ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

SYNTHESIS OF AMPHIPHILIC CARBON QUANTUM DOTS THROUGH CARBONIZATION OF SUPRAMOLECULES

M.Sc. THESIS

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Department of Nanoscience and Nanoengineering

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

SUPRAMOLEKÜLLERİN KARBONİZASYONU İLE AMFİFİLİK KARBON KUANTUM NOKTALARININ SENTEZİ

YÜKSEK LİSANS TEZİ

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HAZİRAN 2021

İbrahim Yağız COŞKUN, a **M.Sc.** student of **ITU Graduate School** student ID **513181008,** successfully defended the **thesis** entitled **"SYNTHESIS OF AMPHIPHILIC CARBON QUANTUM DOTS THROUGH CARBONIZATION OF SUPRAMOLECULES"**, which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Assist. Prof. Dr. Caner ÜNLÜ** Istanbul Technical University	……..
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Date of Submission : 24 May 2021
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To my family,

FOREWORD

First of all, I would like to thank my thesis supervisor Caner ÜNLÜ, who has accepted me into his laboratory and allowed me to study there, sharing all his knowledge and experience, guiding, supporting. Beyond being a faculty member, he has always been a friend for us as the BeeDot laboratory group. He pioneered the emergence of such a study in a short period of 4 months. If he hadn't accepted me into his lab, I wouldn't have come up with such a study.

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June 2021

İbrahim Yağız COŞKUN
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TABLE OF CONTENTS

Page

ABBREVIATIONS

CP-DOT **:** Calix[4]pyrrole Dot
CQD **:** Carbon Quantum Dot
DMF **:** Dimethylformamide
FTIR **:** Fourier Transform Infrared Spectroscopy
GQD **:** Graphene Quantum Dot
LED **:** Light Emitting Diode
MWCNT **:** Multi-walled Carbon Nanotube
PLA **:** Pulsed Laser Ablation
QD **:** Quantum Dot
TEM **:** Transmission Electron Microscopy
TOP **:** Tri-n-octylphosphine
TOPO **:** Tri-n-octylphosphine Oxide
T-DOT **:** Toluene Dot
XPS **:** X-Ray Photoelectron Spectroscopy

LIST OF FIGURES

Page

SYNTHESIS OF AMPHIPHILIC CARBON QUANTUM DOTS THROUGH CARBONIZATION OF SUPRAMOLECULES

SUMMARY

Quantum dots are zero-dimensional nanoparticles, also known as artificial atoms. The reason why they are called zero-dimensional nanoparticles is that quantum dots have dimensions of less than 100 nm on the x, y, and z axes. They were first found in 1980 by Alexey I. Ekimov. In the following years, the foundations of quantum dot research were laid with the contributions of Alexander Efros and Louis Brus. Later, these three scientists were awarded R.W. Wood award due to discovering quantum dots.

Behind the unique fluorescence properties that quantum dots exhibit is a physical explanation known as the quantum confinement effect. Briefly, the quantum confinement effect is an effect that occurs in consequence of the energy band structures becoming discrete state from the continuous state with changing the dimensions of the materials. As a result, the change in the size of quantum dots causes them to emit light in different colors.

Quantum dots have been the focus of attention of scientists and researchers, especially with their fluorescence properties since their discovery. As a result, quantum dot technology has become a state-of-the-art research area that many scientists from different disciplines work on. While research on drug delivery and their usability in cancer treatment continues with a great interest in the field of medicine, quantum dots in the field of electronics have caused a breakthrough innovation, especially in display systems. In addition, they are not limited to display systems also are referred to as promising nanoparticles in studies on quantum computing. Another important field of study is green technology, which has become increasingly important in recent years. Quantum dots have important advantages, such as purifying drinking water from heavy metals and increasing the efficiency of solar panels used in the field of sustainable energy.

On the other hand, heavy metals such as cadmium, mercury, and lead have been used in the synthesis of quantum dots for many years. Although they show properties such as bright photoluminescence and high photostability, metal-based quantum dots have negative effects on the environment and human health. Even though the fluorescence properties of carbon-based quantum dots are one step behind compared to metal-based quantum dots, their being environmentally friendly and not observed any negative effects on human health has led research in quantum dot technology to carbon-based quantum dots.

The synthesis of both metallic and carbon-based quantum dots is accomplished through two basic approaches, top-down and bottom-up approaches, which are the source of nanomaterial fabrication methods. The organometallic synthesis method, which is one of the bottom-up approach methods, is used in the synthesis of metallic-based quantum dots. In carbon-based quantum dot synthesis, both top-down and

bottom-up approaches are preferred, but mostly bottom-up methods such as hydrothermal-solvothermal synthesis and microwave-assisted synthesis are used.

In this thesis, Calix[4]pyrrole from the calixpyrrole family, a family known in the field of supramolecular chemistry, was used as a carbon source. Calix[4]pyrrole is a supramolecule formed by the bonding of 4 pyrrole molecules with non-covalent intermolecular bonds. Calix[4]pyrrole carbon quantum dots (CP-DOTs) were synthesized in the study by using the solvothermal synthesis method. However, unlike the literature, instead of using polar solvent, Toluene, which is an apolar solvent, was used in the thesis. As a result of the syntheses made at different temperatures and times, it was found that the optimum values were achieved with 200°C 8 hour parameters.

The characterization of CP-DOTs has been done both optically and structurally. While UV-Vis Spectrophotometer and Fluorescence Spectrofluorometer were used in optical analyzes, TEM, XPS and FTIR were used for structural analysis.

While HRTEM results give an idea that CP-DOTs have graphitic carbon structure, this hypothesis is confirmed by XPS and FTIR results. XPS data show that the nitrogen atom in the Calix[4]pyrrole structure has moved away from the structure after the synthesis. While the structure of CP-DOTs consists only of carbon atoms, it is also observed that the oxygen atoms which come from the air in the Teflon environment are also added to the structure. FTIR measurements indicate the presence of carboxyl and hydroxyl groups on the surface of CP-DOTs. Optical analysis results are compatible with structural analysis results and support structural analysis results. The observed absorbance, emission, and excitation values of CP-DOTs show typical carbon quantum dot behavior. It was observed that the produced CP-DOTs showed amphiphilic property by examining their behaviors in different solvent environments. CP-DOTs with amphiphilic property offer usability in different application areas.

SUPRAMOLEKÜLLERİN KARBONİZASYONU İLE AMFİFİLİK KARBON KUANTUM NOKTALARININ SENTEZİ

ÖZET

Kuantum noktalar yapay atomlar olarak da bilinen sıfır boyutlu nanopartiküllerdir. Sıfır boyutlu nanopartikül olarak adlandırılmalarının sebebi kuantum noktaların x, y ve z ekseninde boyutlarının 100 nanometrenin altında olmasından kaynaklanır. İlk kez 1980 yılında Alexey I. Ekimov tarafından bulunmuşlardır. Ekimov çalışmasında eriyik cam matriks içerisinde bakır klorür nanokristalleri sentezlemiştir. Takip eden yıllarda Alexander Efros nanokristaller hakkında ilk teorik açıklamayı yazmıştır ve açıklamasında nanokristallerin elektronlarını hapsederek nasıl fluoresans davranış sergilediklerini göstermiştir. Louis Brus ise, Bell Laboratuvarları'nda çalışırken, kadmiyum sülfür kullanarak ilk kez kolloidal kuantum noktaları elde etmiştir. Yapılan bu çalışmalar kuantum nokta araştırmalarının temellerini oluşturur. Bu üç bilim insanına kuantum noktalarını keşfettikleri için 2006 yılında Optical Society of America tarafından R.W. Wood ödülü verilmiştir.

Kuantum noktaların çalışma prensibi şu şekildedir; normalde sıfır boyutlu nanopartiküllerin elektronları değerlik bandında stabil halde durur. Dışarıdan enerji uygulandığında eğer uygulanan enerjinin değeri bant boşluğunun enerji değerinden yüksekse elektronlar iletim bandına geçerler. İletim bandındaki yüksek enerjili elektronlar kararsız haldedir. Kararlı hale tekrar geçmek için değerlik bandına dönmek isterler. Ancak bulundukları iletim bandının enerji değeri değerlik bandının enerji değerinden fazla olduğundan sahip oldukları yüksek enerjiyi vermek zorundadırlar. Elektronlar sahip oldukları bu enerjiyi değerlik bandına geçerken elektromanyetik dalga olarak yayarlar. Yayılan bu elektromanyetik dalgalar farklı emisyon renkleri olarak gözlemlenir.

Kuantum noktaların gösterdikleri eşsiz fluoresans özelliklerinin ardında kuantum hapsi etkisi olarak bilinen fiziki bir açıklama vardır. Kuantum hapsi etkisi şu şekilde açıklanabilir; Boyutların x, y ve z ekseninde 100 nanometrenin altına inmesi nanopartiküllerin elektronlarının hapsolmasına neden olur. Bu durum enerji bant yapılarını değiştirir. Yığın malzemelerde devamlı halde bulunan enerji bant yapıları kuantum noktalarda ayrık hale gelir. Ayrık halde, elektronlar değerlik ve iletim bantlarında belirli enerji seviyelerinde bulunurlar. Boyutsal küçülme aynı zamanda bant boşluğu değerlerini değiştirir. Büyük kuantum noktaların (5-6 nm boyutlu) bant boşluğu küçük kuantum noktaların (2-3 nm boyutlu) bant boşluğuna göre daha dardır. Bu yüzden 5-6 nm boyutlu kuantum noktaları uyarmak için gereken enerji daha azdır. Uyarılma sonucunda düşük frekansa sahip emisyon renkleri yayarlar. Diğer yandan, 2-3 nm boyutlu kuantum noktaların uyarılması için gereken enerji yüksektir ve uyarıldıklarında yüksek frekansa sahip emisyon renkleri yaydıkları gözlemlenir.

Kuantum noktalar keşfedildikleri tarihten itibaren özellikle sergiledikleri fluoresans özellikleri ile bilim insanları ve araştırmacıların ilgi odağı olmuştur. Bunun sonucu olarak günümüzde kuantum nokta teknolojisi farklı bilim dallarından birçok bilim

insanının üzerinde çalıştığı son teknoloji bir araştırma alanı haline gelmiştir. Tıp alanında ilaç taşınımı ve kanser tedavisinde kullanılabilirlikleri üzerine yapılan araştırmalar büyük bir ilgi ile devam ederken, elektronik alanında kuantum noktalar özellikle görüntüleme sistemlerinde çığır açıcı bir yeniliğe sebep olmuşlardır. Kuantum noktalar ayrıca görüntüleme sistemleri ile sınırlı kalmayıp kuantum hesaplama üzerine yapılan çalışmalarda umut vade edici nanopartikül olarak anılmaktadırlar. Bir diğer önemli çalışma alanı ise son yıllarda gittikçe artan bir öneme sahip olan yeşil teknolojidir. İçme sularının ağır metallerden arındırılması, sürdürülebilir enerji alanında güneş panellerinde kullanılarak verim artışının sağlanması gibi kuantum noktaların önemli avantajları vardır.

Uzun yıllar boyunca kuantum noktaların sentezinde kadmiyum, civa ve kurşun gibi ağır metaller kullanılmıştır. Parlak fotoluminesans ve yüksek fotostabilite gibi özellikler göstermelerine karşın metalik bazlı kuantum noktaların çevreye ve insan sağlığına olumsuz etkileri bulunmaktadır. Karbon bazlı kuantum noktaların metal bazlı kuantum noktalara göre fluoresans özellikleri bir adım geride kalsa da çevreci olmaları ve insan sağlığına herhangi bir olumsuz yan etkilerinin gözlemlenmemesi kuantum nokta teknolojisindeki araştırmaları karbon bazlı kuantum noktalara yönlendirmiştir.

