FLUORESCENCE AND PHOSPHORESCENCE OF CARBON QUANTUM DOTS FROM WOOD ASH

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

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Declaration of Originality

This is to attest that the thesis entitled "**Fluorescence and Phosphorescence of carbon quantum dots from wood ash**" submitted by ***GURU CHARAN DAS*** for the partial fulfillment of the requirements for the award of Bachelor of Technology degree in Biotechnology Engineering at National Institute of Technology, Rourkela during the session 2015-2016 is a genuine work carried out by him under my supervision and guidance. To the best of my knowledge, contains no material previously published, nor any material presented by me for the award of any degree or diploma of NIT Rourkela or any other institution.

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ABSTRACT

The synthesis of fluorescent carbon quantum dots (CQDs) has been developed by the Centrifugation of Burned wood ash sample which was considered as carbon source in the presence of distilled water. The concentration of wood ash was 10mg in 50ml of distilled water. Carbon quantum dots have not shown quality result of photo luminescence with distilled water under UV radiation, later which was used as control or reference. With the use of additives like amino acids and polymers, the carbon quantum dots showed better result of photoluminescence and phosphorescence under UV radiation. FESEM analysis revealed the size of carbon quantum dots which were around 10-12 nm in size. The excitation and emission spectrum was seen in the Spectrofluorimetry and it also showed 2θ values upon XRD analysis. These carbon quantum dots have excellent properties and are biocompatible in nature. More study and analysis can be done to get excellent results.

Keywords: Carbon Quantum Dots, Bio-imaging Agents, Photo Luminescence, Phosphorescence.

CONTENTS

CHAPTER 1

INTRODUCTION:

Carbon quantum dots (CQDs) are derived from a carbon source (Burnt wood ash). Usually CQDs were extracted from graphite sources. Photo luminescent carbon quantum dots are gaining more attention due to their novel applications and unique properties thus ranging from field of nanotechnology to biomedical fields. The mostly used Photoluminescence materials are chemicals and organic dyes. However, the applications of quantum dots are limited in biomedical fields because of photo bleaching, quenching of the dye and toxicity. The fluorescent carbon quantum dots can be featured as new class of carbon Nano material are now good and efficient alternative for the common fluorescent materials, which shows satisfactory photo luminescence properties, biocompatibility and high solubility in water.

In the last few years, there had been progress in improving the synthesis, applications and properties of carbon quantum dots. The top down methods include laser ablation produce photo luminescence carbon quantum dots, where the carbon quantum dots are formed from larger carbon materials. These methods are discriminating procedures and require toxicant chemicals and special equipment. Generally, bottom up approaches consists of microwave/ultrasonic preparation, plasma treatment, hydrothermal/ acidic oxidation route. Many among these synthesis methods involve expensive, toxic starting materials, high temperature, long reaction time and surface passivation. The mentioned synthesis methods are lengthy and required strong acids and after treatment with the help of surface coating materials which are required to improvise the water solubility and photo luminescence properties. For the growth in the field of economic chemistry, it is thus required to produce self-coating luminescent carbon quantum dots. Example of the method of fabrication of carbon quantum dots without surface coating is carbonization of glucose. In Specific, it is possible to manage the size, shape, and physical properties of the carbon Nano particles by carefully selecting the carbon source and surface modifier. However, all these above-mentioned methods can be accountable for some degree of drawbacks such as requirement of complex, time-consuming processes, high temperature, severe synthetic conditions, and high cost, which is restricting their wide range of applications. Substantial technique, electrochemical oxidation synthesis, Arc discharge have been proposed to production of carbon quantum dots with simple composition, structure, morphology and size by a simple and cheap process is not yet promising [20]. So further more sophisticated methods and techniques are being developed by various countries and organization for reducing these lengthy and complex procedures to simpler ones. In this project we will be qualitatively analyzing the Photoluminescence and Phosphorescence nature of Carbon Quantum Dots in the presence of additives like Amino Acids and Polymers.

CHAPTER 2

LITERATURE REVIEW

2. Review on various Synthetic methods for synthesis of CQDs

The artificial ideas for carbon quantum dots can be break down into two major groups: top-down and bottom-up methods. The Top-down strategy, in which the longer carbon particles are broken down to littler carbon quantum dots and consists of electric arc discharge, electrochemically oxidation and excision techniques with the help of laser. The Bottom-up strategy consists of thermodynamic methods, synthesis, microwave/ultrasonic technique, solution chemistry techniques from which carbon quantum dots were extracted.

