# ONE- POT SYNTHESIS OF FLUORESCENT CARBON DOTS FROM POTATO STARCH

**PROJECT REPORT**

**Submitted to**

**MAHATMA GANDHI UNIVERSITY, KOTTAYAM**

***In partial fulfillment of requirement for the award of degree of***

**MASTER OF SCIENCE IN CHEMISTRY**

**by**

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**DEPARTMENT OF CHEMISTRY**

**PAVANATMA COLLEGE, MURICKASSERY**

**2020-2022**

# CERTIFICATE

This is to certify that the project report entitled "**ONE-POT SYNTHESIS OF FLUORESCENT CARBON DOTS FROM POTATO STARCH**" is an authentic record of project work carried out by Ms. **Arya Venugopal (Reg No: 200011010683)** under the supervision and guidance of **Dr. Jithin Joy**, Assistant Professor, Department of Chemistry, Newman College ,Thodupuzha ,for partial fulfilment of requirements for the Master of Science in Chemistry under the faculty of Mahatma Gandhi University, Kottayam.


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# DECLARATION

It is hereby declared that, the work entitled: "***One-pot synthesis of fluorescent carbon dots from potato starch***" carried out by me under the supervision of Dr. Jithin Joy, Assistant professor, Newman College Thodupuzha, affiliated to Mahatma Gandhi University in partial fulfillment for the award of the Master of Science in Chemistry is a record of original project work done by me at Newman College Thodupuzha.

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# ABSTRACT

Carbon dots are novel zero-dimensional luminescent carbon based nanomaterials and represent a new form of nano carbon materials which have gained widespread attention in recent years especially in chemical sensors, bioimaging, nanomedicine, solar cells, LED and electrocatalysis. In this study a facile synthesis of fluorescence carbon dots(CDs) from potato starch was performed through hydrothermal treatment. The obtained CDs with quantum yield of 8.64% have good dispersibility due to the soluble functional groups on their surfaces. These are characterized by UV visible spectroscopy, Fluorescence spectroscopy , FTIR spectroscopy and also compensate for the deficiencies of traditional materials in terms of cytotoxicity, environmental and bio hazard.

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# CHAPTER 1 INTRODUCTION

Nanotechnology involves research and technology development at the atomic, molecular or macromolecular levels in the range of approximately 1-100nm to provide fundamental information about phenomenons and materials at the nanoscale. Basically nanotechnology is used to create structures, devices and systems that have novel properties and functions because of their size. The wide range of applications of nanotechnology includes medicine, electronics, military applications, computing, space science and many more.

Nanomaterials are cornerstones of nanoscience and nanotechnology. Nanomaterials are defined as a set of substances where at least one dimension is less than approximately or 100 nm. These materials are of great interest because at this scale, unique optical, magnetic, electrical and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine and other fields.

Luminescent carbon dots (CDs) represent a new form of nanocarbon materials which have gained widespread attention in recent years, especially in chemical sensors, bioimaging, nanomedicine, solar cells, light-emitting diodes(LED) and electrocatalysis. CDs can be prepared simply and inexpensively by multiple techniques such as the arc-discharge method, microwave pyrolysis, hydrothermal method and electrochemical synthesis. CDs show excellent physical and chemical properties like high crystallization, good dispersibility, photoluminescence properties. In particular, the small size, superconductivity, and rapid electron transfer of CDs endow the CDs-based composite with improved electrical conductivity and catalytic activity. Besides, CDs have abundant functional groups on the surface which could facilitate the preparation of multi-component electrical active catalysts. The interactions inside these multi-component catalysts may further enhance the catalytic performance by promoting charge transfer which plays an important role in electrochemistry.

## 1.1 FEATURES OF CARBON DOTS

Carbon dots(CDs) are novel zero-dimensional carbon-based nanomaterials known for their relatively small size and strong fluorescence characteristics. To make these materials fluorescent, their size and surface chemical groups must be carefully adjusted in order to finely tune the electronic structures . CDs not only inherit the excellent optical properties of traditional semiconductor quantum dots, but also compensate for the deficiencies of the traditional materials in terms of cytotoxicity, environmental and biohazard . In addition, CDs are also featured with good water solubility , chemical stability, photobleaching resistance , ease of surface functionalization and large scale preparation . Basically all nanosized materials that consist of mainly carbon skeleton can be called C-dots . They possess at least one dimension smaller than 10 nm in size and fluorescence as its characteristic properties . Among the electronic and physicochemical characteristics of CDs , their optical properties and their fluorescence emissions in particular have attracted increasing interest in recent years. For many years semiconductor quantum dots have been extensively investigated for their strong and tunable fluorescence emission properties, which enable their applications in biosensing and bioimaging. However, semiconductor quantum dots possess certain limitations such as high toxicity due to the use of heavy metals in their production . It is known that heavy metals are highly toxic even at relatively low levels , which may prove prohibitive to any clinical studies. This prompted the creation of CDs to replace semiconductor quantum dots due to their low toxicity, biocompatibility, low cost and chemical inertness in addition to having similar fluorescence properties.

The accidental discovery of CDs during the separation and purification of single-walled carbon nanotubes(SWCNTs) by Xu et al. in 2004 triggered subsequent studies to exploit the fluorescence properties of CDs and create a new class of viable fluorescent nanoparticles. Fluorescent carbon nanoparticles received their name “carbon quantum dots” in 2006 from Sun et al. who proposed a synthetic route to produce CDs with much enhanced fluorescence emissions via surface passivation. CDs are synthesized by two routes, namely the top-down route and the bottom-up route. CDs are typically quasi-spherical nanoparticles composed of amorphous to nanocrystalline cores with predominantly graphitic or turbostratic carbon (sp2 carbon) or graphene and graphene oxide sheets fused by diamond-like sp3 hybridized carbon insertions. Oxidized CDs contain

considerable amounts of carboxyl moieties at their surface. Depending on the synthetic route , the oxygen content in the oxidized CDs ranges from 5 to 50%(weight). Upon surface passivation , the fluorescence properties of CDs are enhanced. Surface functionalization also modifies their physical properties , like their solubility in aqueous and non-aqueous solvents.

Two classes of fluorescence emission mechanisms have been proposed for CDs , the first class of fluorescence emission mechanism is that of band gap transitions caused by conjugated pi-domains, while the second class involves more intricate origins associated with surface defects in CDs. For the first class of fluorescence mechanism, bandgap transitions arise from conjugated pi-domains which are isolated by creating sp2 hybridized islands rich in pi-electrons through the reduction of graphene oxides obtained by using Hummers method of oxidizing and exfoliating graphite flakes. They are created in a way that there are no pi-connections between the sp2 islands, because any pi-connections between the sp2 islands would lead to interisland quenching of desired fluorescence emissions. In this type of band gap transitions , single-layer graphene sheets have to be used to prevent interlayer quenching. The single-layer graphene sheets are used as precursors for electronically slicing into isolated pi-conjugated domains, which resemble large aromatic molecules with extended pi-conjugation of specific electronic energy band gap for optical absorption and fluorescence emissions. Such electronic transitions display strong absorption in the UV region, but weak or no fluorescence emissions. The strong absorption is likely due to light absorption by a large amount of high density pi-electrons in the sp2 hybridized islands, which form excitonic states while the weak emissions are possibly a result of quenching via radiationless relaxations to the ground state during exciton migration to energy traps.

The second class of the fluorescence mechanism arises from surface-related defective sites - generally any sites that have non-perfect sp2 domains will result in surface energy traps. Both sp2 and sp3 hybridized carbons and other functionalized surface defects, such as carbonyl-related localized electronic states, present in CDs contribute to their multicolor emissions that are concentrated in the blue and green regions of the visible light spectrum. These surface defects behave like aromatic molecules that are individually incorporated into solid hosts, exhibiting multicolor surface defects with different excitation and emission properties. The bright surface defect-derived fluorescence of CDs is due to the recombination of electron-hole pairs in the

strongly localized pi and pi * electronic levels of the sp2 site.

The advances of science and its conjugation with interdisciplinary fields emerged in carbon dots making, their controlled characterization and applications into faster, cheaper as well as more reliable products in various scientific domains. The understanding of the generation process, control on making processes and selected applications of carbon dots such as energy storage, environmental monitoring, catalysis, drug delivery, drug targeting and other biomedical applications etc. are among the most promising applications of carbon dots and thus a thrust area of research today.