Metalik ve karbon bazlı kuantum noktaların sentezi, nanomalzeme üretme yöntemlerinin kaynağı olan iki temel yaklaşımla yani yukarıdan aşağıya ve aşağıdan yukarıya yaklaşımlarıyla gerçekleştirilir. Metalik bazlı kuantum noktaların sentezinde özellikle aşağıdan yukarıya yaklaşım metodlarından biri olan organometalik sentez yöntemi kullanılmaktadır. Karbon bazlı kuantum nokta sentezinde ise hem yukarıdan aşağıya hem de aşağıdan yukarıya yaklaşımları tercih edilmekle birlikte daha çok aşağıdan yukarıya yaklaşım metodlarından olan hidrotermal-solvotermal sentez ve mikrodalga destekli sentez gibi yöntemler kullanılır.

Bu tez kapsamında supramoleküler kimya alanında bilinen bir aile olan calixpyrrole ailesinden Calix[4]pyrrole karbon kaynağı olarak kullanılmıştır. Calix[4]pyrrole, 4 adet pyrrole molekülünün kovalent olmayan moleküllerarası bağlar ile bağlanması sonucu oluşan bir supramoleküldür.

Calix[4]pyrrole karbon kuantum noktaların (CP-DOTs) sentezlenmesi aşamasında çalışmada solvotermal sentez yöntemi kullanılmıştır. Ancak literatürden farklı olarak tezde polar çözgen kullanmak yerine apolar çözgen olan toluene kullanılmıştır. Farklı sıcaklık ve sürelerde yapılan sentezler sonucunda optimum değerlerin 200°C 8 saat parametreleri ile sağlandığı bulunmuştur.

CP-DOT'ların karakterizasyonu hem optik hem de yapısal olarak yapılmıştır. Optik analizlerde UV-Vis Spektrofotometresi ve Fluoresans Spektrofluorometresi kullanılırken, yapısal analizler için TEM, XPS ve FTIR'den yararlanılmıştır.

HRTEM sonuçları, CP-DOT'ların grafitik karbon yapıya sahip olduğu konusunda bir fikir verirken bu hipotez XPS ve FTIR sonuçları ile doğrulanmaktadır. XPS dataları sentez sonrasında Calix[4]pyrrole yapısında bulunan azot atomunun yapıdan uzaklaştığını göstermektedir. CP-DOT'ların yapısı yalnızca karbon atomundan oluşurken teflon içerisindeki havada bulunan oksijen atomlarının yapıya katıldığı da gözlenmektedir.

FTIR ölçümleri, CP-DOT'ların yüzeyinde karboksil ve hidroksil grupları bulunduğunu işaret eder. Optik analiz sonuçları yapılan yapısal analiz sonuçları ile uyumludur ve yapısal analiz sonuçlarını desteklemektedir.

CP-DOT'ların gözlemlenen absorbans, yayma ve uyarma değerleri tipik karbon kuantum nokta davranışı göstermektedir. Üretilen CP-DOT'ların farklı çözücü ortamındaki davranışları incelenerek amfifilik özellik gösterdikleri gözlemlenmiştir. Amfifilik özellik gösteren CP-DOT'lar farklı uygulama alanlarında kullanılabilirlik sunmaktadır.

1. INTRODUCTION

1.1 History of Quantum Dots

Quantum dots (QDs) are zero-dimensional nanoparticles. They are called with this brief definition because their all dimensions are below 100 nanometers. Generally, they have between 2 and 5-nanometer size. Also, they are sometimes known as "artificial atoms".

Alexey I. Ekimov discovered these nanoparticles at the end of the 1970s. He synthesized nanocrystals of copper chloride (CuCl) in the molten glass matrix. Then Ekimov's research and observations were published in 1981 [1]. Alexander Efros wrote the first theoretical explanation that how these nanocrystals show fluorescent behavior by confining their electrons. His theory was published in 1982 [2]. Louis Brus who inspired by Alexey I. Ekimov produced quantum dots in liquid form while he was working at Bell Laboratories. In this way, he obtained first colloidal quantum dots by using cadmium sulphide (CdS). His research was released in 1983 [3]. These three researchers (Alexey I. Ekimov, Alexander Efros and Louis Brus) shared R.W. Wood award given by Optical Society of America in 2006 with discovering quantum dots.

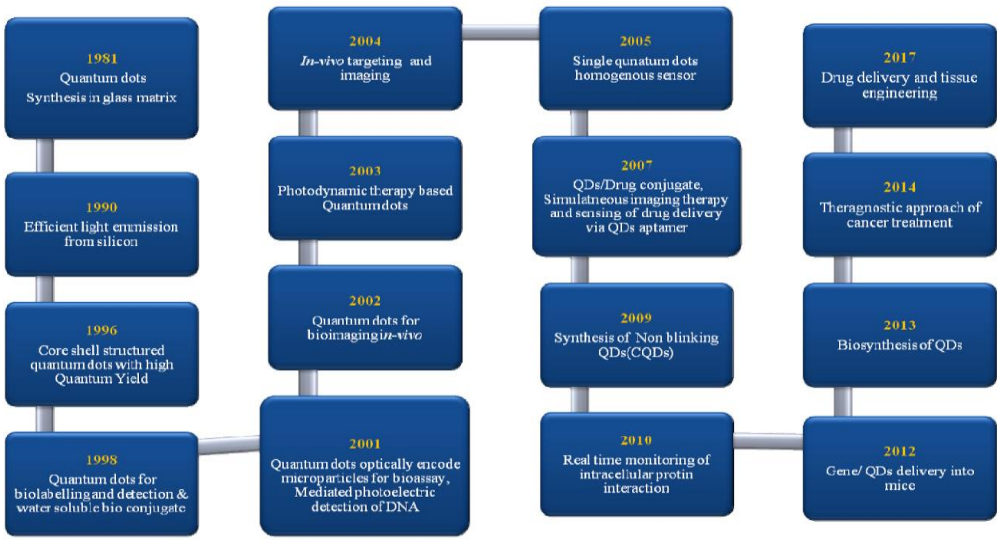

Figure 1.1 : Timeline of the development of quantum dots [4].

After the discovery in the 1980s, quantum dots have received increasing attention from different research and application fields. In particular, their unique optoelectronic properties played a game-changing role in display systems. These artificial atoms, which are not limited to electronic applications but also used in biological applications, offered alternative methods to drug delivery systems used in cancer treatments.

1.2 The Science Behind Quantum Dots

The science behind this unique property is called the "Quantum Confinement Effect" for short. Before explaining what the "Quantum Confinement Effect" is, it is necessary to briefly talk about the energy band structure. The energy band structure consists of conduction band, band gap and valence band. These bands describe the energy levels where electrons are or are not found.

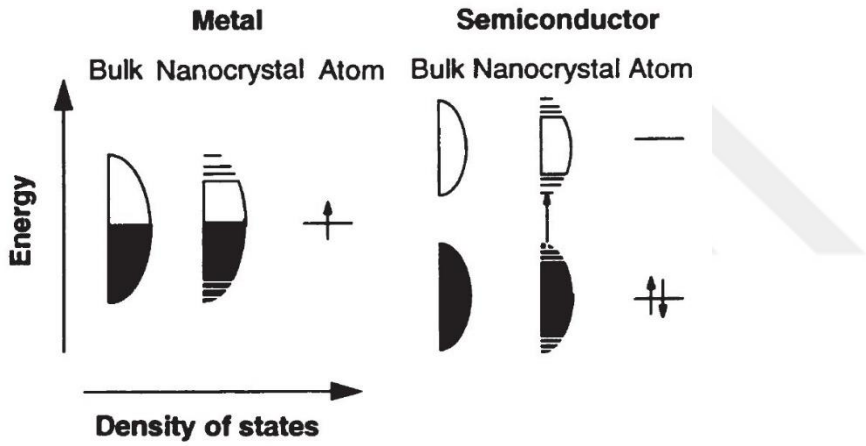

Figure 1.2 : Schematic illustration of the density of states in metals and semiconductors [5].

If an electron is excited enough energy from the stable state it is in, it can pass to a higher energy level by making a band change. In this case, the electron movement takes place from the valence band towards the conduction band. However, the electron passing to the conduction band has high energy and is not in a stable state. It returns to the valence band to be in stable state again. Since the energy level in the valence band is lower, it emits its high energy as electromagnetic waves, as illustrated in Figure 1.3 [6].

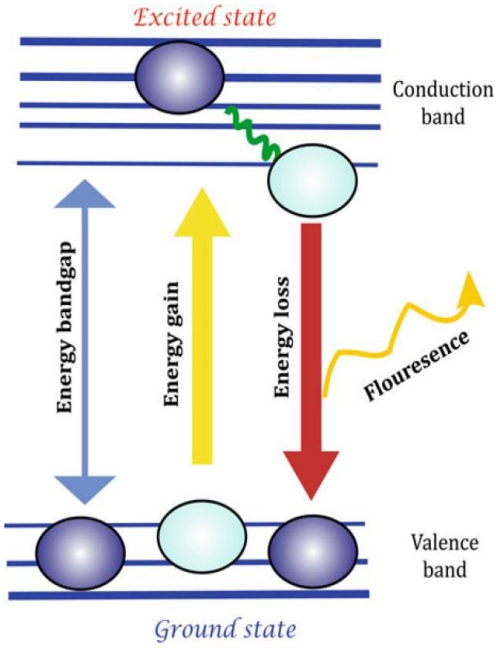

Figure 1.3 : Diagram of excitation and emission of quantum dots [7].

Materials are divided into three as conductor, semiconductor, and insulator according to their energy band structure. Conductors have a continuous energy band structure in which the conduction and valence bands are either very close to or intertwined. However, in semiconductors and insulators, there is one more band structure that called band gap. The band gap is the forbidden zone for electrons that cannot be found in this gap. For electrons to pass from the valence band to the conduction band, they must be excited with a higher energy than this band gap. In semiconductors, the band gap is narrower than in insulators relatively. This ensures that the band structures of the semiconductors are adjustable, and they can become conductors and insulators when desired.

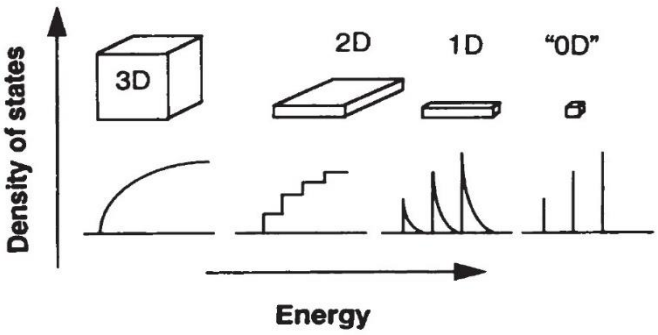

Figure 1.4 : Density of states in one band of a semiconductor as a function of dimension [5].

In fact, quantum dots are also semiconductor nanoparticles, but with a difference, they are in nanoscale. In the this scale, the situation works differently from the macroscale. There is no limit to prevent the motion of electrons in bulk materials. However, when the dimensions are shrank and a zero-dimensional nanoparticle is obtained, electrons are confined from all dimensions. This situation changes the energy band structures and causes the continuous band structure to become discrete, as seen in Figure 1.4. Electrons can now be found at certain energy levels in conduction and valence bands. Band gap values change due to this dimensional reduction. The band gap of a nanoparticle of 5 - 6 nm in size is narrower than a nanoparticle of 2 - 3 nm in size. Big quantum dots are required less energy to excite. While they become stable state, they emit electromagnetic waves that have a lower frequency and glow red. On the contrary, small quantum dots are required higher energy. They emit higher frequency waves and glow violet or blue, as shown in Figure 1.5. Briefly, energy band structures can be changed by manipulating the size of nanoparticles. This nanoscale situation is called the "Quantum Confinement Effect" [8].