2.1. Top-down strategies

2.1.1Electric Arc-discharge Methods

By purifying the single walled Nano tubes or carbon quantum dots were discovered derived from arc-discharge soot. A Φ3 ×70 mm hole was drilled in a Φ6 × 300mm pure graphite rod and was filled with 1:1 molar ratio of graphite and Y-Ni alloy ($YNi2$) powder. The cathode was a Φ10mm graphite rod with an end towards anode in order to increase the cathode deposit. A current of 40-100 ampere was generated in a helium atmosphere at a pressure of 100-700 torr. After that the soot was extracted by $CS2$, and then washed with 1:1 hydrochloric acid (HCL) and dried at 100 Celsius. The estimated soot produced by direct current arc discharge technique with graphite rods containing Y-Ni alloy and washed with $CS2$ and HCL was containing 40% single walled carbon Nano tubes or carbon quantum dots. [6]

2.1.2 Electrochemical Oxidation of Graphite

The electrochemical fabrication of carbon quantum dots of sizes 1.2-3 nm was done using alkali. In this it was demonstrated the design of photo catalyst (TiO/CQDs and SiO2/CQDs complex system). Graphite which possess honeycomb layer by cutting gives ultra-small particles which lead to small fragments of graphite producing carbon quantum dots. This may offer a straight and superficial strategy to prepare high quality of carbon quantum dots. The graphite rod acts as both anode and cathode and NaOH/EtOH as electrolyte. This synthesized the carbon quantum dots with a current intensity of 10-200mA cm-2. This result revealed that the alkali environment is a key factor and the OH- group is necessary for the formation of carbon quantum dots by the electrochemical oxidation process.

2.1.3 Laser-Excision Methods

The carbon quantum dots were produced using laser excision technique. They have done it by hot- pressing graphite powder and the following steps of baking and annealing under argon flow at 850-900 Celsius and 70-75 kPa. In this technique the surface is modified for better fluorescence results of carbon quantum dots. Different polymeric agents were used i.e. PEG (polyethylene glycol) [5]. After that the highly photo luminescent carbon quantum dots were separated by the dialysis method and after that followed by centrifugation. For high quantum yield of around 15-20% 13C powder is used and rigorous control. A single step procedure was introduced in which a pulsed ND: YAG laser was used. This method is still not much significant and is costly.

2.2 Bottom-up Approaches

2.2.1 Thermodynamic Methods

From a simplified source of carbon quantum dots which is the soot that is derived from the burnt wood ash or gas burners. Multicolor photo luminescence carbon quantum dots of size less than 2nm have already been produced from the burning soot of wax candles by the treatment of oxidizing acid and the introduction of COOH and OH groups into the surface of carbon quantum dots. Further the extracted particles are purified by gel electrophoresis. The control over the structure and physical properties of carbon quantum dots can be achieved by the careful selection of carbon sources and the surface modifiers. Blue photoluminescence carbon quantum dots can be prepared from ethylene diamine tetra acetic acid salts. Basically, most of the artificial methods are longer in procedure and requires strong acids and after treatment steps to maximize the photo luminescence properties and solubility in water. The carbonization of sucrose by controlled method had obtained high production of carbon quantum dots. Some other groups which can give high quantum yield by taking different molecular precursors are galactose and glucose etc.

2.2.2 Microwave/Ultrasonic Synthesis

In Microwave synthesis technique 5g of citric acid was precisely measured as the molecular precursor of carbon dots. Then 0.1M of TOAB aqueous solution was prepared and 2ml, 6ml, 9ml and 8ml of TOAB solution was then transferred. Then the solution was heated with the help of a domestic microwave oven (at maximum 500 watt). After heating the prepared solution, the volume decreased was clearly visible along with the change of color from transparent to yellowish-red. Then after 2-3 min the yellowish color was very much observed in all the concentration of carbon quantum dots. To confirm the formation of carbon quantum dots, the product was illuminated with Ultra Violet light at 360 nm. Also the blue color photo luminescence of carbon quantum dots was visualized. These bottom-up strategies are not much convenient procedures [10]. They are very lengthy procedures. They require surface modifiers and molecular precursors.

CHAPTER 3

MATERIALS USED AND METHODS

Materials Required:

- Burned Wood Ash.
- Distilled Water.

Apparatus required:

- Falcon Tubes.
- Micro centrifuge Tubes.
- Centrifuge machine
- Auto Pipette.
- Cylindrical glass vials.
- UV Transilluminator.

Chemicals used:

- Amino Acids.
- Ionic salts.
- Polymers.

PROCEDURE:

3.1-Preparation of Wood Ash Sample:

- 15mL of distilled water was taken in the Falcon tubes using auto pipette.
- Weighed 3gm Burnt wood ash using weighing machine.
- Added the Wood Ash in the Falcon Tubes.
- Centrifuged at 3000 rpm for 10 minutes.
- Transferred the supernatant into micro centrifuge tubes.

- Then we centrifuged at 13,000 rpm for 10 minutes.
- Took 1mL from the supernatant.
- Now our sample was ready.

3.2-Preparation of Wood Ash Sample(CDQs) +Additives (Amino Acids)

- Transferred 2mL Wood Ash sample into the cylindrical glass vials.
- Weighed 100mg from the following Amino Acids.

