

**SYNTHESIS AND CHARACTERIZATION OF FLUORESCENCE CARBON  
QUANTUM DOTS FROM RENEWABLE SOURCES**

**RAUDHAH BINTI MOHD SALLEH**

**(XRZ7H5)**

**A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE  
REQUIREMENTS FOR THE MASTER OF SCIENCE  
(MATERIAL SCIENCE)**

**FACULTY OF SCIENCE**

**EÖTVÖS LORÁND TUDOMÁNYEGYETEM**

**2019/2020**

## AUTHOR DECLARATION

**Name:** Raudhah Binti Mohd Salleh

**Neptun ID:** XRZ7H5

**ELTE University, Faculty of Science, major:** MSc Material Science

**Title of diploma work:** Synthesis and Characterization of Fluorescence Carbon Quantum Dots from Renewable Sources

As the author of the diploma work I declare, with disciplinary responsibility that my thesis is my own intellectual product and the result of my own work. Furthermore, I declare that I have consistently applied the standard rules references and citations.

I acknowledge that the following cases are considered plagiarism:

- using a literal quotation without quotation mark and adding citation;
- referencing content without citing the source;
- representing another person's published thoughts as my own thoughts.

Furthermore, I declare that the printed and electronically versions of the submitted diploma work are textually and contextually identical.

Budapest, 2020 May 25



---

(Raudhah Binti Mohd Salleh)

## ACKNOWLEDGEMENT

I would like to take this opportunity to express my greatest gratitude towards my project supervisor, Dr Gyulai Gergo and Fatima Ounzi who guided me throughout the project. They had given me valuable information and suggestions to complete this thesis successfully. Their supervision, guidance, encouragement and patient given throughout the project are greatly appreciated. These studies were supported by grant (VEKOP-2.3.3-15-2017-00020) from the European Union and the State of Hungary, co-financed by the European Regional Development Fund. This work was completed in the ELTE Institutional Excellence Program (1783-3/2018/FEKUTSTRAT) and ELTE Thematic Excellence Programme (SZINT+) supported by the Hungarian Ministry for Innovation and Technology. Sincere thanks are extended to the Tempus Public Foundation for granting me the Stipendium Hungaricum scholarship throughout this thesis journey. My appreciation also extend to my family in Malaysia and my course mates who had given me moral support, prayers and unconditional love to ensure the project is completed successfully on time.

## Table of Content

<b>Content</b>	<b>PAGE</b>
Author Declaration	ii
Acknowledgement	iii
Table of Contents	iv
List of Abbreviations	vi
<b>Chapter 1: INTRODUCTION</b>	<b>1</b>
<b>Chapter 2: LITERATURE REVIEW</b>	
2.0 Carbon Dots (CDs)	2
2.1 Synthesis of CDs	2
2.1.1 Bottom-up method	3
2.1.2 Top-down method	5
2.2 Characterization of CDs	7
2.3 Luminescent Properties	8
2.3.1 Photoluminescence	8
2.3.1.1 PL Mechanism	8
2.3.1.2 Effect of excitation wavelength on the CDs	9
2.3.1.3 Effect of pH value for solution on the CDs	10
2.3.1.4 Effect of size of CDs on the PL	10
2.3.2 Enhancing photoluminescence of CDs	11
2.3.2.1 Surface passivation	11
2.3.2.2 Reduction strategies	12
2.3.2.3 Doping	12
2.3.2.4 Chemical means	13

2.4 Up conversion luminescence (UCL)	15
<b>Chapter 3: MATERIAL AND METHODOLOGY</b>	
<b>PART 1: Preparation CDs by using citric acid and urea</b>	
3.1 Raw materials preparations	16
3.2 Apparatus and equipment	16
3.3 Sample preparation	
3.3.1 Molar ratio and kinetic study by using reactor	16
3.3.2 Molar ratio study by using domestic microwave	17
3.4 CDs testing and characterization	17
<b>PART 2: Renewable CDs by using plant</b>	
3.1 Raw materials preparation	
3.1.1 Plant	17
3.1.2 Double distilled water	17
3.1.3 Chloroform	17
3.2 Experimental flow diagram	
3.2.1 Water extraction	18
3.2.2 Solvent Extraction	18
<b>Chapter 4: RESULTS AND DISCUSSION</b>	
<b>PART 1: Preparation of carbon dot by using citric acid and urea</b>	
4.2.1 Microwave assisted reaction	19
4.2.2 Reactor-assisted reaction method (Study on the molecular ratio, volume effect and time reaction)	21
4.2.3 Reaction-assisted reaction method (Kinetics study for A093)	23
<b>PART 2: Preparation of carbon dot by using plants</b>	
4.1 Fluorescence color on the sample	24
<b>Chapter 5: CONCLUSIONS</b>	25
<b>Chapter 6: SUMMARY</b>	25

**LIST OF ABBREVIATIONS**

<b>CDs</b>	Carbon Dots
<b>CQDs</b>	Carbon Quantum Dots
<b>FTIR</b>	Fourier-Transform Infrared Spectroscopy
<b>HRTEM</b>	High-Resolution Transmission Electron Microscopy
<b>IL</b>	Ionic Liquid
<b>MWCO</b>	Multi Wall Carbon Nanotubes
<b>N-CDs</b>	Nitrogen Carbon Dots
<b>O-CDs</b>	Oxygen Carbon Dots
<b>PPEI –EI</b>	Propionylethylenimine-co-ethylenimine
<b>S-CDs</b>	Sulfur Carbon Dots
<b>SWCNTs</b>	Single Wall Carbon Nanotubes
<b>TEM</b>	Transmission Electron Microscope
<b>QY</b>	Quantum Yield
<b>UCL</b>	Up Conversion Photoluminescence
<b>XRD</b>	X-ray Diffraction

## **CHAPTER 1: INTRODUCTION**

Carbonic nanomaterials such as nanodiamonds, fullerenes, graphene, carbon nanotubes and fluorescent carbon nanoparticle have motivated extensive studies on them because of their great potential in a variety of technical applications. Their electronic, physicochemical characteristics, optical and fluorescence properties have attracted rising interest in recent years. Nonetheless, traditional semiconductor quantum dots have certain limitations such as low biocompatibility and high toxicity due to heavy metals used even at relatively small concentrations. Meanwhile the CDs produced in the early stage usually have low quantum yield and solubility.

The green CDs are made from ‘green precursors’ as a source of carbon where the term of ‘green precursor’ refers to any substances which are natural or are derived from renewable products or sources. Therefore, to achieve environmental-friendly, cost-effective and simple method with exciting properties, various green carbon sources were tried and investigated for the creation of CQDs.

Pioneering to this fundamental, it was reported from Liu et al., that they used grass as carbon source with hydrothermal treatment at 180°C. The result had shown the CDs doped with nitrogen, were soluble in water and exhibited 6.2% quantum yield.

## **CHAPTER 2: LITERATURE REVIEW**

### **2.0 Carbon dots (CDs)**

Carbon dots (CDs) have size below 10nm. They are zero-dimensional carbon nanomaterials that consist of an amorphous or crystalline core with an oxidized carbon surface with carboxyl groups and  $sp^2$  carbon [1].

CDs exhibit optical properties like photoluminescence, chemiluminescence and electroluminescence. The chemical and physical properties of CDs vary dramatically by tuning their size, composition, shape and presence of heteroatoms such as oxygen, phosphorus, nitrogen, sulfur and boron [3]. CDs could have a wide range of applications such as chemical sensing, bioimaging, explosive detection, drug delivery, food safety photocatalysis, agriculture and energy conversion.

CDs are stable in aqueous solution and can be derived from organic compounds [2]. Since the building block of CDs is synthesized primarily out of carbon, thus the nanoparticle created is more biocompatible and less toxic compared to traditional semiconductor quantum dots that usually contain heavy metals.

### **2.1 Synthesis of CDs**

There were many sources that can be used to synthesize CDs by using synthetic or natural resources. Sharma et al., 2017 stated that natural resources can be obtained from human derivatives, leaves and plants, waste material, vegetables, animal derivatives, food and beverages and fruits [4].

Xu et al. discovered CDs in 2004 from the side products of single wall carbon nanotubes (SWCNTs) during the purification process [5]. After 2 years, they managed to synthesize stable photoluminescent carbon nanoparticles with variation of size and called it “carbon quantum dots” (CQDs) [6].

One of the unique feature of CDs is that they can contain carboxyl, hydroxyl, carbonyl, amino and epoxy groups that can be used in binding with organic or inorganic moieties [7]. The functionalities allow the CDs surface to bind with hydrophilic or hydrophobic molecules which is important for solvent stability especially in water [8].



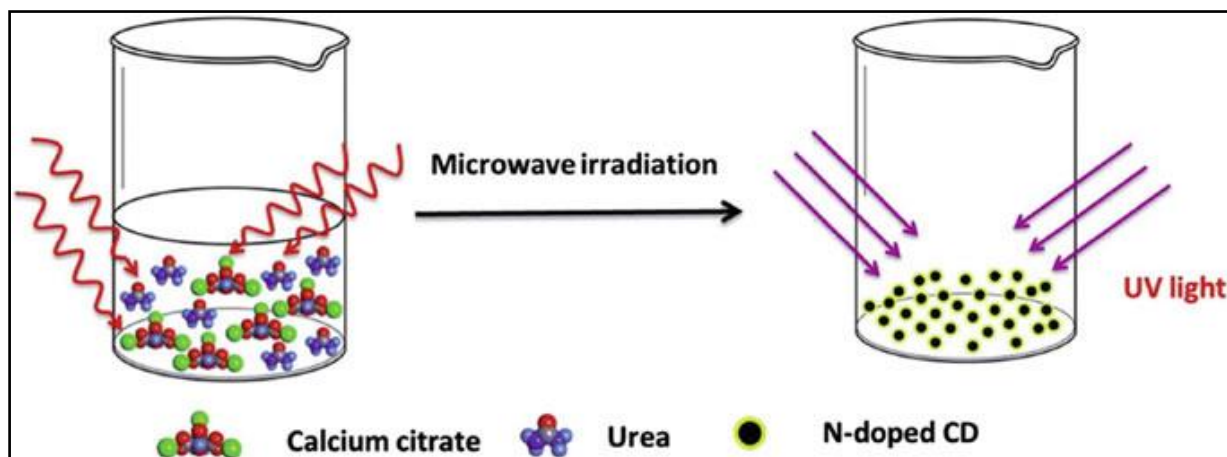
The development of CDs in the last few years involved two main methods, top-down and bottom-up techniques. For bottom-up, it involves microwave irradiation, hydrothermal and pyrolysis methods. Meanwhile, the top-down method involves laser ablation, electrochemical oxidation and arc discharge method.