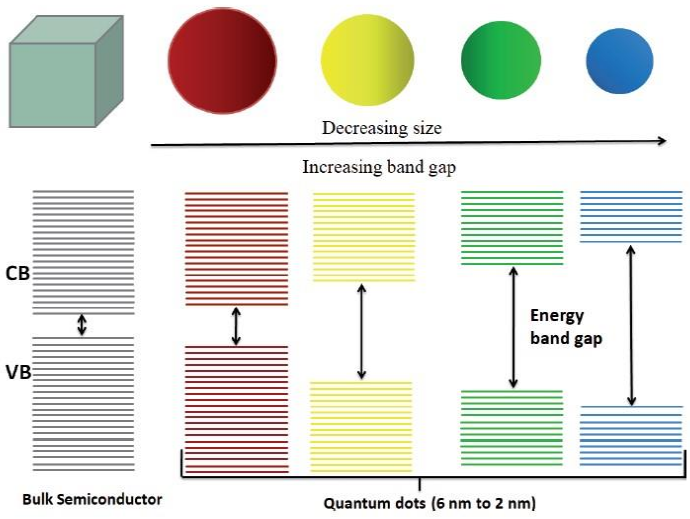

Figure 1.5 : Diagram of band structure changing with dimensional reduction [8].

1.3 Types of Quantum Dots

Metallic quantum dots have been the most studied since the discovery in the 1980s. In Figure 1.6, different metallic quantum dots are presented according to their emission wavelengths. Cadmium [9], mercury [10], and lead [11] based quantum dots have broad UV excitation, narrow emission, bright photoluminescence, and high photostability.

These properties have enabled them to find application areas in biomedical research, sensors, and photovoltaic systems. However, the biggest disadvantage of these quantum dots is that they contain heavy metals. These metals, which have negative effects on the environment and human health, cause restrictions especially in biomedical applications. They cause carcinogenic and toxic effects on the human body. Many studies have shown that they cause fatal damage to the nervous, cardiovascular, and respiratory systems [12]. In order to avoid this problem, metals such as indium [13,14], silver [15], zinc [16], and copper [17] with less toxic effects than heavy metals have started to be preferred.

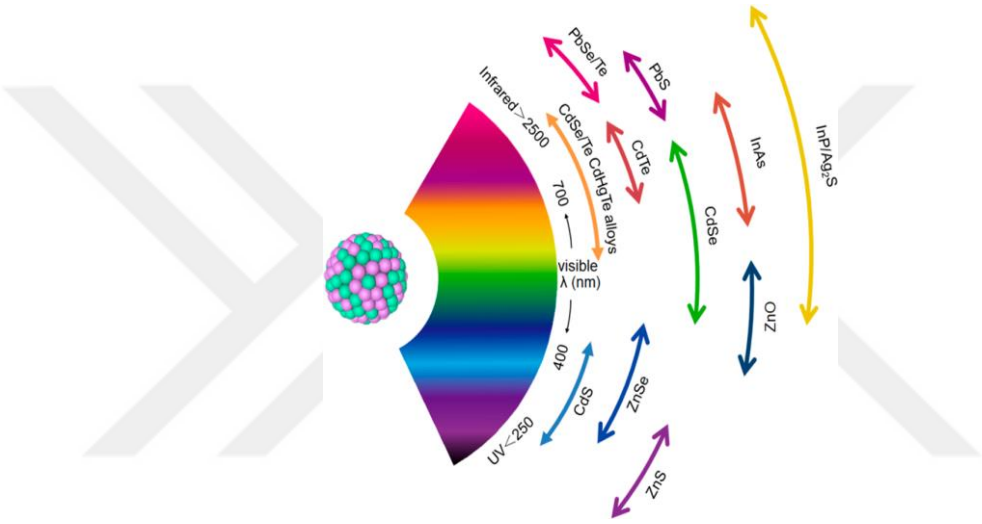

Figure 1.6 : Metallic-based QDs scaled as a function of their emission color [18].

The discovery of carbon-based quantum dots for the first time in 2006 [19] and the subsequent development of photoluminescence properties brought quantum dot researches to a different point. Although their quantum yields are lower than those of heavy metals, their being biocompatible, environmentally friendly, reproducible, and low-cost highlights carbon-based quantum dots.

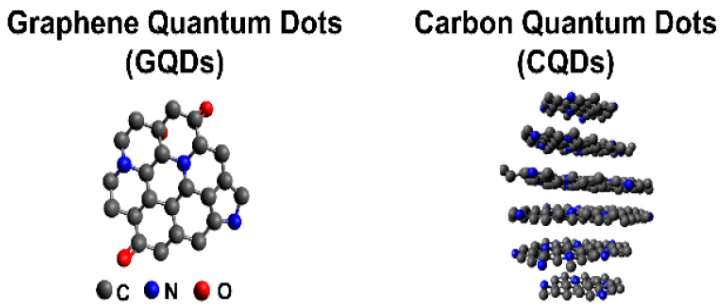

Figure 1.7 : Classification of carbon-based quantum dots [20].

1.4 Preparation of Quantum Dots

1.4.1 Preparation of metallic-based quantum dots

Generally, two different methods are used for the preparation of quantum dots. One is top-down and the other is bottom-up approach.

In earlier stage, metallic quantum dots were tried to produce by lithography that is one of the top-down approaches. However, obtained quantum dots have non-homogeneous size distribution, low reproducibility, low optical properties, and crystal defects. With all these results shown that the top-down approach cannot be used for advanced applications [21].

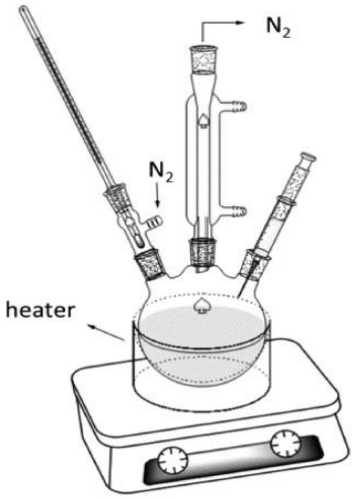

Figure 1.8 : Diagram for a hot-injection organometallic synthesis of QDs [18].

Therefore, the bottom-up approach has been accepted and developed in the synthesis of metallic quantum dots. Organometallic synthesis is one of the methods used in the bottom-up approach. Murray et al.[22] demonstrated a simple production route for the preparation of cadmium based (CdE, E = S, Se, Te) quantum dots using this method for the first time. Simply in their study, they first mixed the cadmium and one of the sulphur, selenium, tellurium precursors with the Tri-n-octylphosphine (TOP) solution separately, then injected these two solutions into the heated Tri-n-octylphosphine oxide (TOPO) solution. After several hours of reactions at temperatures ranging from 220° to 320°C, they obtained cadmium-based quantum dots. At the same time, this synthesis made by injecting precursors on the heated solvent is called hot-injection organometallic synthesis.

General hot-injection organometallic synthesis setup is demonstrated in Figure 1.8. In order to avoid the toxic effects of the precursors that used and to develop more environmentally friendly organometallic synthesis, different precursors and solvents were preferred in subsequent researches.

The difficulty of controlling the reaction temperature during the injection of precursors causes different products to be obtained in different preparations in hot injection organometallic synthesis. This leads to reducing the reproducibility of each batch. Hence, the non-injection organometallic synthesis method is developed for improving reproducibility. In this method, precursors and solvent are put into the batch reactor together and then the temperature is increased. Cao et al.[23] used this method to obtain high-quality cadmium sulphide quantum dots in their research. They also added nucleation initiators to the batch reactor. The nucleation and growth stages of CdS quantum dots are separated from each other with these initiators. High-quality quantum dots are obtained with both organometallic synthesis approaches.

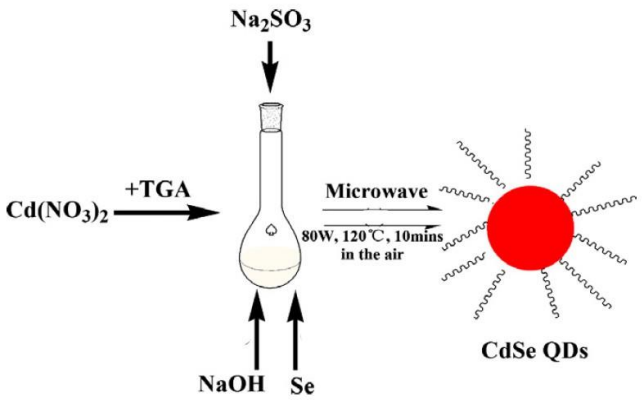

Figure 1.9 : Microwave assisted synthesis of CdSe quantum dots [25].

However, in order for these quantum dots to be usable in biological and biomedical applications, they must be well dispersed in water. This limitation adds an extra phase transfer process to the quantum dots that produced. Aqueous synthesis methods such as hydrothermal synthesis, microwave irradiation, and ultrasonic treatment enable the production of environmentally friendly quantum dots that are compatible with biological applications. Roy et al.[24] synthesized silicon quantum dots by hydrothermal method for intracellular imaging and drug delivery. After dissolving d-glucose used as a reducing agent and stabilizer in distilled water, silicon precursor solution was added.

The final solution prepared was placed in the Teflon-line autoclave and continuous heating was applied. After the 16 hour process at 160°C, silicon quantum dots were obtained. CdSe quantum dots prepared by microwave-assisted synthesis were used in white led applications, as shown in Figure 1.9.

Xuan et al.[25] suggested that the combination of phosphors and QDs in LEDs can be a solution to obtain white light sources with high color rendering properties. Chen et al.[26] obtained smaller and uniform particle size distribution with perovskite quantum dots prepared by ultrasonic synthesis method and created a wide color scale with different chemical compositions.

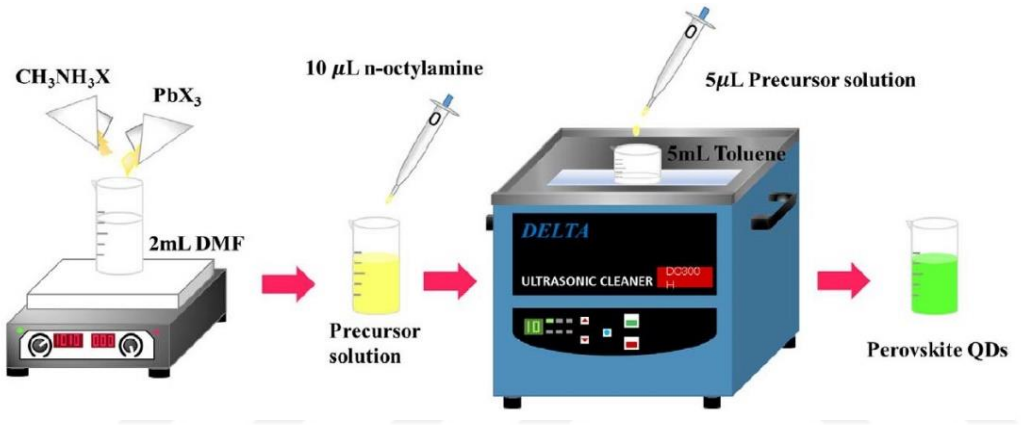

Figure 1.10 : Diagram of ultrasonic synthesis method for perovskite QDs [26].

1.4.2 Preparation of carbon-based quantum dots

There are two approach options in the synthesis of carbon-based quantum dots; One is the top-down approaches in which bulk carbon materials are cut down into smaller pieces by chemical, electrochemical and physical methods, and the other is the bottom-up approaches where quantum dot synthesis starts from carbon atoms by using many different carbon sources as a precursor. Easy control to size distribution, low cost, and no need for advanced techniques have led to increase in interest in bottom-up approach methods. In the following sections, the synthesis methods of carbon quantum dots (CQDs) and graphene quantum dots (GQDs) will be explained under separate headings.