- D- Alanine
- L- Asparagine
- L- Cysteine
- L-Glutamine
- L-Leucine
- L-Methionine
- L-Proline
- L-Tyrosine
- L-Tryptophan
- Thymidine
- L-Valine
- L-Threonine
- L-Glutamic acid
- L-Isoleucine
- Added 100mg each Amino Acids to the Wood Ash sample or Carbon Quantum Dots.
- Mixed the solution by shaking the glass vials with hands.
- Note: Some of the Amino Acids were not properly soluble in the solution sample of Carbon Quantum Dots.
- Checked the Photoluminescence under and Phosphorescence of the Carbon Quantum Dots + Amino Acids sample.

3.3- Preparation of Wood Ash sample(CDQs) + Additives (Polymers)

- Transferred 2mL Wood Ash sample into cylindrical.
- Weighed 100mg from the following polymers:
- Polymethylmethacrylate.
- PolyvinlyPyrolidone
- Polyvinyl alcohol.
- Polyethylene glycol.
- Polysorbate 20.
- Polysorbate 40.
- Polysorbate 60.
- Polysorbate 80.

- Added the weighed 100mg Polymers each to the Wood Ash sample or Carbon Quantum Dots into 8 separate glass vials.
- After that mixed properly by shaking the glass vials.
- Note: Some polymers were not properly soluble in Carbon Quantum Dots sample.
- Checked Fluorescence and Phosphorescence of the Wood Ash sample + Additives.

CHARACTERIZATION:

The size of particle and zeta potential of carbon quantum dots was measured and found to be 10-12nm in size and -19 mV respectively. The particle size was measured by NanoSEM. The zeta potential was measured by an analyzer which analyzes the particles size (Nano ZS 90, 7 Malvern). The crystallinity of carbon quantum dots was measured by Burker D8 X-ray diffractometer. Fluorescence spectroscopy was performed with Perkin Elmer LS55 spectrophotometer at various excitation energies ranging from 250 to 450 nm and thus giving the emission energies.

CHAPTER 4

RESULT AND DISCUSSIONS

4.1 PREPARATION OF SAMPLES (Wood Ash)

Fig 4.1 Preparation of CQDs from Wood Ash

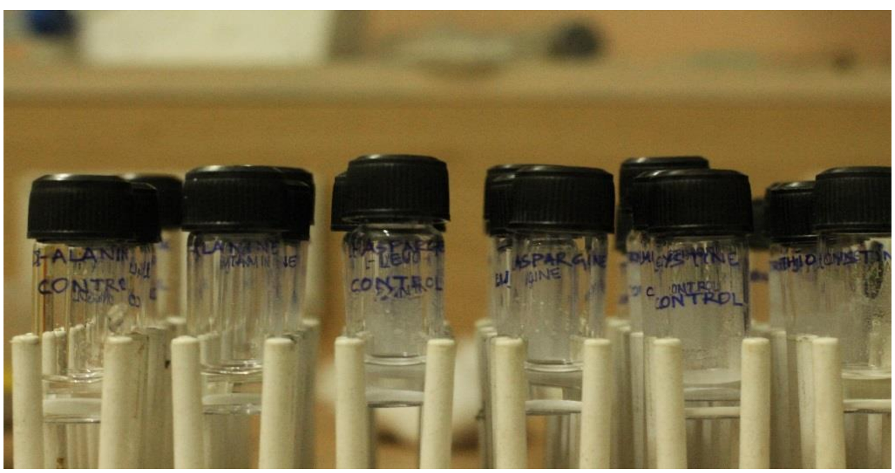


Fig 4.2 Preparation of Wood Ash Sample + Additives (Amino Acids)

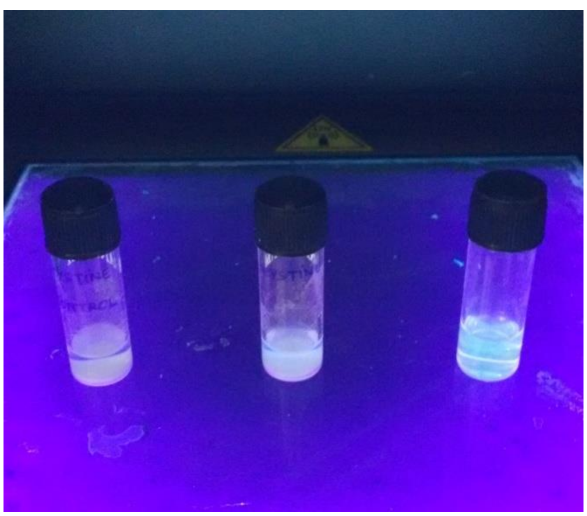
Fig 4.3 Preparation of Sample CDQs + Additives (Polymers)

Fig 4.4 UV Transilluminator for observing the Fluorescence and Phosphorescence of the wood ash samples + Additives (Amino Acids and Polymers)

Top 10 Samples:

