent carbon dots using glucose, adenosine and cytidine biomolecules as precursors. Two types of N-CDs were synthesized using adenosine and cytidine as the precursors, individually. The three CDs were synthesised by one-step hydrothermal method and purification of glucose CDs were completed by dialysing using dialysis bags (24 hrs). No purification treatments were required for other two CDs. By using optical spectroscopy, we characterized the three carbon dots. The spectra showed shifted peaks for all the three carbon dot samples compared to precursors biomolecules. Due to difference in N-content of precursors and their final products, different fluorescent intensities were observed. These CDs, synthesised by the three biomolecules via eco-friendly procedure had shown good chemical and optical stabilities.

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