1.4.2.1 Top-down approaches for preparation of carbon quantum dots

Laser ablation

In the laser ablation method, high temperature and pressure are applied locally to the bulk carbon material in the solvent. Nanoparticles are obtained without any impurities. The advantage of this method is that the process time is short and easy.

However, the size and shape of the carbon quantum dots produced by laser ablation show inhomogeneity and the quantum yields do not reach the desired values. Cui et al.[27] developed a homemade dual-beam Pulsed Laser Ablation (PLA) system, as presented in Figure 1.11, to shorten the laser ablation time and increase the yield in the preparation process of CQDs.

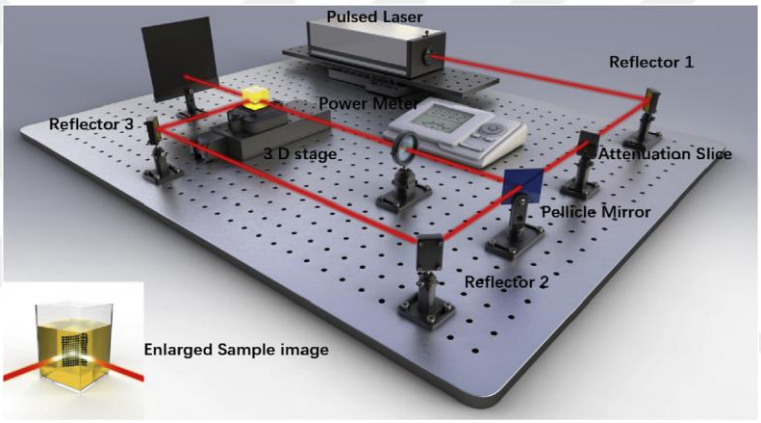

Figure 1.11 : Home-made dual beam PLA system developed by Cui et al.[27].

Electrochemical oxidation

It is the method of obtaining quantum dots by applying a voltage to the carbon source in the electrolyte. Typically, a conventional 3-electrode cell system is used for this method, as schemed in the Figure 1.12. Graphite rod, carbon nanotube, carbon paste, and carbon fiber are preferred as carbon resources. The electrode materials and electrolyte solutions play an important role in determining the properties of the quantum dots. Liu et al.[28] used graphite electrode, platinum foil electrode, and Ag/AgCl electrode in their studies. Also, alkaline alcohol was used as an electrolyte. Iron ion detection, cell imaging, and cytotoxicity measurements were made with the produced carbon quantum dots.

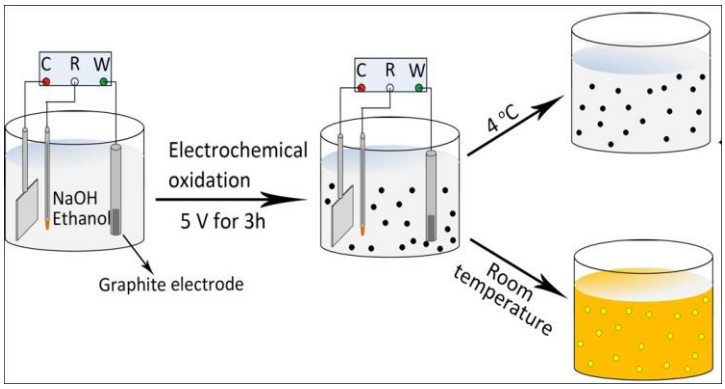

Figure 1.12 : 3-electrode cell system and diagram of electrochemical oxidation method [28].

Arc discharge

Fluorescence carbon quantum dots were first detected during the purification of single-walled carbon nanotubes by arc discharge method by Xu et al.[29]. This method has been used by lijima [30] for the production of carbon nanotubes for the first time before. In the inert gas environment, the arc is created by applying a voltage between anode containing the carbon precursor and the graphite rod cathode. Arc current creates a high-temperature plasma ranging from 4000 to 6000 K. This formed plasma sublimates the carbon precursor into the gas phase. The carbon atoms in the gas phase with the temperature gradient accumulate on the cathode and crystallize. In this way, nanoparticles are formed.

Ultrasonic wave assisted synthesis

In this method, quantum dots are produced as a result of the physical breakdown of the carbon source in a chemical liquid medium with the help of ultrasonic waves. However, this method requires post-treatment in order to obtain the final product. Li et al.[31] used activated carbon as a carbon source in their studies. They applied the ultrasonic treatment to the suspension they obtained by mixing activated carbon with hydrogen peroxide. After their purification process, they obtained carbon nanoparticles with sizes ranging from 100-150 nm. In other their study, they used glucose as a carbon source [32]. Park et al.[33] applied ultrasonic synthesis to a food waste-ethanol mixture to generate carbon quantum dots in a completely environmentally friendly approach.

As a result of their large-scale synthesis, they produced 120 grams of carbon quantum dots from 100 kilograms of food waste. They inferred with cytotoxicity analysis that these green carbon quantum dots can be used in biomedical applications.

Chemical oxidation

In chemical oxidation, which is one of the other chemical top-down approaches, the oxidation property of strong acids is used. Quantum dots are synthesized as a result of the controlled oxidation of the carbon source with acid. Functional groups formed at the surface of carbon quantum dots by controlled oxidation provide good solubility in water, but this may reduce the yield of photoluminescence.

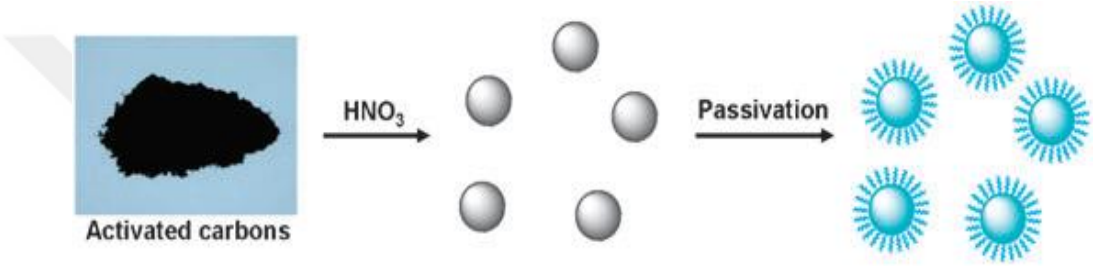

Figure 1.13 : Chemical oxidation process applied by Qiao et al.[34].

Qiao et al.[34] applied chemical oxidation synthesis to 3 different activated carbon sources and obtained multicolored photoluminescent carbon quantum dots.

1.4.2.2 Bottom-up approaches for preparation of carbon quantum dots

Pyrolysis method

In the pyrolysis synthesis method, which does not require an extra purification process, quantum dots are obtained by holding the carbon precursors at the decomposing temperature at a certain period of time. Li et al.[35] produced carbon quantum dots with this synthesis method to be used in the detection of iron ions as a chemical sensor. In order to evaluate the quantum yield of carbon quantum dots, synthesis was performed in 3 different periods of 24, 48 and 72 hours. Quantum yield of CQDs were measured as 71.1, 65.5 and 64.8 for each synthesis time respectively.

Microwave-assisted synthesis

Microwave-assisted synthesis is one of the bottom-up approaches preferred by researchers as it provides advantages such as low cost, environmental friendliness and time savings. Intense electromagnetic waves break the chemical bonds of carbon precursors to form quantum dots.

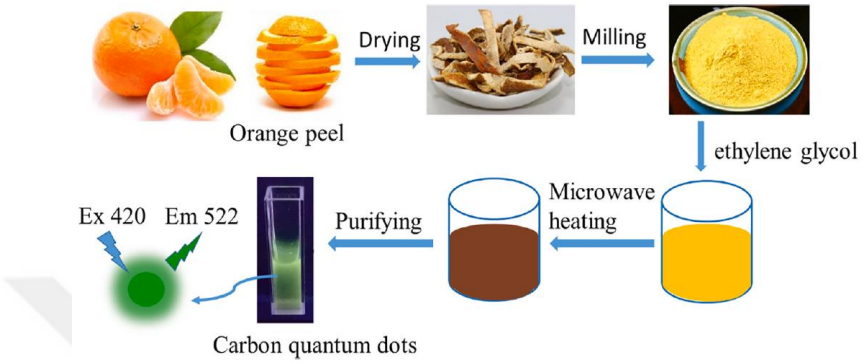

Figure 1.14 : From orange peel to quantum dots by microwave-assisted synthesis route [36].

This synthesis method, which is frequently used in different studies, has been used by Hu et al.[36] to detect E.coli bacteria in milk. In their experiments, orange peel is used as a carbon precursor. All stages of microwave-assisted synthesis are illustrated in Figure 1.14. After obtaining carbon quantum dots with microwave-assisted synthesis, they combined these dots with magnetic nanoparticles. Carbon quantum dot magnetic nanoparticles used as fluorescent probes provide an effective method for the identification and quantification of E.coli bacteria. In another study, Dong et al.[37] combined reduced graphene oxide layers with carbon quantum dots prepared by microwave assisted synthesis to develop potassium ion batteries. Quantum dots provide more active space by opening between layers of graphene. This ensures rapid adsorption and desorption of potassium ions to the electrode.

Solvothermal and hydrothermal synthesis method

It is a method of preparing quantum dots by mixing carbon precursors with polar or apolar solvents and exposed to high temperature and pressure. When water is used as a solvent, synthesis is called hydrothermal. It is often preferred by researchers for its ease of processing, being an environmentally friendly method and low cost to synthesize quantum dots. Mitochondria is an organelle that has an important and critical role in physiological processes that are vital for human life.

Damage or loss of function of the mitochondria causes diseases. The limited use of materials used as mitochondrial probes has led researchers to different materials. Gao et al.[38] used carbon quantum dots prepared by solvothermal synthesis for mitochondria imaging and distinguishing cancer cells from normal cells.

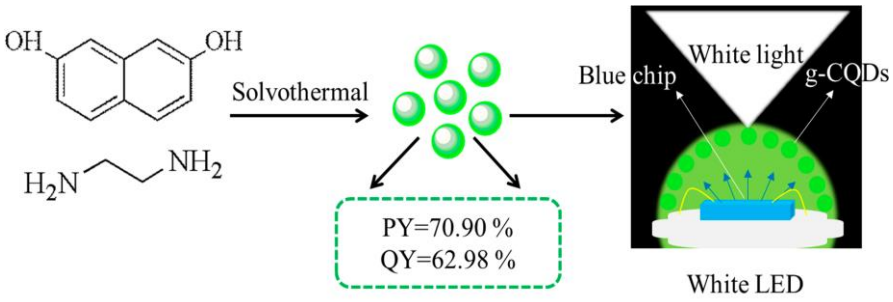

Figure 1.15 : Solvothermal synthesis of carbon quantum dots and white LED application [39].

In another study, research was made on the use of carbon quantum dots prepared by solvothermal synthesis for illumination in LED devices, as demonstrated in Figure 1.15.

Zheng et al.[39] obtained carbon quantum dots with high quantum efficiency in their study. They emphasized that the amount of ethylenediamine, reaction temperature, and reaction time have an important effect on product yield and quantum yield. They found that the high amount of carbon increased the product yield, high nitrogen content and rich functional hydroxyl groups increased the quantum yield.

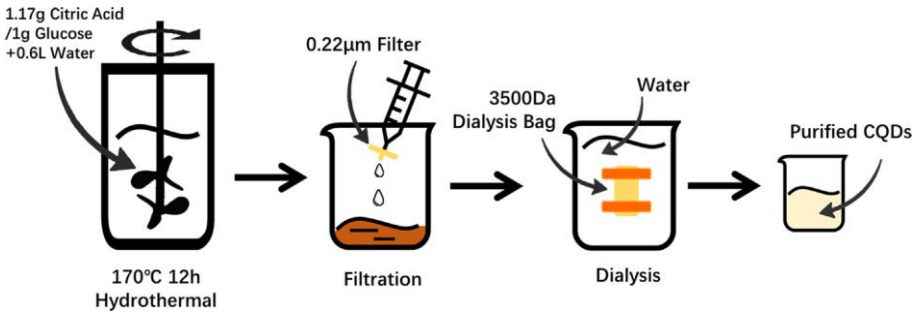

Figure 1.16 : Schematic representation of CQDs synthesis using citric acid and glucose [40].