## 1.2 STRUCTURE OF CARBON DOTS

Carbon quantum dots from different structures may be either graphitic or amorphous. The size of CQDs can be tuned by different nanocomposites. CDs are characteristically quasi spherical carbon nanoparticles composed of amorphous to crystalline carbon bases. It is primarily made up of sp2-graphitic carbon or graphene and graphene oxide sheets combined through the insertion of sp3-hybridized carbon that exhibits fluorescence properties. There are two main morphologies of carbon dots;disc shaped with 1-3 stacked sheets of aromatic carbon rings and quasi-spherical with a core-shell arrangement having crystalline and amorphous properties. Carbon dots have their excitation wavelength-dependent or independent emission with each having their own benefits in microscopic fluorescent imaging. Some carbon dots have an affinity for a particular cell type , organelle or chemical. This property allows the carbon dots to be used as sensors in a biological environment and can even provide quantitative information if the quenching or intensity of their fluorescence is dependent on the concentration of the analyte. Carbon dots are the youngest members of nanoworld. They are commonly spherical in shape having average diameter less than 10 nm. Carbon dots have only sp2 hybridized carbon framework whereas carbon dots are composed of sp2 and sp3 hybrid carbon networks. Moreover, they can be easily functionalized with hydroxyl, carboxyl, carbonyl, amino and epoxy groups over their surfaces thereby offering extra advantages for binding with both inorganic and organic moieties. Bare carbon nanoparticles do not exhibit any kind of photoluminescent activities while their surface modifications lead to exhibit strong photoluminescent signals. Surface modification of carbon dots by different

functionalities, passivating agent and solvent, reflects a smart variation in their properties.

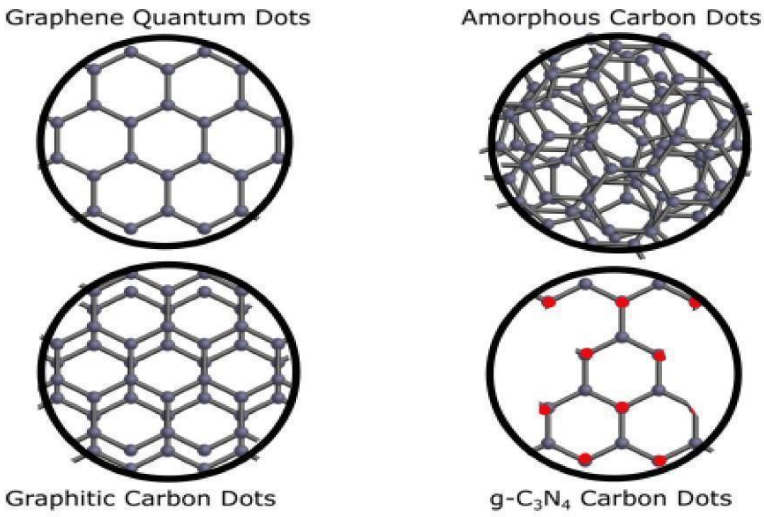


**Fig 1. 2 Structure of carbon dots**

They consist of clusters of carbon with various other atoms such as nitrogen, oxygen, sulfur, and phosphorus. They exhibit excellent excitation tunable emission properties. Carbon dots show high QYs ranging from 5% to 80%. The surface of carbon dots can be functionalized with polar functional groups such as carboxyl, hydroxyl and amine. These functional groups can be further conjugated with biomolecules for imaging and other biomedical applications.

## 1.3 SYNTHESIS OF CARBON DOTS

Synthetic methods of carbon dots can be classified into two groups;top-down and bottom-up methods. In the top-down process, the macromolecule is destroyed or dispersed into small-sized carbon dots by physical or chemical methods ;while the bottom-up approach mainly refers to the polymerization and carbonization of a series of small molecules into carbon dots through chemical reaction.

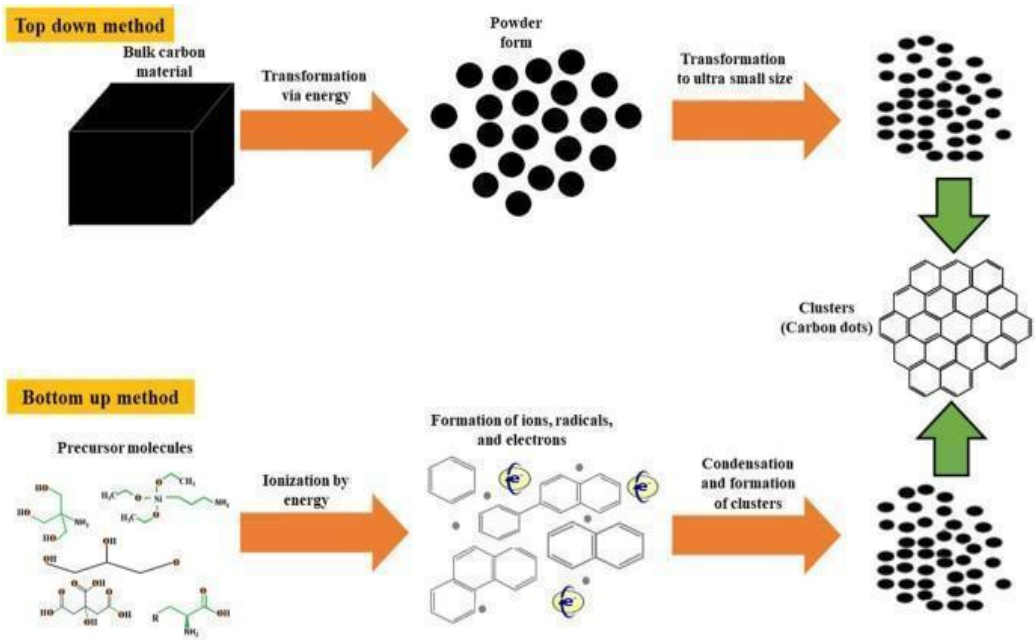


**Fig 1. 3 Synthesis of carbon dots**

## 1.3.1 TOP - DOWN METHODS

## Arc Discharge Method

It is a method to reorganize the carbon atoms decomposed from the bulk carbon precursors in the anodic electrode driven by the gas plasma generated in a sealed reactor. The temperature in the reactor can reach as high as 4000 K under electric current in order to produce a high-energy plasma.

In the cathode the carbon vapor assembles to form carbon dots. The preparation of carbon dots by arc discharge method originated in 2004 (Xu et al. ), obtained three kinds of carbon nanoparticles with different relative molecular mass and fluorescence properties accidentally when preparing single-walled carbon nanotubes(SWCNTs) by arc discharge method. The as-prepared carbon dots can emit blue-green, yellow and orange fluorescence at 365 nm. Further experiment demonstrated that the surface of carbon dots was attacked by a hydrophilic carboxyl group. The carbon dots obtained by this method have good water solubility, however, in general they possess a large

large particle size distribution in view of how different sizes of carbon particles are formed during

the discharge process. The large particle size would extensively decrease the specific surface area of carbon dots , which may limit the active reaction sites during the electrocatalytic process.

## Laser Ablation(LA)

Laser ablation is a synthetic method that involves the use of a laser and a carbon source for the synthesis of carbon dots. Sun et al. , used a method to generate fluorescent C-dot , where they firstly mixed graphite powder and cement and then heat-treated it to obtain a carbon source. Furthermore , by using a laser source carbon was removed from the surface by using an argon gas vapor steam at 900 degree celsius and 75 KPa to obtain carbon nanoparticles. Such synthesized carbon nanoparticle sizes were variable, which exhibited no photoluminescence. The sample was then treated with polyethylene glycol(PEG1500N) or poly propionyl ethylene-imine-ethyleneimine after being refluxed in aqueous nitric acid over 12h(PPEI-EI). The PL of passivated C-dots with a diameter at about 5 nm was very powerful, whose fluorescence quantum yields ranged from 4% to 10% at 400 nm excitation.

Likewise, Gonsalves et al. , produced carbon nanoparticles by embolization immediately from a carbon target dissolved in non-ionized liquid;the carbon particles that resulted would not exhibit fluorescence. The carbon nanomaterials were deposited in aqueous nitric acid and then allowed to stand for 12h to enable the carbon nanoparticles surface , after which PEG200 was applied to the mixture and boiled under reflux for 28h, followed by mercapto-succinic acid and warmed for 31 h. Then, the colorless mixture turned to light brown, fluorescent C-dots via a size distribution of 267 nm. The scale of the poly ethyl glycol(PEG) chain as well as the existence of other parameters have no impact on the long-term destruction of the activated C-dot ;however , other metals including Hg2+, Ca2+, Ni2+, Zn2+, Cu2+, Cd2+ions disperse. Therefore it has no impact on the fluorescence of C-dots , so it could be employed to monitor iodine.