The morphology of CDs can be affected by the preparation method. The biggest CDs reported so far is 60 nm. Top-down CDs are usually either spherical nanoparticles or nanosheets with relatively big sizes. Meanwhile, bottom-up CDs, are usually considered as carbon quantum dots and TEM confirmed its lateral size less than 10 nm.

### 2.1.1 Bottom-up method

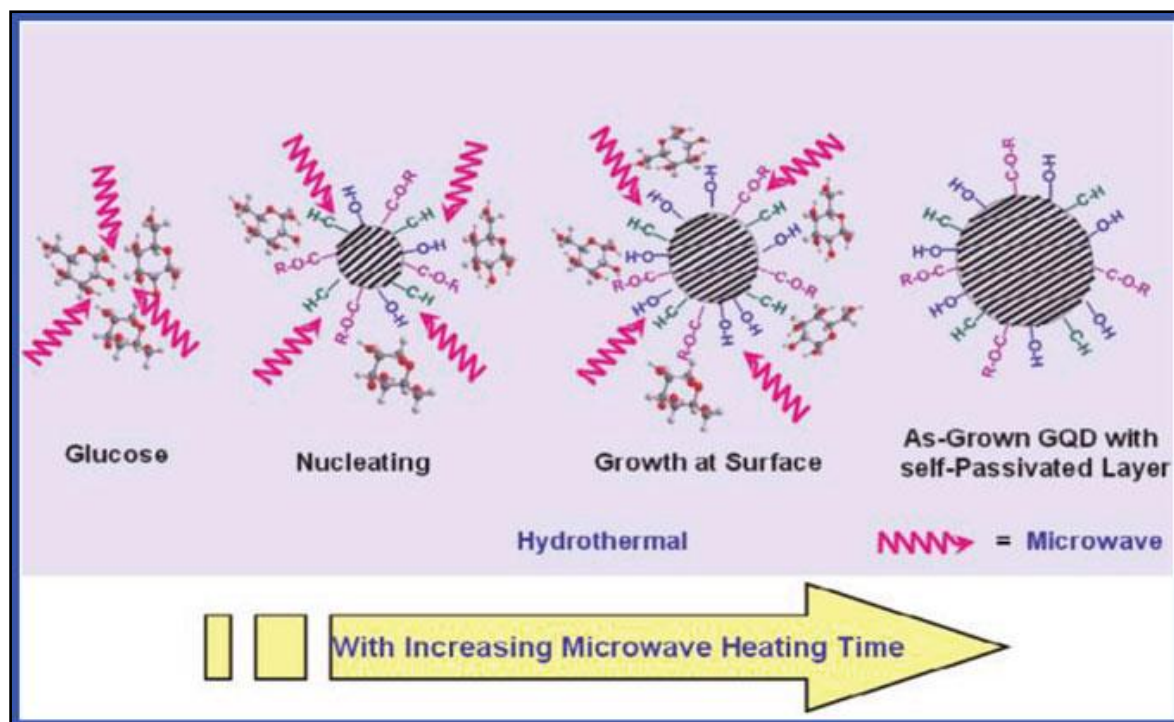
Microwave irradiation with the benefits of time saving, energy efficient and eco-friendly nature received significant attention in the scientific research. In this method, the small organic molecule is carbonized by microwave heating within short period of time. Zhu et al. in 2009 reported the first synthetizations of CDs from carbohydrates source with excellent photophysical properties [9]. Liu et al. in 2011 synthesized CDs from glycerol and bind with 4,7,10-trioxo- 1,13-tridecylenediamine with 12% of quantum yield (QY) due to the presence of amino groups (NH<sub>2</sub>) over the surface of CDs [10]. In 2016, Feng et al. produced CDs with QY of 46% from silkworm chrysalis. These nanoparticles were used in bioimaging due to their properties of low toxicity and photoluminescent nature [11]. Liu et al.,2018 reported photoluminescent CDs from citric acid, L-cysteine and dextrin with 22% of QY. They demonstrated their photostability and could be used for the detection of Cu<sup>2+</sup> in drinking water [12].

High temperature carbonization process for making CDs has been conducted in solvents rather than water. This is because the treatment of carbon sources within *non-coordinating solvents* such as nonpolar or organic solvents will produce highly luminescent CDs. This add-on step was inspired by synthesis pathway of inorganic quantum dots where the nonpolar solvents were believed to assembly and transform the nanoparticles into crystalline colloids. In other words, the nonpolar solvents enhanced the reactivity of the CDs and the amine residues.



**Figure 2.1** Synthesis of N-doped CDs using microwave heating method. The process applies the microwave irradiation of a heterogeneous mixture of calcium nitrate powder and solubilized urea.

Hydrothermal and solvothermal methods have advantages of being a nontoxic, environment friendly, low cost and easy operational techniques. It works by sealing the organic precursor in a hydrothermal reactor and held during the reaction under high temperature and high pressure. Zhang et al.,2010 produced CDs from ascorbic acid with ethanol as solvent [13] and Pang et al.,2017 reported synthesis of co-doped nitrogen and sulfur that derived from the methionine [14]. In the same year, Shen et al. synthesized photoluminescent CDs from the extract of carbohydrates of sweet potato for detection of  $\text{Fe}^{3+}$  with high QY [15].



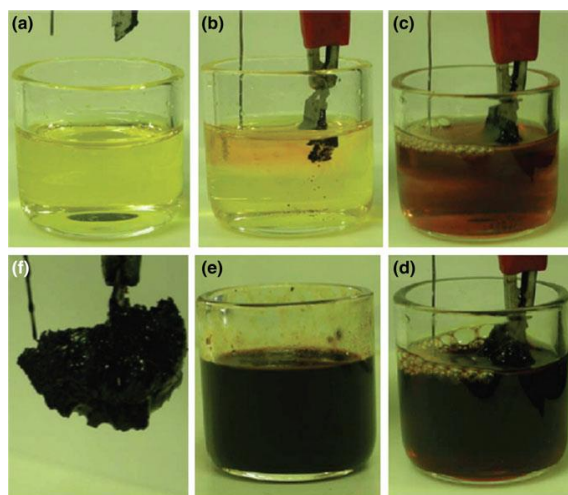
**Figure 2.2** Pathway for nucleation and growth of CDs by hydrothermal method and glucose as a carbon source.

In pyrolysis method, researchers synthesized CDs from organic compound that undergoes chemical reactions with strong acid or alkali under very high temperature. Martindale et al., 2015 synthesized CDs from citric acid at 180°C with average diameter of ~6nm to generate hydrogen fuel for solar energy [16]. Guo et al., 2016 synthesized CDs from keratin hair by one-step pyrolysis method under 200°C for 1h. The CDs produced were used to detect  $\text{Hg}^{2+}$  with higher selectivity and sensitivity [17]. In 2017, Rong et al. synthesized high photoluminescent CDs of nitrogen-doped CDs (N-CDs) from guanidium chloride and citric acid. The CDs were used to detect metal ions and for bioimaging [18].

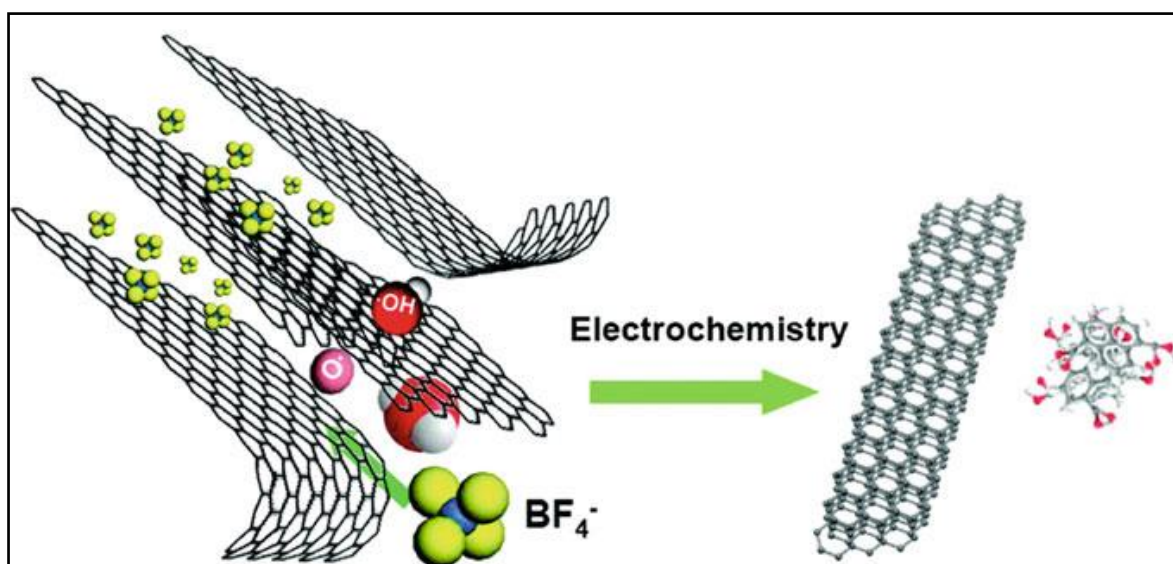
### 2.1.2 Top-down method

In top-down, electrochemical oxidation is used to synthesize ultrapure CDs from larger molecular matter such as carbon nanotube, carbon fiber or graphite using an electrolytic process. In this method, the larger organic molecules are used as electrode in the presence of electrolytes. Zhou et al., 2007 synthesized CDs from multiwall carbon nanotubes with tetrabutylammonium perchlorate as electrolyte [19]. Two years later, Zheng et al. synthesized CDs that has potential as biosensor using graphite as electrode in

the presence of phosphate buffer at neutral pH [20]. In 2017, CDs were synthesized with polyaniline hybrid with high QY and purity. It was also tested has high capacitance and used in energy-related devices [21]. Figure 2.3 shows an experimental setup of an electrochemical cells that apply graphite electrode as carbon source and ionic liquid (IL) as an electrolyte for CDs.