Photocatalysis applications are carried out in order to prevent environmental pollution such as the treatment of waste-water and the purification of air. In this context, titanium dioxide is frequently used as photocatalytic material.

In order to increase the photocatalytic activity of titanium dioxide, Shen et al.[40] prepared carbon quantum dots from citric acid and glucose separately by using hydrothermal synthesis. In Figure 1.16, it is shown that representation of the hydrothermal synthesis stages used by Shen et al. Later, they applied the hydrothermal synthesis method again to combine titanium dioxide and carbon quantum dots. As a result of their experimental study, it was observed that carbon quantum dots produced from glucose increased the photocatalytic activity of titanium dioxide more than those produced from citric acid.

In their separate study, Zhao and Wang used the heteroatom doping approach to improve the fluorescence properties of carbon quantum dots by hydrothermal synthesis and carbon quantum dots were doped with nitrogen. Zhao et al.[41] aimed to visualize the dopamine chemical in the human body easily and cheaply with nitrogen-doped carbon quantum dots prepared in their studies. Wang and his group [42] used nitrogen-doped carbon quantum dots to detect the chemical reactive picric acid that causes environmental pollution.

1.4.2.3 Top-down approaches for preparation of graphene quantum dots

Electrochemical exfoliation

It is a top-down approach in which different bulk carbon sources such as carbon fiber, graphite, and coal are electrochemically exfoliated using a two-electrode system. In electrochemical experiments where the working electrode is the carbon source, the platinum rod is used as the counter electrode. Chu et al.[43] used nitrogen-containing electrolyte to dope graphene quantum dots with nitrogen in their study.

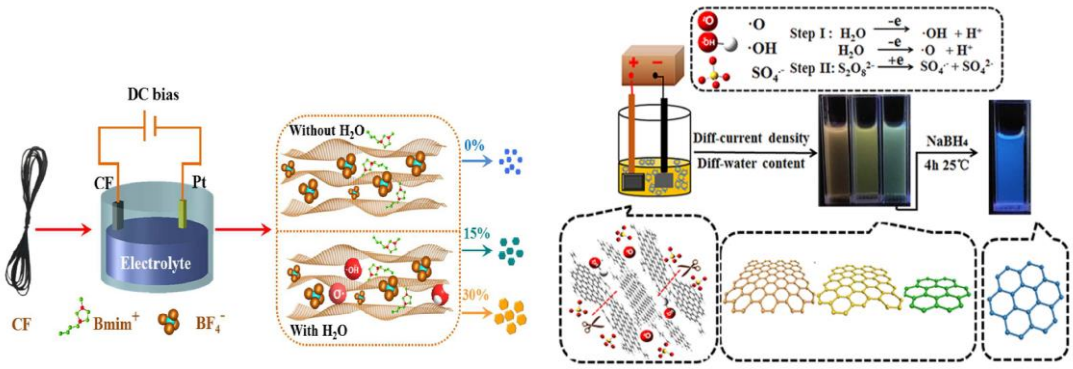

Figure 1.17 : Electrochemical exfoliation method with different carbon resources, carbon fiber and coke respectively [44, 45].

Ultrasonic wave assisted exfoliation

It is a synthesis method in which the weak van der Waals bonds between the layered structure that forms the carbon source are broken by ultrasonic waves and graphene quantum dots are obtained, as illustrated in Figure 1.18.

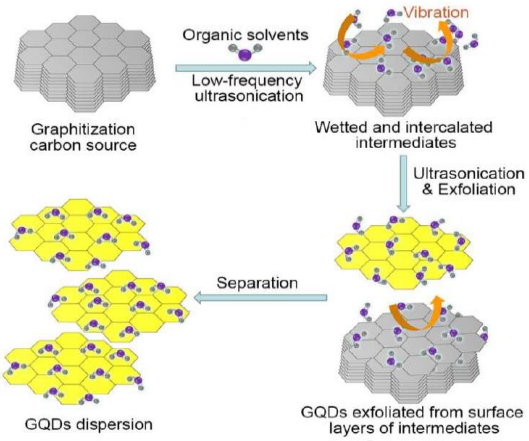

Figure 1.18 : Schematic illustration of the preparative process of GQDs by ultrasonic-assisted exfoliation [46].

In an experiment where carbon sources with different defect densities were selected, graphene quantum dots were synthesized by the ultrasonic exfoliation method. The change in defect density caused graphene quantum dots to exhibit different photoluminescence properties. In addition, Lu et al.[46] studied the solvent effect by synthesizing graphene quantum dots with different solvents.

Acidic exfoliation

In the acidic exfoliation method, which is similar to other exfoliation methods, the carbon source is mixed with concentrated acids. The mixture, which is kept for a certain time and temperature, is then purified to obtain graphene quantum dots. Shao and colleagues [47] used activated carbon and concentrated nitric acid to synthesize graphene quantum dots in their experiments. They concluded that the graphene quantum dots they synthesized were a novel candidate of near-infrared fluorophores.

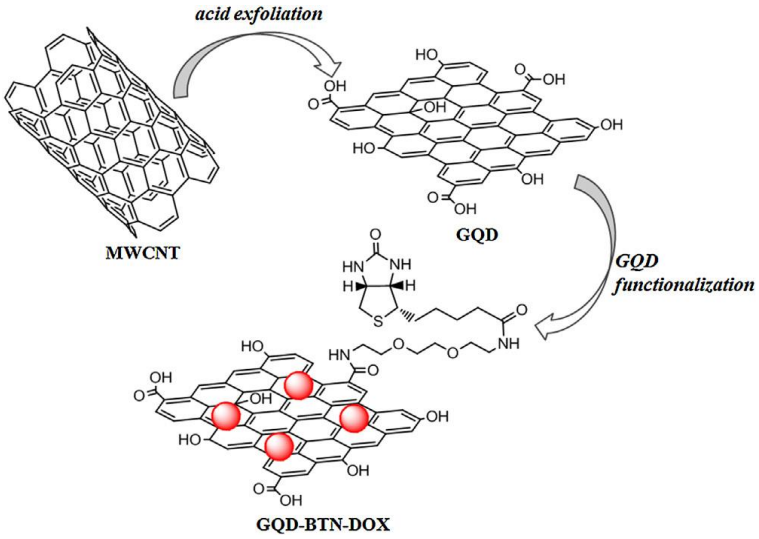

Figure 1.19 : GQDs synthesis by acidic exfoliation from multi-walled carbon nanotubes [48].

Iannazzo et al.[48], on the other hand, used multi-walled carbon nanotubes (MWCNTs) as a carbon source in their studies. In Figure 1.19, acidic exfoliation synthesis is shown. For graphene quantum dot synthesis, multi-walled carbon nanotubes were treated with the nitric acid sulfuric acid mixture in a ratio of one to three. Iannazzo and his group used these graphene quantum dots for drug delivery to cancer cells.

1.4.2.4 Bottom-up approaches for preparation of graphene quantum dots

Carbonization

Bottom-up approaches applied in the synthesis of graphene quantum dots show similarities with the synthesis methods of carbon quantum dots. The carbonization method, which is one of these synthesis methods, is the method in which graphene quantum dots are synthesized as a result of the carbon source directly exposed to a certain temperature. Li et al.[49], synthesizing graphene oxide quantum dots for the detection of copper ions, used citric acid as a carbon source. The group, which carried out their experiments at 3 different temperatures, observed that the increase in temperature increased the size of the quantum dot-like structures formed and that a porous structure was formed by causing aggregation. In another study, More and his study group [50] examined how the change of process parameters changes the properties of the graphene quantum dots synthesized by carbonization.

Microwave-assisted synthesis

The microwave-assisted synthesis method, which provides easy usage, time-saving and high-efficiency advantage compared to other methods, is often preferred in the bottom-up approach. Li and his group [51] emphasized that high quantum efficiency graphene quantum dots prepared by microwave-assisted synthesis can be used in optoelectronic devices and biomedical applications.

Solvothermal and hydrothermal synthesis method

Liu and his study group [52] produced bright blue fluorescent graphene quantum dots with 20 percent quantum efficiency by hydrothermal synthesis using lignite-derived humic acid as a precursor. They emphasized that the reason for using humic acid in particular is to reduce the cost in large-scale production compared to other precursors. After mixing humic acid with aqueous ammonium hydroxide, a 1mol / L NaOH solution was added to the mixture to optimize the pH. The final solution waited in the oven at 200°C for 12 hours and synthesis was carried out. In addition, the working group conducted an ion detection experiment using different metal ions with the graphene quantum dots they produced. They have shown that graphene quantum dots, which have strong cyan emission, react to copper ions, showing that they can be used to detect these ions.

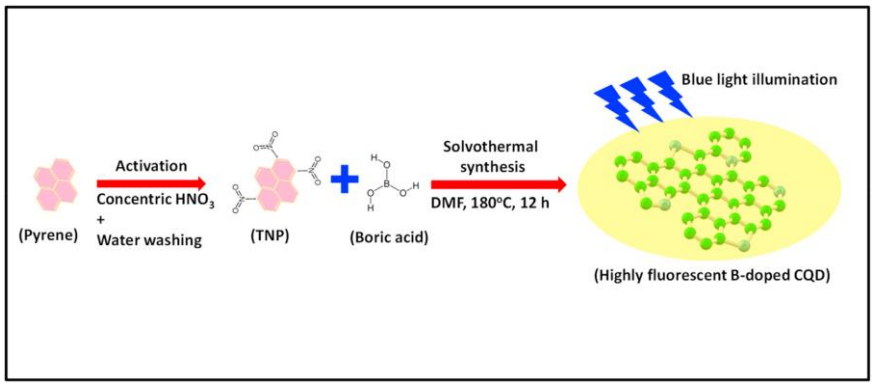

Figure 1.20 : Illustration of the solvothermal synthesis of B-doped GQD samples [53].

In another study, Juang et al.[53] produced boron-doped graphene quantum dots with different chemical ratios by solvothermal synthesis. The group using boric acid and trinitropyene for synthesis used dimethylformamide (DMF) as solvent. The chemical ratio between boric acid and trinitropyrene has been cited as a critical factor adjusting the boron concentration in graphene quantum dot lattices.

1.5 Characterization Techniques of Quantum Dots

1.5.1 Fluorescence spectroscopy

Fluorescence spectroscopy is a characterization technique in which the fluorescence properties of materials are analyzed. A beam of light with different wavelengths is directed into the material. These electromagnetic waves excite the electrons of the material. The electrons cross the band gap and go into the excited state. As the electrons return to the ground state, they emit light depending on the electromagnetic wave they absorb. The fluorescence spectrum reflects information about the electronic structure and state of the material [54].

1.5.2 Raman spectroscopy

The sample reflects, absorbs, or scatters a monochromatic electromagnetic wave sent on it from a light source. The small amount of light that is inelastically scattered has a different frequency from the light source. This scattering is called Raman scattering and detailed information about the chemical structure and bonds of the material is obtained with the analysis of this scattering [55].

1.5.3 Fourier transform infrared spectroscopy

In this non-destructive characterization technique, materials are exposed to IR radiation. IR photons have enough energy to cause the bonds that connect the atoms to vibrate. The chemical bonds in the material absorb IR radiation of a certain wavelength and frequency that match their vibration modes. The spectrum produced by measuring the radiation absorption frequency is used to identify compounds and functional groups [56].

1.5.4 Transmission electron microscopy

The high-energy electron beam is sent onto the material. The electrons transmitted and/or diffracted through the material are collected by the lenses and the image of the sample is obtained. This technique allows the investigation of material morphology and structure at a nanometric scale. Besides, secondary signals resulting from the interaction of the sample with the electron beam provide information on the composition of the sample [57].