SL. No.	Wood ash Sample+ Amino Acids and Polymers	Fluorescence	Phosphorescence
1.	L-cysteine	-	-
2.	L-Glutamine	+	+
3.	L-Leucine	+	-
4.	L-Proline	+	-
5.	L-Tryptophan	+	-
6.	L-Tyrosine	+	++
7.	L-Valine	++	+
8.	PolyvinlyPyrolidone	+	-
9.	Polyethylene glycol	+	-
10.	Polysorbate 40	-	++

<u>Fluorescence Results:</u>



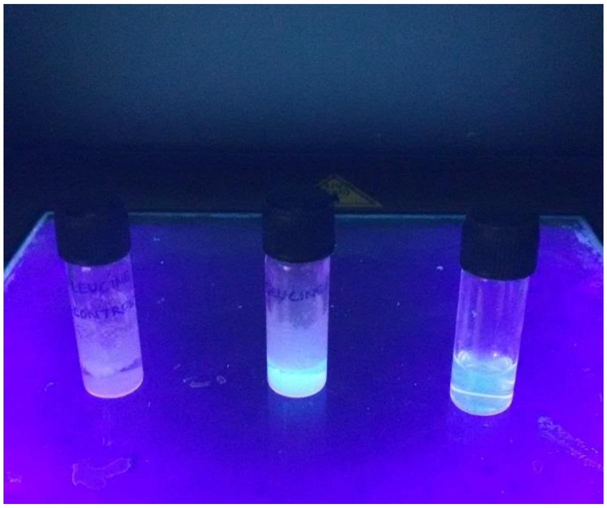
A **B** **C**

Fig 4.5 Samples (CQDs) + L-Cysteine

Where, **A**= Control= Distilled Water+ Amino Acid.
B= Carbon Quantum Dots + Amino Acid.
C= Carbon Quantum Dots.

