

# The Synthesis of Carbon Quantum Dots

Master's Thesis

Master of Materials Science

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### *Abstract*

Carbon quantum dots (CQDs) are a new class of carbon nanomaterials that have emerged recently and have gained much focus due to their unique properties and desired advantages of low toxicity, ecologically friendliness, low cost, and simple preparation routes. A study was conducted to investigate the effect of solvent used and the technique used in the synthesis in the resulting carbon quantum dots. Two types of reaction procedures, microwave-assisted heating, and refluxing the solution over an oil bath, were deployed. These materials were prepared, using citric acid and urea precursors and double distilled water and DMSO as solvents. The CQDs fabricated were highly fluorescent under UV-light and had a high quantum yield. Fluorescence spectroscopy, atomic force microscopy (AFM) and UV-visible spectroscopy was utilized to characterize the morphology, size and fluorescence properties of the prepared CQDs



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### ***Abbreviations***

CQDs	Carbon Quantum Dots
nm	Nanometer
MV	Microwave
PL	Photoluminescent
PEG	Poly (ethylene glycol)
SWNTs	Single-walled carbon nanotubes
TEM	Transmission electron microscopy
FTIR	Fourier-transform infrared spectroscopy
DOX	Doxorubicin
HepG2	Human epithelial type 2
PBS	Phosphate-buffered Saline
DMSO	Dimethyl sulfoxide

## Chapter 1

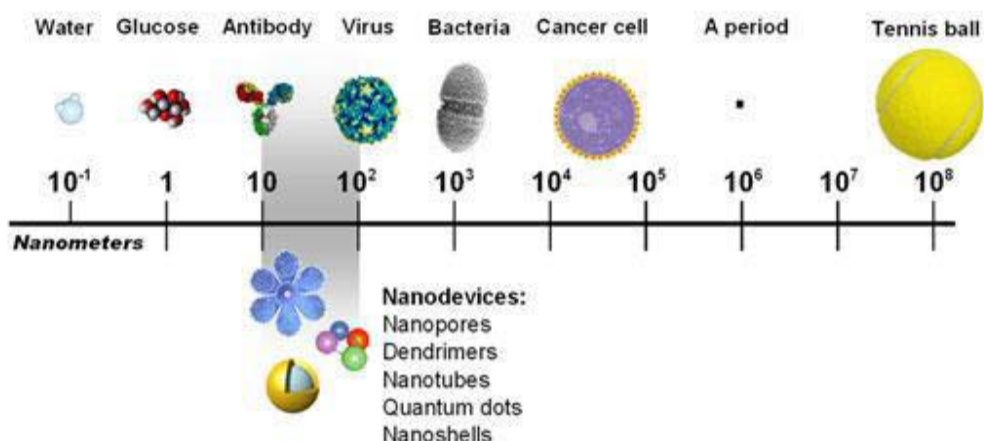
### 1.1. Background

Nanoscale materials in both chemistry and physics covers a broad area of science, such as engineering and future technical developments.

The National Nanotechnology Initiative has defined nanotechnology as working at the atomic, molecular and supramolecular levels so nanoscale refers to the length less than 100 nm and sometimes extended to several hundred of nanometers, nanomaterials have a wide range size from 0.1 to 1000 nm (Fig.1). The small sizes make them have unique features which are different from their corresponding bulk because of their large surface area to volume ratio, which is much larger. The large surface area allowing for catalytic promotion of reactions, increase their ability to adsorb and carry other compounds as well.

Nanomaterials become the focus of applied research leading to important technological applications in different area such as catalysis, sensing, nanoelectronics, and medicine as drug delivery and drug carriers as well.

The study of manipulating matter at atomic and molecular scale and dealing with design, synthesis, characterization, and application of nanomaterials is known as Nanotechnology. Nowadays nanotechnology is used in various application such as electronics, agriculture, environmental, and nanomedicine. As it stands now nanomaterials have an effective role in medical and biological field. In this work we focused on Carbon Quantum Dots (CQDs).CQDs are semiconducting nanoparticles that are entirely made up of carbonaceous materials.



**Figure (1). The scale of nanomaterial systems.**

Carbon quantum dots (CQDs) were first obtained by Xu et al in 2004 accidentally during the purification of single-walled carbon nanotubes (SWCNs) by arc discharge method (Xu et al., 2004) and they were improved for strong photoluminescence (PL) effects through laser ablation of the carbon target as a mixture of graphite powder and cement in 2006. The obtained CQDs could emit blue-green, yellow, and orange fluorescence at 365 nm. CQDs are zero-dimensional spherical shaped carbon nanoparticles (Pang et al., 2017), which are usually surface passivated and functionalized with organic or biomolecules. These photoluminescent (PL) materials are small nano-meter sized (2-10nm) pure or composite materials with excellent properties, thus making them interesting and emerging candidates for new and exceptional applications in biomaterials and nanotechnology research fields (X. Wang et al., 2011).

These materials can be designed to have various functional groups including hydroxyl, carboxyl, carbonyl, ether, and epoxy groups. In addition it is easy to functionalize them with amine, phosphorous, sulphur, and boron-containing heteroatoms containing functional groups with the different organic, polymeric, and biological materials used during the preparation process. Therefore, the fluorescent properties can be manipulated by the size and extent of functional groups on the surface of the CQDs by using different precursors and fabrication methods (Sagbas & Sahiner, 2019).

Up to date, their synthesis strategies, modification methods and application fields have been evolved. The synthesis approaches of CQDs can be elucidated into two groups; top-down and bottom-up approaches (Y. Wang & Hu, 2014). In the top-down process, the macromolecule is destroyed or dispersed into small-sized CQDs by physical or chemical methods. While in the bottom-up approach mainly refers to the polymerization and carbonization of a series of small molecules into CQDs through chemical reaction.

In the past few years, great attempts have been made to come up with better synthetic routes and more detailed fundamental studies. At present there are many approaches that have been described and reported for the synthesis of CQDs to improve their optical properties. They can be prepared easily and affordably by multiple techniques or methods, such as arc-discharge, laser ablation, microwave irradiation, hydrothermal method, solvent refluxing and electrochemical synthesis. These methods can synthesise monodispersed CQDs with precisely defined molecular structure and size. It is of great preference to control the size during the preparation process.



Generally, a high number of carbon precursors can be used in the preparation of photoluminescent CQDs. The precursors widely vary from organic compounds and natural products have been reported. Several natural resources containing a high number of carbon precursors have been reported. Recently, green synthetic approaches were introduced. Amongst natural resources and precursors, natural sources become widely used as green precursors, because they have great advantages in biomedicine since they are simple, repeatable, ecologically friendly, and cost effective for the synthesis of CQDs.

In the literature, many CQDs were prepared from different carbon sources including the carbonization of various fruit juices, orange waste, onion waste, watermelon, pomelo peels, sweet pepper, capsicum, honey, lemon, grass, urea, citric acid and plant leaves. In accord with past studies, citric acid is one of the most common raw materials used in the fabrication of CQDs because it consists of carbonyl, carboxyl and hydroxyl groups. The chosen precursors often determine the physicochemical properties of the resulting CQDs such as the size, crystallinity, nitrogen content, fluorescence characteristics including quantum yield, colloidal stability, and biocompatibility.

Carbon quantum dots (CQDs) have drawn a lot of attention because of their relatively strong fluorescence characteristics and photocatalytic properties. The physicochemical properties of CQDs can be manipulated by altering the concentration of precursors, reaction time, solution pH and reaction temperature. As a group of newly emerged fluorescent nanomaterials, CQDs have shown immense potential as versatile nanomaterials for a wide range of applications. These are said to be promising materials for applications in numerous fields including environmental, nanotechnology and life sciences because for their special properties (Baker & Baker, 2010).

- Unique photostability: stability and composition of CQDs lead to their greater photostability when compared with organic dyes and traditional QDs.
- Broader excitation and narrow emission: CQDs have a more sharply defined emission peak and broader excitation spectra than organic dyes and other cadmium based QDs.
- Biological properties: They have superior biologic properties, such as hydrophilicity, non-toxicity, chemical stability, and good biocompatibility.
- Excellent Luminescence: They have similar or greater luminescence as compared with other QDs.

- Aqueous stability: CQDs have high aqueous stability as compared with other nanoparticles such as cadmium based QDs.
- Electronic properties: Outstanding electronic properties of CQDs as electron donors and acceptors that causes the electrochemical luminescence and chemiluminescence, which empowers them with broad potential in optronics, catalysis, and sensors.
- Chemical inertness: The chemical stability of CQDs is very high as compared with other QDs (traditional or metallic).

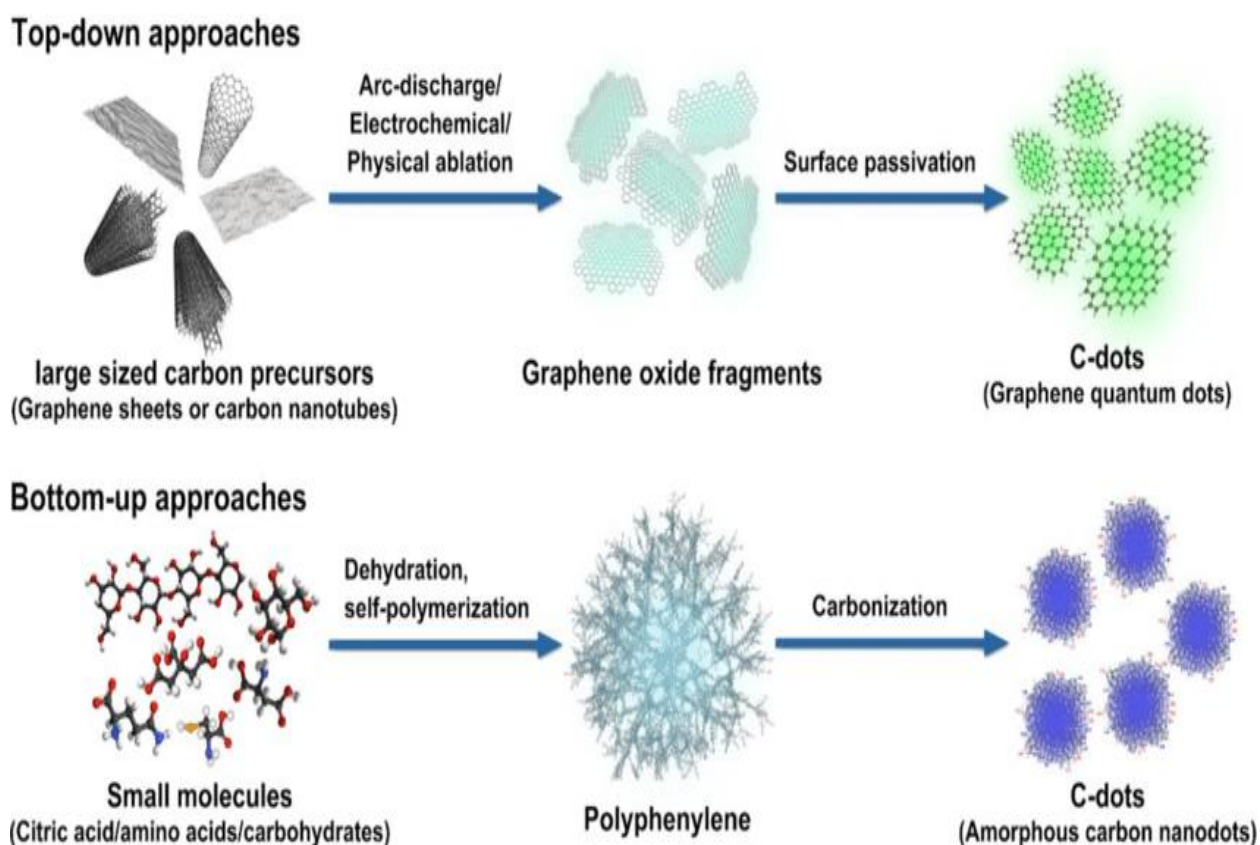
These materials have excellent fluorescent properties such as broad excitation spectra, narrow and tunable emission wavelength, and high photostability against photo bleaching and blinking compared to the other fluorescent semiconductor quantum dots. Thus, CQDs can be applied in analytical nano-sciences, nanotechnologies and sensor fabrication due to their distinctive chemical inertness and excellent biocompatibility. Besides that, it can also be applied in the detection of biomolecules, sensing of heavy metals and photocatalytic processes.