1.5.5 X-Ray photoelectron spectroscopy

X-Ray Photoelectron Spectroscopy is a surface-sensitive characterization technique. The sample surface is analyzed at nanometric depth. Information is collected on the sample's elemental composition, empirical formula, and the chemical and electronic states of the elements that form the sample. X-Ray Photoelectron Spectroscopy is based on the photoelectric effect. The sample surface is excited by incident photons coming from the X-Ray source. As a result of this excitation, the core electrons of the atoms on the surface break off from the atom and emit. Some of the incident photon energy is used to exceed the binding energy of core electrons. The remaining energy is the kinetic energy of the core electrons. The XPS spectrum is obtained by collecting the core electrons with different kinetic energies that are detached from the surface by the electron energy analyzer [58].

2. METHOD

2.1 Material

Supramolecular chemistry, defined by Jean Marie Lehn as "chemistry beyond the molecule," is an interdisciplinary field of science that includes the chemical, physical and biological contents of molecular assemblies. Schematic diagram of supramolecular chemistry is presented in Figure 2.1. The concept of supramolecule is defined as a highly complex formation formed by two or more chemical entities bound together with intermolecular forces. While molecular chemistry is based on covalent bonds, supramolecular chemistry is based on non-covalent intermolecular bonds. These bonds are electrostatic interactions, hydrogen bonding, weak Van der Waals forces, π-π interactions etc. [59-63].

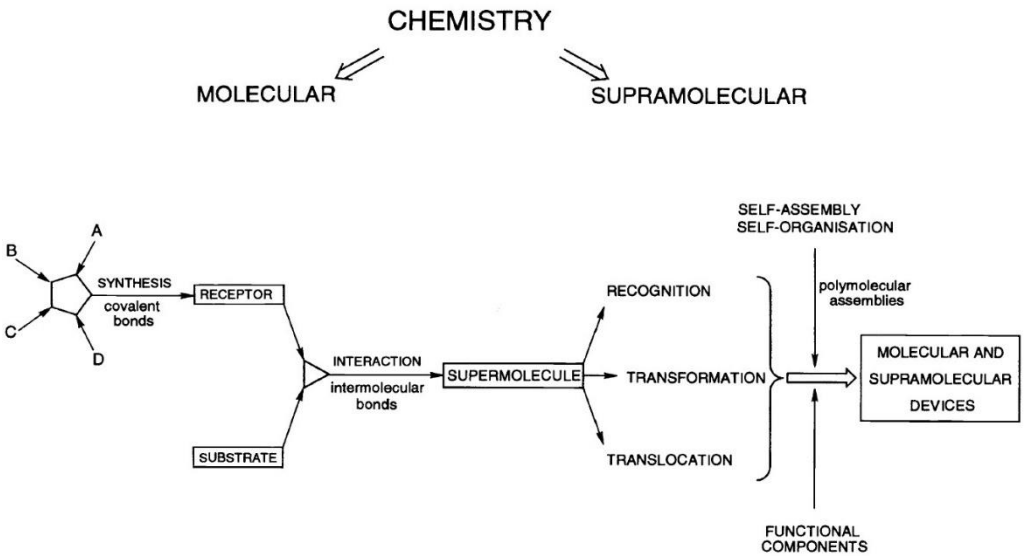

Figure 2.1 : Diagram of from molecular to supramolecular chemistry [61].

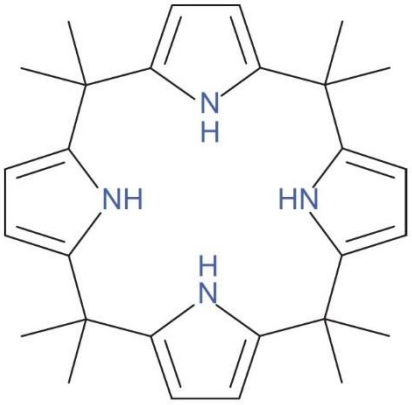

Figure 2.2 : Structure of Calix[4]pyrrole [65].

Calix[n]pyrroles are one of the supermolecule family. The number "n" represents the pyrrole number in the macrocycle. The carbon source used to synthesize quantum dots in the thesis is calix[4]pyrrole. In the calixpyrrole family, calix[4]pyrrole is the smallest and simplest macrocycle, as shown in Figure 2.2. As a result of the reaction of pyrrole and acetone in acid medium, it can be synthesized in high yield with a single-step procedure. Calix[4]pyrrole and its derivatives are used in a wide range of applications. One of them acts as an anchor group for the separation of polluting species from water and provides new possibilities in water decontamination. Another important application area is its usage as an ion-selective sensor [64,65].

2.2 Synthesis of Amphiphilic Quantum Dots

The solvothermal synthesis method was used to synthesize quantum dots. Calix[4]pyrrole and toluene were chosen as the carbon source and the solvent respectively. Calix[4]pyrrole is received from Aydoğan Lab. All the chemicals were purchased from Sigma Aldrich with highest purity unless otherwise is mentioned.

First of all, 20 mg of Calix[4]pyrrole and 20 ml of Toluene are mixed in a 50 ml beaker on a magnetic stirrer. Then magnetic stirrer is run at 60^0 C and 400 rpm until calix[4]pyrrole precursor is completely dissolved in toluene in the mixture. The prepared solution is then transferred to the teflon-lined autoclave. 20 ml of Toluene is put into another teflon-lined autoclave to be a reference sample. In order to find the optimum values, syntheses were carried out at different temperatures and durations.

The emission colors of CP-DOTs synthesized at different temperatures and durations are shown in Figure 2.3. Furthermore, the solvothermal synthesis stages are illustrated in Figure 2.4.

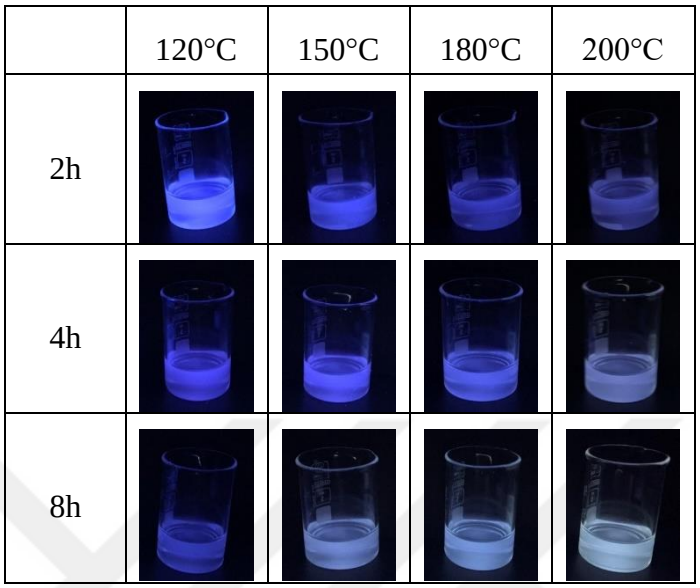

Figure 2.3 : Under UV lamp (365 nm), emission colors of CP-DOTs.

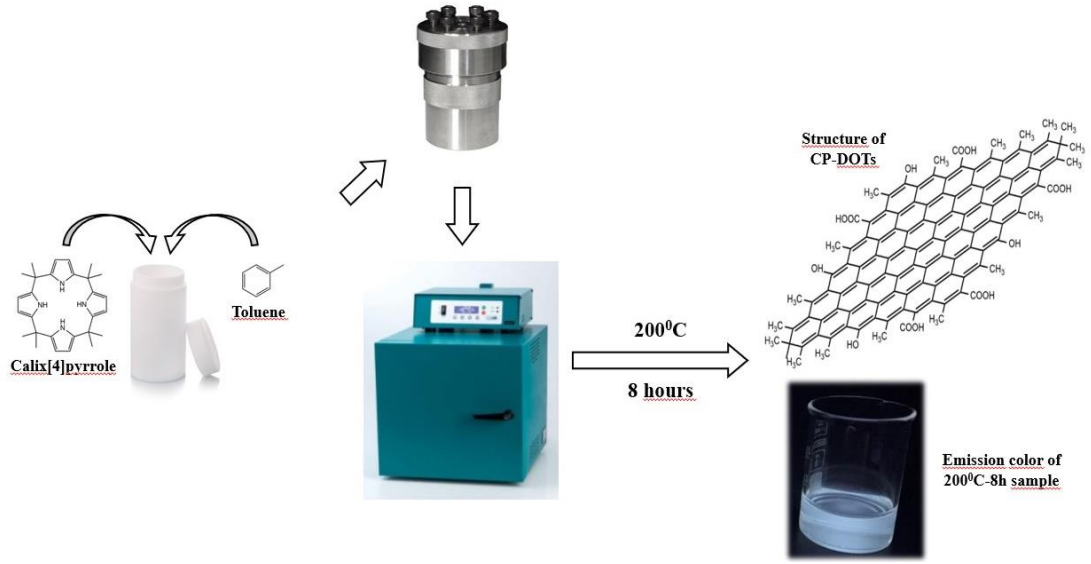

Figure 2.4 : Illustration of solvothermal synthesis stages of CP-DOTs.

After the process was over, the colloidal solution is passed through filter paper to remove macro-sized impurities. For further purification, the colloidal quantum dot solution is centrifuged at 14500 rpm for 30 minutes.

After each synthesis process, 40 ml of Aqua Regia (HCl/HNO_3, ratio 3:1) is prepared in teflon which containing calix[4]pyrrole solution in order to prevent contamination before the new synthesis and kept for 1 hour.

The Teflon which containing the as-received toluene is put in the base bath and kept for 1 hour. After waiting for 1 hour, the teflones are rinsed with distilled water, and acetone is placed in them. The teflones which were kept in acetone for 30 minutes before proceeding to the next synthesis are then rinsed again with pure water and dried in the oven.

2.3 Characterization

2.3.1 Optical characterization

After synthesis, the emission colors and brightness of the amphiphilic quantum dots were observed under a UV lamp with a wavelength of 366 nm. In the next step, for investigation of optical properties, the absorption spectra of the quantum dots were recorded with the Scinco Neosys-2000 Double-beam Ultraviolet-visible (UV-Vis) Spectrophotometer. Excitation and emission spectra were taken with Varian Cary Eclipse Fluorescence Spectrofluorimeter to understand the fluorescence properties.

2.3.2 Structural characterization

High-Resolution Transmission Electron Microscopy (HR-TEM), X-Ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR), and Raman Spectroscopy were used for the structural characterization of quantum dots. JEOL JEM-ARM200CFEG UHR-TEM was used to make dimensional analysis and to take information about the shape and formation of synthesized quantum dots.

XPS measurements, in which elemental and structural analyzes were made, were taken with Thermo Scientific K-Alpha with a monochromatic 1486.68 eV Al Kα X-ray line source and a 400 μm beam size. The chemical structure and bonds of carbons forming quantum dots were determined by Perkin Elmer ATR-FTIR Spectrophotometer and Renishaw inVia Raman Microscope.

3. RESULTS AND DISCUSSION

CP-DOTs synthesized with parameters of 200°C 8 hours in the examinations carried out under UV lamp provided the determination of optimum synthesis parameters as 200°C 8 hours with their stable and brighter emission colors compared to other samples. As seen in Figure 3.1, observing the behavior of CP-DOTs in different solvents, it was concluded that CP-DOTs exhibit amphiphilic property.