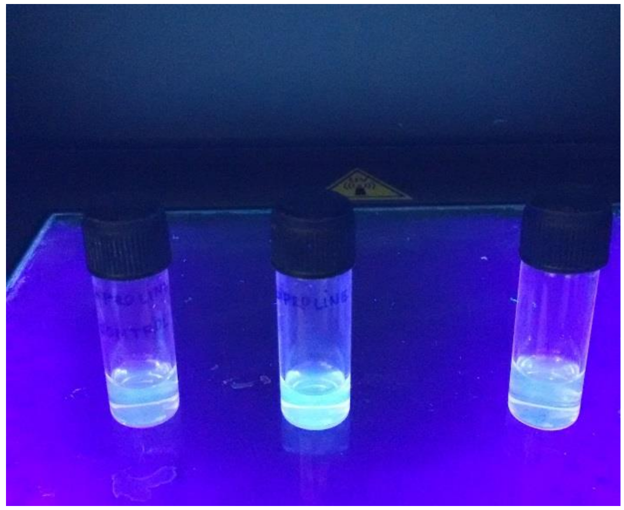
A **B** **C**

Fig 4.6 Samples + L-Glutamine



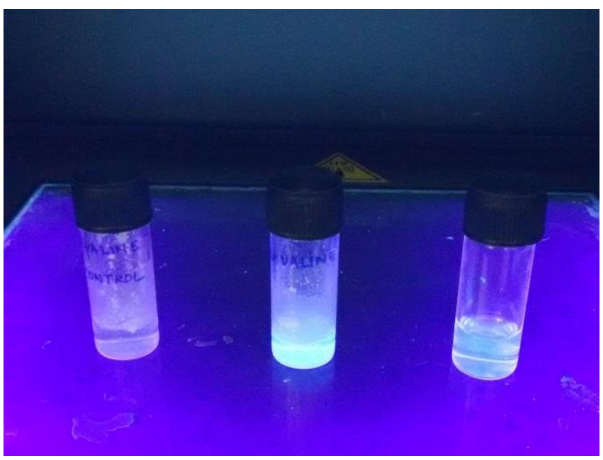
A B C

Fig 4.7 Sample + L-Leucine



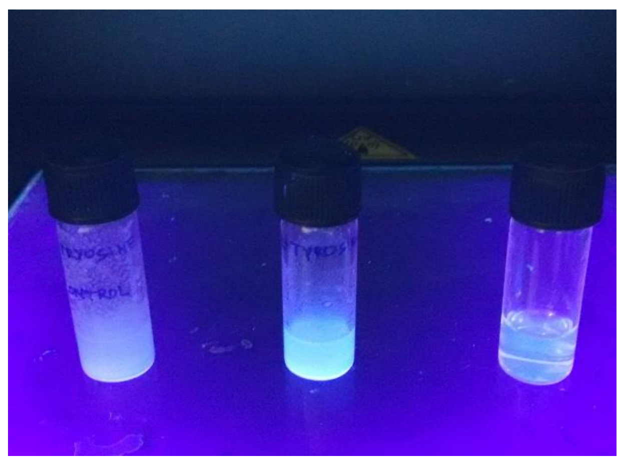
A B C

Fig 4.8 Sample + L-Proline



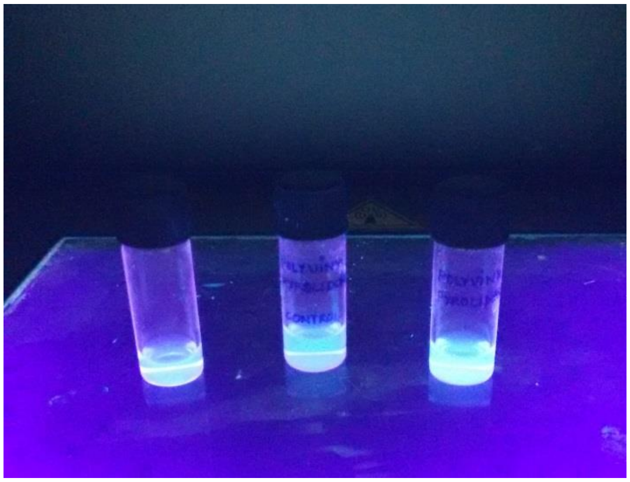
A B C

Fig 4.9 Sample + L-Tyrosine



A B C

Fig 4.10 Sample + L-Valine



A B C

Fig 4.11 Sample + PolyvinlyPyrolidone

A B C

Fig 4.12 Sample + Polyethylene glycol

Where, **A**= Carbon Quantum Dots.
B= Carbon Quantum Dots + Polymers
C= Control=Distilled water+ Polymers

A B C

Fig 4.13 Sample + Polysorbate 40

Phosphorescence Results:

AMINO ACIDS

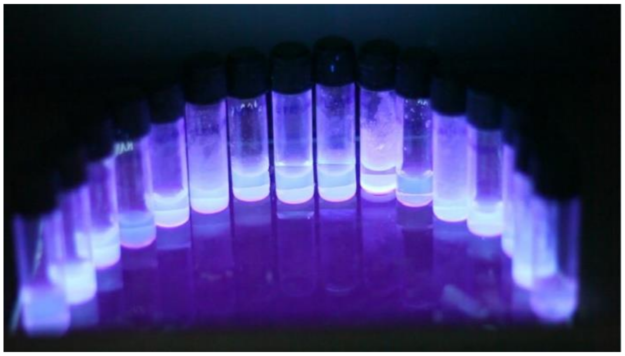


Fig4.14

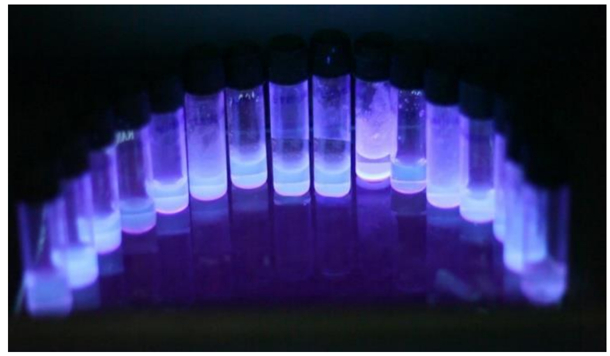


Fig 4.15

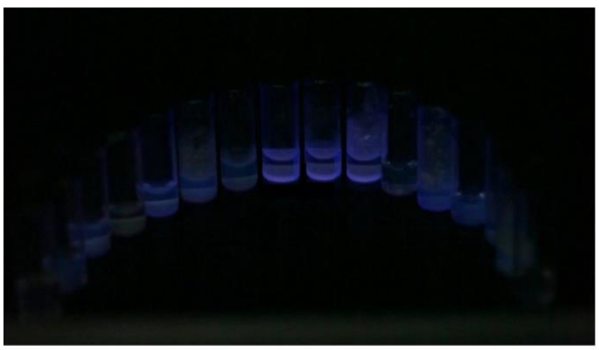


Fig 4.16

Fig 4.17

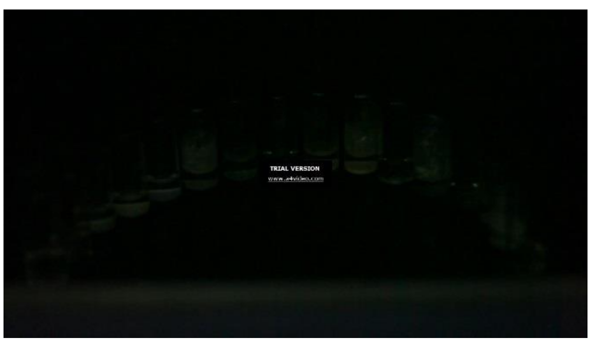


Fig 4.18

From Fig 4.14 to Fig 4.18 the result shows that some amino acids exhibit Phosphorescence nature with Carbon Quantum Dots.