By dispersing ultrasonic laser radiation throughout a PEG1500N mixture over 4h, a uniform black suspension has been produced . C-dots were achieved from a color precipitate following centrifugation(5000 rpm). The average thickness of the C-dot microstructure could affect quantum fluorescence performance, which could be regulated by changing the pulse width of a laser pulse. Laser ablation has a number of advantages, including ease of use and the ability to produce a variety

of nanostructures. However , in order to meet the carbon mark, this approach necessitates a large amount of carbon materials. Carbon nanostructures produced by laser radiation have a wide range of sizes, and large particles could be conveniently separated by centrifugation , which leads to effective utilization of carbon nanoparticles and carbon materials. In comparison to chemical oxidation, liquid form laser ablation produces carbon quantum dots in a much faster and safer one-step procedure with fewer initial chemicals and residues.

## Electrochemical Method

The electrochemical method is a simple and convenient preparation technique, which can be carried out under normal temperature and pressure conditions. Synthesis of carbon quantum dots by electrochemistry method has been widely used for the sake that it is easy to tune the particle size and photoluminescence performance of the synthesized carbon quantum dots. In 2015, Hou et al. , prepared a blue -emission carbon quantum dots with an averaged particle size of 2. 4 nm by electrochemical carbonization of sodium citrate and urea in deionized water, which can be utilized as a highly sensitive detector for Hg2+ in waste water.

Electrochemical carbonization is stable and a one-step process. Zhou et al. produced carbon dots by electrochemical action of multi wall carbon nanotubes in aceto-nitrile solution containing 0. 1 M tetrabutyl-ammonium perchlorate(TBAP) as the supporting electrolyte. Upon cycling the potential is maintained between -2. 0 and 2. 0 V at a scan rate of 500 Mv/s, the transparent electrolyte solution changed into dark brown solution. The solution shows blue luminescence under the UV lamp. After purifying the dark brown solution and removing the electro nitrile , finally carbon dots were obtained.

## Microwave Assisted Synthesis

Microwave-assisted synthesis is a simple and cost-effective process for synthesizing carbon dots by irradiating electromagnetic radiation with wavelength ranging from 1mm to 1nm by the reaction mixture of the precursor molecules. Zhu et al. used microwave irradiation to make fluorescent carbon dots with a size of ~3. 7 nm. They heated saccharides and polyethylene glycol aqueous solution in a

domestic microwave oven (500W) for almost 3 properties and excitation minutes. Microwave irradiation of organic molecules is a fast and inexpensive method to synthesize C-dots. Microwave offers instant and uniform heating to the substrate, hence it is very easy to operate and lessens the reaction time also. Many green precursors such as dextrin, glucose, rose, rice, citric acid, egg, raw cashew gum etc. from which carbon dots can be easily prepared.

Feng et al. have synthesized carbon dots using dried rose flowers as precursors. The synthesized carbon dots have a size range from 4-6 nm in diameter which shows blue fluorescence in the presence of UV light and good ultrasensitive detection property of Tetracycline in real samples.

## Thermal Decomposition

The thermal decomposition technique has also been widely used as another traditional bottom-up approach for the synthesis of carbon dots. A material or compound is chemically decomposed in ordinary thermal decomposition by heat action. The thermal reactions to decomposition are typically endothermic. The advantage of this method includes ease of use, time taking cheap price and large-scale manufacturing.

Wang et al, reported highly luminescent CDs as the passivation agent by the thermal decomposition of citric acid as the source of carbon and organ silane, N-(Beta-aminoethyl)-alpha-aminopropyl methyl dimethoxysilane (AEAPMS). They only heated the reaction mixture for one minute at 240 degree Celsius and the observed CD diameter was ~ 0. 9 nm. Wang et al after that produced the CDs from citric acid by using this method. They heated citric acid for 30 min on a hot place at 200 degree Celsius, neutralized it with a solution of NaOH and finally solubilized it for purification. The size of CDs within the 0.7 to 1 nm range was observed. These CDs demonstrate both independent photo luminescent dependent properties.

## 1.3.2 BOTTOM-UP METHODS

### Carbonization Synthesis

Various precursor molecules can be carbonized easily; thus, this is one of the cheapest, recognized, convenient, and superfast single-step techniques for CD manufacturing. Carbonization is a chemical process in which continuous pyrolysis in an inert environment, solid materials with higher carbon content are formed from organic materials. Wei et al. , used this technique to produce N-doped carbon dots. They used a much faster method than glucose and ethylene-prepared carbon dots were observed between 1 and 7 nm, along with 48% of QY.

### Pyrolysis Synthesis Method

Among the bottom-up approaches, the pyrolysis method has been well established due to the rapid synthesis and commercialization. Zhu et al. reported a facile microwave pyrolysis approach to synthesis carbon dots by combining poly ethylene glycol (PEG 200) and a saccharide (Glucose, Fructose, etc) in water to form a transparent solution, followed by heating in a microwave oven. The obtained carbon dots exhibited excitation dependent photoluminescent properties. This is a simple, fast and environmentally friendly preparation method for the synthesis of carbon dots rich in oxygen containing groups, which would become the coordination sites of metal ions for the design of carbon based electrocatalysts.

### Hydrothermal / Solvothermal Synthesis

In particular, the hydrothermal method is one of the most commonly used procedures in carbon dots synthesis, because the setup is simple and the outcome particle is almost uniform in size with high QY. In a typical approach, small organic molecules or polymers are dissolved in water or organic solvents to form the reaction precursor, which was then transferred to a Teflon lined stainless steel autoclave. The organic molecule or polymer merged together at a relatively high temperature to form carbon seeding cores and then grow into carbon dots with a particular size of 10 nm. The highest

QY of carbon dots obtained was about 80%, which is almost equal to fluorescent dyes. The carbon dots were synthesized by using citric acid and ethylene diamine as carbon and nitrogen sources with high product yield under hydrothermal process, featuring as a desirable bio sensor for the detection of Fe3+ in living cells. Biomolecules with rich carbon and nitrogen resources can be used to finely tune the inner structures of carbon dots under hydrothermal condensation. The synthetic process and controllable heteroatom doping makes this method a promising approach to develop and fabricate novel electrocatalysts with tunable doping composition and electronic structure.

## Ultrasonic Treatment

In this technique, carbon precursors along with acids, alkali and other oxidants are kept under high ultrasound waves due to which there is a breakage of carbon particles into very small nanoparticles. There is continuous cavitation of the molecules. The use of high energy ultrasonic waves avoids the complex post-treatment process, thereby realizing the facile synthesis of carbon dots with a small size. Li et al. , prepared a fluorescent carbon dot along with the ability of water solubility. They used activated carbon employing the ultrasonic treatment approach helped through one step H2O2. The TEM findings showed that the surface of prepared carbon dots was rich in hydroxyl groups along with a detected size range of 5 to 10 nm.

## 1.4 PROPERTIES OF CARBON DOTS

The carbon quantum dots have unique physical, chemical and optical properties. The chemical property of carbon dots is highly important among all the properties due to their photoluminescent phenomenon, chirality and UV absorption. Typically carbon dots can act as both electron acceptors and donors.

### 1.4.1 PHYSICAL AND CHEMICAL PROPERTIES

#### Absorbance

The optical absorption peaks of carbon dots in the UV-visible region is usually estimated as $\pi - \pi^*$ transition of sp2 conjugated carbon and n-$\pi^*$ transition of hybridization with heteroatoms such as N, S, P etc.

Absorption property can be manipulated through surface passivation or modification process.

Jiang et al. developed a facile hydrothermal method to synthesize red, green and blue luminescent carbon dots by using three isomers of phenylenediamines. The UV-visible absorption spectra of the obtained carbon dots showed an analogous pattern.

The absorption transitions of these three carbon dots were red shifted, indicating the electronic band gaps of the carbon dots were smaller than their corresponding precursors.

#### Photoluminescence

The most fascinating feature of carbon dots is their tunable photoluminescence properties arising from quantum confinement effects.

The photoluminescence quantum yield of bare carbon dots is low (typically less than 10%) due to the emissive traps on the surface.

In order to enhance the brightness of carbon dots, surface passivation is necessary.

Carbon dots with different colors have been synthesized, ranging from UV to red, but most of them

emit commonly in blue and green regions.

Undesirable for multicolour imaging, most of the carbon dots show broad emission spectra because of the large heterogeneity resulting from poorly controllable synthesis processes.

One uniform feature of the photoluminescence for carbon dots is the distinct dependance of the emission wavelength and intensity.