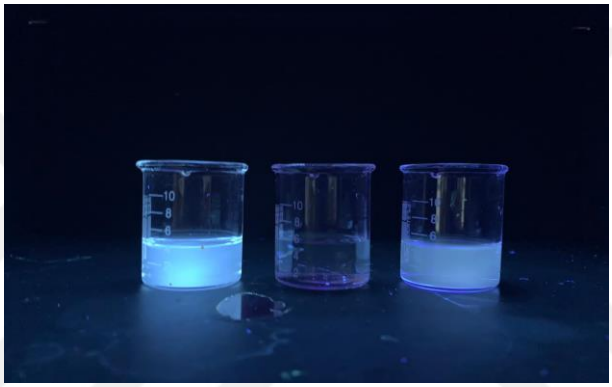

Figure 3.1 : Amphiphilic property of CP-DOTs. Ethanol, deionized water, and methanol were used as a solvent from left to right.

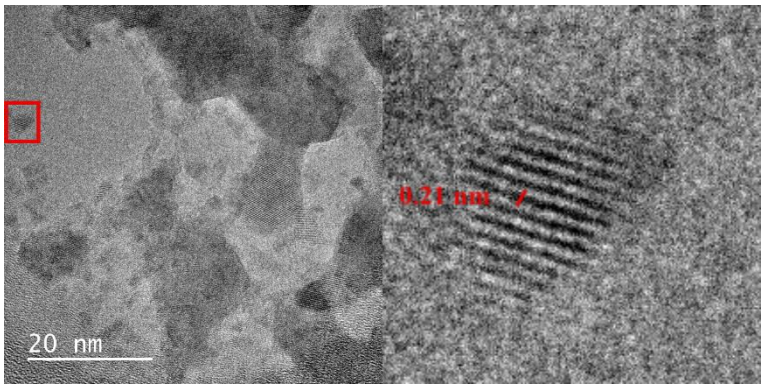

Figure 3.2 : HRTEM images of synthesized CP-DOTs.

As shown in Figure 3.2, CP-DOTs were clearly visualized with HRTEM. Besides quantum dots that appear singular, there are also agglomerated ones. Quantum dots range in size from 2 nm to 5 nm [36,47,53].

At the zoomed-in image, the lattice spacing distance of the quantum dot was measured as 0.21 nm [27,39,40]. This spacing distance value indicates that quantum dots have a graphitic carbon structure. All these values are consistent with the literature.

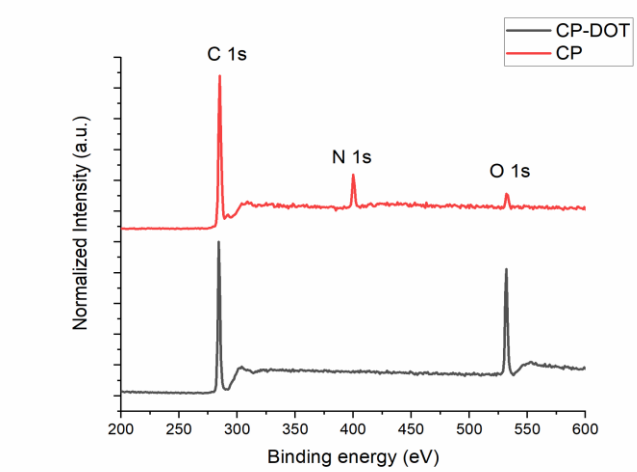

Figure 3.3 : XPS spectra of as-prepared Calix[4]pyrrole and CP-DOTs.

The nitrogen contained in the pyrroles that form calix[4]pyrrole has been completely lost after synthesis. The complete disappearance of the nitrogen atom within the quantum dots shows that the synthesized quantum dots do not contain any extra atoms other than carbon and the structure consists entirely of carbon and oxygen, as shown in Figure 3.3. In addition, the increase in the amount of oxygen in the structure of the quantum dots indicates that the presence of air in the Teflon environment dissolves in toluene during the synthesis, and oxygen coming from the air adapts to the structure, possibly the surface, of the quantum dots.

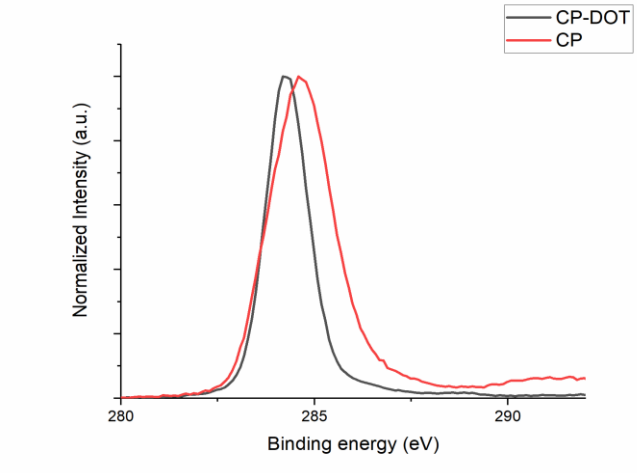

Figure 3.4 : XPS spectra of CP-DOT and as-prepared calix[4]pyrrole focused on C 1s peak.

As can easily be seen from Figure 3.4, as-prepared calix[4]pyrrole has a large peak centered at 285 eV, while XPS measurement of CP-DOTs has less energy than 285 eV and gives a narrower peak.

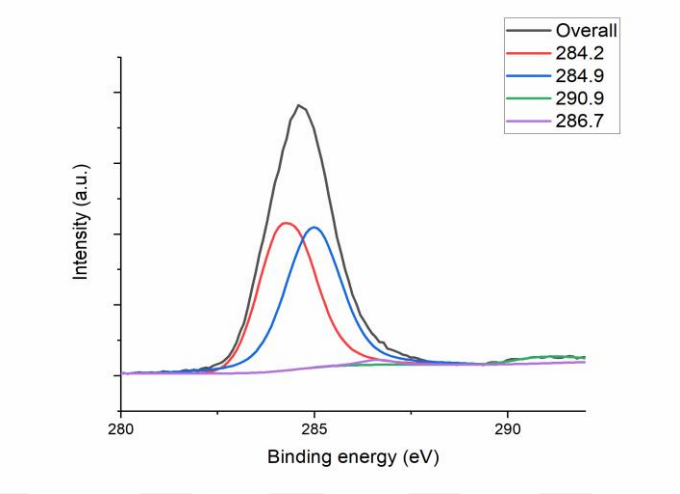

Figure 3.5 : XPS spectrum of as-prepared calix[4]pyrrole focused on C 1s peak.

In Figure 3.5, broad-band is observed in the C 1s peak of the as-prepared calix[4]pyrrole, and this peak is convoluted to two main peaks. The peak centered at 285 eV consists of a combination of two different peaks of very close intensity, of which the left one has 284.2 eV and the right one has 284.9 eV. This situation shows that the carbon atoms have both sp^2 and sp^3 hybridizations in the structure.

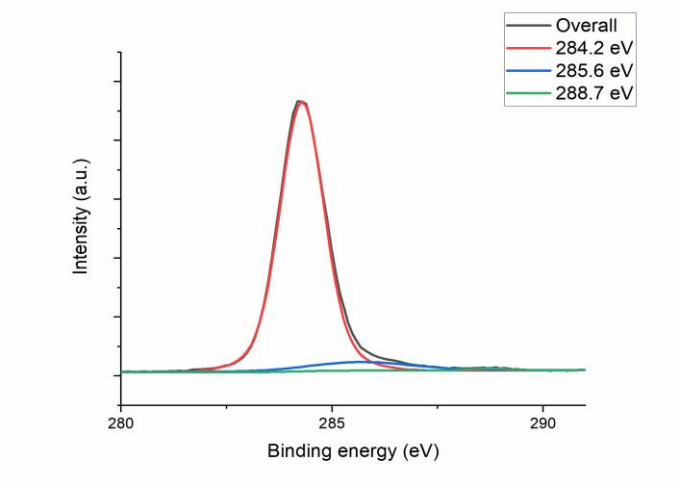

Figure 3.6 : XPS spectrum of CP-DOT focused on C 1s peak.

However, in Figure 3.6, C 1s peak of the CP-DOT narrowed and shifted to the region of less energy. Only one peak at 284.2 eV is convoluted. This shows that sp^2 hybridization has become dominant within the structure.

In addition, C=O peak is observed at 285.6eV. C=O peak in the XPS spectrum verifies that there is oxygen in the structure of CP-DOT.

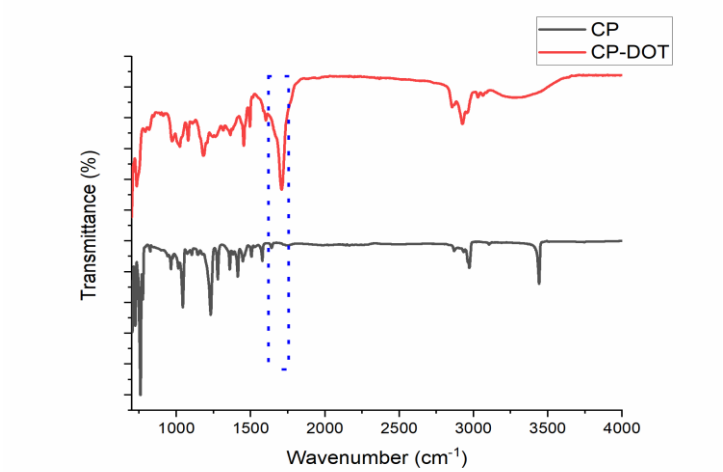

Figure 3.7 : FTIR spectra of as-prepared Calix[4]pyrrole and CP-DOTs.

In Figure 3.7, the most important change between the two FTIR graphs occurred at 1750 cm^{-1}. While a downward peak is observed at this point in the CP-DOT plot, there is no change in the as-prepared calix[4]pyrrole plot at the same point. The peak around at 1750 cm^{-1} points that there are carboxyl groups on the surface of CP-DOTs. Additionally, the band attributed to the hydroxyl peaks were observed between 3250 and 3500 cm^{-1}. On the contrary, these bands mentioned above were not observed in as-prepared calix[4]pyrrole FTIR graph.

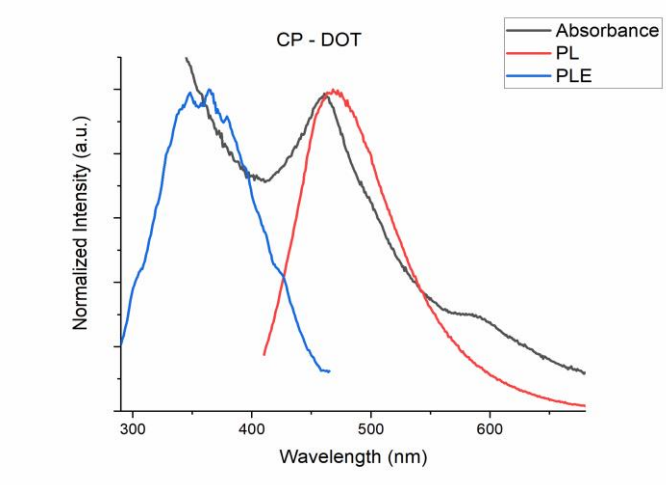

Figure 3.8 : Absorbance, emission, and excitation spectra of CP-DOTs in one graph.

The absorbance spectrum and excitation-emission spectra of the CP-DOTs are given together in the Figure 3.8.

The wavelength range in which the quantum dots absorb the incident light and the wavelengths in which they show fluorescence properties coincide. These observed values are typical carbon quantum dot emission, excitation and absorbance values.

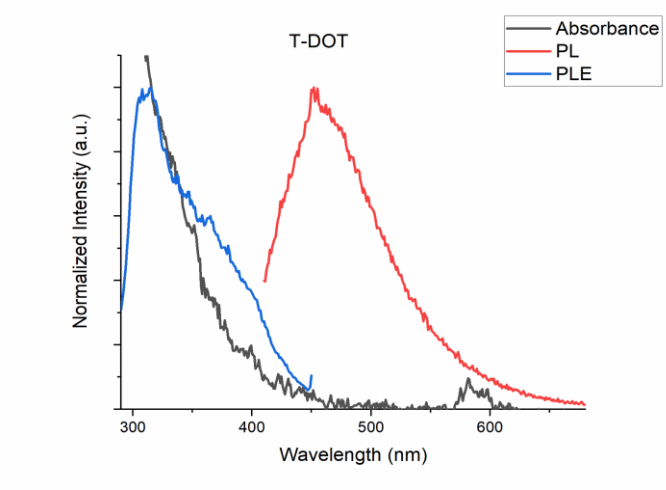

Figure 3.9 : Absorbance, emission, and excitation spectra of T-DOTs in one graph.