**Figure 2.3** Progress of electrochemical reaction of graphite anode inside electrolyte solution comprising the IL 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF<sub>4</sub>]). The changes of colour from pale yellow to brownish shows the presence of nanoparticle and box (f) is the graphite electrode after reaction.



**Figure 2.4** Proposed mechanisms of the ions that originated from LI penetrate between the graphite sheets while generating carbon nanotubes and CDs.

Using laser ablation, the size of CDs can be varied. In this method, complex organic macromolecules are placed under laser radiation operated in continuous waves or in pulsed mode and the nano-sized carbon particles will be detached from the larger

molecular structures. The first synthesized CDs from this method were reported by Sun et al., 2006 from graphite powder [22]. In 2018, photoluminescent CDs of 3nm size were reported from carbon glassy particles with polyethylene glycol. The prepared CDs were applied in bio imaging of cancer epithelial human cells [23].

The synthesis of CDs from arc discharge method apply direct current arc voltage across two graphite electrodes. Bottini et al. 2006 synthesized CDs from pristine and SWCNTs with bright photoluminescence in the blue-green region and violet-blue region, respectively [24]. In 2014, boron and nitrogen-doped QDs were synthesized.  $B_2H_6$  was used for doping boron and  $NH_3$  for doping nitrogen [25].

## 2.2 Characterization of CDs

Characterization of CDs can be divided into structural and photophysical properties. The structural characterization involves Transmission electron microscopy (TEM), High-resolution TEM (HRTEM), X-ray diffraction (XRD), Raman scattering, X-ray photoelectron spectroscopy and Fourier Transform infrared (FTIR) spectroscopy [26].

TEM is primary technique for visualizing and give information on particle size distribution, morphology and organization of the crystalline. HRTEM can provide information upon the periodicity of the graphitic core, thus reflecting its crystalline nature. XRD helps to confirm the nature of the CDs by providing the information about the unit cell dimensions and crystal spacing measurements. Features of the CDs are revealed by Raman scattering using the ratio of the of D and G bands. The D band corresponds to disordered  $sp^2$  at around  $1350\text{ cm}^{-1}$  and G band comes from the in-plane stretching vibration mode  $E_{2g}$  at around  $1600\text{ cm}^{-1}$ . XPS shows the information on specific atomic units present that relating to the CDs surface. Lastly, the FTIR commonly complements the XPS through recording typical vibration bands to illuminate distinct functional units [26].

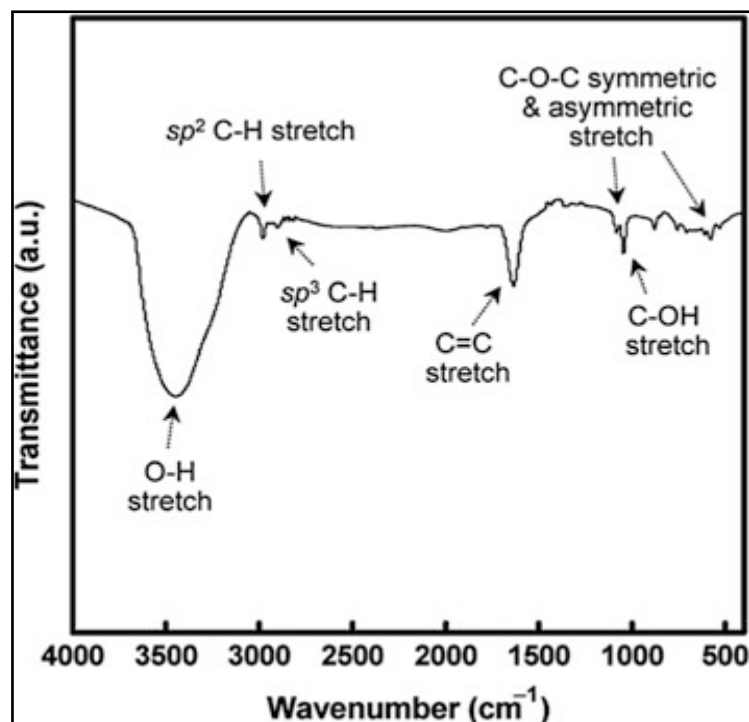


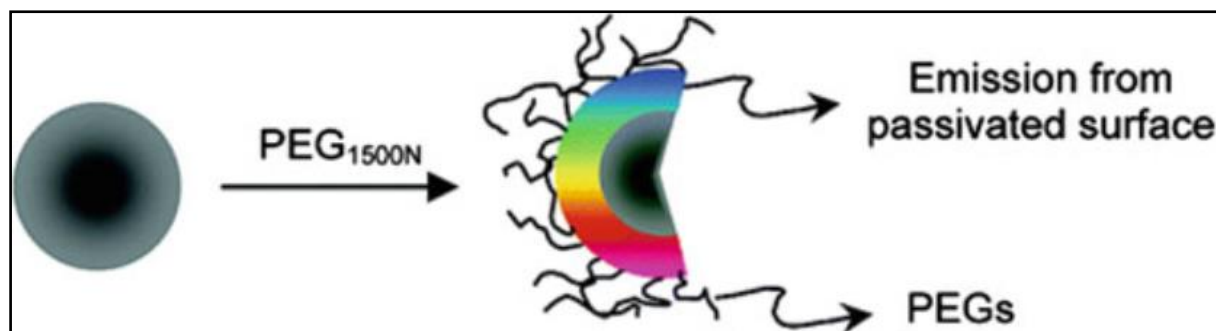
Figure 2.5 Spectrum of FTIR for CDs sample.

## 2.3 Luminescent Properties

### 2.3.1 Photoluminescence

#### 2.3.1.1 PL Mechanism

Photoluminescence is the light emission of matter in any form after the process of absorption of photons. As one of their most fascinating features, photoluminescence on CDs commonly considered to be either intrinsic state emission or defect (surface) state emission. Sun et al., start the surface passivation with some organic polymer to enhance the low luminescent CDs emit bright photoluminescence and they proposed the later photoluminescence should be attributed to the radiative recombination of the excitation from the surface defects CDs that have been passivized. The compound used in the study was polyethylene glycol, PEG as figure below.



**Figure 2.6** Surface passivation of CDs surface with PEG to enhance their luminescence property.

Firstly, the photoluminescence of CDs can be improved via surface passivation with polymer and organic molecules. Secondly, the photoluminescence properties could be tuned by modifying the surface functional groups or oxidation degree. In contrast to other nanoparticles, particularly Qdots, the fluorescence emission has been linked to the “quantum effect” where the nanoparticle of the semiconductor dictates coalescence of energy levels allowing the excitation of electrons from the valence band into the conducting band in the form of discrete energies.

### 2.3.1.2 Effect of excitation wavelength on the CDs

Wavelength dependency or independency is mostly related to the variety of sizes which is also called polydispersity. It may also be due to the surface adsorbed functional groups too. For CDs, the particles formed will differ in size, thus it has wavelength dependency. However, if membrane filtering is performed, the particle formed usually has relatively the same size and rarely effect the wavelength.

Y-P Sun and colleagues passivized the CDs with other molecular species of polymer such as propionylethylenimine-co-ethylenimine (PPEI-EI) and proven the compound helps in generated the photoluminescent of CDs just like PEG. As the excitation wavelengths were progressively increased from 400 to 600nm, the emission spectrum red-shifted gradually but the emission intensities reduced dramatically. In additional, the surface passivation enhances the proliferation of CDs, thus it turns them more hydrophilic and useful for biological application such as bioimaging. Usually, CDs that show excitation-independent photoluminescence have higher photoluminescence quantum yield than CDs exhibiting excitation –dependent photoluminescence.

### 2.3.1.3 Effect of pH value for solution on the CDs

Pan et al., found that the CDs could exhibit strong photoluminescence in alkaline solution rather than acidic solutions and the effect can be reversible. They used CDs by the free zigzag sites with a carbene-like triplet ground to explain pH-dependent photoluminescence. The reason might be due to zigzag sites in the CDs were free and photoluminescence active under alkaline conditions rather than protonated and inactive under acidic solutions [27].

However, most CDs showed different responses at different pH values. There are reports where the photoluminescence of CDs were relatively strong in neutral but decreased in strong acid or strong alkaline solutions [43, 29]. Others found that some CDs have almost pH independent photoluminescence [30]. Therefore, it can be concluded that the pH response of CD photoluminescence is highly dependent on the synthesis method.

### 2.3.1.4 Effect of size of CDs on the PL

As discussed before, the photoluminescence of CDs could be attributed to the surface states or the small  $sp^2$  clusters. Nevertheless, there were evidences showed that the photoluminescence could be affected by their size. Sun et al., found that larger size CDs with average 30-50 nm diameter and same surface passivation were much less luminescent compared to smaller CDs with less than 10 nm diameter [31].

According to that observation, they proposed that the ratio of surface-to-volume is important upon surface passivation and the photoluminescence could be affected by their size.

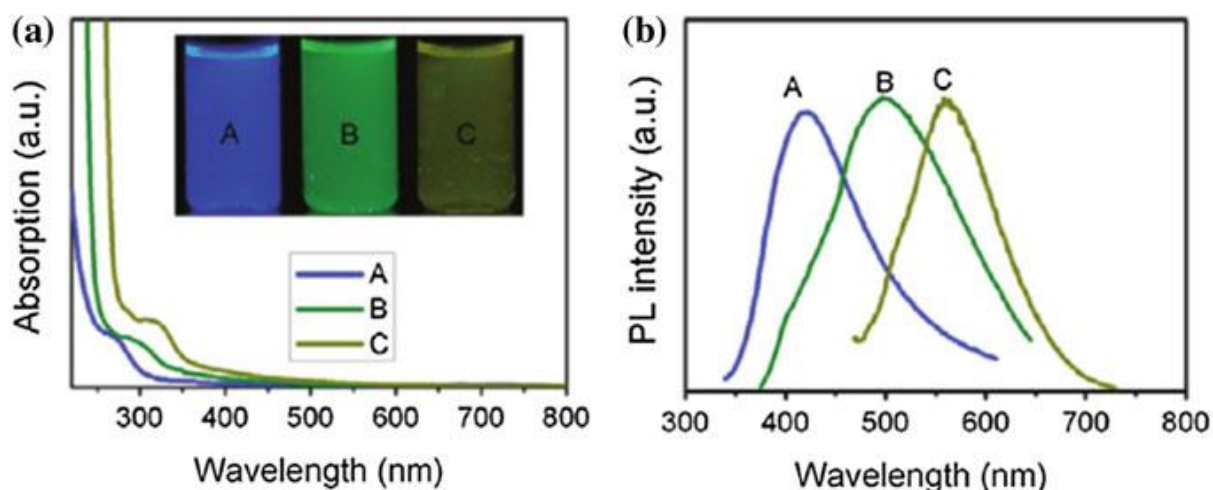
Pang et al., separated the obtained CDs from alkali-assisted electrochemical oxidation of graphite into two fraction sizes ( $1.9 \pm 0.3$  and  $3.2 \pm 0.5$  nm) using dialysis membranes. They found that larger CDs emitted yellow photoluminescence while the smaller CDs emitted blue photoluminescence [32].