## Chapter 2

### 1. Literature review

#### 2.1. Preparation of Carbon Quantum Dots

A range of synthetic methods have been developed to enhance the properties and functionality CQDs using the two main classified approaches which are top-down and bottom up method as shown on **Figure (2)**.



**Figure (2).** Schematic diagram of two types of preparation approaches of Carbon quantum dots.

##### 2.1.1. Top-down method

As mentioned before in top-down approaches, CQDs are prepared by fragmentation that involves breaking down or cleaving larger carbon structures, such as graphite, carbon nanotubes, carbon soot, activated carbon and graphite oxide, to smaller ones by using acid oxidation, arc discharge, laser ablation, ultrasonic/electrochemical exfoliation, or hydrothermal/solvothermal exfoliation methods (Park et al., 2016). However, they are difficult, tedious, expensive, of low production yield (X. Wang et al., 2011).

#### 2.1.1.1. Laser Ablation.

Laser ablation is a method of breaking down one part of material to create a microfeature using a laser beam. This method works by irradiating the precursors that are immersed in water.

The timescale of the interaction between the laser beam and the material is the most critical factor for fabricating ideal structures. In this method, synthesis of fluorescent CQDs is accomplished by laser irradiation of carbon target. (Sun et al., 2006) described that they initially heated a blend of cement and graphite powder in order to prepare a carbon target, then fabricated CNPs by means of laser ablation/removal of the carbon target in a stream of argon gas conveying water vapor at 900 °C and 75 kPs.

This method uses a high-energy laser pulse to irradiate the surface of the target to a thermodynamic state in which high temperature and high pressure are generated, rapidly heats up and evaporates into a plasma state, and then the vapor crystallizes to form nanoparticles. It was reported a facile approach to synthesize CQDs via laser irradiation of carbon precursor, which was dispersed in different ordinary organic solvents (J. Liu et al., 2009). It was previously reported the application of this technique using crystalline graphite microparticles (Singh et al., 2019). The starting material was dissolved in water, and *ns* pulsed fibre laser (wavelength 1070 nm, pulse duration around 50 *ns* and pulse repetition between 1 and 500 kHz) was employed. The laser beam was focused onto the graphite in water dispersion at a depth of 5 mm from the air-liquid interface. Heat energy caused significant fragmentation of carbon materials into smaller particles. This method requires continuous stirring to avoid precipitations (Das et al., 2018). It was observed that the sizes of CQDs could be varied by altering the laser irradiation time and optimising other parameters such as pulse repetition rate, pulse duration, laser power and laser wavelength. CQDs

The obtained CQDs exhibited visible and tunable photoluminescence (PL). Further, demonstrated the surface state of the CQDs can be modified by selecting proper organic solvent during the laser irradiation process in order to tune the PL properties of the synthesized CQDs. Laser ablation is an effective method to prepare CQDs with narrow size distribution, good water solubility, and fluorescence characteristics (Fan et al., 2020).

#### 2.1.1.2. Arc Discharge

Arc discharge 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 4,000K under electric current in order to produce a high-energy plasma. In the cathode the carbon vapor assembly to form CQDs. The preparation of CQDs by arc discharge method was originated in 2004 by (Xu et al., 2004). The CQDs that were prepared through this method have good water solubility, however, in general they possess a large particle size distribution in view of different sizes of carbon particles are formed during the discharge process which would later decrease the specific surface area of the CQDs and limit the electrocatalysis processes. Although the first reported fluorescent CQDs were prepared by this method, but there are limited studies about CQDs preparation using the arc discharge method.

#### 2.1.1.3. 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 CQDs by this method has been widely reported for the sake that it is simple to tune the particle size and PL performance of the synthesized CQDs. Even though electrochemical soaking is said to be a powerful method to prepare CQDs using various bulk carbon materials as precursors. To prepare CQDs in which this method uses two graphite rods as electrodes. The electrolyte used was distilled water and current at static potentials of 15-60 V was provided to the electrodes. This method can generate hydroxide ions and protons due to the hydrolysis of water molecules. Based on a previous study, CQDs have been prepared by heating ammonium citrate at 180 °C for 3 h using ambient air (Ratnayake et al., 2019). This method is also known as oxidation of molecular precursors, but it does not require concentrated acid. For instance, L-Cysteine, sodium hydroxide and hydrogen peroxide were mixed with ultrapure water and then stirred at 90 °C for 12 h. The product obtained was purified by using a dialysis membrane for 12 h, and a strong green fluorescence of CQDs was observed (Liang et al., 2019).

The electrochemical process-induced a high number of oxygen molecules and intercalation of hydroxide ions between graphite layers of defect-induced graphite rod. Besides that, this method has large throughput and produces CQDs with amorphous core and highly luminescent properties(Kaur et al., 2018). However, there are only a few reports about electrochemically carbonizing small molecules to CQDs. The CQDs with amorphous core that were prepared through this method exhibited excellent excitation and size dependent PL properties without complicated purification and passivation procedures.

### 2.1.2. Bottom-up method

In the bottom-up approaches, small precursors such as carbohydrates, citrate and nanocomposites are carbonized through hydrothermal, microwave, and thermal pyrolysis methods. Hydrothermal/ solvothermal methods (Yang et al., 2020) and microwave irradiation are basic methods of bottom-up approach. In general, the bottom-up approach is useful to produce large scale of CQDs synthesis (Park et al., 2016).

#### 2.1.2.1. Microwave Pyrolysis

Microwave (MW) assisted synthesis fulfils the promise of being a rapid and facile technique as an alternative energy input source and has been widely used because of its control for internal and volumetric heating of materials (X. Wang et al., 2011). Among the bottom-up CQDs production methods the microwave-assisted process is one of the prominent methods in terms of significantly reducing the reaction time. The CQDs preparation process has three main steps:

- Polymerization,
- Dehydration,
- Carbonization

which take place by microwave irradiation methods. The MW consists of synchronized perpendicular oscillations of electric and magnetic fields. The MW energy absorbed by carbon materials and transformed in the form of heat is called dielectric heating. The MW-assisted heating can also be used for the selective heating purposes as its interaction with materials with different dielectric properties is based on a selective coupling with the higher tangent loss material.

These waves penetrate the irradiated material, and heat is produced throughout the volume of the material at molecular/atomic level, resulting in fast and uniform volumetric heating. (Zhu et al., 2009) reported a simple microwave pyrolysis approach to prepare CQDs by mixing poly (ethylene glycol) (PEG) and polysaccharide (glucose, fructose, etc.) in water to form a transparent solution, followed by heating in a microwave oven (Z. H. Zhang et al., 2009). Similarly, in another previous study, an amount of ascorbic acid was previously added into a polyethylene glycol solution and heated under microwave reactor at 700 W and 200 °C for 1 minute (Singh et al., 2019). The colour of the solution at the end of the reaction slowly changed from yellow to brown, indicating the formation of CQDs through the dehydration process. The

produced CQDs exhibited no perceptible shift of the PL peak over an excitation range from 320 to 380 nm were observed.

(J. Liu et al., 2009) Promoted microwave-mediated pyrolysis of citric acid with various amine molecules to synthesize highly luminescent CQDs. The amine molecules, especially primary amine molecules enhance the PL performance. The resultant CQDs through this method are highly biocompatible and had a great potential for biomedical applications.

The MW assisted syntheses of carbon materials have several advantages compared to other methods. The major advantage of using MW heating for carbon material processing is the contactless heat transfer to the reactant sample as the energy is generated directly within the material through molecular interaction with the electromagnetic field. One of the supreme and noteworthy advantages of this method, which constraints on specific shape and size of CQDs dependence on the experimental parameter.

#### 2.1.2.2. Hydrothermal/solvothermal treatment

This method is a low cost, ecologically friendly and non-toxic route to produce carbon-based materials from various precursors. Solvothermal carbonization followed by extraction with an organic solvent is a popular approach to prepare CQDs. A solution of organic precursor is sealed and reacted in a hydrothermal reactor at high temperature. Many CQDs in previous studies were prepared through this method, from many precursors such as glucose, citric acid, chitosan, banana juice, and protein.

(J. Liu et al., 2009) synthesised amino functionalized in one-step fluorescent CQDs by hydrothermal carbonization of chitosan at 180°C for 12 hours. The amino-functionalized Fluorescent CQDs can be used directly in bioimaging of living molecules.

(Zhu et al., 2009) reported the highest QY of CQDs up to about 80%, which were almost equal to fluorescent dyes. The CQDs were synthesized by using citric acid and ethylene diamine as carbon and nitrogen sources with high product yield using hydrothermal process, which were later used for the detection of Fe<sup>3+</sup> in living cells. In another study, CQDs have been synthesised via the hydrothermal method using vitamin C in water and ethanol solution at 180 °C for 5 h. Then, the product was dialysed for 24 h to remove impurities(Z. Zhang et al., 2018). Similarly to another report, pomelo was used as a raw material in CQDs production through hydrothermal route at 200 °C for 7 h (Copur et al., 2019). The pomelo juice was mixed with distilled water. During the hydrothermal process, it was dehydrated due to the polymerisation and carbonisation among the organic molecules of protein and oligosaccharide to produce single-

crystalline CQDs. The average particle size obtained was 2-4 nm with good fluorescence(Jiang et al., 2019).

## 2.2. Methods used to characterise CQDs

Several instruments or analyses are commonly used to characterise the CQDs;

PL spectrophotometer has been employed previously to study the optical properties of CQDs. PL behaviour depends on the particle sizes that can be excited by a particular wavelength. Smaller particles will exhibit PL effect at lower wavelength while larger particles will have PL effect at higher wavelength. (Gyulai et al., 2019) established that the luminescence quantum yield (QY) is mainly dependent on the shell part of the CQDs, more specifically on the overall oxygen content, and the amount of carboxylic type groups play the most important role in determination of the fluorescence intensity.

Photoluminescence is the most intriguing characterization of C-dots, both from the view of fundamental research and practical application, one uniform feature of the PL for CQDs is the distinct dependence of the emission wavelength and intensity.

Transform Infrared Spectroscopy (FTIR) is used for the determination of functional groups that are present on the surface of CQDs.

Transmission electron microscopy (TEM) can be carried out to obtain the data on surface morphology, nanostructure and particle size of CQDs. In many cases has been used to investigate the nanostructures of the synthesised CQDs and to estimate the sizes of CQDs down to quantum scale.

CQDs have average sizes between 2 -10 nm. Based on previous reports, CQDs showed nearly spherical shaped and uniformly sized particles indicating the crystalline nature of CQDs.

UV Vis absorption spectra over a range of 200 – 800 nm can be used to check the optical behaviour of CQDs, while photoluminescence (PL) can be used to analyse the emission and excitation light within a detection range of 200-800 nm. CQDs typically exhibit strong light absorption in the UV region with a tail extending into the visible range. The maximum absorption peak at is usually approximately 250 nm regions, respectively.(Park et al., 2016). Strong UV absorption is usually shown by CQDs prepared using various techniques, but still the positions of absorption peaks of UV are entirely different for different techniques used for the preparation of CQDs



XRD is efficiently used to characterize C-dots and to obtain information of particle size, phase purity, and crystal structure. XRD also determines the crystalline phases of CQDs.

### 2.3. Applications of CQDs

CQDs have received an increasing amount of attention because of their significant advantages such as biocompatible, non-toxicity, photostable, and easily functionalized with good photoluminescence and water solubility. Owing to these unique properties, they have been used in numerous fields, including bioimaging, catalysis, electronics, biosensing, chemical sensing, power, targeted drug delivery, and other biomedical applications.