The photoluminescence strength of the carbon dots solution first increased and then decreased as the concentration increased under an irradiation at 417 nm wavelength with various concentrations.

One of the most fascinating features of carbon dots, both from fundamental and application oriented perspectives is their photoluminescence.

One unique feature of the photoluminescence of carbon dots was a clear λex dependance of the emission wavelength and the intensity.

The photoluminescence properties of the carbon dots can be tuned via modification of electrons or energy transfer.

## Phosphorescence

The phosphorescence properties of carbon dots were discovered recently.

A pure organic room temperature phosphorescent (RTP) material was obtained based on water soluble carbon dots and its phosphorescent lifetime was lengthened to the sub second order (~ 380 ms).

Preliminary investigations suggested that phosphorescence originated from the triplet excited state of aromatic carbonyls on the surface of the carbon dots.

By dispersing the carbon dots into a polyvinyl alcohol (PVA) matrix, clear phosphorescence could be observed at room temperature when exited with UV light.

## Chemiluminescence

The chemiluminescence properties of carbon dots were firstly discovered when the carbon dots co-existed with some oxidants, such as KMnO4 and Cerium (iv).

The electron paramagnetic resonance (EPR) reveals that oxidants, such as KMnO4 and Cerium (iv), can inject holes into the carbon dots. This process increases the population of the holes in the carbon dots and accelerates the electron-hole annihilation, resulting in energy release in the form of chemiluminescence emission.

Chemiluminescence intensity was dependent on the concentration of the carbon dots in a certain range.

Increasing the temperature had a positive effect on the chemiluminescence due to the thermal equilibrium of the electron distribution in the carbon dots.

For this system, the chemiluminescence properties can be designed by changing their surface groups.

The chemiluminescence of carbon dots creates new opportunities for their potential in the determination of reductive substances.

The dual role of carbon dots as an electron donor and acceptor offers great potential in optronics and catalysis.

## Electrochemical Luminescence (ECL)

To understand how the composition, morphology, and surface structure of carbon dots affect the photoluminescence and electrochemical luminescence in certain applications.

The carbon dots with low and high oxidation levels, denoted as r-CDs and o-CDs, were synthesized via a carbonization-extraction strategy and carbonization-oxidation process, respectively.

The results showed that the electrochemical response was controlled by the diffusion of the o-CDs onto the electrode surface.

The electrochemical luminescence wave started at 1. 10 V and reached its peak value at 1. 30 V, which is consistent with the oxidation peak in the cyclic voltammograms (CVs); thus, the ECL emission was direct oxidation of o-CDs.

## Ultraviolet-Visible Absorption

The basic chemical structure of CDs can be significantly elucidated by the typical UV-vis spectral analysis.

The presence of π-π* (C=C) and n-π* (C=O, C-N, C-S, etc. ) transition of the CDs skeleton indicates the type of surface functional groups, routes of CD synthesis, precursors, and chemical environment.

The presence of heteroatoms (such as N, O, P, B, S and Se) in the CD's molecular structure also results in the fluctuations of the UV-vis peaks.

The N, S-CDs fabricated from 3-aminothiophenol via a one-pot hydrothermal method showed two absorption shoulders at 298 nm, and 354 nm attributed to n-π* transition and heteroatoms N and S surface states defect, respectively.

## Chirality Of Cds(Emerging Property)

Among the two types of CD synthesis approaches, the "bottom-up" approach usually generates better chiral CDs as the precursor molecules themselves are chiral and therefore do not need the introduction of chiral ligands during the synthesis process.

In another approach to enhance the material property for biomedical applications, chiral CDs derived from glutamic acid were doped into gels as the latter display superior biocompatibility.

An important aspect of such a doping process is the requirement of chiral match ability between the CD and the gelator, which would otherwise lead to the disintegration of the gel.

It was shown that the doping of the chiral CD with the gelator(N, N-bis(octadecyl)-D-amino glutamic diamide) to form gel resulted in the fluorescence enhancement of the CD.

Using chiral CD synthesized from citric acid and L-aspartic acid, an on-off and off-on fluorescence sensor was developed to detect both Sn2+ ion and L-Lysine enantiomer.

## 1.4.2 BIOLOGICAL PROPERTIES OF CARBON DOTS

Impressive progress has been made in engineering bright carbon dots bio proves with good stability. Systematic cytotoxicity valuations were carried out on both raw carbon dots and passivated carbon dots during the last few years.

Sun's group employed carbon dots produced by the arc discharge of graphite rods, and then refluxed in HNO3 for 12 hours for cytotoxicity assay.

The bare carbon dots were apparently non toxic to cells upto a relatively high concentration of 0. 4 mg m/L.

CDs are mostly known for their fascinating biocompatibility and relatively less toxicity, thus fulfilling the required conditions for diverse applications.

Since CDs are free from toxic heavy metals and possess high photostability, these are used in the bioimaging fields and medical diagnosis as well.

## 1.5 APPLICATIONS OF CARBON DOTS

Although using excellent properties such as low toxicity and good bio compatibility makes carbon dots ideal materials for bio imaging, biosensors and drug delivery applications, carbon dots can however offer advantages in catalysis, sensors and optronics based on their excellent optical and electronic properties.

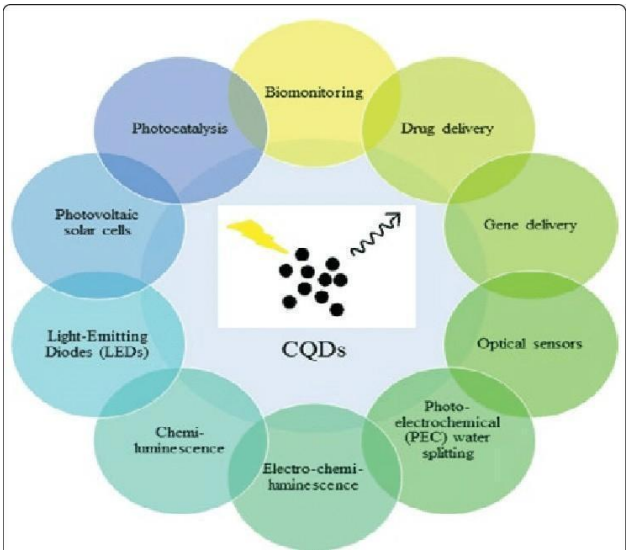


**Fig 1. 5 Applications of Carbon dots**

### 1.5.1 BIOIMAGING

Because of the fluorescence emissions and the biocompatibility property, carbon dots are being used for bio imaging.

In vivo images can be generated by injecting solvents carrying carbon dots into living organisms for identifications or treatment purposes.

Organic dye-conjugates are used as an efficient fluorescent H2S probe.

H2S presence may change blue to green emission of organic dye-conjugated-CQDs. Therefore,

organic dye-conjugated-CQDs are able to imagine changes in the physiologically important rates of H2S.

Some of the CDs have been used for the diagnosis of cancer and photo therapies. For instance, 200µl of CQDs and wheat straw were given to the mice from the tail vein, and later on the fluorescence property was investigated.

Due to excellent fluorescence , low toxicity and biocompatibility, C-dots can be used in cellular imaging and multimodal bioimaging of tissues and cells.

N, S co-doped C-dots were applied for biological applications, they were directly applied in the imaging of peritoneal macrophages of mice without any further functionalization which represents that C-dots had penetrated into the peritoneal macrophages of mice.

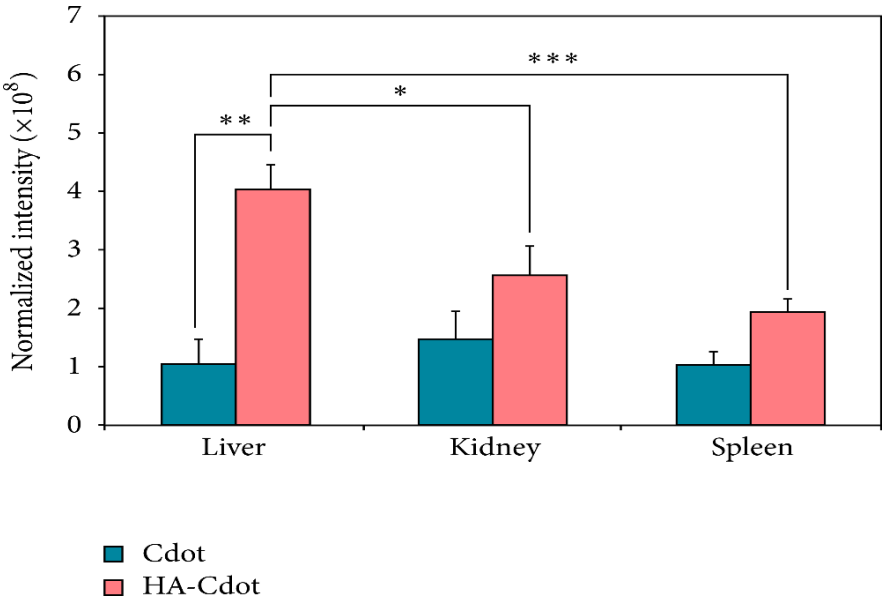


**Fig 1. 5. 1 Quantitative fluorescence analysis of Cdots and HA-Cdots conjugated in the dissected organs**

## 1.5.2 SENSING

CQDs have been used as a biosensor for their versatility in alteration, high water solubility, nontoxicity, good photostability and excellent biocompatibility.