POLYMERS:

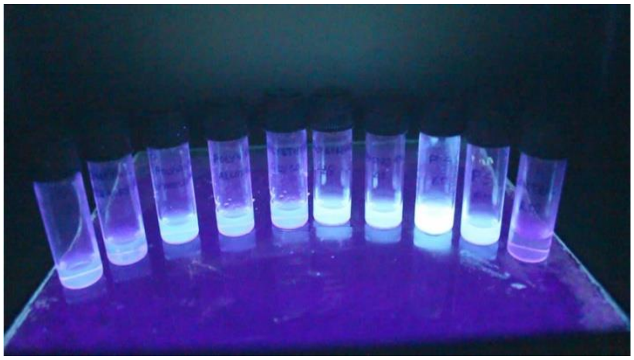


Fig 4.19

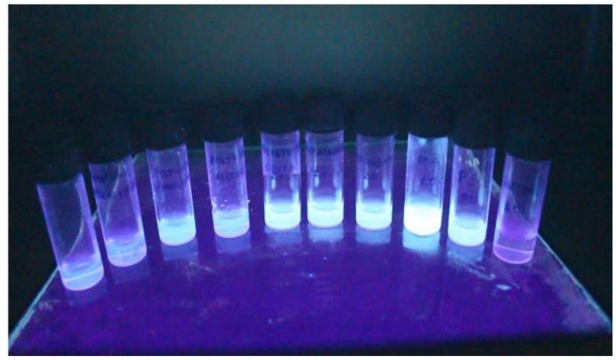


Fig 4.20

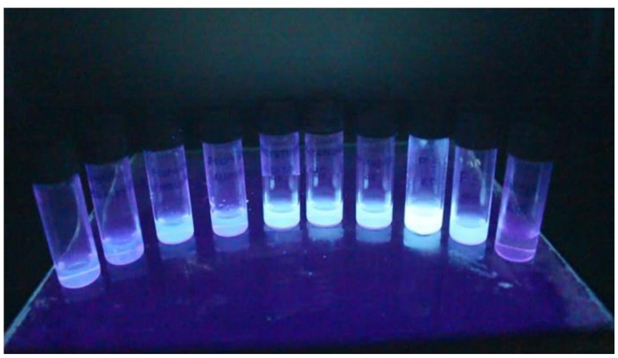


Fig 4.21

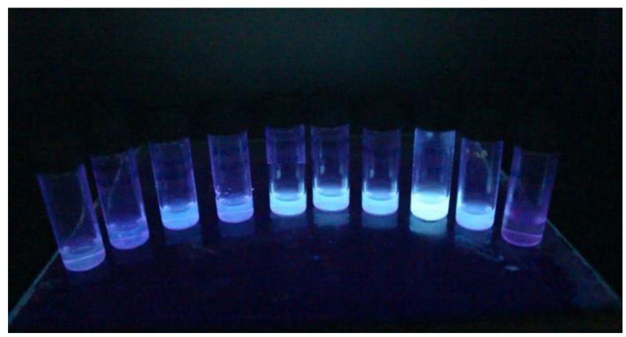


Fig 4.22

Fig 4.23

Fig 4.24

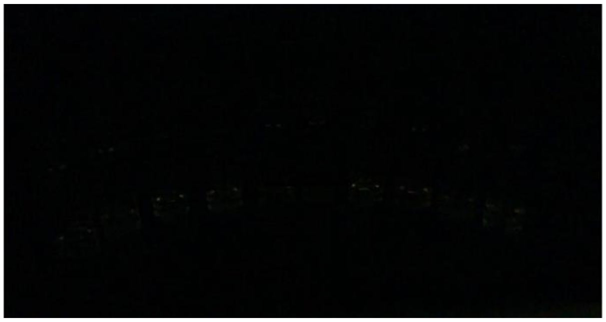


Fig 4.25

From Fig 4.19 to Fig 4.25 shows that some Polymers exhibit Phosphorescence nature with Carbon Quantum Dots.

5. FESEM ANALYSIS:

The carbon quantum dots were observed in multiple sizes during the FESEM analysis with the help of NanoSEM. The majority of particles were small around 10-12 nm in size upon magnifying. Thus the size of the particles was confirmed which are in nanometers in size.