Lee et al., separated the obtained CDs from alkali-assisted electrochemical oxidation of graphite using column chromatography. They found that as the size of CDs



increased gradually from 1.2 to 3.8nm, the photoluminescence emission red-shifted from UV light to near-infrared light [33].

Peng et al., synthesized CDs by chemically oxidizing carbon nanofibres and separated into different size distribution 1-4 nm, 4-8 nm, and 7-11 nm. The size differences were obtained by tuning their reaction temperature. The colour of the solution changed from blue and green to yellow with increasing size of CDs particle as figure below [34].



**Figure 2.7** (Left) UV-vis spectra of A,B and C correspond to different temperature 120, 100 and 80 °c. (Right) Photoluminescence spectra of CDs with difference emission colour excited at 318, 331 and 429 nm.

It should be considered that the size-effects on the photoluminescence spectra were only shown same or quite similar if the same method preparation applied, as they present similar surface states. Otherwise, different preparation method of CDs may have quite different photoluminescence properties even though the size distributions are similar.

### 2.3.2 Enhancing photoluminescence of CDs

#### 2.3.2.1 Surface passivation

Usually top-down methods are easier to prepare for CDs with different photoluminescence ranging from blue to red. However, the quantum yield obtained was relatively low; less than 3%. Thus, there were many efforts carried out to improve the photoluminescence. One of the popular methods is passivizing the surface states by some

organic polymers. Sun et al., passivized using PEG as mentioned in above discussion and succeed to achieve a quantum yield from relatively 4% to 10%. Despite involving a long-time refluxing procedure, some researches still try to develop a one-step procedure; integrating the synthesis and passivation.

Hu et al., used a pulse Nd:YAG laser to irradiate graphite or carbon black dispersed under ultrasonication in diamine hydrate, diethanolamine or PEG 200. The obtained CDs could emit similar strong PL properties as those of post-passivated CDs [35]. In addition, for bottom-up synthesis, the passivation agents could be added up directly into the organic precursor. As for example, Gianelis et al., synthesized series of ammonium carboxylate complexes through acid base combination between organic amines and organic acid. During the thermal treatment, one acts as carbon source and the other part acts as the surface modifier [36].

#### 2.3.2.2 Reduction strategies

Reducing CDs with some strong reductants are able to improve the photoluminescence quantum yield of the CDs. Zheng et al., used  $\text{NaBH}_4$  and found out there were no obvious changes of morphologies but the emission spectrum blue-shifted from 520 to 470 nm and the quantum yield increased from 2 – 24 % [39]. Dong et al., used hydrazine for chemically oxidizing XC-72 carbon and observed that the photoluminescence spectrum blue-shifted from 525 to 455 nm [40].

#### 2.3.2.3 Doping

Sun et al., suggested that doping was a new weapon to obtain highly photoluminescence CDs. They coated CDs with zinc oxide or zinc sulfide and later passivized with PEG 1500. Surprisingly the quantum yield obtained was much higher than undoped CDs; 50 and 45% [37].

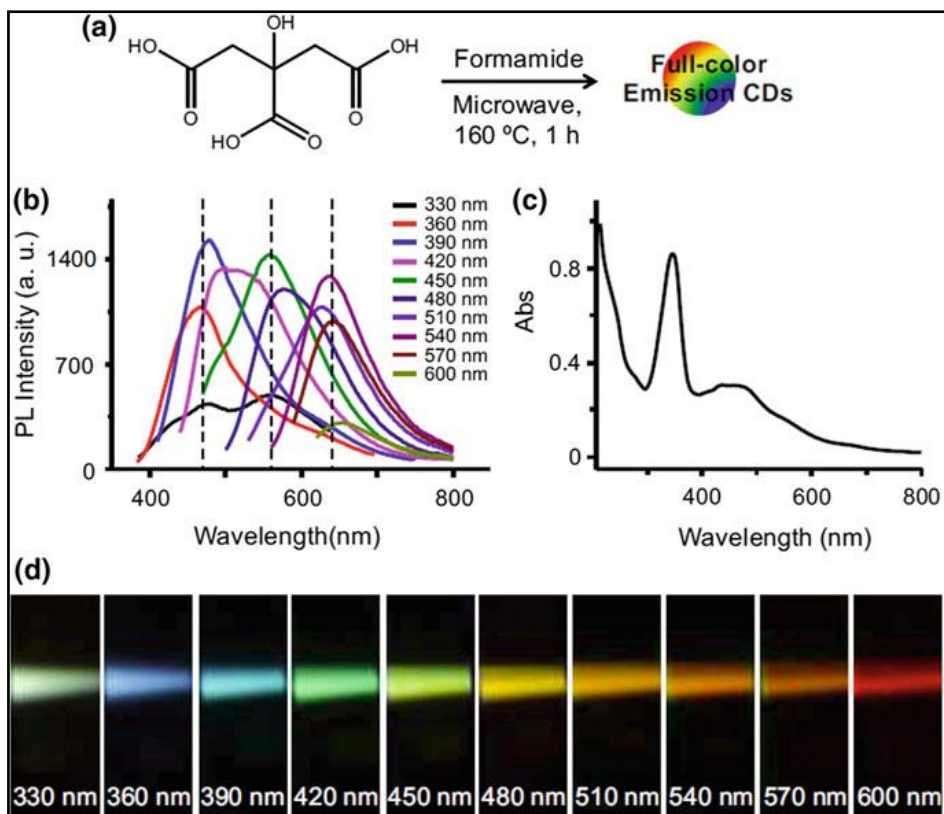


**Figure 2.8** CDs doped with ZnS. (*Left*) – Image of ZnS lattice planes within CDs (circled) under HRTEM. (*Right*) – Fluorescence in present in all solutions of CDs/semiconductor composites under UV irradiation.

Besides that, other studies also tried to dope CDs resulting in nitrogen N-doped CDs (N-CDs), nitrogen and sulfur doped N,S-CDs and oxygen doped O-CDs. It was found that doping with Nitrogen could introduce new kind of surface states. The electrons trapped by the new surface might be able to facilitate a high yield of radiative recombination and their density could be increased intensely with the co-doped sulfur atoms, thus resulting in further enhancement of photoluminescence [38].

#### 2.3.2.4 Chemical Means

Modulation of the functional or structural properties of CDs via chemical means has become prominent research in controlling the excitation-dependent emission profiles of CDs [26]. H Lin et al., synthesized CDs with emission “full color” upon excitation at different wavelengths [27]. The multicolor properties of the CDs in figure 2.8 were related to the multi-functional groups on the surface particularly aromatic residues like C=N, C=O and C-N bonds.



**Figure 2.9 (a) Synthesis scheme of CDs. (b) Fluorescence emission peaks at different excitation wavelength. (c) Broad absorbance peak spectrum from UV-VIS relative to the presence of multiple energies absorbed. (d) Luminescence colours at different wavelength.**

Beside aromatic residues, the CDs were also passivized through esterification reactions and exhibited “on-off” photoluminescence. The research was conducted using citric acid as a carbon precursor and shown diminished fluorescence in highly acidic conditions. However, the additional step of esterification upon hydroxide and carboxylic acid residues with alcohols managed to produce highly fluorescent CDs [28].

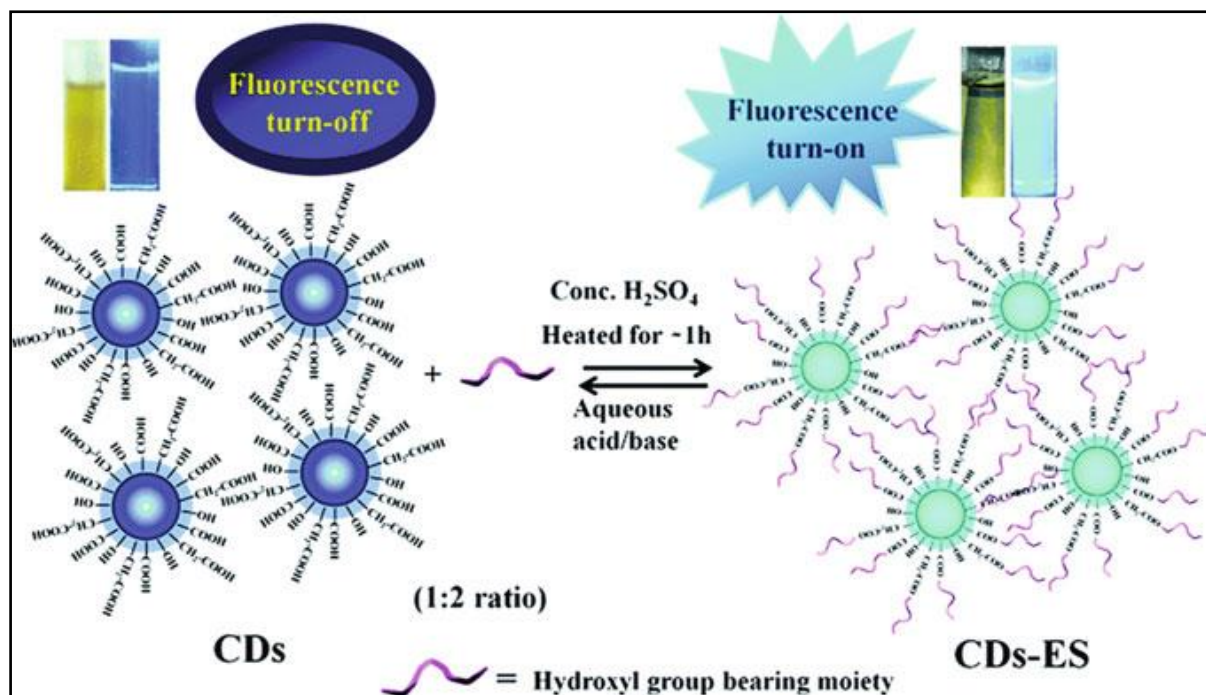


Figure 2.10 (Left) CDs in citric acid with low fluorescence at pH=1. (Right) CDs in acid undergo esterification with alcohol bearing moieties and show increasing fluorescence.