Biosensors based on materials based on CQD and CQs may be used to track cellular copper, glucose,

pH, H2O2 trace levels and nucleic acid visually.

The fluorescence of CQDs reacts effectively to pH, local polarity and the existence of metal ions in solution, which further extends their capacity for nano sensing applications, for example in pollutant analysis.

Carbon dots have been used widely for sensing of temperature, pH, light, phase, solvent, pressure and multi sensitivity.

## 1.5.3 DRUG DELIVERY

Carbon quantum dots exhibit non toxicity and biocompatibility which enables them to be used in wide range applications including drug carriers, fluorescent tracers and monitoring drug release. This is evidenced through the use of carbon dots as photosensitizers in photodynamic therapy for cancer cell destruction.

The major advantage of C-dot based drug delivery is that the carriers are non-toxic, photoluminescent and bio compatible in nature.

Due to their small size and enhanced surface area, there is faster uptake of C-dots as a carrier by the cells and there is a minimum adverse effect on the carrier molecule.

It has been used efficiently for the release of doxorubicin.

C-dots have also been used for the delivery of SN 38 by using PEGylated nanographene.

By using graphene quantum dots, pancreatic cells were investigated.

## 1.5.4 OPTRONICS

Carbon dots have the ability to act as materials for dye-sensitized solar cells, organic solar cells, super capacitors and tools for light pollution.

Carbon dots can be used as photosensitizers in dye-sensitized solar cells and the performance of photoelectric conversion is greatly enhanced.

Hybrid silica-based sol embedded in carbon dots can be used as clear fluorescent paint.

The optical properties of carbon dots can be enhanced and improved by synthesizing multicolour

emitting carbon dots.
The optical properties of carbon dots can be enhanced and improved by synthesizing multicolour emitting carbon dots.
Carbon dots are widely used in LEDs, photovoltaic cells, electroluminescent CD-based LEDs and CDs in perovskite solar cells.

The small size and reactive nature of carbon dots makes them highly suitable for visualization of latent fingerprints, due to which they can be easily bound with the ridge of the fingerprints.
One major advantage with the use of carbon dots for latent fingerprinting is that there is no effect of aging of organic and inorganic content from the fingerprint samples.

## 1.5.5 CATALYSIS

With their high surface area-to-volume ratio and their versatile functional groups, CDs find application in catalysis. CDs synthesized from willow bark were used as a photocatalyst for the fabrication of a Au nanoparticle/reduced graphene oxide nanocomposite, demonstrating that the CDs effectively reduced both materials.
The resulting nanocomposite was used in a system that catalyzes the reaction of glucose and oxygen into $H_2O_2$ allowing it to be an indirect method of glucose sensing *via* the detection of $H_2O_2$.
In another study, Essner *et al.* synthesized CDs from citric acid. They first
used their CDs to reduce HAuCl4 to Au nanoparticle/CD hybrids at room temperature.

## 1.5.6 LED DEVICES

Guo et al. synthesized a series of multicolor CDs by the thermolysis of an epoxy group containing polystyrene microspheres.
CDs produced under 200, 300, and 400°C could emit blue, orange, and white fluorescence with the excitation of single wavelength ultraviolet, respectively, and the fluorescent quantum yield is 47%.
With the excellent properties, those CDs could be used as the above-mentioned three color LED

devices.

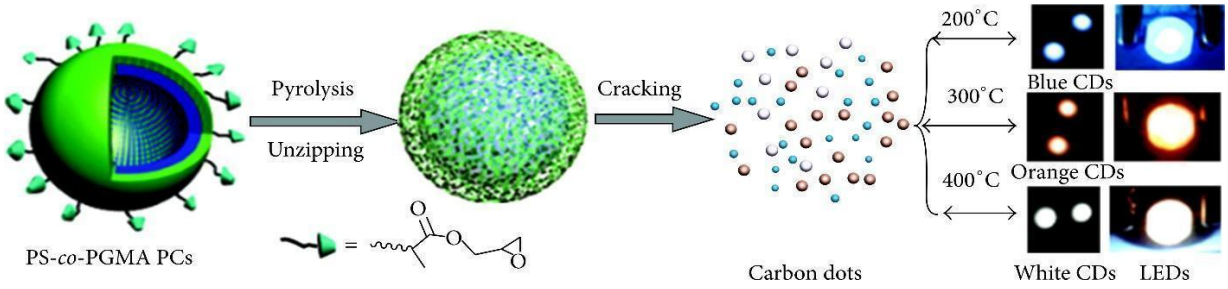


**Fig 1. 5. 6 LED Devices**

## 1.5.7 CHEMICAL SENSING

Fluorescent carbon dots, due to their excellent optical properties, chemical stability, and good solubility in water, in the field of chemical sensing under great attention, are widely used in metal ion detection, anion detection, small organic molecules, and biomolecules detection.

Like the semiconductor quantum dots, CDs by the interaction with the analyte can change the efficiency of recombination between the surfaces of the electron-hole pairs, which occurred in the fluorescence enhancement and quenching treatment to achieve quantitative or qualitative analysis of the measured object.

## 1.5.8 METAL ION PROBE

Carbon dots as a new fluorescent probe in solution are easily quenched efficiently by electron acceptor and thus can effectively detect metal ions in solution and determine the concentration of metal ions in a certain concentration range, to achieve the trace analysis of metal ions. $Hg^{2+}$ is one of the most toxic heavy metal ions in the environment, and has received the attention of scientific researchers. Currently, based on CDs as sensors, scientists have developed a variety of methods to detect $Hg^{2+}$.

Lu et al. prepared a new type of CDs from grapefruit peel through the hydrothermal method. As the

$Hg^{2+}$ can effectively quench the fluorescence of CDs, a new method for the detection of $Hg^{2+}$ Was developed, the detection limit of 0.23 nm,and this method has been successfully applied to the detection of $Hg^{2+}$ in the river.

## 1.5.9 ANIONS AND SMALL MOLECULE DETECTION

Unlike heavy metal, ions detect fluorescence quenching mechanism CDs, anionic or small molecules generally by restoring fluorescence of the quenched CDs to achieve the purpose of detection.

Zong et al. selected spherical mesoporous Silica as a nano reactor, added to the solution of citric acid and three other inorganic salts( NaCl, LiCl and $KNO_3$)and ultrasound to obtain CDs.

The study found that the CDs can bond with $Cu^{2+}$ specifically and quench the fluorescence of CDs. while adding L-cysteine in the solution of CDs- $Cu^{2+}$ , $Cu^{2+}$ could be released from the surface of the CDs, thereby recovering the fluorescence of CDs.

## 1.5.10 NANOMEDICINE

Besides being carriers, CDs themselves behave with therapeutic performances such as antibacterial activity, anticancer activity, antiviral activity and antioxidant activity. Compared with drug molecules, these drug CPDs show better biocompatibility and water solubility as well as stronger fluorescence and can be used as efficient bioimaging probes for theranostics.

Yang's group prepared Met-CPDs by hydrothermal treatment of metronidazole, a wide spectrum antibiotic against obligate anaerobes.

Compared with metronidazole, Met-CPDs behaved with better aqueous solubility and excellent biocompatibility because of the formation of new functional groups carboxyl, hydroxyl and amino groups.

Biological experimental data demonstrated that the Met-CPDs showed excellent selective antibacterial activity against obligate anaerobes due to the contained nitro group, pharmacophore, which was in accordance with the main mode of action of metronidazole.

## 1.5.11 PHOTOTHERAPY

Phototherapy, including photodynamic therapy(PDT) and photothermal therapy(PTT), is a form of non-invasive therapeutic treatment that converts the irradiating light into reactive oxygen species(e.g., •OH,$O_2^{\bullet-}$ and $^1O_2$ )and heat with the help of photosensitizers, inducing local apoptosis of cancer cells.