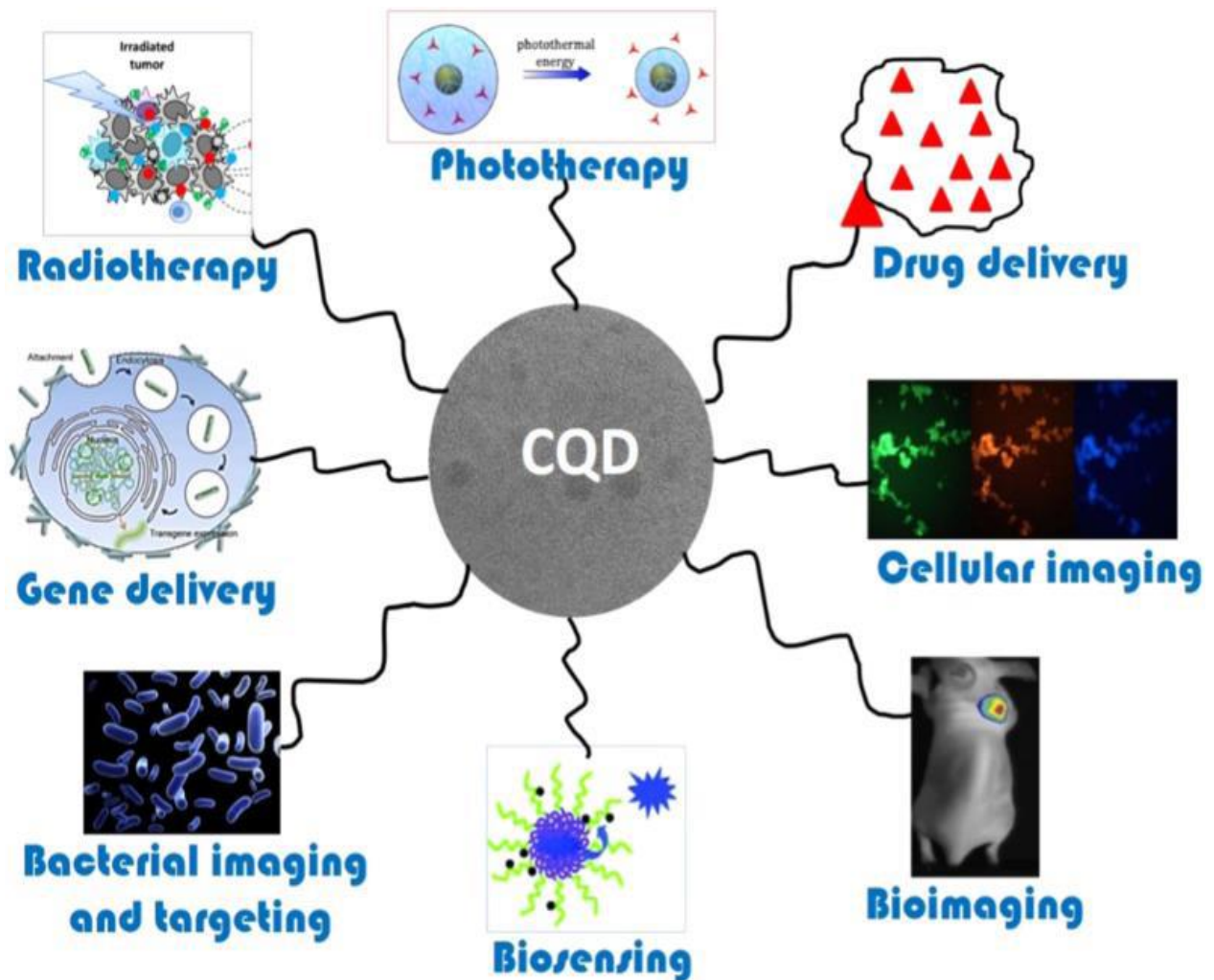


Figure (3). Application of Carbon quantum dots.

### 2.3.1. Bioimaging

CQDs play an important role in biomedical applications. Bioimaging is one of the essential applications, which can be defined as the process in which images of living organisms are produced with the help of techniques such as magnetic resonance imaging (MRI), X-rays, and ultrasound. Nanotechnology have found a way to visualize cells in microorganisms by using CQDs as fluorescent imaging probes. There has been growing interest in the use of fluorescence CQDs in bioimaging of cells and tissues of different living systems for *in vivo* and *in vitro* biomedical applications, owing to their excellent biocompatibility, small size (2-10nm), excellent PL, and multicoloured fluorescence properties of CQDs. Since, carbon is non-toxic and environmentally friend.

The carbon cores of CQDs themselves are not toxic and any cytotoxicity of CQDs is primarily due to surface passivating. These traits make CQDs very desirable as alternatives to semiconductor quantum dots to visualise biological systems both *in vitro* and *in vivo* (Yan et al., 2014). *In vivo* imaging of plant cells is more complicated in comparison with animal cells because of the complex cell structure(Sagbas & Sahiner, 2019). CQDs can easily penetrate the cell membrane and act as a fluorescence material to visualize the human and animal cells. Before imaging, cells are usually incubated with CQDs so that the CQDs can be internalised by the cells(Cao et al., 1946).

The prepared NCQDs were used as luminescent nanothermometer to determine the temperature in cells as the NCQDs are highly affected by external temperature (Lu et al., 2018). The aqueous N-CQDs dispersion (20 µg/mL,0.5 mL) was incubated with human hepatoblastoma (HepG2) cancer cells in culture medium for 4 h at 37 °C. Thereafter, the cells were washed three times with PBS buffer to remove the excess N-CQDs and fixed by 75% ethanol solution for 30 min. The imaging of cancer cells was determined by confocal laser scanning microscope (CLSM). They observed that the NQCDs can withstand a harsh environment due to their flouroscent stability and can be applied in monitoring the intracellular temperature.

### 2.3.2. Chemical Sensing

An interesting application of CQDs is in the field of chemical sensing. The detection of heavy metals such as Hg<sup>2+</sup>. Mercury ion is considered as one of the most hazardous and toxic cations

on the environment and human health.  $\text{Hg}^{2+}$  can accumulate in the human body, cause DNA damage, mitosis impairment and permanent damage to the central nervous system even in a low concentration. CQDs were then used for chemical sensing due to their low toxicity, water solubility, high photostability and superior chemical stability. The interaction between CQDs and chemical leads to the quenching/enhancement of CQDs fluorescence. One of the first attempts of utilising CQDs in chemical sensing is the selective detection of  $\text{Hg}^{2+}$  in aqueous solutions and live cells.

(Yan et al., 2014) has reported the  $\text{Hg}^{2+}$  CQD systems for selective detection of  $\text{Hg}^{2+}$  in aqueous solution as well as in live cells. The CQDs were synthesised using citric acid anhydrous (0.42 g) and ethylenediamine (536 mL) were dissolved in deionized water (10 mL). Then the solution was transferred to a poly(tetrafluoroethylene) autoclave (15 mL) and heated at  $200^{\circ}\text{C}$  for 5 h. The obtained solid was dissolved in ethanol and remove the insoluble precipitate by centrifugation at 4000 rpm for 15 min. The obtained CQDs possesses high quantum yields of 65.5 and 55.4%, respectively. They then studied the effective and selective quenching of fluorescence emissions of CQD-1 and CQD-2 by  $\text{Hg}^{2+}$ . Both CQDs acted as selective and sensitive fluorescent probes for the detection of traces of  $\text{Hg}^{2+}$  in both aqueous solutions and live cells.

(M. L. Liu et al., 2019) reported a procedure for selective detection of  $\text{Cu}^{6+}$  in aqueous samples such as tap water by CQDs prepared with lysine and bovine serum albumin. The detection of  $\text{Cr}^{6+}$  was determined based on the decreases of the CQD emission wavelengths. In the absence of  $\text{Cr}^{6+}$ , the emission of CQDs can be observed at 425 nm constantly.

Hematin ( $\text{Fe}^{3+}$ ) is the most abundant essential trace element for plants, animals including humans. As an oxygen carrier in haemoglobin and a cofactor in many enzymatic reactions, it plays an important role in cellular metabolism and enzyme catalysis. The deficiency of  $\text{Fe}^{3+}$  leads to anaemia, liver and kidney damages, diabetes, and heart diseases. Also, the excessive  $\text{Fe}^{3+}$  in living cells is associated with serious diseases.

(Hong et al., 2019) described how they prepared the CQDs that were used for the detection of  $\text{Fe}^{3+}$ . The results show that only  $\text{Fe}^{3+}$  give significant quenching effect on the fluorescence of F-CQDs, indicating the high selectivity of F-CQDs for the detection of  $\text{Fe}^{3+}$ .

(Rani et al., 2020) synthesised nitrogen and phosphorus doped CQDs. This composite can generate a bright blue-green emission and exhibit great photo-stability in high salt conditions. Therefore, it could be used to detect  $\text{Fe}^{3+}$  sensitively in aqueous solution without the

interference from other ions in which the lowest detectable concentration of  $\text{Fe}^{3+}$  was determined to be  $0.05 \mu\text{M}$ .

Again, in another study (Liang et al., 2019) prepared CDQs that were used for the detection of  $\text{Fe}^{3+}$ . These CQDs were prepared in a typical procedure by dissolving L-cysteine and NaOH (1.0 M) in ultra-pure water, the mixture was allowed to stir at  $90^\circ\text{C}$  for 12 h, and the colourless mixed solution gradually turned to bright yellow. Finally, the prepared CQDs solution was purified via a dialysis membrane for 12 h with ultrapure water.

(Lu et al., 2018) has reported the NCQDs that were prepared from watermelon juice. In a typical procedure, 50 mL of fresh-squeezed watermelon juice and 5 mL of ethanol were sealed into a Teflon equipped stainless steel autoclave (100 mL) and heated at  $180^\circ\text{C}$  for 3 h. After the reaction, the resulted solution was centrifuged at 5000 rpm for 10min to remove big particles. The obtained supernatant was then dialyzed against water for 24 h to afford aqueous solution of N-CQDs. The prepared N-CQDs were used for the detection of  $\text{Fe}^{3+}$ .

Other applications of CQDs in chemical sensing included the detections of  $\text{Pb}^{2+}$ ,  $\text{Cr(VI)}$  and  $\text{Ag}^+$ . As mentioned above, CQDs are able to exhibit multicolour emissions, which is a huge advantage that sets them apart from the majority of labelling agents. This allows researchers to control and choose the excitation and emission wavelengths.

### 2.3.3. Drug delivery

In drug delivery, the drug is dissolved, entrapped, encapsulated or attached to nanoparticles matrix and depends upon the method of preparation.

Carbon based nanoparticles have attracted attention in drug delivery in recent years due to their ability to act as a platform for the attachment of several drugs. The CQDs which are mainly composed of C, N, O and H atoms are excellent candidates for drug delivery systems as well. (Yuan et al., 2017) conducted a study where Doxorubicin (DOX) was loaded on CQDs for drug delivery. DOX is one of the most used model anticancer drugs in drug delivery systems which is highly regarded in cancer therapy due to its broad spectrum efficacy. CQDs were synthesized by hydrothermal treatment of milk which was heated at  $180^\circ\text{C}$  for 2 h. This heat treatment changed the colour of the mixture from a white solution to a brown one. Thereafter, the solution was centrifuged at 2000rpm to remove solid particles and obtain pure CQDs. The DOX loading, the CQDs and DOX were incubated in PBS at pH 7.4.

DOX was conjugated to the CDs through electrostatic interactions via the multiple surface CD functional groups. On the other hand, the electrostatic interaction between positively charged DOX and negatively charged CQDs as well as hydrophilicity of the CQDs which promotes hydrogen bonding between DOX and CQDs are the main proposed mechanisms for observed enhanced drug loading on the CQDs. The application of CQDs in drug delivery systems could result in a more localized drug loaded. CQDs in tumour cells compared to the using drug alone.

### 2.3. Aim of the study

- To study how the effect of the reaction methods in the preparation of carbon quantum dots.
- To study the effect of the solvent on the fluorescence of the CDQs.
- Characterization of the product (Optical, size and structural properties) using UV-absorption, AFM, DLS and fluorescence analysis.

## Chapter 3 Experimental

### 3.1. Materials

Citric acid and Urea (Reanal) were used in the fabrication of carbon quantum dots. Double distilled water and DMSO were deployed as solvents in this study. Dimethyl sulfoxide (DMSO) and absolute ethanol were purchased from VWR International and were of analytical grade. Double distilled water was checked by its conductivity ( $<5$  mS) and surface tension ( $>72.0$  mN/m at  $25 \pm 0.5$  °C). All the chemicals used in this study were of analytical grade from Sigma-Aldrich.

### 3.2. Methodology

#### 3.2.1 Preparation of Carbon Quantum Dots

The CQDs were fabricated using two types of reaction procedures involving a simple microwave radiation and reflux methods using citric acid as a carbon source and urea as a nitrogen source. Double distilled water and DMSO were used as solvents. In a typical procedure, 1.92g of citric acid and 0.60g of urea were dissolved in 10ml of double distilled water in a quartz tube and the mixture was sonicated for a few minutes until a clear solution was obtained. The reaction mixture was heated in a commercial microwave oven (800 W) for 5 min while the reaction mixture changed its colour from transparent to black, indicating the

formation of CQDs. It is important to note that the temperature is unknown and cannot be controlled on the commercial microwave. In the solvothermal method similar reaction mixtures were refluxed over an oil bath at a temperature of 180 °C for 16 h. After cooling it naturally at room temperature, samples were purified thoroughly.