Comparison of absorbance and fluorescence measurements of T-DOTs synthesized as reference sample reveals a completely different result from CP-DOTs. As seen in the Figure 3.9, there is no absorbance peak coinciding with the peak in the 450 nm where the peak sees the maximum values in the excitation measurement. Likewise, while the peak obtained as a result of the emission measurement reaches its highest intensity at 320 nm, there is no peak that meets this in the absorbance graph.

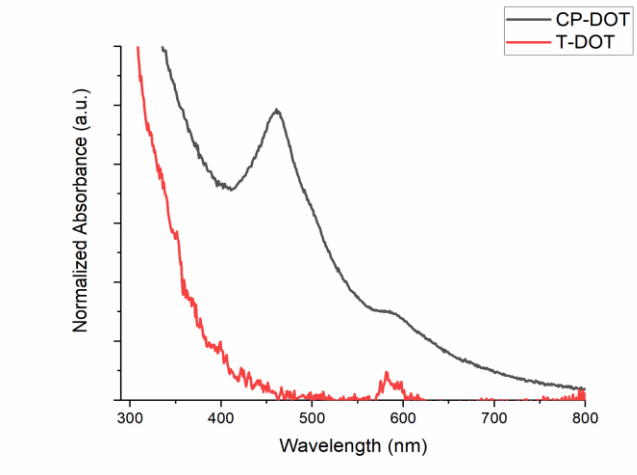

Figure 3.10 : Comparison of absorbance spectra of CP-DOT and T-DOT.

The fact that they absorb the electromagnetic wave from different wavelengths explains that CP-DOT and T-DOTs are quantum dots with different structures.

When CP-DOT was compared with T-DOT, CP-DOT has a much sharper and more intense crystal band transition, as shown in Figure 3.10.

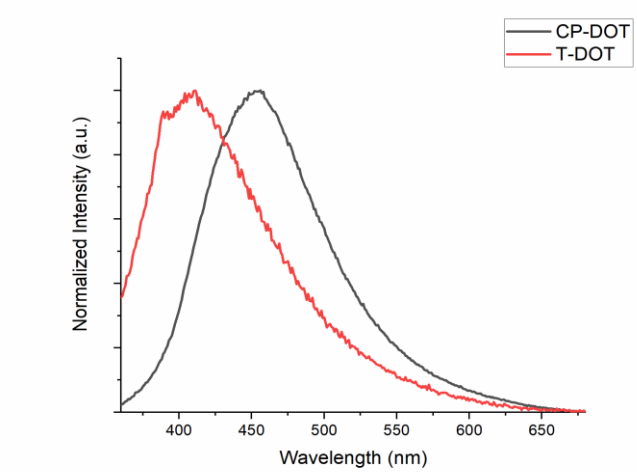

Figure 3.11 : Comparison of emission spectra of CP-DOT and T-DOT.

While CP-DOT emits a blue emission color at 455 nm wavelength in excitation measurement, T-DOT emits purple at around 410 nm. The difference in Figure 3.11 exhibit that CP-DOT has a narrower emission in the region with less energy. In addition, CP-DOT has a more homogeneous size distribution. On the other hand, T-DOT deviated from the Gaussian distribution and demonstrated an emission character with more than one peak.

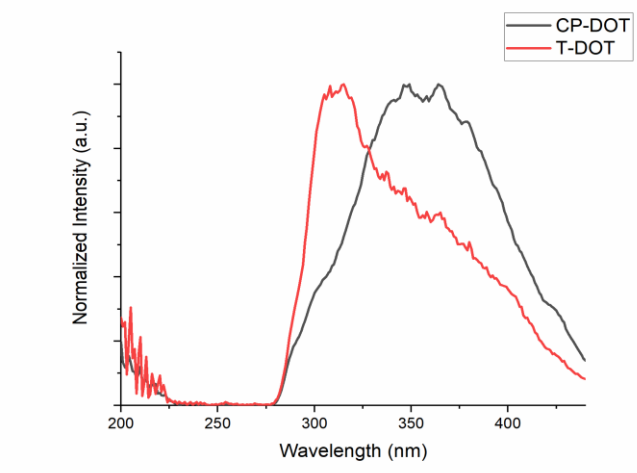

Figure 3.12 : Comparison of excitation spectra of CP-DOT and T-DOT.

Figure 3.12 shows that excitation values in the T-DOT graph take the highest values in the near UV region. There is no peak centered on a single wavelength, as the wavelength increases the intensity of the excitation values decreases.

On the other hand, in the same figure CP-DOT graph has a wide peak centered between 350-375 nm. CP-DOT can be excited in a wider bandwidth and quantum yields are more uniformly distributed within that band.

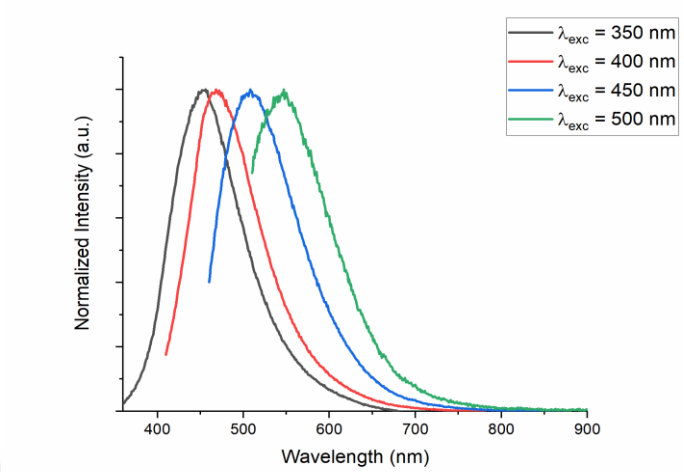

Figure 3.13 : Emission spectra of CP-DOT with different excitation wavelengths, the y-axis shows normalized intensity.

It is clear from the graph that the synthesized CP-DOTs show excitation-dependent properties, as seen in Figure 3.13. As the wavelength of the incident electromagnetic wave changes, CP-DOTs show an emission starting from 450 nm to 550 nm. Observing different emission peaks in accordance with different wavelengths is a typical carbon quantum dot behavior. This behavior proves that there are carboxyl groups on the surface of CP-DOTs.

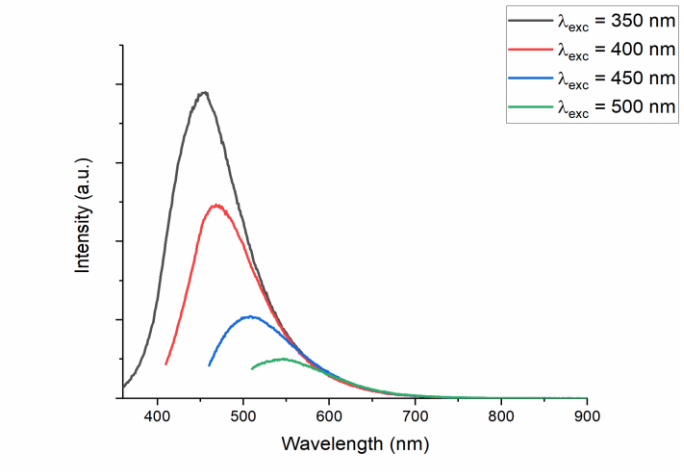

Figure 3.14 : Emission spectra of CP-DOT with different excitation wavelengths, the y-axis shows measured intensity.

In Figure 3.14, the wavelength at which the strongest emission occurs as a result of excitation is 350 nm. The intensity of the emission values made by the quantum dots decreases with increasing wavelengths. This also indicates that CP-DOTs emit the brightest at 350 nm.

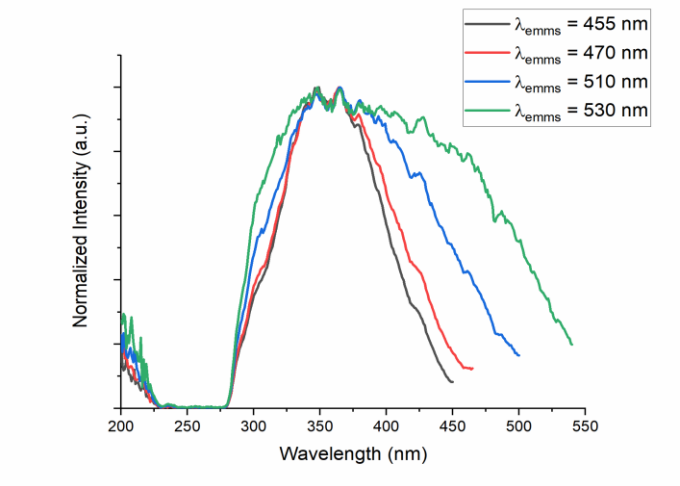

Figure 3.15 : Excitation spectra of CP-DOT with different emission wavelengths.

As a result of emission measurements made at different wavelengths, the wavelength of 360 nm, as seen in Figure 3.15, where the peak has the highest intensity, does not change, as the value of the incident wavelength increases, the peak expands.

4. CONCLUSION

In this thesis, Calix[4]pyrrole from the calixpyrrole family, a family known in the field of supramolecular chemistry, was used as a carbon source. Quantum dots were synthesized using the solvothermal synthesis method at different time and temperature values in order to obtain optimum properties. The fact that the carbon quantum dots synthesized with 200°C - 8 hour parameters in the examinations carried out under UV lamp have a stable appearance and a brighter emission color compared to other samples shown that these values are the optimum synthesis parameters.

High-Resolution TEM was used for visual and structural analysis. It has been observed that quantum dots are successfully formed in HRTEM images. Measuring the lattice spacing distance as 0,21 nm gave the conclusion that the synthesized quantum dots have a graphitic carbon structure. Measurements were taken with XPS and FTIR in order to make an in-depth structural analysis of synthesized carbon quantum dots and to verify the graphitic carbon structure hypothesis obtained with HRTEM images. As a result of XPS measurements, it was seen that the structure of CP-DOTs was completely composed of sp^2 hybridized C=C bonds. The presence of C=O bonds in the structure has revealed that there is oxygen in the structure of quantum dots. It was revealed by FTIR measurements that CP-DOTs have carboxyl and hydroxyl groups on their surface and that the structure is completely different from Calix[4]pyrrole, which is used as a carbon source.

At the stage of optical analysis, the absorbance, emission, and excitation properties of CP-DOTs were examined. In order to compare optical analysis results, toluene, which was used as a solvent during synthesis, was also synthesized with 200°C - 8 hour parameters and T-DOTs were formed. As a result of optical analysis, it was seen that CP-DOTs and T-DOTs have completely different structures. The absorbance measurements of the CP-DOTs match the typical carbon quantum dot behavior and show an intense crystal band transition. While CP-DOTs exhibited a homogeneous size distribution in the emission measurements, it was seen that the quantum yields in the excitation measurements were more uniformly distributed. At the same time, their

excitation-dependent feature, which is the typical carbon quantum dot behavior in emission measurements, confirms that there are carboxyl groups on the surface of CP-DOTs.

CP-DOTs produced by solvothermal synthesis formed a completely new graphitic carbon structure independent of calix[4]pyrrole and toluene. As a result of the analyzes, it has been proven that CP-DOTs exhibit typical carbon quantum dot behavior. CP-DOTs, which show amphiphilic property by dissolving in different solvents, offer usability in different application areas.

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