CDs have gained much attention as promising photo therapeutic agents due to their unique optical properties, high water solubility and high photostability.

Molecular dyes(e.g,. porphyrin, diketopyrrolopyrrole, Ru or Mn- functionalized CDs) were used for improving the PDT efficacy (e.g,. QY,$^1O_2$ yield)and multimodal imaging guided PDT in vivo.

To avoid the drawbacks of the mono-mode therapy,synergistic PDT and PTT are adapted to cancer therapy.

Red/NIR emitting CPDs prepared from CA and urea, polythiophene, and diphenyl diselenide were recognized as effective theranostic agents for PTT.

**CHAPTER 2** **EXPERIMENTAL SETUP**

## 2.1 MATERIALS AND METHODS

- Potato starch solution
- $Zn(NO_3)_2 \cdot 6H2O$
- Oxalic acid dihydrate
- Naphthol blue-black(NBB)
- Sodium hypochlorite solution
- 2-propanol

**Figure 2. 1 A. Potato starch solution**

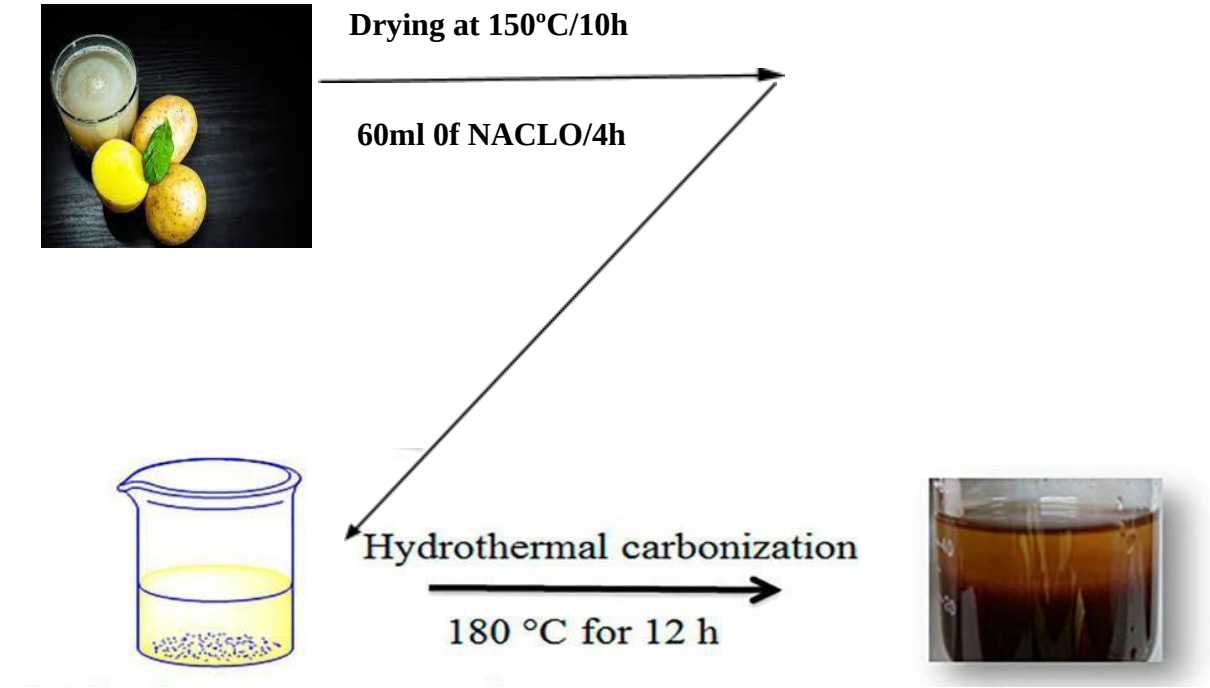


**Figure 2. 1 B. Formation of C-dots from the hydrothermal carbonization of potato starch solution**

## 2.2 HYDROTHERMAL CARBONIZATION OF POTATO STARCH SOLUTION

Potatoes were collected from a local vegetable market near Thodupuzha. They were peeled off and washed with distilled water to remove mud and dust particles. After washing they are crushed using a grinder and the potato starch solution obtained is kept inside a microwave oven at 150ºC for 10h for carbonization. Then 2ml of the pretreated potato starch solution was washed in 100ml of an aqueous 0. 1M H2SO4 solution and rinsed with water, followed by filtering and heating in an oven at 150ºC for 2h. The obtained solution was then mixed with 60ml of a sodium hypochlorite solution, kept at room temperature for 4h and then washed in water until the pH of the water

reached 7. The oxidized potato starch solution (in 25ml of water) was placed in a Teflon -lined autoclave and kept at 180ºC for 12h. The autoclave was allowed to cool down naturally, and the obtained brown solution was washed with dichloromethane to remove the unreacted organic moieties. The aqueous solution was centrifuged at 5000 rpm for 15 min to separate the solvent from the mixture and finally dried at 100ºC for 2h. The yield of the C-dots calculated from weight of raw material (2 ml of potato starch solution) and weight of product (0. 24 g C-dots) was 12. 3%.

## 2.3 PREPARATION OF C-DOT-LOADED ZNO

C-dot -loaded ZnO was prepared by the solution dispersion method. A 0. 9 g sample of ZnO and 0. 1 g of C-dots were dispersed in 2-propanol and water, respectively. The latter was added to the former and stirred for 4 h. The resultant precipitate was filtered and washed with water several times. The product was then heated in an oven at 100ºC for 3h. The calculated content of C-dots in the catalyst is 10wt%.

## 2.4 ANALYSIS OF OXIDIZED CARBON DOTS

### 2.4.1 ULTRAVIOLET-VISIBLE(UV-VISIBLE) SPECTROSCOPY

The optical properties of Carbon dots were analyzed by UV visible spectroscopy; this technique is useful to observe the region of absorption, which on Carbon dots is typically in the UV region. optical properties of diluted carbon dots suspension were analyzed with Perkin Elmer uv-visible Lambda 365 equipment. The UV region of light is considered to be from 200 nm to 400nm. Visible light is considered to be from 400 nm to 750 nm. The absorbance measurements were performed in the 200 to 800 nm wavelength range.

The absorption wavelengths of modified carbon dots will increase correspondingly or the absorption peak will be enhanced.

The primary method of characterization is obtaining a UV spectrum to observe the region of absorption and a visible spectrum to determine the region of light emission for fluorescence.

The ultraviolet-visible(UV-visible) absorption spectra were recorded using a Jasco V-670 spectrometer.

## 2.4.2 FLUORESCENCE SPECTROSCOPY

For better understanding the photoluminescence features of prepared carbon dots in a biological water-soluble environment, the fluorescence emission is measured by dissolving the protonated carbon dots numbers in deionized water.
Fluorescence spectra were obtained using a Hitachi F-7000 fluorescence spectrometer.

## 2.4.3 FOURIER TRANSFORM INFRARED SPECTROSCOPY(FTIR)

For determination of the functional groups that are present on the surface of carbon dots, FTIR or Fourier transform infrared spectroscopy has also been used. Carbon dots are mostly oxygen, carbon and hydrogen. due to the development of carbon dots by partial oxidation of of carbon precursor, carboxyl or carboxylic acid groups, hydroxyl groups and epoxy/ether Groups are abundant on the surface of C-dots and so far for the investigation of this groups containing oxygen ft-ir is a useful device.
Before applying, changes were required to be made with C-dots for balancing out potential Wells on the energy surface, lesser toxicity and higher fluorescence Quantum yield. altered C-dots can be characterized using infrared Spectroscopy so as to decide if they were passivated adequately.

# CHAPTER 3 RESULTS AND DISCUSSION

An environmentally friendly feature of the hydrothermal carbonization method used in the whole process is the unnecessary use of either a strong acid or an organic reagent. The present preparation of carbon dots in an aqueous medium has the advantage of being considerably cheaper and absolutely “green”. The produced C-dots were readily soluble in water to form a stable, yellowish and transparent aqueous solution without precipitation for months;this method can be used as a facile approach to synthesize C-dots.

## 3.1 CHARACTERIZATION OF CDs

### 3.1.1 OPTICAL PROPERTIES OF THE SYNTHESIZED CARBON DOTS

The optical properties of the synthesized Carbon dots were obtained using UV-Visible and Fluorescence spectroscopy. The excitation spectra of synthesized Carbon dots are displayed Below. The synthesized Carbon dots revealed two distinct peaks at 277 nm and 315 nm. They arise due to π- π* and n- π * transitions associated with C=C bond and carbonyl/hydroxyl groups, respectively. Addition of aqueous ammonia during the hydrothermal reaction caused the conversion of phenolic -OH to ammonium phenolate ions resulting in changes of absorption values of Carbon dots. The excitation spectrum of synthesized Carbon dots had two prominent peaks at 289 nm and 315 nm, which could be correlated to the absorption spectrum of the prepared Carbon dots.