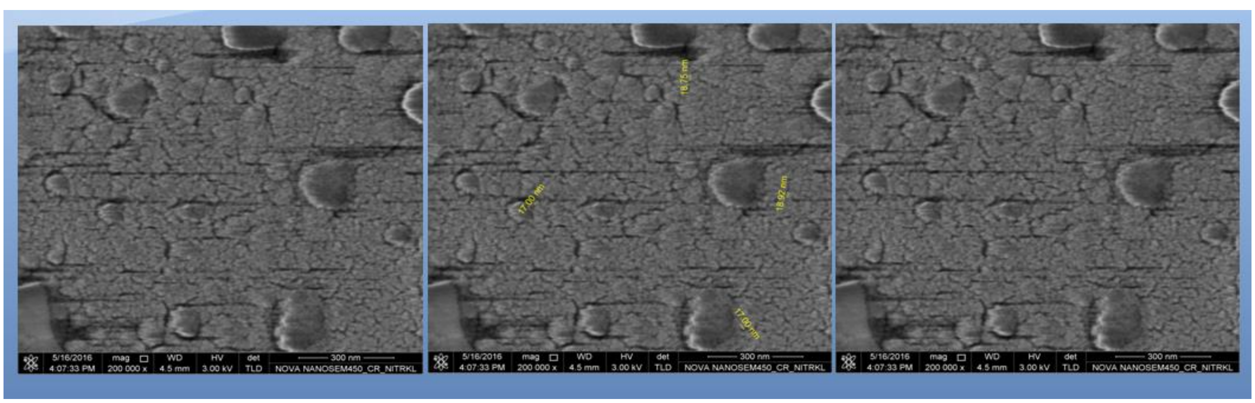


Fig 5.1 Nano SEM images of Carbon Quantum Dots.

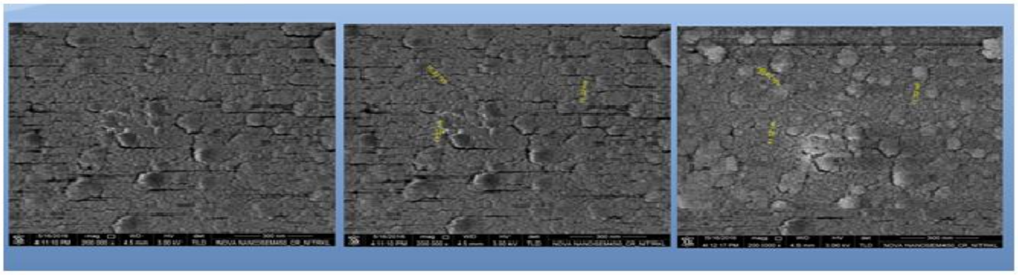


Fig 5.2 Nano SEM images of Carbon Quantum Dots.

6. X-RAY DIFFRACTION (XRD):

In the XRD analysis of the carbon quantum dots the size and nature of the crystallite were revealed. We found multiple peaks in the following shown fig 5.3. From the figure we can conclude that 2θ values are obtained. The 2θ value found for the quantum dots is 36.

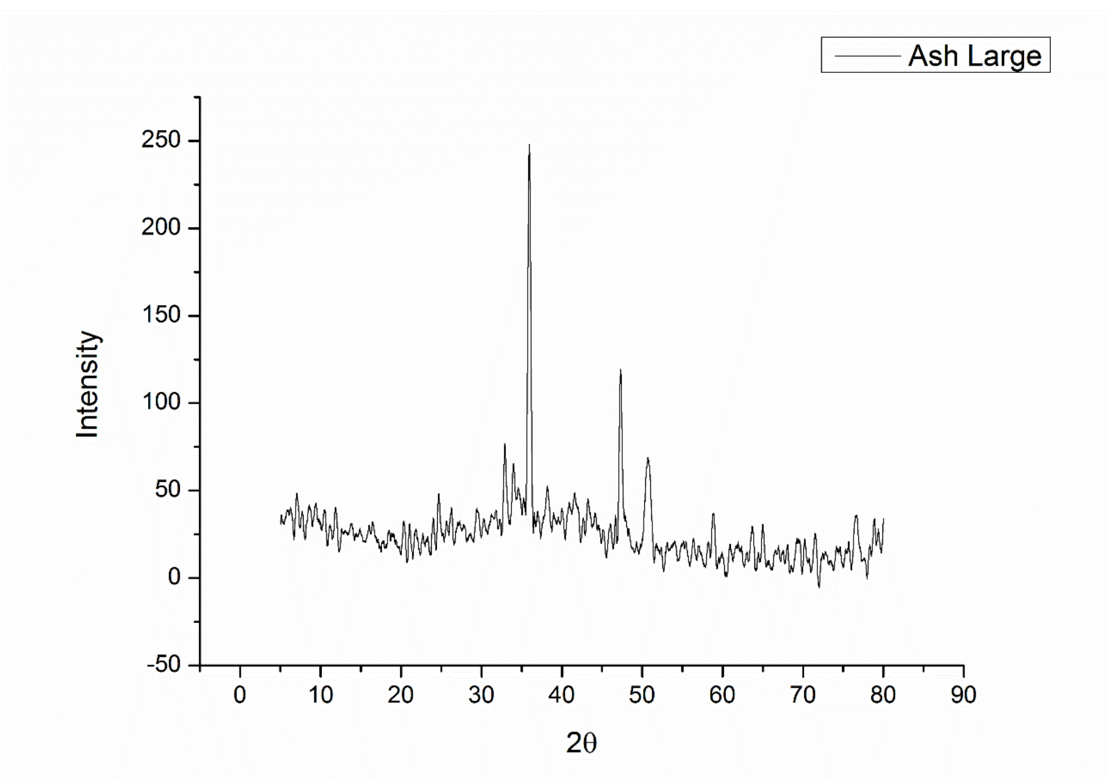


Fig. 5.3

7. SPECTRO FLUORIMETRY:

Spectrofluorimetry is a tool which provides information about the molecular structure which may be derived from the excitation and emission spectra. Fluorescence spectrum intensity depends on the excitation wavelength. Here the excitation wavelength range is from 250-350nm. Different excitation peaks can be seen in the following data graph Fig 5.4. The emission peaks can be seen in the range of 400-600nm.