#### 2.4 Up Conversion Luminescence (UCL)

UCL an anti-stokes process whereby low-energy absorbed photons are converted into higher-energy emissions. UCL has advantages for weak background interference, long lifetime, low excitation energy and strong tissue penetration. These interesting features for nanostructures can be applied in anti-counterfeit, bioimaging, therapy and many more [42]. Sun et al., reported a small aliquot of the aqueous solution of surface passivized CDs was drop on cover glass and evaporated its water. Then it was measured by a confocal fluorescence microscope equipped with laser. The CDs exhibited very high intensity emission when excited with either 458 nm or 800 nm wavelength laser. Thus, they proposed that the emission originating from the 800nm excitation was two-photon luminescent [41].

## **CHAPTER 3: MATERIALS AND METHODOLOGY**

### **PART 1: Preparation CDs from citric acid and urea.**

#### **3.1 Raw materials preparations**

Citric acid and urea used were getting from the ELTE Lab storage.

#### **3.2 Apparatus and equipment**

- I. Weighing scale
- II. Spatula
- III. Parafilm
- IV. Centrifugator
- V. Evaporator
- VI. Glucose membrane

#### **3.3 Sample preparation**

##### **3.3.1 Molar ratio and kinetic study by using reactor**

Citric acid and urea were incorporated together with different mass ratio according to table below:

<b>Sample code</b>	<b>Mass CA/UREA (g)</b>	<b>Time</b>	<b>Volume (ml)</b>	<b>Note</b>
A091	0.32/0.20	5h	15	
A092	0.96/0.60	5h	15	
A093	0.96/0.60	Kinetic studies	15	Time (5, 15, 30, 60, 120, 180, 240, 300 mins)
A094	0.96/0.60	1h	15	
A095	0.16/0.10	1h	5	
A096	0.32/0.20	1h	5	

Citric acid and urea were weighted as per described in table above. Then all the samples were synthesized using reactor and kept in same temperature at 180°C, same power at 200 and same solvent used; water. Meanwhile, the time reaction and volume were varying according to the purpose of the study.

### 3.3.2 Molar ratio study by using domestic microwave

Sample code	Mass CA/UREA (g)
CDD1	0.1/0.9
CDD2	0.2/0.8
CDD3	0.3/0.7
CDD4	0.4/0.6
CDD5	0.5/0.5

Citric acid and urea were weighted as per described in table above. Then all the samples were synthesized using domestic microwave and kept in same volume at 5 ml, same time reaction at 10 minutes and same solvent used; water. Lastly, temperature was not able to control by using domestic microwave technique.

### 3.4 CDs testing and characterization

All the samples that were synthesized in the reactor undergo UV-VIS analysis. All the samples that were synthesized in the microwave-assisted reaction method had the fluorescence result by using Varian Cary Eclipse fluorescence spectrophotometer. 3D spectra were recorded in the 250-500 nm excitation and 250-800 nm emission range.

## PART 2:

### 3.1 Raw materials preparations

#### 3.1.1 Plants

2 types of plants used; Celery (*Apium Graveolens*) and Coriander (*Coriandrium Sativum*)

#### 3.1.2 Double distilled water (DDW)

DDW mainly used for extraction of the plant was self-prepared in the ELTE lab.

#### 3.1.3 Chloroform

Chloroform or dichloromethane for plant extraction.

### 3.2 Experimental flow

### **3.2.1 Water extraction**

50 g of plant were mixed with 100ml distilled water as to prepare the sample before they were blended until soft and filtered. The sample was centrifuged for 10 minutes at 20000 rpm. Then, the sample was filtered for second time and took into microwave for 1, 4, and 6 hours. All the samples were kept at temperature 180°C, pressure 19.0 and power 50 during the reaction. After that, the sample was concentrated using rotary vapor. Last but not least, the sample undergoes dialysis and concentrated using lyophilization technique.

### **3.2.2 Solvent extraction**

50 g of plant were mixed with 100ml distilled water as to prepare the sample before they were blended until soft and filtered. The sample was centrifuged for 10 minutes at 20000 rpm. Then, the sample was filtered for second time and chloroform was added. Next, the sample was took into separatory funnel and transferred into centrifugator again. 10 ml of centrifuged sample (without any distilled water was added) was taken and put inside the microwave for 1, 4, and 6 hours. Last but not least, the sample undergoes dialysis and concentrated using lyophilization technique.

Both supernatant and precipitation are kept for further analysis before and after filtration, centrifugation and separation steps.



## **4.0 RESULTS AND DISCUSSION**

### **PART 1: Preparation of carbon dot by using citric acid and urea**

#### **1. Microwave assisted reaction**

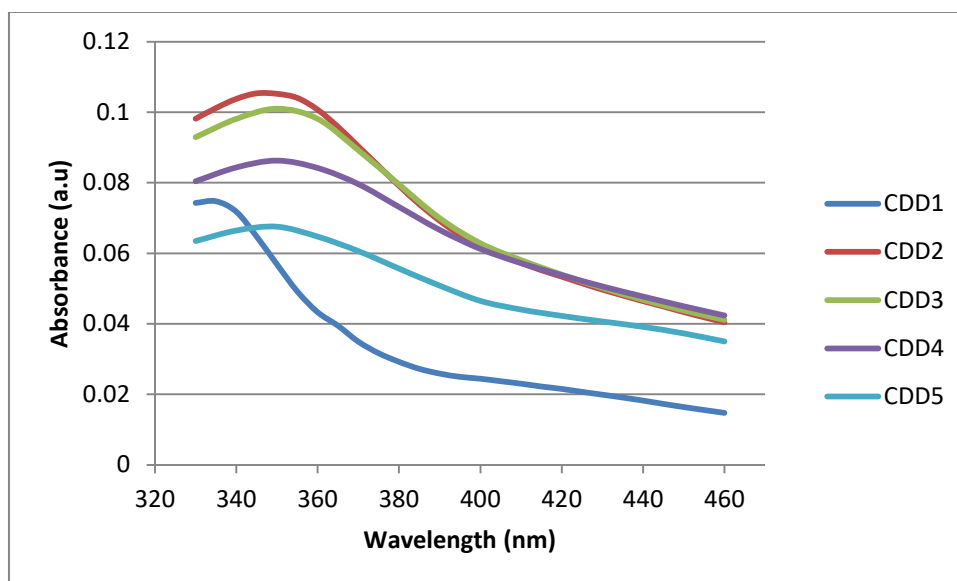
Table 3.1 below shows the relationship of the different molar ratio of citric acid and urea to the wavelength. Citric acid and urea were mixed together and the UV spectra of the originating solution were recorded. The time elapsed for each sample was kept constant for 10 minutes. The values of maximum absorbance were also shown at the specific wavelength for every sample.

Sample	Molar ratio (CA:Urea)	Absorbance (a.u)	Wavelength (nm)
CDD1	0.1/0.9	0.07	335
CDD2	0.2/0.8	0.11	345
CDD3	0.3/0.7	0.10	350
CDD4	0.4/0.6	0.09	350
CDD5	0.5/0.5	0.07	350

**Table 4.1 Difference molar ratio of CA and Urea relatives to the absorbance and wavelength under microwave-assisted technique.**

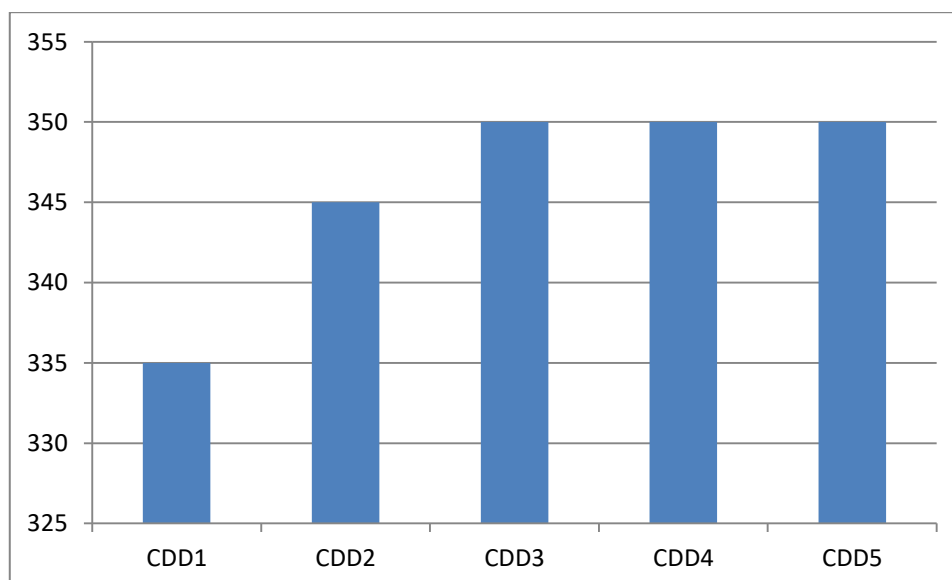
The UV-Vis spectra recorded for each molar ratio using microwave-assisted technique can be seen in figure 3.1. The absorbance spectra range lies between 330nm to 450 nm. It shows that the value of the absorbance increase when the citric acid is used for 10% and 20% of the sample and decrease as per citric acid is added from 60%, 80% and 100% in the sample.

As seen in figure below, the absorption peaks appeared in all samples are significantly blue shifted. This absorption shift takes place due to the quantum confinement effect. The result indicates that a blue shift has been observed with increasing urea composition and most likely corresponds to the  $n \rightarrow \pi^*$  transitions.