The detailed fluorescence study on the Carbon dots was carried out under various excitation wavelengths from 265 nm to 380 nm with the wavelength interval of 5 nm and then the maximum emission intensity was observed at 315 nm. The excitation dependent emission spectra are given below. The fluorescent intensity was gradually increased and there was no notable shift during the increase of excitation wavelength from 265 nm to 315 nm and this could be due to the π- π* transitions of graphitic carbon cores. Moreover, the emission intensity decreased as the excitation wavelength increased from 315 nm to 380 nm and the emission peaks were red shifted.

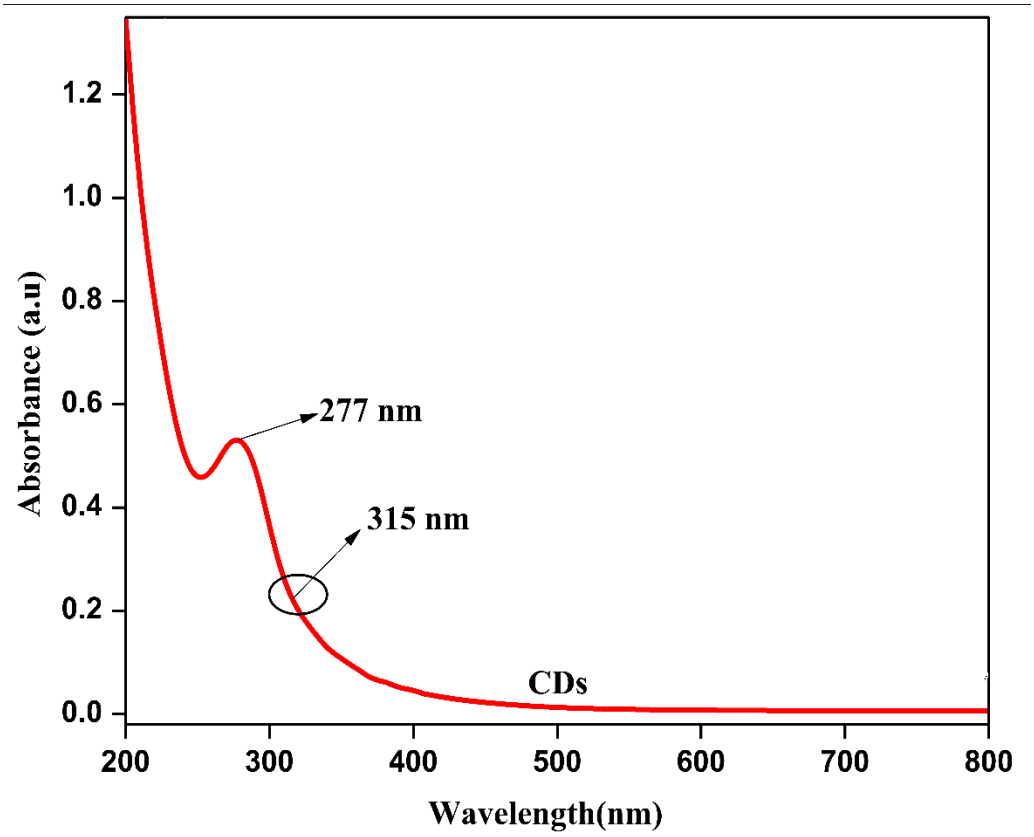


**Figure : UV-Vis spectra of synthesized CDs**

## 3.1.2 EXCITATION DEPENDENT EMISSION

The most common and attractive photo physical property of carbon dots (CDs) is the excitation dependent emission. This is ascribed to different sizes of CDs and distribution of different surface states because of the presence of various organic functional groups over the surface of the CDs. Typically, in the case of small size CDs (<5 nm) emission maxima strongly depends on excitation wavelength. Due to this reason, the emission intensity was gradually increased while increasing excitation wavelength from 265 to 315 nmin fluorescent spectra. Since, the excitation was selectively made in the region of π- π* transition no notable shift was observed due to the absence of multi-fluorescence centers. After increasing excitation wavelength from 315 to 380 nm which is specific of n- π* transition region, the emission intensity got shifted to higher wavelength (i.e. red shift) which can be attributed to the presence of amine functionalities in Carbon dots. The radiative recombination (π* to n transitions) of carbonyl/amine functionalities in the surface is the major reason for arising excitation

dependent emission spectra of Carbon dots. The maximal intensity (405 nm) of Carbon dots was noticed at the excitation wavelength of 315 nm. Hence, this confirmed that the synthesized Carbon dots are suitable candidates for bioimaging and biolabeling applications due to the wide ranges of fluorescent spectra.