Sample volume was filled to 13ml of double distilled water or DMSO (depending on which solvent was used on the synthesis) and it was centrifuged for 10 minutes, at 2000 rpm to remove aggregates. Further it was put in the rotary evaporator to get rid of the solvent. The sample was thoroughly purified through dialysis using a dialysis membrane for 24 hours to remove unreacted molecules and get pure CQDs. Finally, the particles were dispersed in water and lyophilized for storage. Similar purification steps were applied for all the samples in this study. All the CQDs in this study were synthesized in conditions similar to those described above for both double distilled water and DMSO. Samples with corresponding reaction time, temperature and reaction procedure that was used are summarised in Table 1.

**Table 1. Preparation of CQDs with different solvent and different reaction technique.**

Sample code	Molar ratio	Used Technique	Solvent	Time	T°C	Volume(mL)
T01	1:1	Refluxing system (RS)	Water	16 h	180°C	10
T02	1:1	Microwave (MV)	Water	10 min	n/a	10
T03	1:1	Reflux system (RS)	DMSO	16 h	180°C	10
T04	1:1	Microwave (MV)	DMSO	10 min	n/a	10

Again, the CQDs were synthesized through a simple microwave radiation method using citric acid as a carbon source and urea as a nitrogen source. Double distilled water was used for all the experiments. Firstly, 1.92g of citric acid and 0.60g of urea is dissolved in 5ml of double distilled water in a quartz tube and the mixture was sonicated for a few minutes until a clear solution was obtained. The mixture was then treated in a CEM Discover microwave system for 1 hour, at 150°C and 50W. When exposed to microwave radiation, the colour of the solution changed to light brownish, indicating the formation of CQDs. After cooling it naturally at room

temperature a light brownish solution was observed. Sample volume was filled to 13ml of double distilled water and it was centrifuged for 10 minutes, at 2000 rpm to remove aggregates. Further it was put in the rotary evaporator to get rid of the solvent. The sample was thoroughly purified by dialysis using a dialysis membrane for 24 hours to remove unreacted molecules and get pure CQDs. Similar steps were applied in all the samples with different concentration for citric acid and urea (1:1, 1:2 and 1:3), at different temperature (150°, 180°) and reaction time (1 hour, 2 hours, 4 hours, 6 hours and 16 hours). All the CQDs in this study were synthesized in conditions similar to those described above. Samples with corresponding reaction time, temperature and the colour that was observed for each sample are listed in Table 2.

**Table 2. Preparation of CQDs with different molar ratio, time and temperature.**

Sample code	Molar ratio	Time (hours)	Temperature(°C)
T-06	1:1	1	150
T-07	1:1	1	180
T-08	1:1	2	150
T-09	1:1	2	180
T-10	1:1	6	150
T-11	1:1	6	180
T-12	1:1	16	150
T-13	1:1	4	159
T-14	1:1	16	180
T-15	1:1	4	180
T-16	1:2	1	150
T-17	1:2	1	180
T-18	1:2	2	150
T-19	1:2	2	180
T-20	1:2	16	150
T-21	1:2	16	180
T-22	1:2	4	150
T-23	1:2	4	180

### 3.2.2 Fluorescence properties

The optical properties were studied using two techniques, UV-VIS spectroscopy and fluorescence spectrometer. 3-D spectra were recorded using diluted samples dispersed in double distilled water or DMSO. The measured intensity was normalized using the integral of Raman-scattering spectrum of pure water. The quantum yield of the samples at 350 nm excitation wavelength was determined using quinine sulfate as a standard. UV-absorbance at 350 nm (Analytic Jena, Specord 40) and the emission spectrum integral were measured for series of samples and standard concentrations.

### 3.2.3 Size determination

Atomic force microscopy (AFM) and dynamic light scattering (DLS) were used to investigate particle size of the prepared CQDs. The DLS system (Brookhaven Instruments, USA) consists of a BI-200SM goniometer and a BI-9000AT digital autocorrelator. As a light source a Coherent Genesis MX488-1000STM laser-diode system operating at 488 nm wavelength and emitting vertically polarized light was used. Measurements were carried out at a detection angle of 90° and a temperature of 25 °C with nanoparticle samples appropriately diluted with doubly distilled water. The recorded autocorrelation functions were analysed by the second order cumulant expansion and Contin method.

AFM was established to study the morphology of the sample in a non-contact mode. Highly diluted aqueous and DMSO dispersions of the particles were deposited on freshly cleaved mica. The samples were dried in vacuum for at least 2 hrs before the measurement. Surface was imaged using a Nanosurf Flex-Axiom atomic force microscope system operating in non-contact mode, using Budget Sensors Tap190Al-G silicon cantilever with a force constant of 48 N/m. Vertical accuracy of the instrument in this mode is around 0.05 nm. Each sample was imaged in 1×1 μm<sup>2</sup> areas at 10 randomly selected locations.



## Chapter 4

### 4.1. Results and Discussions

#### 4.1.1 Synthesis

Carbon quantum dots (CQDs) were successfully prepared using two different reaction procedures, from citric acid and urea precursors, applying conditions summarized in Table 1 and Table 2. In the refluxing experiments the reaction mixture turned from colourless to black colour gradually during the 16 h preparation. All the samples were purified through dialysis using a membrane for 24 h and lyophilized, the sample prepared in DMSO was isolated as a black powder while the one prepared in water had a dark green, sticky resin-like appearance. In this study it was investigated how the solvent used and reaction procedure affect the final product. In this work we wanted to broaden the experimental conditions (molar ratio, temperature and synthesis duration) study them in more detail, using CEM discover microwave reactor, which has superior control over temperature, input power and pressure. However, due to circumstances samples(T06-T23) could not be investigated further.

Sample to sample batches were comparable in appearance. The samples that were prepared via a microwave method for 5 min reaction appeared dark brown to black powdery materials after drying and their appearance being similar in case of both water and DMSO solvents. It was observed that products differ in polarity. Samples that were prepared in double distilled water were dissolvable in water (T01&T02). This observation provided evidence that samples prepared in water can be dispersed in water without aggregation and they have a high hydrophilic surface. Also, particles prepared in DMSO could only be re-dispersed in DMSO (T03&T04). However, when dispersed in water, small precipitates were observed suggesting a hydrophobic character. All samples could be readily re-dispersed in their respective solvents after lyophilization without using any lyoprotectants.

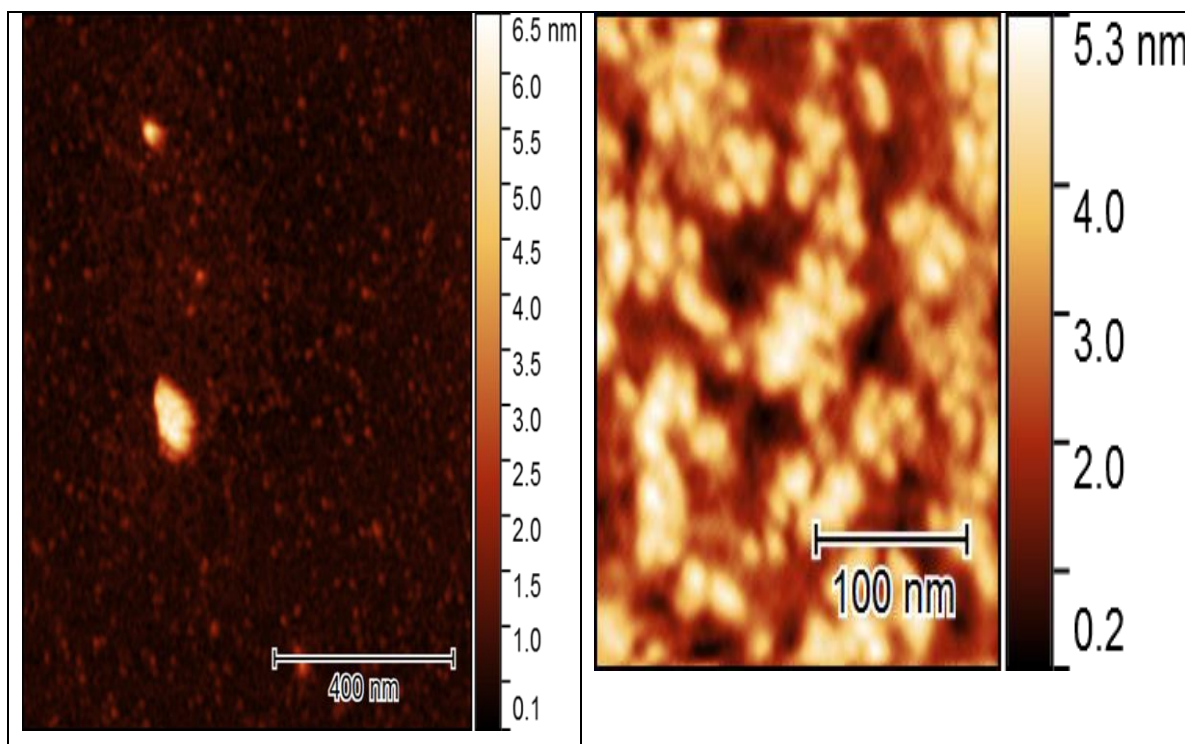
In the aqueous medium used for biological experiments it is necessary for the CQDs to be dispersed. To achieve this, we developed a method to transfer the CQD3 and CQD4 samples into aqueous medium using controlled precipitation. 10 mg particles were dispersed in 2 mL of DMSO then added drop wise to 10 mL of water under magnetic stirring (500 rpm). The resulting sol was then dialyzed against 3×2 L water using 3500 MWCO regenerated cellulose membrane. Under these conditions CQD3 formed a stable sol without any signs of aggregation or sedimentation even after 1 month of storage. CQD4, however, precipitated and sedimented

on a timescale of minutes. This indicates that there is a significant difference in the polarity between the two samples and CQD4 is the most hydrophobic particle.

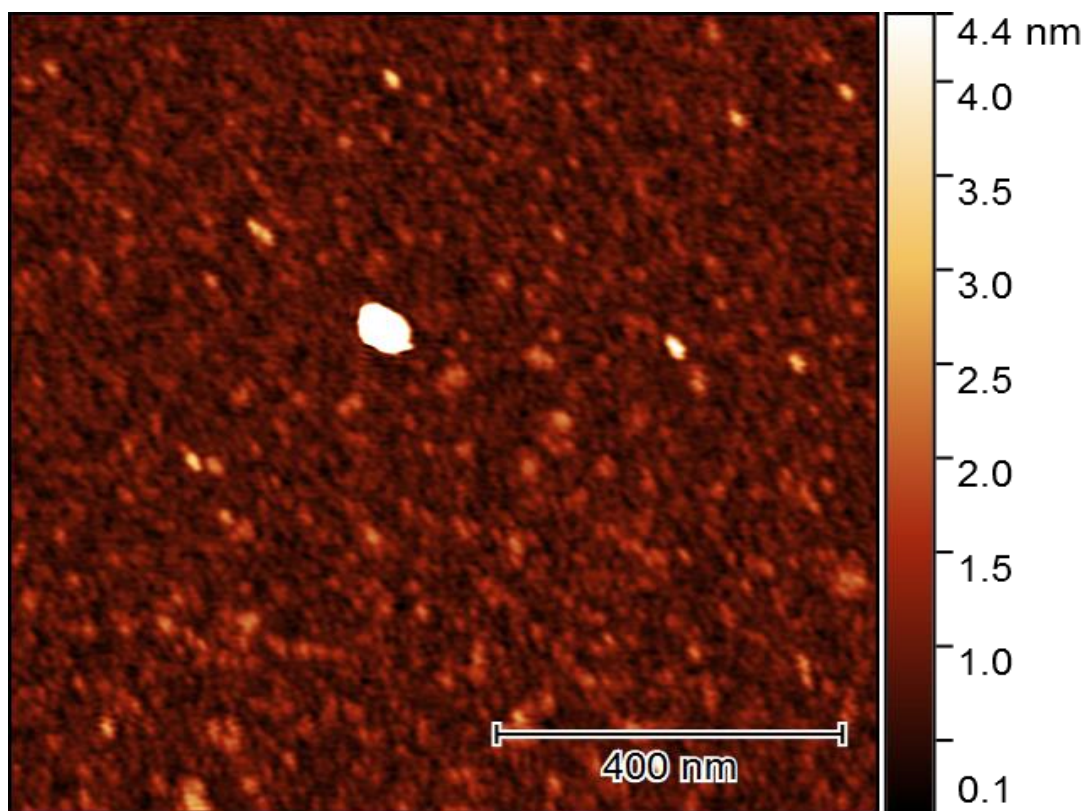
#### 4.1.2 Size

The morphological characterization of the prepared carbon quantum dots was studied using atomic force microscopy (AFM). The images of the synthesized carbon quantum dots T02, T03 and T04 are shown in Fig. 4, Fig 5 and Fig. 6. The AFM images illustrates that the as-synthesized CQDs are particles in nature, appear to be spherical in shape and have a narrow size distribution. The left image of CDs highlights their small nature. The results suggest that the average size of the carbon quantum dots is 1-2 nm. Dynamic light scattering (DLS) measurements also back up the small size of the particles as a meaningful size could be determined, indicating that hydrodynamic diameters are below 10 nm. There were no particular particles found for sample T01 on the AFM, this sample was prepared through the refluxing method for 16 h at 180°C and double distilled water was used as a solvent. This shows that these reaction conditions were not suitable to reach the particle formation stage. Therefore, this particle was not studied further.