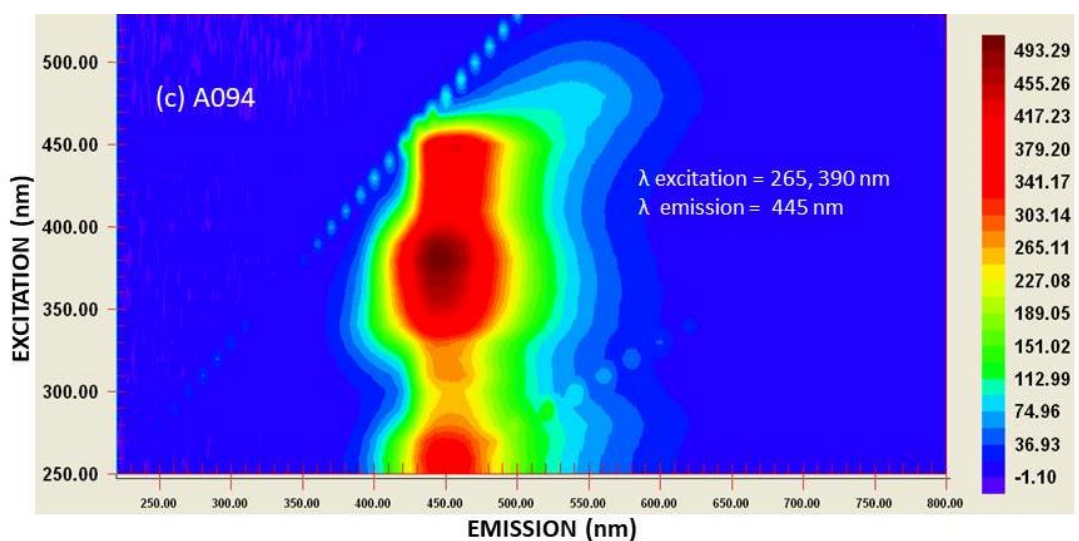
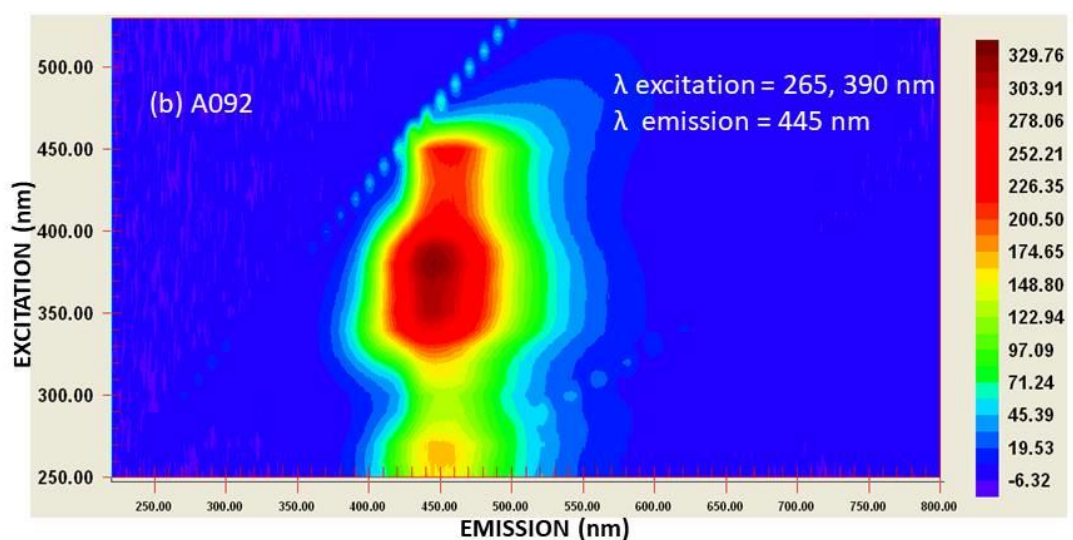
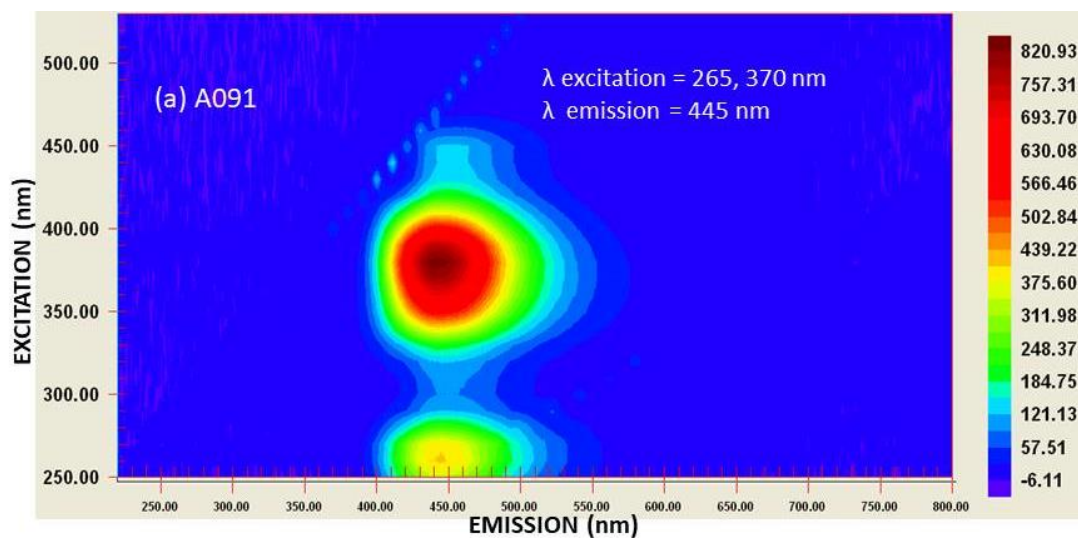
**Figure 4.1: Relationship absorbance and wavelength for difference molar ratio citric acid and urea using microwave-assisted technique.**

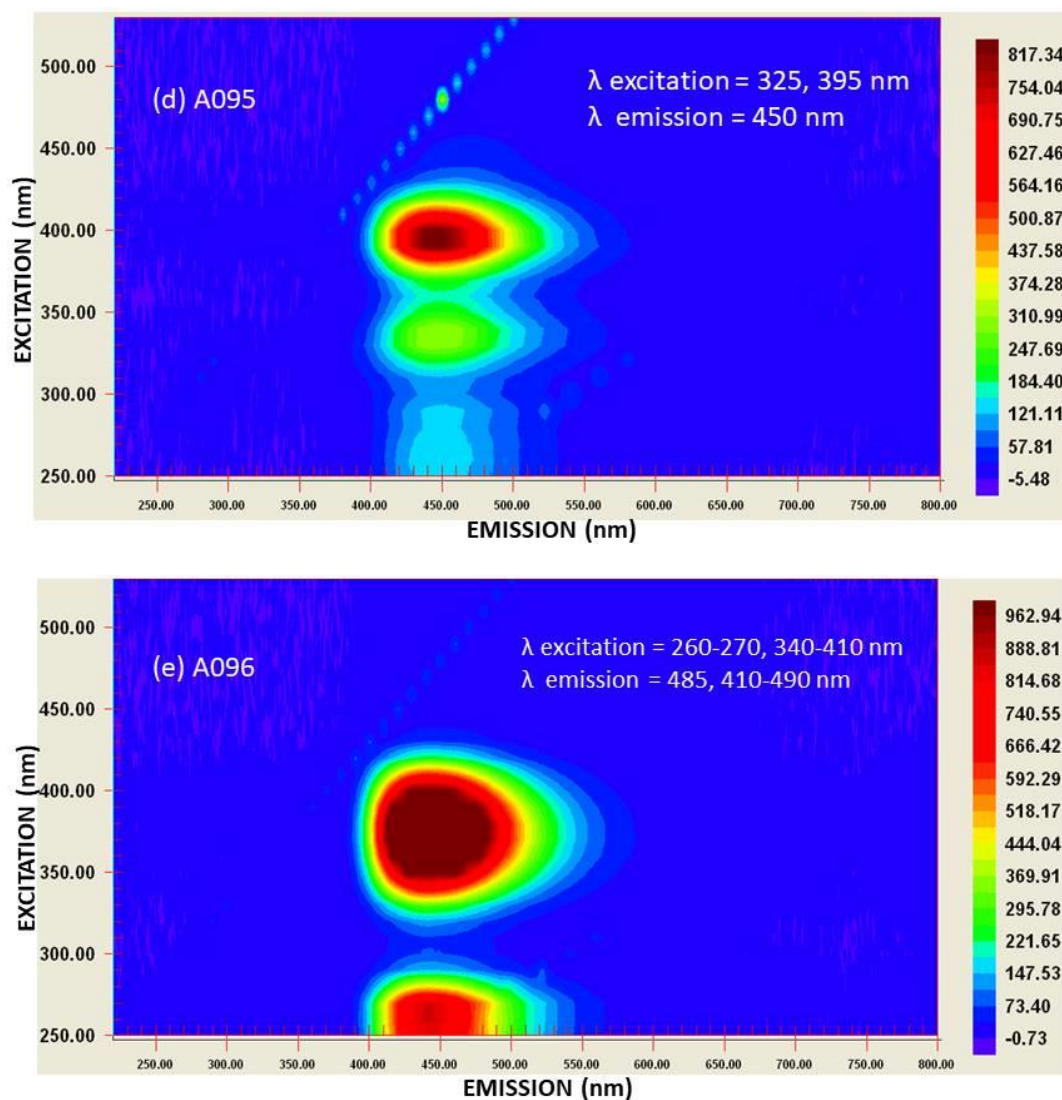
Figure 4.2 shows the relationship distribution of molar ratio to the wavelength of citric acid and urea by using microwave-assisted wavelength. The maximum absorptions peak at the wavelength increase as the citric acid is used up from 20% until 60% and then remains constant at 350 nm for 80% and 100% amount of citric acid.