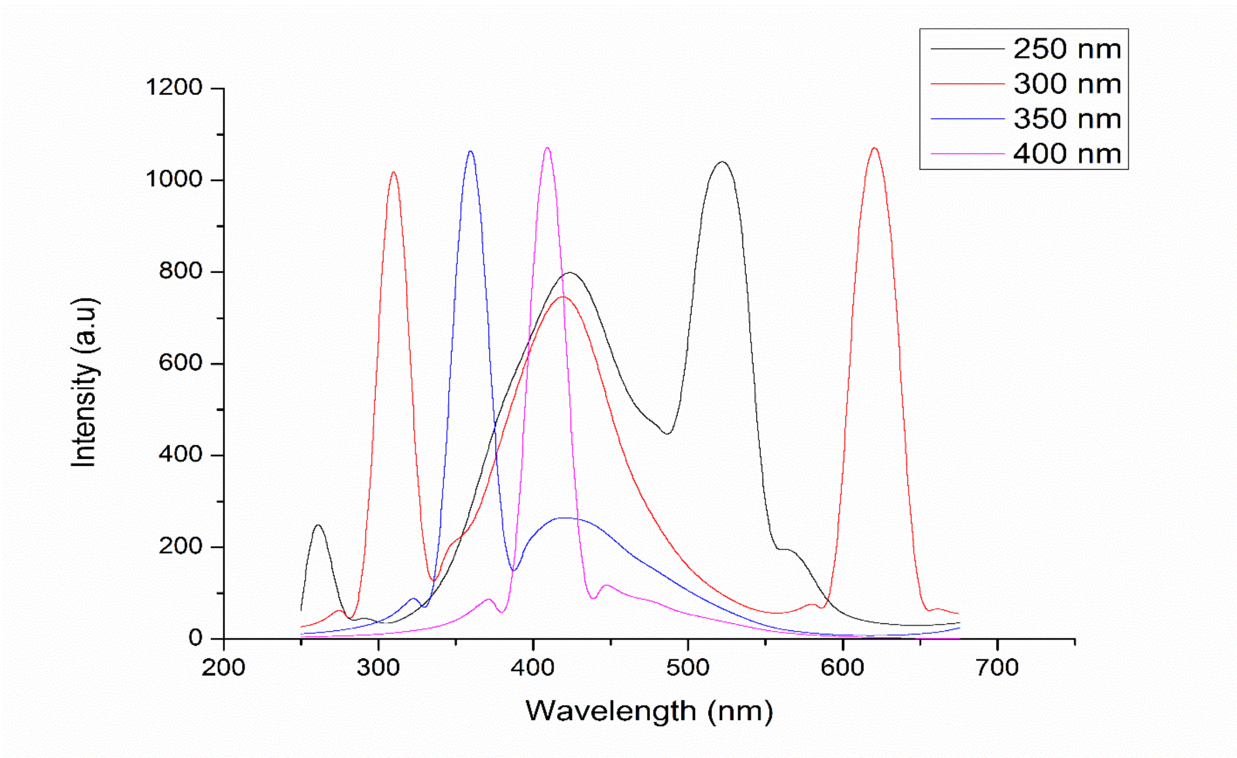


Fig 5.4

CHAPTER 5

CONCLUSION

After executing the above procedures, we came into a conclusion that we have synthesized carbon quantum dots from burnt wood ash by centrifugation method with distilled water. These carbon quantum dots displayed unique and novel properties gave better result of photoluminescence and phosphorescence. Photoluminescence property of CQDs can be used for bio imaging in cells and organisms. The carbon quantum dots revealed their crystalline property upon doing the XRD analysis. There were both particles of smaller size and larger size. Upon excitation they showed multiple peaks from which we can find out the 2θ value. The Spectrofluorimetry results showed absorption and emission spectrum. From the Photo Luminescence and Phosphorescence data from the wood ash sample + additives (amino acids and polymers), we visualize the increase and decrease of fluorescence of the sample. Some sample showed more phosphorescence than others. The ionic salt does not exhibit Photoluminescence property. Thus in case of Ionic salts mixed with Carbon Quantum Dots we can conclude that Ionic Acids does not show Fluorescence with Carbon Quantum Dots. We visualize the increase and decrease of fluorescence of the sample. Some sample showed more phosphorescence than others. Previously no works have been done on amino acids. In this project we have obtained data showing fluorescence and phosphorescence on the amino acids. This the preliminary work done on the carbon quantum dots. Further work can be done in this field.

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