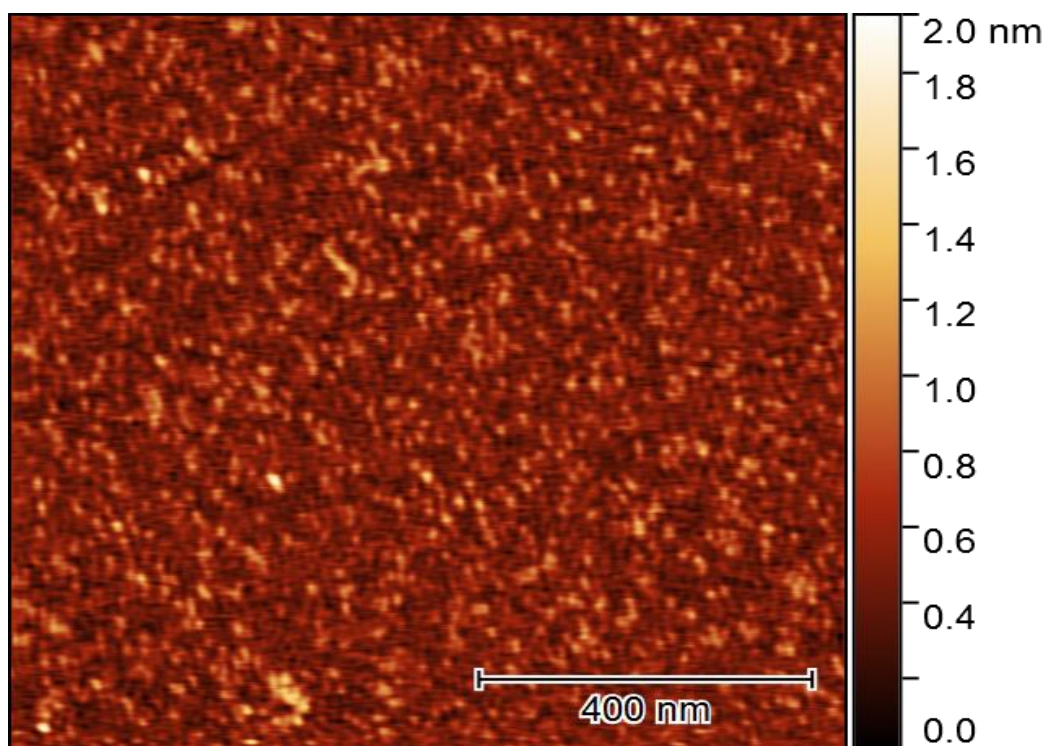
T02 particles had an average diameter of  $(1.7 \pm 0.1)$ . Comparably, the average size of T03 was slightly smaller, at  $(1.2 \pm 0.1)$  nm while T04 particles had an average diameter of  $(0.9 \pm 0.1)$  nm. It could be noted that there is a slight difference in the diameter of the particles, this is due to the fact that the carbon quantum dots were prepared under different reaction conditions. In the case of aqueous microwave assisted heating (T02), due to the lower boiling temperature of water particle formation was slower resulting in bigger particles. The high boiling point of DMSO (189 °C) could help to accelerate the particle formation step as the higher temperature favours the carbonization step leading to more compact particles.



**Figure(4).** AFM image for sample T02 synthesized using double distilled water solvent.



**Figure(5).** AFM image for sample T03 synthesized using DMSO solvent.



**Figure(6).** AFM image for sample T04 synthesised using DMSO solvent.

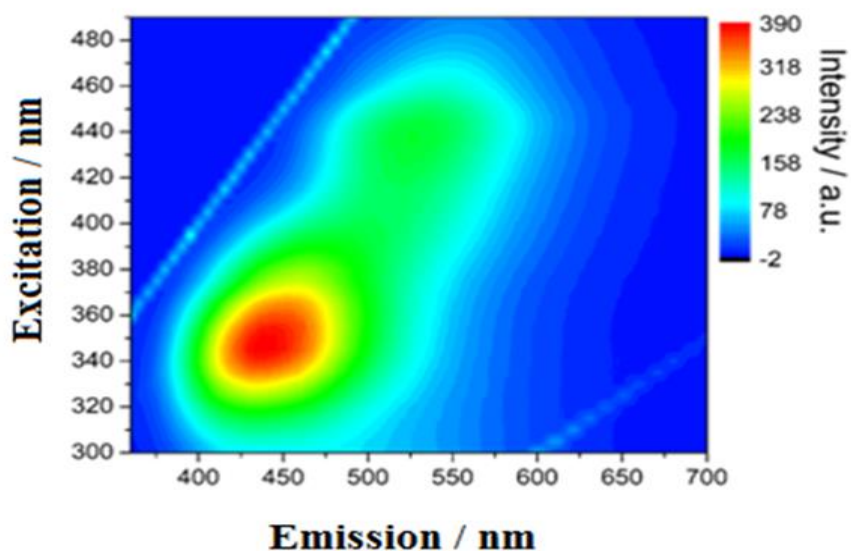
#### 4.1.3 Fluorescence properties

The analysis of optical properties of carbon quantum dots, holds the key for their future applications in optoelectronic devices and biological sensors. Herein, the effect of solvent and reaction method on the sample product were established. The Fluorescence properties of the particles were investigated using fluorescence spectrophotometry. Fluorescence is one of the most fascinating features of CQDs, both from fundamental and application-oriented perspectives UV-Vis absorption and fluorescence (FL) emission spectra of the as-synthesized carbon quantum dots were recorded. The developed CQDs (T02, T03 and T04) were investigated under ultraviolet and day-light irradiation, respectively. Under day-light illumination, the CQD solution appeared as black liquid at high concentration and transparent at high dilution. Under ultraviolet radiation, the diluted, transparent CQD solutions emitted an intense bright blueish luminescence colour, indicating that they are highly fluorescent.

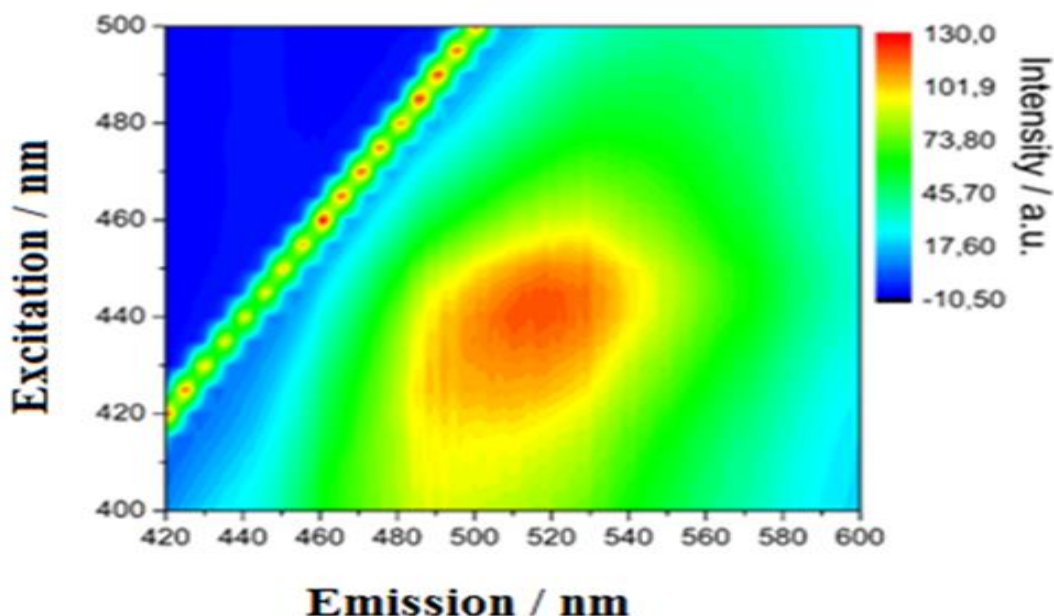


**Figure (6).** An image of a carbon quantum dot particle sample under UV-light.

The emitted light intensity as a function of emission and photoluminescence excitation is presented in 3-D spectrum. SampleT02 (Aqueous product) showed one luminescence region centred around 350 nm excitation with a maximum fluorescence emission appear at 445 nm, respectively, as shown in Fig. 7 of the supporting information.



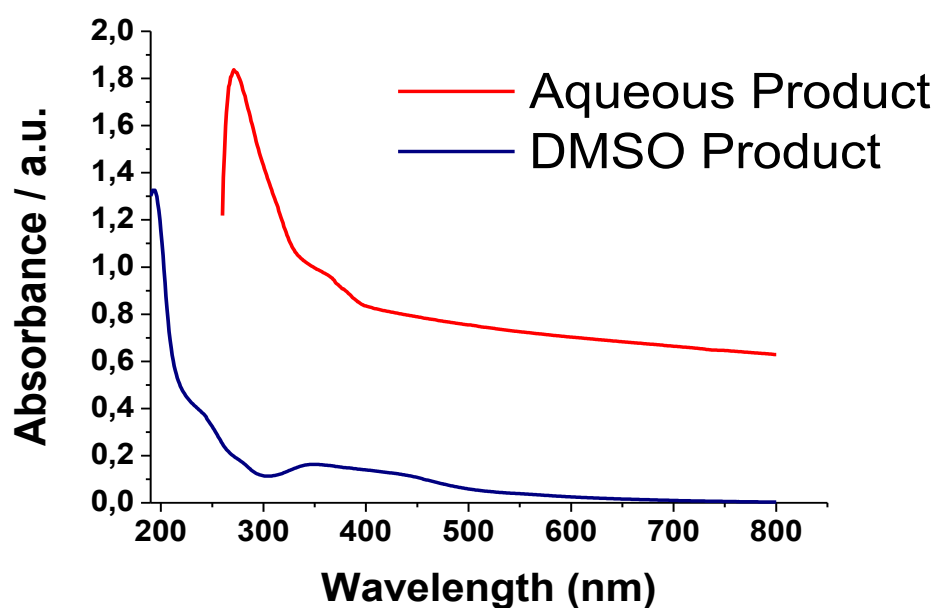
**Figure (7)** 3D Fluorescence spectrum for sample T02(aqueous product).



**Figure (8). 3D Fluorescence spectrum for sample T03 (DMSO product)**

On the other hand, T03 (DMSO product) showed luminescence regions around 450 nm excitation and emission at around 518 nm, as shown in Fig. 7. According to previous studies, the shift in emission peak positions with different excitation wavelengths arises not only from the different sizes of CQDs, but also from different emissive sites on the CQDs. At certain excitation wavelengths, some corresponding emissive sites would be excited and fluoresce, resulting in the excitation-dependent behaviours of the emission spectra.

In the UV –VIS spectrum, the prepared carbon quantum dots exhibit an absorbance peak at 367 nm for the aqueous product, and 350 nm from the DMSO product as shown in Fig. 9. A strong absorbance peak is observed for the aqueous product compared to that of DMSO product.