**Figure 4.2: Relationship distribution of molar ratio to the wavelength of citric acid and urea by using microwave-assisted wavelength.**

## 2. Microwave-assisted reaction method (Study on the molecular ratio, volume effect and time reaction)





**Figure 4.3 (a-e) Excitation and emission fluorescence spectrum for synthesis quantum dot of citric acid and urea in reactor.**

Sample	Molar ratio (CA:Urea)	Vol. (ml)	Time (h)	$\lambda$ max. excitation (nm)		$\lambda$ max. emission (nm)	
A091	0.32/0.2	15	5	265	370	445	
A092	0.96/0.6	15	5	265	390	445	
A094	0.96/0.6	15	1	265	390	445	
A095	0.16/0.1	5	1	325	395	450	
A096	0.32/0.2	5	1	260-270	340-410	485	410-490

**Table 4.2 Relationship maximum excitation and emission on different molar ratio and volume in the production of quantum dot using reactor.**

For concentration comparison in large volume, we have A091 and A092 samples. Both of them have the same volume of 15ml and 5 hours reaction time. A092 has

concentration three times higher than the A091. Both of A091 and A092 shows maximum excitation 265nm and 370nm whereas the maximum emission at 445nm.

For concentration comparison in small volume 5ml, we have sample A095 and A096. A096 has concentration two times higher than A095 and they show different behavior from the 15ml. A096 has smaller maximum excitation at 260-270nm and 340-410nm than A095 at 325nm and 395nm. Nonetheless, maximum emission shows the opposite trend; A096 has higher emission at 485nm and 410-490 than A095 at 450. It shows that the higher the molar ratio, the wavelength broadened and reduced.

For time comparison in the same concentration constituent, we have sample A092 and A094. A092 was prepared in 5 hours meanwhile A094 was prepared in 1 hour. Both of them shows the same maximum excitation set at 265nm and 390nm and the same emission than 445nm. During the synthesization of CDs for 1 hour, the maximum excitation moves slightly toward lower energies with increasing size particle. This condition was consistent with quantum confinement effects idea.

### 3. Domestic microwave-assisted reaction method (Kinetics study for A093)

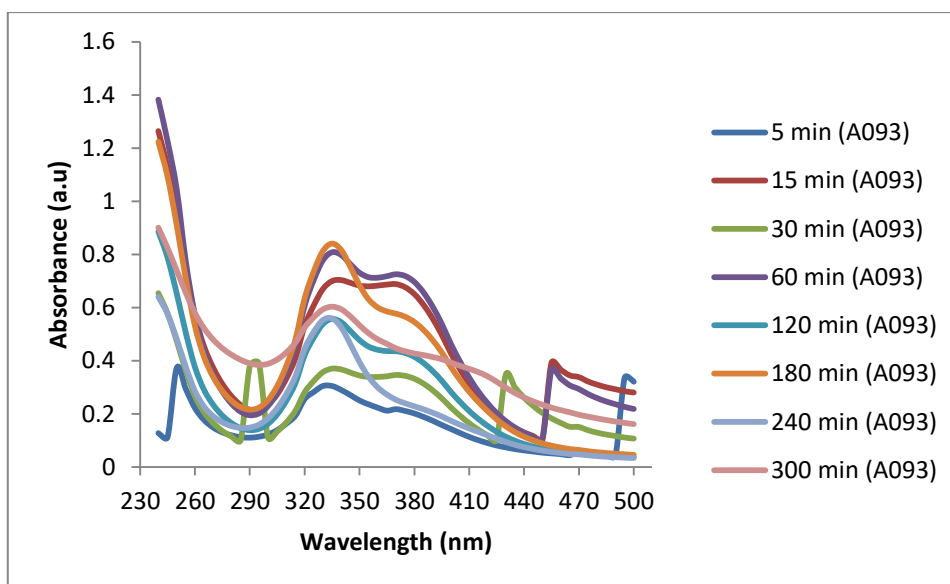


Figure 4.4 Absorbance spectra of different CDs prepared with increasing reaction time.

Sample	Absorbance (a.u)	$\lambda$ max (nm)
A093_05	0.37	250
A093_15	1.26	240
A093_30	0.65	240
A093_60	1.38	240
A093_120	0.87	240
A093_180	1.22	240
A093_240	0.64	240
A093_300	0.90	240

**Table 4.3: Relationship of kinetic study for A093 with ratio 0.96:0.6 of citric acid and urea. The reaction times were varied from 5, 15, 30, 60, 120, 180, 240 and 300 minutes. The range of the spectrometer was set between 240nm to 500nm.**

As the time increases, the wavelength maintain after 15 minutes at 240nm. However, the absorbance values alternate increasing and decreasing at each time recorded. It is obviously shown that sample A093 at minute 180 has the optimum value of absorbance. Nonetheless, beyond 430nm, each time reactant shows significant behavior respectively. This would logically relate that over time, particle will become larger. This is equivalent to less energy needed to excite an electron, hence the longer wavelength observed.

In addition, the breakdown of quantum mechanics as objects become too large and enters the realm of classic physics. Each graph seems to trail off quite faster and shows little changes when the size becomes too great.

## **PART 2: Preparation of carbon dot by using plants**

For both water extraction and solvent extraction, there were two observations,

1. All of the samples were tested using laser pointer and shown fluorescence color.
2. As the time-frame inside the microwave increasing for 1,4 and 6 hours, the color of the samples became paler and emitting at shorter wavelength

Other characterizations and tests were not able to conduct due to pandemic Covid-19 occurred.

## **CHAPTER 5: CONCLUSION**

In conclusion, for the renewable CDs from citric acid and urea shows, different technique, concentration and time reaction could enhance significant behaviour of the CDs and shows different optical properties. Meanwhile, renewable of CDs from Celery and Coriander leaves could be able to create using reactor. In further suggestions, of course a lot of more experiments need to be carried out to tailor the properties of the products.

## **CHAPTER 6: SUMMARY**

### **SYNTHESIS AND CHARACTERIZATION OF FLUORESCENCE CARBON QUANTUM DOTS FROM RENEWABLE SOURCES**

**Raudhah Binti Mohd Salleh**, MSc student in Material Science

Place of Diploma work: Laboratory of Interfaces and Nanostructures, ELTE Budapest

Supervisor: **Dr Gyulai Gergő, Fatima Ouanzi**

The primary goal of my work was to synthesize and characterize fluorescence carbon quantum dots (CDs) from different molar ratio of citric acid with urea and plants used as precursors. There were three main studies in this research.

Firstly, citric acid and urea with different molar ratios were pyrolyzed in a domestic microwave. All the samples were synthesized in 10 minutes, using 5ml volume of water as solvent. It shows that the UV-Vis absorbance increased as the citric acid content of the precursor mixture increased up to 20% of molar ratio.

Secondly, citric acid and urea with different molar ratios were synthesized in a hydrothermal microwave reactor. The precursor mixtures, dissolved in water were kept at 180°C for a given time. At this part, the molar ratio and the volume were varied and compared as to study the effect of experimental conditions on the UV-Vis absorbance and its maximum wavelength as well as fluorescence properties. As a result, it was found that the reaction volume does have a significant effect on the maximum fluorescence excitation and emission wavelengths of the sample. This implies that simply changing the reaction volume, the chemical nature of the forming CDs can be different.

The effect of reaction time on the properties of the products was also studied using fixed precursor molar ratios of citric acid and urea. We found that as the reaction time progress that after an initial shift in the absorption maximum the overall shape of the spectra do not change, while the absorption value changes non-linearly. This indicates that the CDs form quite rapidly, and with increased reaction time only the conversion is affected.

To study if more complex renewable precursors, like plant materials can be used to synthesize CDs, celery and coriander were used as starting materials. Processed samples derived from the plants were subjected to different amounts of time to microwave irradiation in hydrothermal conditions using the microwave reactor. After purification of the samples it was found that under UV light the samples developed a distinct visible fluorescence, indicating the presence of CDs. In the future further studies are needed to be carried out to study in detail the fluorescence and morphological properties of these plant derived CDs.



**REFERENCES:**

- 1 Shao, T., Wang, G., An, X., Zhuo, S., Xia, Y., & Zhu, C. (2014). A reformative oxidation strategy using high concentration nitric acid for enhancing the emission performance of graphene quantum dots. *RSC Adv.*, 4(89), 47977-47981. doi:10.1039/c4ra06935h
- 2 Lim, S. Y., Shen, W., & Gao, Z. (2015). Carbon quantum dots and their applications. *Chemical Society Reviews*, 44(1), 362-381. doi:10.1039/c4cs00269e
- 3 Tuerhong, M., Xu, Y., & Yin, X. (2017). Review on Carbon Dots and Their Applications. *Chinese Journal of Analytical Chemistry*, 45(1), 139-150. doi:10.1016/s1872-2040(16)60990-8
- 4 Sharma, V., Tiwari, P., & Mobin, S. M. (2017). Sustainable carbon-dots: Recent advances in green carbon dots for sensing and bioimaging. *Journal of Materials Chemistry B*, 5(45), 8904-8924. doi:10.1039/c7tb02484c
- 5 Xu, X., Ray, R., Gu, Y., Ploehn, H. J., Gearheart, L., Raker, K., & Scrivens, W. A. (2004). Electrophoretic Analysis and Purification of Fluorescent Single-Walled Carbon Nanotube Fragments. *Journal of the American Chemical Society*, 126(40), 12736-12737. doi:10.1021/ja040082h
- 6 Sun, Y., Zhou, B., Lin, Y., Wang, W., Fernando, K. A., Pathak, P., . . . Xie, S. (2006). Quantum-Sized Carbon Dots for Bright and Colorful Photoluminescence. *Journal of the American Chemical Society*, 128(24), 7756-7757. doi:10.1021/ja062677d
- 7 Ding, C., Zhu, A., & Tian, Y. (2013). Functional Surface Engineering of C-Dots for Fluorescent Biosensing and in Vivo Bioimaging. *Accounts of Chemical Research*, 47(1), 20-30. doi:10.1021/ar400023s
- 8 Yan, Y., Xia, L., & Ma, L. (2019). Solvent-controlled synthesis of multicolor photoluminescent carbon dots for bioimaging. *RSC Advances*, 9(42), 24057-24065. doi:10.1039/c9ra04241e
- 9 Linkov, P. A., Vokhmintcev, K. V., Samokhvalov, P. S., & Nabiev, I. R. (2017). Ultrasmall quantum dots for fluorescent bioimaging in vivo and in vitro. *Optics and Spectroscopy*, 122(1), 8-11. doi:10.1134/s0030400x17010143
- 10 Wu, P., & Yan, X. (2013). Doped quantum dots for chemo/biosensing and bioimaging. *Chemical Society Reviews*, 42(12), 5489. doi:10.1039/c3cs60017c