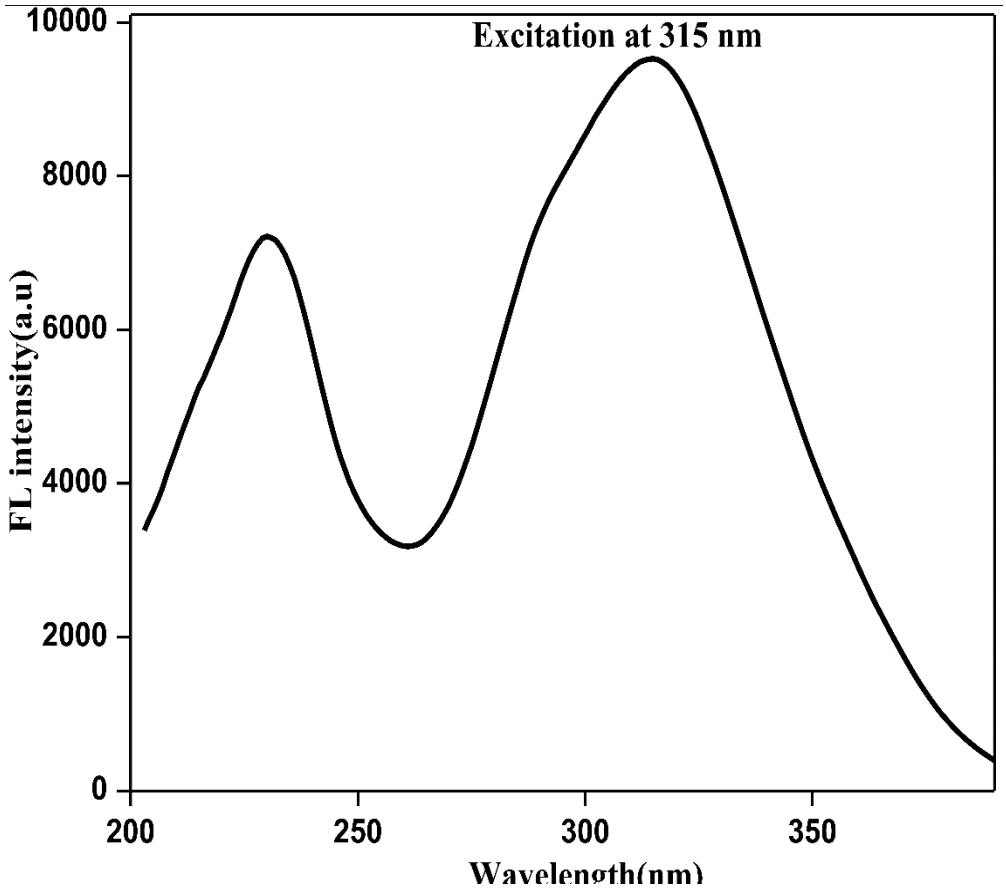


**Figure : Fluorescence excitation spectrum of synthesized N-CDs.**

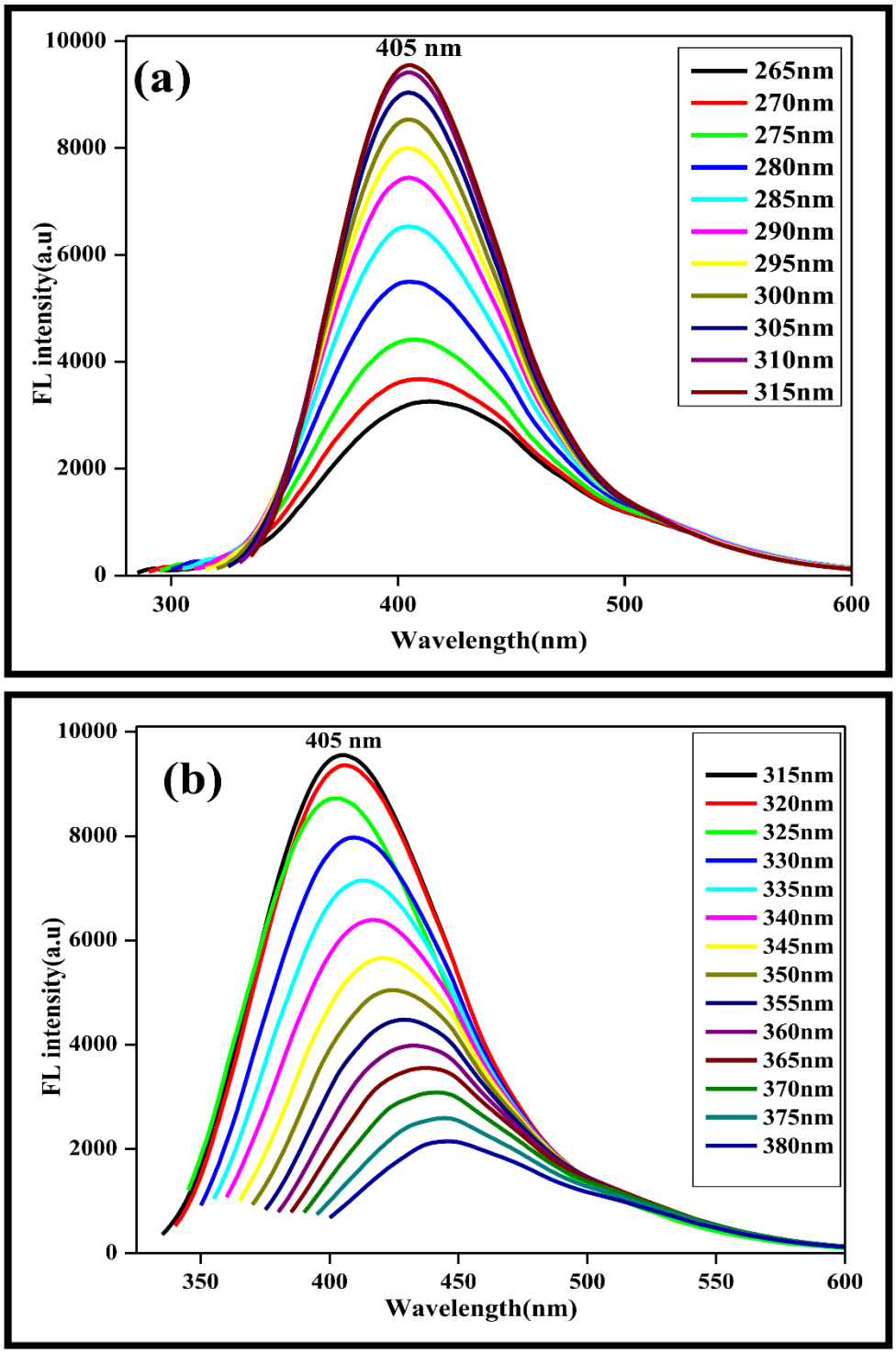


**Figure (a) Fluorescence spectra of synthesized N-CDs at different excitation wavelengths from 265 nm to 315 nm; (b) Fluorescence spectra of synthesized N-CDs at different excitation wavelengths from 315 nm to 380 nm.**

## 3.1.3. EMISSION MECHANISM OF N-CDS

Emission intensity of CDs was enhanced due to the doping of nitrogen through stimulating the upward shift of the Fermi level and electrons in the conduction band. The hexagonal rings of carbon in the CDs were disturbed due to the formation of C–N bonds in the doping process and this tends to create the emission energy traps. The recombination of electron hole-pairs in the strongly localized π and π* electronic levels of $sp^2$ sites trigger the surface defect derived fluorescence. In fact, surface functionalization makes surface defects more stable which facilitate the recombination of surface electrons and holes thereby leading to fluorescent emissions.

## 3.1.4. STRUCTURAL ANALYSIS

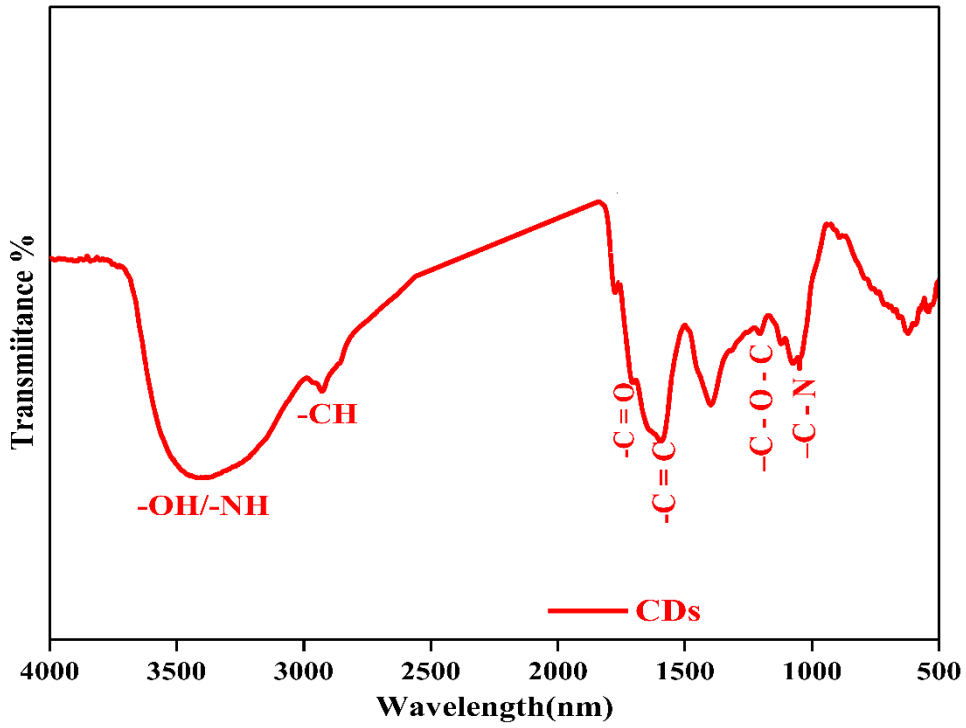


**Figure : FT-IR spectra of prepared CDs.**

The Carbon dots show the absorption bands at 3413, 2926, 1704 and 1114 cm-1, which reveal the functional groups of A. deliciosa have been shifted slightly. In the IR spectrum of the prepared N-CDs, -O-H stretching was observed at 3413 cm-1, which reveals that the doping of nitrogen by amine functionalities and the stretching vibration of -C-H groups had been observed at 2926 $cm^{-1}$. The broad absorption band of prepared Carbon dots appearing at 1644 $cm^{-1}$ corresponds to the characteristic vibration of the C=C bond ($sp^2$) stretching mode. The weak absorption band at 1049 $cm^{-1}$ appears from extract and carbon dots (-C=O and -C-O-C) were broadened. Hence, the presence of acid, amine, hydroxyl and carbonyl moieties over the surface of synthesized Carbon dots could be confirmed from the FT-IR spectrum.

# CHAPTER 4 CONCLUSION

In this study , a green and facile synthesis of fluorescent CDs under the hydrothermal condition(in an aqueous medium at 180℃) from potato starch was developed. The CDs are spherical in shape with the average diameter of 3.39 nm. In addition, the characterisation of CDs showed that they have oxygen containing groups on their surface which are beneficial to the improvement of water solubility and fluorescence. The obtained CDs have good fluorescence with a quantum yield of 8.64%. Furthermore the CDs were also applied in cell imaging at their non toxic concentration, indicating that they are promising multicolor fluorescent probes in biological imaging. The present preparation of carbon dots in an aqueous medium has the advantage of being considerably cheaper and absolutely “green”. This procedure is a facile,eco-friendly method,which may be feasible for large scale production.The produced C-dots Were readily soluble in water to form a stable yellowish and Transparent aqueous solution without precipitation for months; this method can be used as a facile approach to synthesize C-dots.An environmentally friendly feature of the hydrothermal carbonization method used in the whole process is the unnecessity of either a strong acid or an organic reagent.the prepared C-dots are worth attention due to their advantages in green synthesis,high solubility in an aqueous medium, luminescence property and they can have potential applications as fluorescent markers and efficient catalysts in biosciences and energy sciences.

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