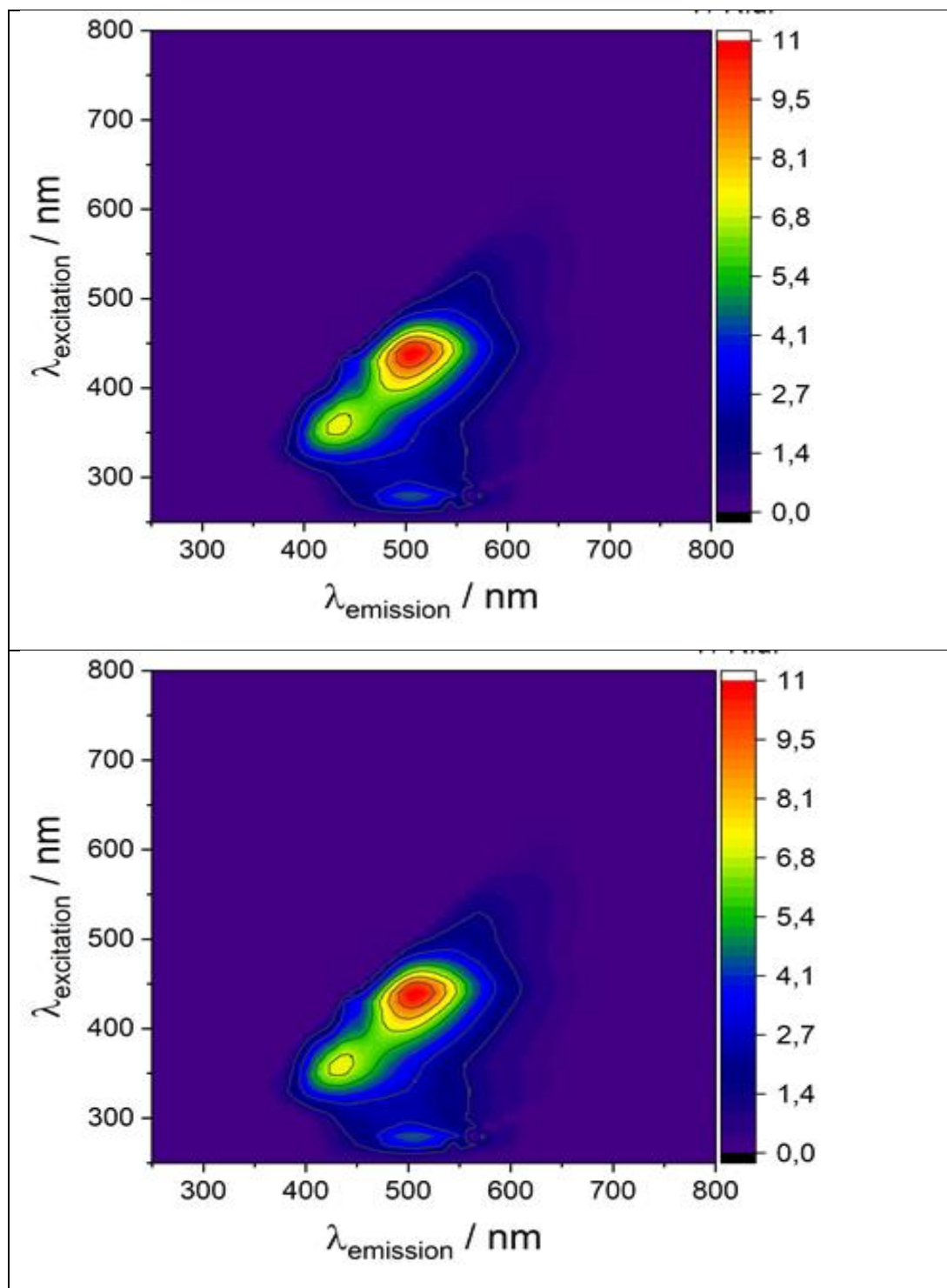
**Figure (9).** UV- VIS spectrum for the aqueous product and DMSO products.

Table.3. Excitation and emission maximum wavelengths of aqueous and DMSO product.

Sample code	$\lambda_{\text{emission}}$	$\lambda_{\text{excitation}}$	$\lambda_{\text{absorption}}$
T02	445	362	367
T03	518	450	350

Together, these results shown on Table 2. demonstrates that the solvent greatly influences the fluorescence characteristic of the carbon quantum dots. The samples that were prepared in DMSO were highly hydrophobic and had a much lower fluorescence, as their peaks were much broader, compared to the aqueous product.

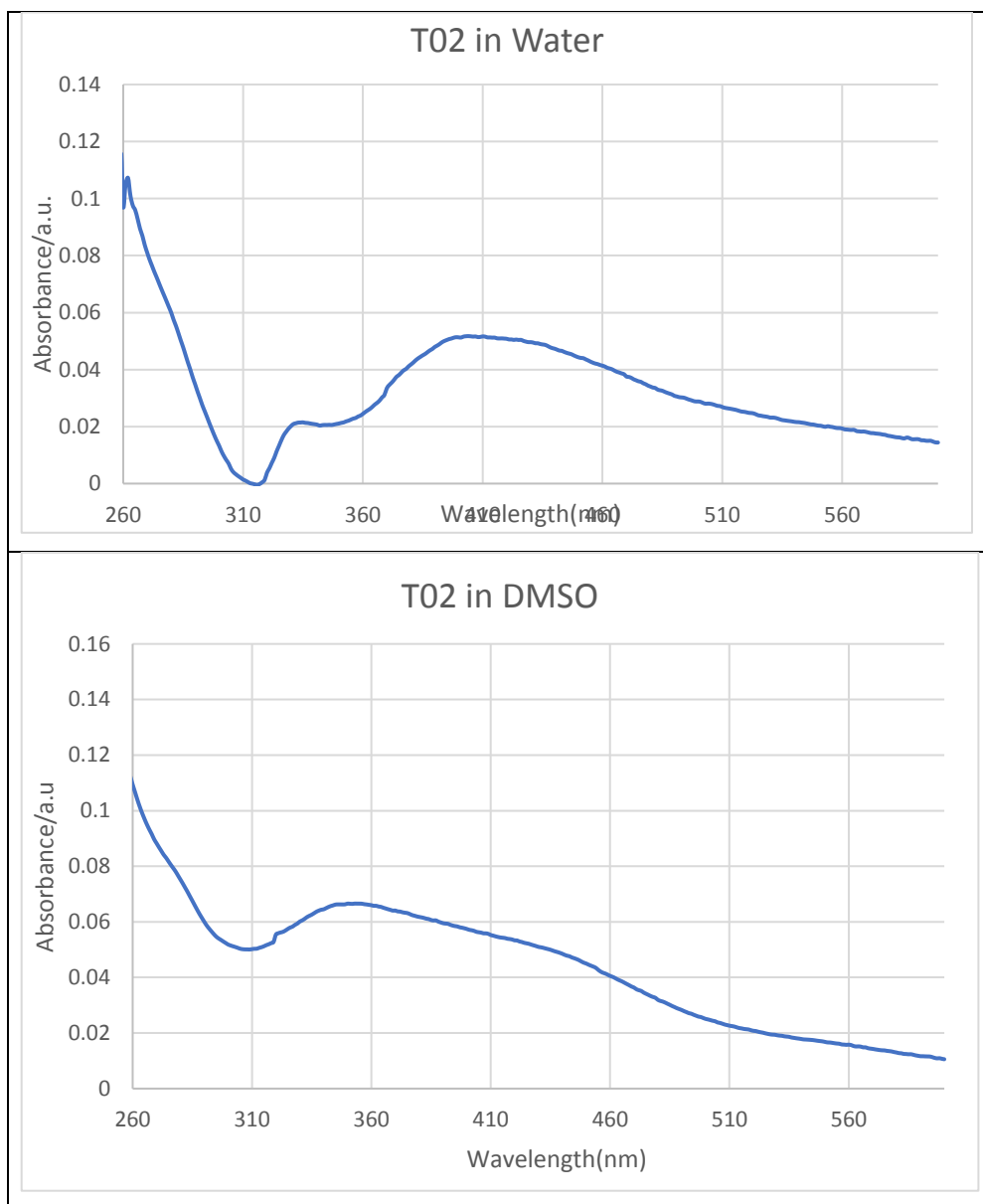
Again, the samples prepared were dispersed in water and DMSO, 3D fluorescence and UV-Vis absorbance spectra was recorded, to study the effect of solvent, on the fluorescence of the product.



**Figure (10). 3D fluorescence of T02 dispersed in water and DMSO.**

In sample T02 (prepared in water), 3 luminescence peaks were observed on the fluorescence spectrum, around 350 nm excitation with 450 nm emission (Peak 1) and 440 nm excitation with 500 nm emission (Peak 2). The presence of a further weak peak could be detected at a



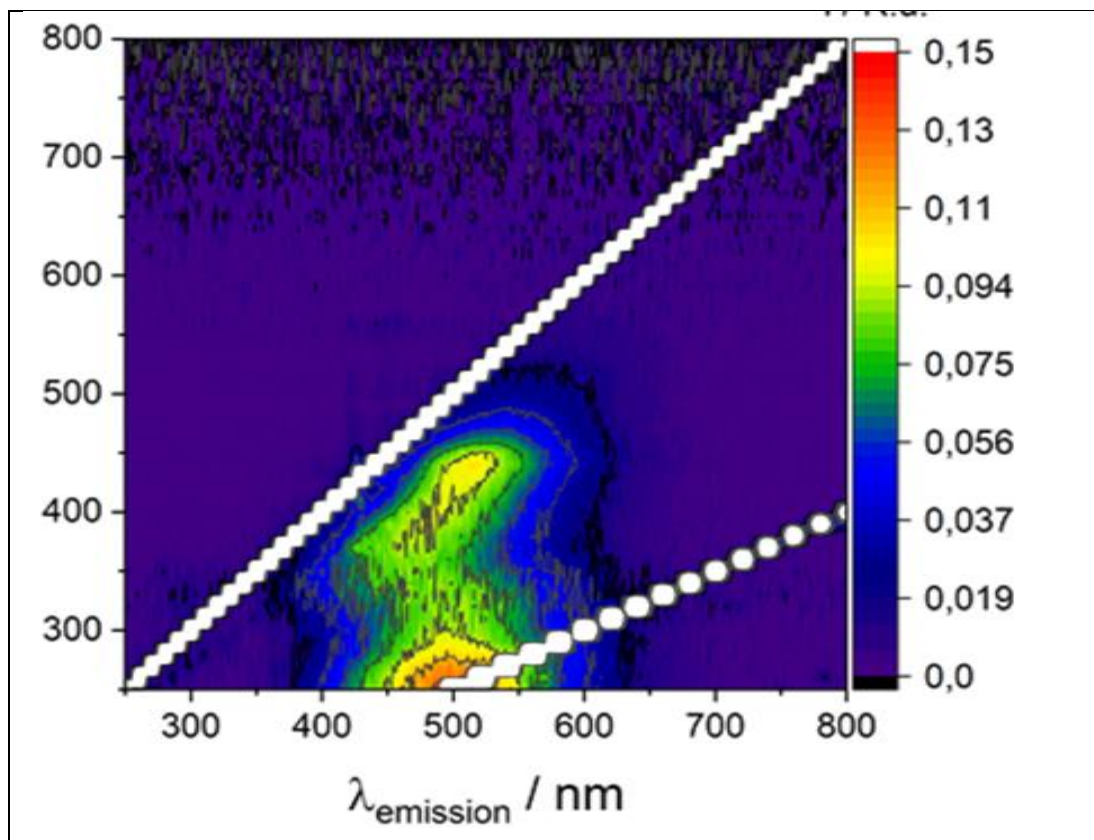


**Figure (11). UV- VIS spectrum of sample T02 in water and DMSO**

smaller wavelength, below 250 nm excitation and around 450 nm emission (Peak 3), as shown on Figure (10). When the sample was dissolved in DMSO, peak 3 became much stronger. Peak 1 and 2 did not change positions, however, the peaks became broader. In the UV-Vis, CQDs typically show optical absorption in the UV region with a tail extending to the visible range for representative spectra the particle exhibited absorbance peak at the 340 nm and the 420 nm range.

Furthermore, samples that were prepared in DMSO solvent (T03) indicated much broader peaks and different fluorescence character compared to samples prepared in water, Shown in Figure 10. T03 sample had main peaks in the Peak 1 and Peak 2 regions, however in DMSO

the region is broadened, and no individual peaks were observed. The shape of the peaks suggests that particles prepared in DMSO have a much lower fluorescence. Peak 3 became even more red shifted to 300–310 nm excitation and 490–510 nm emission. When dissolved in water the overall intensities were greatly reduced, may be due to the fact that they cannot be easily dissolved in water and have a less polar surface character. In the case of UV-Vis characterization, for T03, there we no distinctive peaks either in water or DMSO. As shown on, Figure.