- 11 Feng, J., Wang, W., Hai, X., Yu, Y., & Wang, J. (2016). Green preparation of nitrogen-doped carbon dots derived from silkworm chrysalis for cell imaging. *Journal of Materials Chemistry B*, 4(3), 387-393. doi:10.1039/c5tb01999k
- 12 Liu, Q., Zhang, N., Shi, H., Ji, W., Guo, X., Yuan, W., & Hu, Q. (2018). One-step microwave synthesis of carbon dots for highly sensitive and selective detection of copper ions in aqueous solution. *New Journal of Chemistry*, 42(4), 3097-3101. doi:10.1039/c7nj05000c
- 13 Zhang, B., Liu, C., & Liu, Y. (2010). A Novel One-Step Approach to Synthesize Fluorescent Carbon Nanoparticles. *European Journal of Inorganic Chemistry*, 2010(28), 4411-4414. doi:10.1002/ejic.201000622
- 14 Pang, Y., Gao, H., Wu, S., & Li, X. (2017). Facile synthesis the nitrogen and sulfur co-doped carbon dots for selective fluorescence detection of heavy metal ions. *Materials Letters*, 193, 236-239. doi:10.1016/j.matlet.2017.01.149
- 15 Shen, J., Shang, S., Chen, X., Wang, D., & Cai, Y. (2017). Facile synthesis of fluorescence carbon dots from sweet potato for Fe<sup>3+</sup> sensing and cell imaging. *Materials Science and Engineering: C*, 76, 856-864. doi:10.1016/j.msec.2017.03.178
- 16 Martindale, B. C., Hutton, G. A., Caputo, C. A., & Reisner, E. (2015). Solar Hydrogen Production Using Carbon Quantum Dots and a Molecular Nickel Catalyst. *Journal of the American Chemical Society*, 137(18), 6018-6025. doi:10.1021/jacs.5b01650
- 17 Guo, Y., Zhang, L., Cao, F., & Leng, Y. (2016). Thermal treatment of hair for the synthesis of sustainable carbon quantum dots and the applications for sensing Hg<sup>2+</sup>. *Scientific Reports*, 6(1). doi:10.1038/srep35795
- 18 Rong, M., Feng, Y., Wang, Y., & Chen, X. (2017). One-pot solid phase pyrolysis synthesis of nitrogen-doped carbon dots for Fe<sup>3+</sup> sensing and bioimaging. *Sensors and Actuators B: Chemical*, 245, 868-874. doi:10.1016/j.snb.2017.02.014
- 19 Zhou, J., Booker, C., Li, R., Zhou, X., Sham, T., Sun, X., & Ding, Z. (2007). An Electrochemical Avenue to Blue Luminescent Nanocrystals from Multiwalled Carbon Nanotubes (MWCNTs). *Journal of the American Chemical Society*, 129(4), 744-745. doi:10.1021/ja0669070
- 20 Zheng, L., Chi, Y., Dong, Y., Lin, J., & Wang, B. (2009). Electrochemiluminescence of Water-Soluble Carbon Nanocrystals Released

- Electrochemically from Graphite. *Journal of the American Chemical Society*, 131(13), 4564-4565. doi:10.1021/ja809073f
- 21 Zhao, Z., & Xie, Y. (2017). Enhanced electrochemical performance of carbon quantum dots-polyaniline hybrid. *Journal of Power Sources*, 337, 54-64. doi:10.1016/j.jpowsour.2016.10.110
- 22 Sun, Y., Zhou, B., Lin, Y., Wang, W., Fernando, K. A., Pathak, P., Xie, S. (2006). Quantum-Sized Carbon Dots for Bright and Colorful Photoluminescence. *Journal of the American Chemical Society*, 128(24), 7756-7757. doi:10.1021/ja062677d
- 23 Sun, Y., Zhou, B., Lin, Y., Wang, W., Fernando, K. A., Pathak, P., . . . Xie, S. (2006). Quantum-Sized Carbon Dots for Bright and Colorful Photoluminescence. *Journal of the American Chemical Society*, 128(24), 7756-7757. doi:10.1021/ja062677d
- 24 Bottini, M., Balasubramanian, C., Dawson, M. I., Bergamaschi, A., Bellucci, S., & Mustelin, T. (2006). Isolation and Characterization of Fluorescent Nanoparticles from Pristine and Oxidized Electric Arc-Produced Single-Walled Carbon Nanotubes. *The Journal of Physical Chemistry B*, 110(2), 831-836. doi:10.1021/jp055503b
- 25 Dey, S., Govindaraj, A., Biswas, K., & Rao, C. (2014). Luminescence properties of boron and nitrogen doped graphene quantum dots prepared from arc-discharge-generated doped graphene samples. *Chemical Physics Letters*, 595-596, 203-208. doi:10.1016/j.cplett.2014.02.012
- 26 Wang, Y., & Hu, A. (2014). Carbon quantum dots: Synthesis, properties and applications. *Journal of Materials Chemistry C*, 2(34), 6921. doi:10.1039/c4tc00988f
- 27 Pan, L., Sun, S., Zhang, A., Jiang, K., Zhang, L., Dong, C., . . . Lin, H. (2015). Truly Fluorescent Excitation-Dependent Carbon Dots and Their Applications in Multicolor Cellular Imaging and Multidimensional Sensing. *Advanced Materials*, 27(47), 7782-7787. doi:10.1002/adma.201503821
- 28 Baruah, U., Deka, M. J., & Chowdhury, D. (2014). Reversible on/off switching of fluorescence via esterification of carbon dots. *RSC Advances*, 4(69), 36917. doi:10.1039/c4ra04734f

- 29 Dong, Y., Chen, C., Zheng, X., Gao, L., Cui, Z., Yang, H., Li, C. M. (2012). One-step and high yield simultaneous preparation of single- and multi-layer graphene quantum dots from CX-72 carbon black. *Journal of Materials Chemistry*, 22(18), 8764. doi:10.1039/c2jm30658a
- 30 Zhu, X., Wang, H., Jiao, Q., Xiao, X., Zuo, X., Liang, Y., Wang, L. (2014). Preparation and Characterization of the Fluorescent Carbon Dots Derived from the Lithium-Intercalated Graphite used for Cell Imaging. *Particle & Particle Systems Characterization*, 31(7), 771-777. doi:10.1002/ppsc.201300327
31. Zhu, X., Wang, H., Jiao, Q., Xiao, X., Zuo, X., Liang, Y., Wang, L. (2014). Preparation and Characterization of the Fluorescent Carbon Dots Derived from the Lithium-Intercalated Graphite used for Cell Imaging. *Particle & Particle Systems Characterization*, 31(7), 771-777. doi:10.1002/ppsc.201300327
32. Zhao, Q., Zhang, Z., Huang, B., Peng, J., Zhang, M., & Pang, D. (2008). Facile preparation of low cytotoxicity fluorescent carbon nanocrystals by electrooxidation of graphite. *Chemical Communications*, (41), 5116. doi:10.1039/b812420e
33. Li, H., He, X., Kang, Z., Huang, H., Liu, Y., Liu, J., Lee, S. (2010). Water-Soluble Fluorescent Carbon Quantum Dots and Photocatalyst Design. *Angewandte Chemie International Edition*, 49(26), 4430-4434. doi:10.1002/anie.200906154
34. Peng, J., Gao, W., Gupta, B. K., Liu, Z., Romero-Aburto, R., Ge, L., Ajayan, P. M. (2012). Graphene Quantum Dots Derived from Carbon Fibers. *Nano Letters*, 12(2), 844-849. doi:10.1021/nl2038979
35. Hu, S., Niu, K., Sun, J., Yang, J., Zhao, N., & Du, X. (2009). One-step synthesis of fluorescent carbon nanoparticles by laser irradiation. *J. Mater. Chem.*, 19(4), 484-488. doi:10.1039/b812943f

36. Bourlinos, A. B., Zbořil, R., Petr, J., Bakandritsos, A., Krysmann, M., & Giannelis, E. P. (2011). Luminescent Surface Quaternized Carbon Dots. *Chemistry of Materials*, 24(1), 6-8. doi:10.1021/cm2026637
37. Sun, Y., Wang, X., Lu, F., Cao, L., Meziani, M. J., Luo, P. G., Veca, L. M. (2008). Doped Carbon Nanoparticles as a New Platform for Highly Photoluminescent Dots. *The Journal of Physical Chemistry C*, 112(47), 18295-18298. doi:10.1021/jp8076485
38. Qu, D., Zheng, M., Du, P., Zhou, Y., Zhang, L., Li, D., Sun, Z. (2013). Highly luminescent S, N co-doped graphene quantum dots with broad visible absorption bands for visible light photocatalysts. *Nanoscale*, 5(24), 12272. doi:10.1039/c3nr04402e
39. Li, L., Ji, J., Fei, R., Wang, C., Lu, Q., Zhang, J., Zhu, J. (2012). A Facile Microwave Avenue to Electrochemiluminescent Two-Color Graphene Quantum Dots. *Advanced Functional Materials*, 22(14), 2971-2979. doi:10.1002/adfm.201200166
40. Dong, Y., Dai, R., Dong, T., Chi, Y., & Chen, G. (2014). Photoluminescence, chemiluminescence and anodic electrochemiluminescence of hydrazide-modified graphene quantum dots. *Nanoscale*, 6(19), 11240-11245. doi:10.1039/c4nr02539c
41. Cao, L., Wang, X., Meziani, M. J., Lu, F., Wang, H., Luo, P. G., Sun, Y. (2007). Carbon Dots for Multiphoton Bioimaging. *Journal of the American Chemical Society*, 129(37), 11318-11319. doi:10.1021/ja073527l
42. Chen, C., Li, C., & Shi, Z. (2016). Current Advances in Lanthanide-Doped Upconversion Nanostructures for Detection and Bioapplication. *Advanced Science*, 3(10), 1600029. doi:10.1002/advs.201600029
43. Dong, Y., Zhou, N., Lin, X., Jianpeng, L., Chi, Y., & Chen, G. (2010). Extraction of Electrochemiluminescent Oxidized Carbon Quantum Dots from Activated Carbon. *Chemistry of Materials*, 22(21), 5895-5899. doi:10.1021/cm1018844