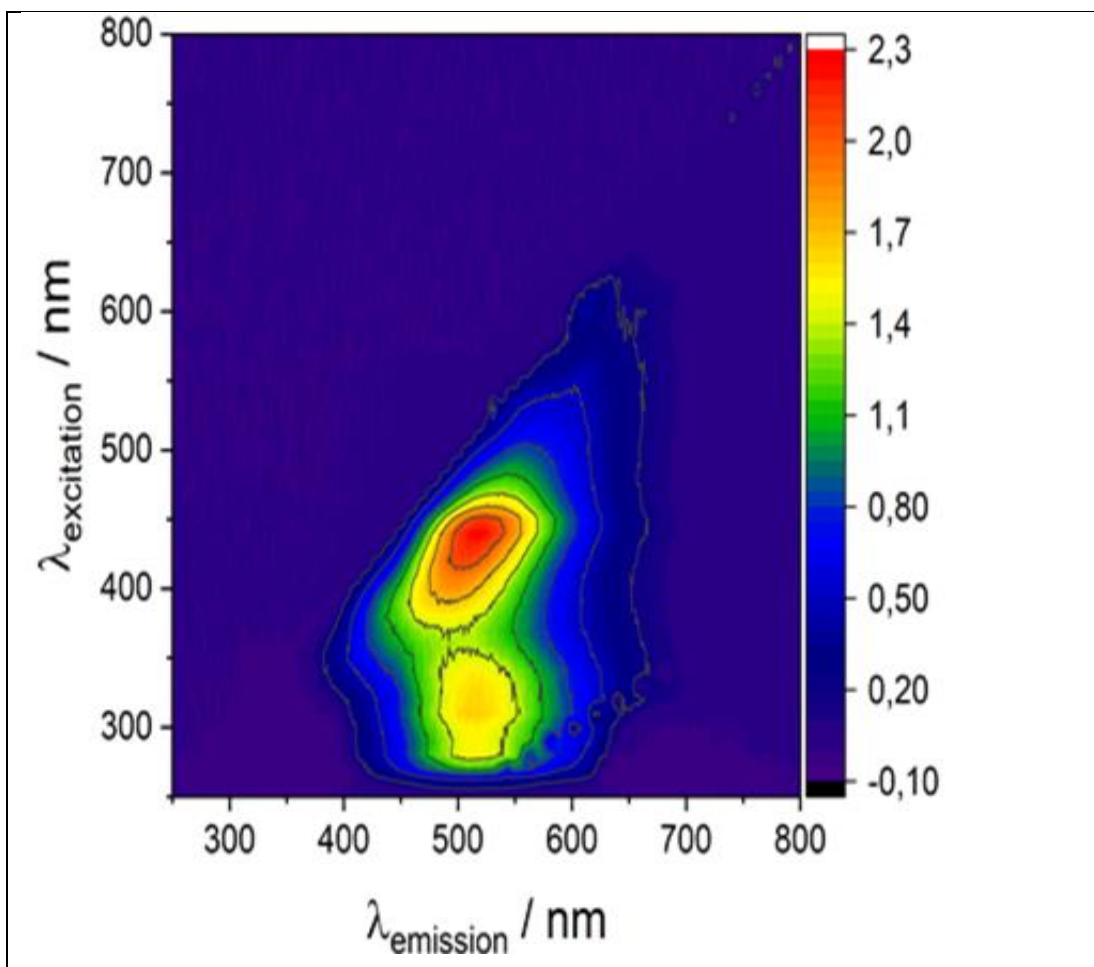
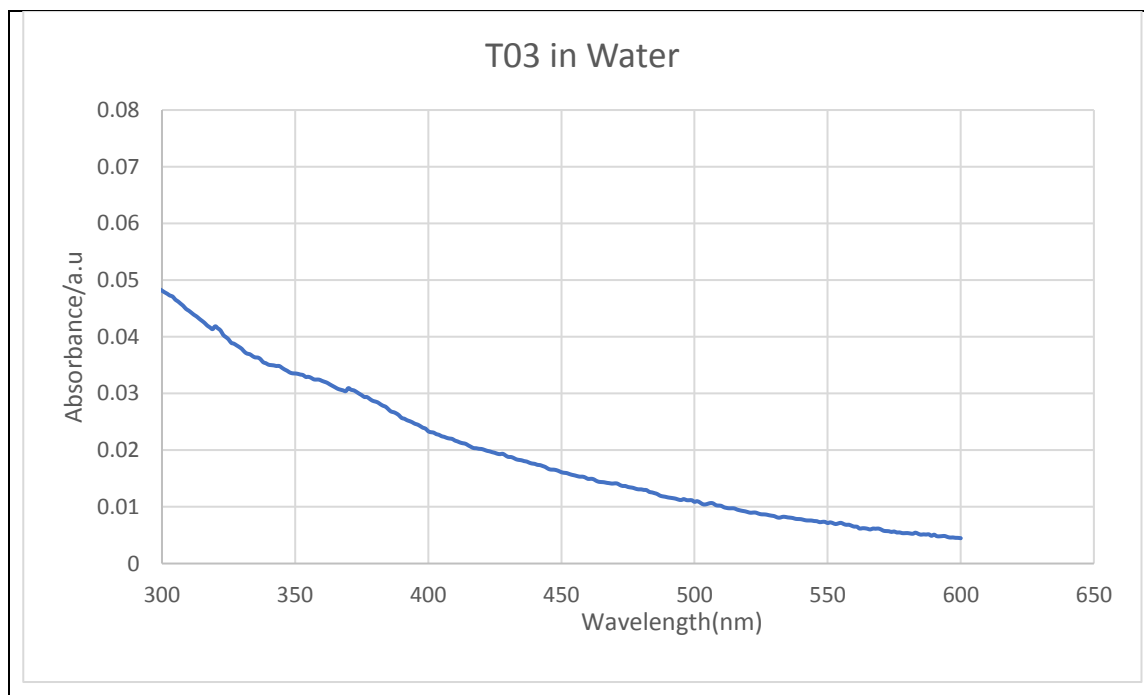
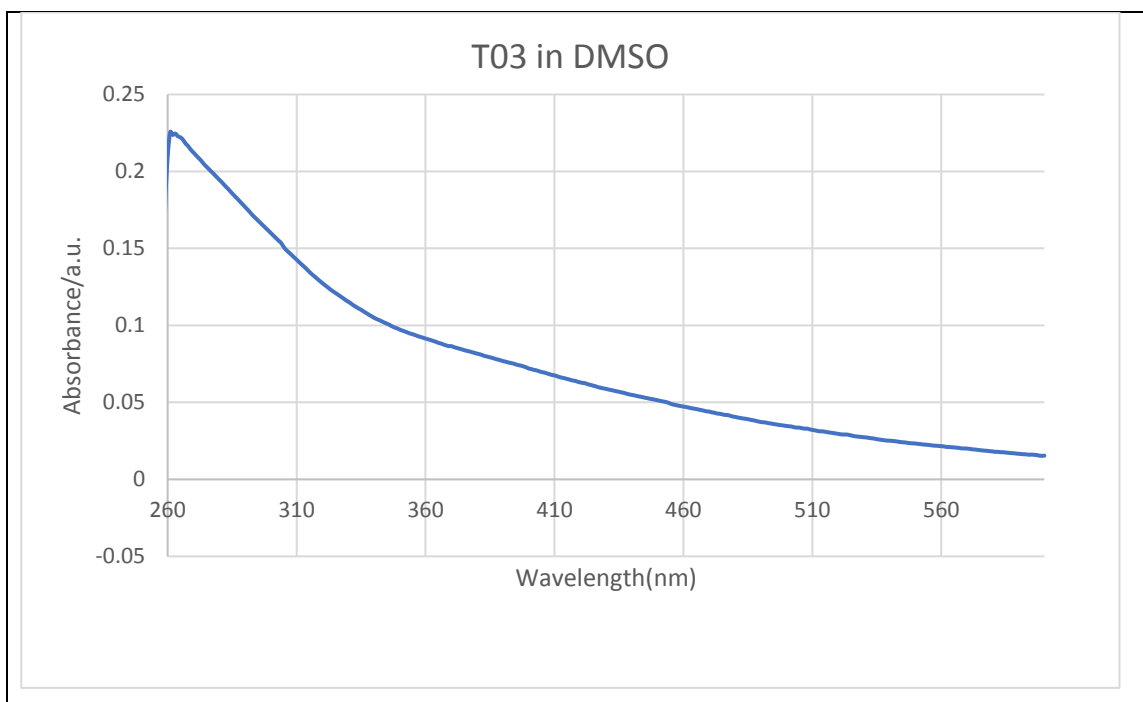


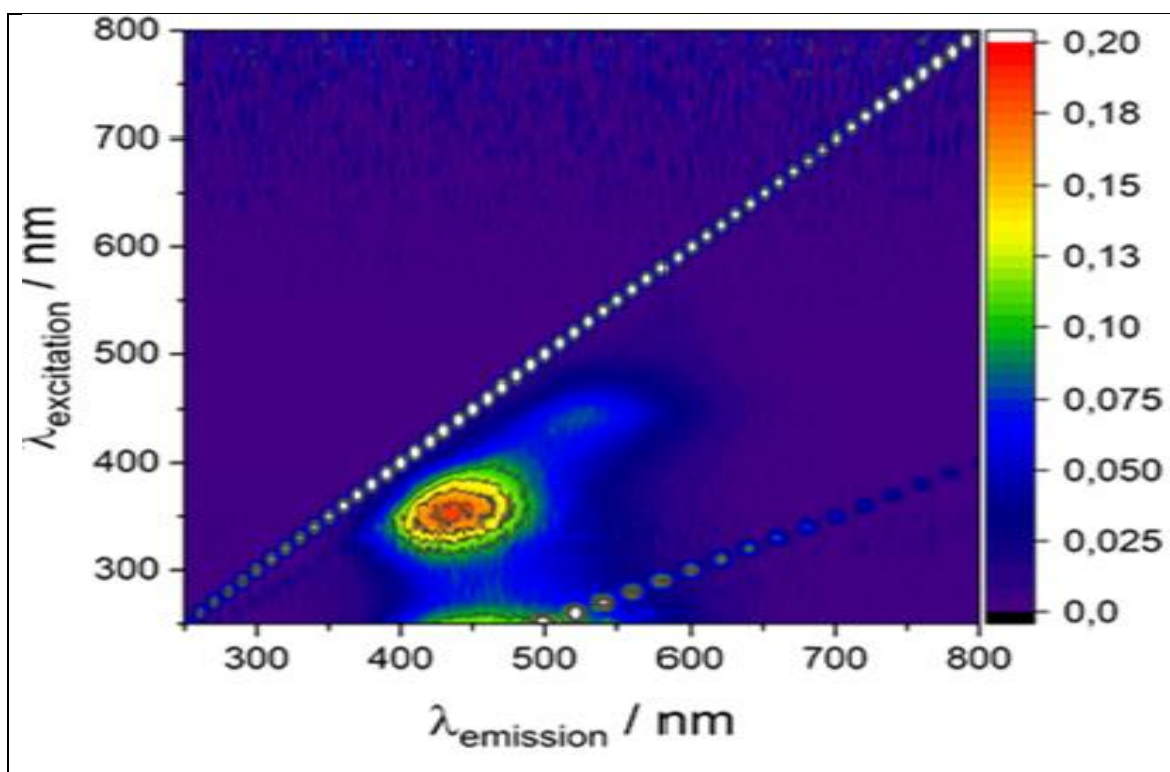
Figure (12).3D fluorescence of T03 dispersed in water and DMSO.

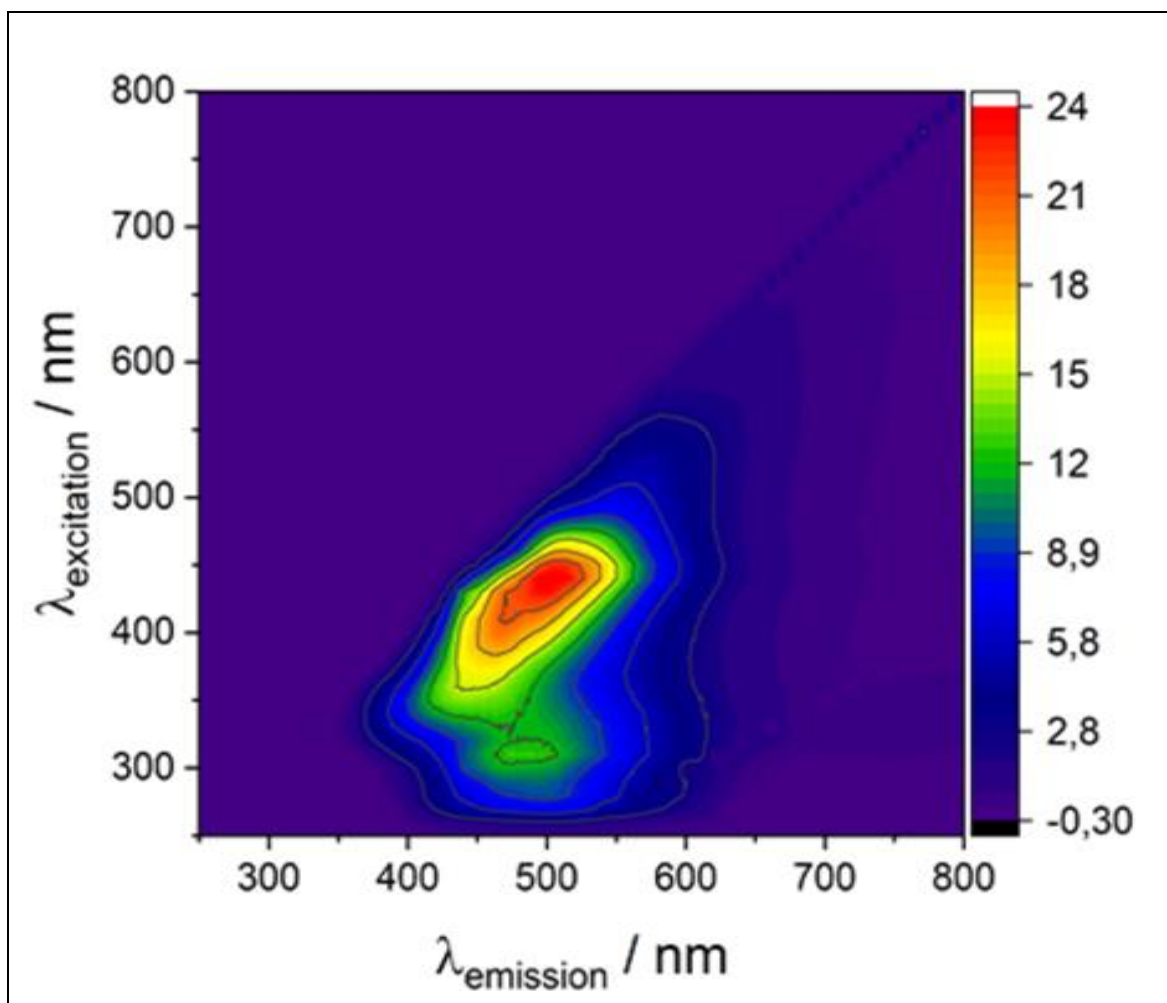




**Figure (13) UV- VIS spectrum of T03 in water and DMSO.**

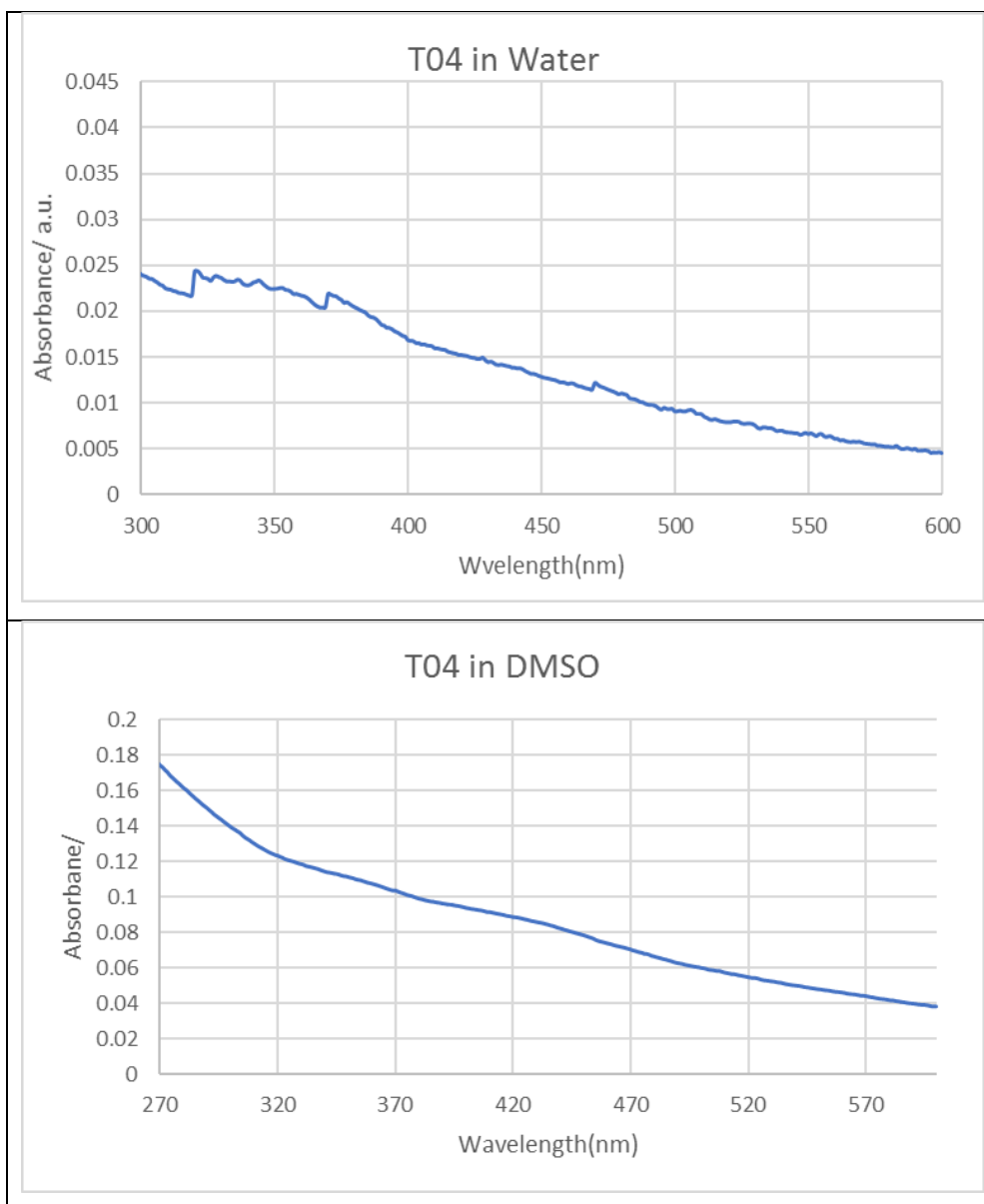
As shown in Fig. (0), T04(DMSO product) had almost the same 3D fluorescence spectrum with sample T03. Similarly, the sample also had two main luminescence in the Peak 1 and Peak 2 regions and the regions were much broader compared to the aqueous product. These results illustrated that the carbon quantum dots prepared with DMSO solvent have a lower fluorescence.





**Figure (14). 3D fluorescence of T04 dispersed in water and DMSO.**

In the case of T04 the shape of the spectrum became almost similar to T02 in water. The fluorescence peaks can be attributed to the various luminescence centres in the particles. Absorption peak 3 corresponds to  $\pi \rightarrow \pi^*$  region of fluorescence transitions of sp<sup>2</sup>-hybridized carbon originating from the conjugated electron structure of the particle core, while the Peak 1 region can be attributed as  $n \rightarrow \pi^*$  transitions at the carbon lattice edge. The lower energy Peak 2 fluorescence is commonly associated with  $n \rightarrow \pi^*$  transitions of surface functional groups of the particles. It is important to note that CQD3 has the most prominent fluorescence in the Peak 3 region, responsible for the core luminescence.



**Figure(15) .UV- VIS spectrum of T04 in water and DMSO.**

**Table 4. Excitation and emission maximum wavelengths of CQDs dispersed in water and DMSO.**

Sample code	Solvent	$\lambda$ emission (nm)	$\lambda$ excitation (nm)	$\lambda$ absorption
T02	Water	440	350	340&320nm
		520	440	
		450	250	
T02	DMSO	430	340	
		500	440	
		500	280	
T03	Water	500	240	No distinctive peak
		510	440	
T03	DMSO	500	320	
		510	400	
		520	310	
T04	Water	450	240	
		440	350	
		530	440	
T04	DMSO	480	310	
		490	437	
		480	310	

## Chapter 5

### 5.1. Conclusion

In this study, we herein have demonstrated how the reaction methods and solvents have an effect on the synthesis and fluorescence of carbon quantum dots. The reaction method has an effect on the properties of the carbon quantum dots. It was found that the used solvent influences the polarity and functionality of the carbon quantum dots. Carbon quantum dots prepared in DMSO when dissolved in water-induced fluorescence than did with the ones prepared in water. While CQDs prepared in water have high fluorescence properties, that would particularly be important for potential applications in bioimaging. The prepared CQDs showed a high quantum yield of 11%. Based on these findings, we wanted to do a comprehensive investigation, since the commercial microwave is a bit inherently unreliable since the temperature cannot be controlled. A further study was conducted to investigate the effect of reaction time, molar ratio and reaction temperature in the resulting product of carbon quantum dots, using CEM discover microwave reactor, which has superior control over temperature, input power, and pressure that was used in this investigation. A simple and one-step method was deployed for the preparation of highly fluorescent CQDs. These materials were prepared through microwave irradiation, using citric acid as a carbon source, urea as a nitrogen source, and double-distilled water as a solvent. Successfully, the CQDs were fabricated and they were fluorescent under UV-light. However, a lot of more experiments and steps needed to be carried out to tailor and characterize the properties of the CQDs. Unfortunately, due to the global pandemic most of the experimental work and analysis of the CQDs could not be completed.



## **Thesis summary**

### **The Synthesis of Carbon Quantum Dots: MSc student in Materials Science.**

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During my Master's studies, I joined the Laboratory of Interfaces and Nanostructures at the Eötvös Loránd University, where I engaged in the research on carbon quantum dots. CQDs play an essential role in bioimaging and drug delivery system, owing to their unique properties.

The objectives of this project were to carry out a critical literature review and determine processing routes worth investigating. To do that we conducted a study to investigate the effect of a solvent and the technique used in the synthesis in the resulting carbon quantum dots. Two types of reaction procedures, microwave-assisted heating, and refluxing the solution over an oil bath, were deployed. These materials were prepared, using citric acid and, urea precursors and double distilled water and DMSO as solvents.

We also wanted to study further the experimental conditions and study them in more detail, by studying the effect of molar ratio, temperature, and time in the synthesis of carbon quantum dots. To study these effects thoroughly, atomic force microscopy (AFM) was employed to determine the morphology of the synthesized particles, the results from the AFM illustrated that the CQDs were particles in nature, have a spherical shape and an average size of 1-2 nm. We further analyzed the optical properties of the carbon quantum dots, using the fluorescence spectrometry and UV-Vis absorption. Fluorescence is one of the most fascinating features of CQDs, both from fundamental and application-oriented perspectives. It was found that the solvent and technique used, have a huge effect on fluorescence properties of the resulting products, as the results confirmed that CDQs prepared in water have a higher fluorescence than those CQDs prepared in DMSO. The solvent used at synthesis also influences the polarity and functionality of the quantum dots. CQDs prepared in DMSO were more hydrophobic.

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# NYILATKOZAT

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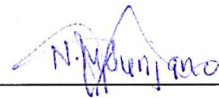
**NEPTUN azonosító:** E7FYDO

**Szakdolgozat címe:**

The Synthesis of Carbon Quantum Dots

A **szakdolgozat** szerzőjeként fegyelmi felelősségem tudatában kijelentem, hogy a dolgozatom önálló szellemi alkotásom, abban a hivatkozások és idézések standard szabályait következetesen alkalmaztam, mások által írt részeket a megfelelő idézés nélkül nem használtam fel.

Budapest, 2020, May 27e



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*a hallgató aláírása*