ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

THE INTERACTION OF Cd-BASED CHALCOGENIDE QUANTUM DOTS WITH RAW PHOTOSYNTHETIC PIGMENTS

M.Sc. THESIS

Sumeyye AYKUT

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(509211271)

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

İŞLENMEMİŞ FOTOSENTETİK PİGMENTLER İLE Cd-İÇEREN KALKOJENİT KUANTUM NOKTALARIN ETKİLEŞİMİ

YÜKSEK LİSANS TEZİ

Sümeyye AYKUT
(509211271)

Kimya Anabilim Dalı

Kimya Programı

Tez Danışmanı: Doç. Dr. Caner ÜNLÜ

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Sümeyye AYKUT, a M.Sc. student of ITU Graduate School student ID 509211271, successfully defended the thesis entitled “THE INTERACTION OF Cd-BASED CHALCOGENIDE QUANTUM DOTS WITH RAW PHOTOSYNTHETIC PIGMENTS”, which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Assoc. Prof. Dr. Caner ÜNLÜ** Istanbul Technical University	.....
Jury Members :	**Asst. Prof. Ufuk Saim GÜNAY** Istanbul Technical University	.....
	Asst. Prof. Ahmet Emin ATİK Acibadem Mehmet Ali Aydinlar University	.....

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To whom have infinite effort for the sake of their believes,

FOREWORD

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Sümeyye AYKUT
(Chemist)

TABLE OF CONTENTS

Page

ABBREVIATIONS

BCN : Boron-Nitride-Carbon Quatum Dots
C-BN : Carbon Dopped-Boron-Nitride Quantum Dots
CQD : Carbon Quantum Dots
CVD : Chemical Vapour Deposition
ETR : Electron Transfer Rate
FTIR : Fourire Transform Infrared Spectrometer
FWHM : Full Width Half Maximum
IR : Infrared Radiation
JCPDS : Joint Committee on Powder Diffraction
LHC : Light Harvesting Capacity
PAR : Photosynthetically Active Radiation
PLE : Photoluminescence Excitation Spectrum
PP : Photosynthetic Pigment
PQY : Photoluminescence Quantum Yield
PS : Photosystem
QD : Quantum Dot
UV : Ultra-violet Radiation
XRD : X-Ray Diffraction

SYMBOLS

Cd	**:** Cadmium
S	**:** Sulphur
Se	**:** Selenium
Te	**:** Tellerium
C	**:** Carbon
O	**:** Oxygen
Mg	**:** Magnesium
Au	**:** Gold
Cd-Mry	**:** Cadmium myristate
Na	**:** Sodium
H	**:** Hydrogen
N	**:** Nitrogen
Cu	**:** Copper

LIST OF TABLES

Page

LIST OF FIGURES

Page

THE INTERACTION OF Cd-BASED CHALCOGENIDE QUANTUM DOTS WITH RAW PHOTOSYNTHETIC PIGMENTS

SUMMARY

The detrimental effects of global warming caused by usage of fossil fuels and toxic gas emission to the atmosphere could be dramatically decreased by environmental sustainability and renewable energy resources. Moreover, coal, oil and gas classified as fossil fuels which almost the whole energy of the world derived from is going to respectively be over in 107, 35 and 37 years. That is why alternative renewable energy sources are quite important according to scientists.

It is possible to utilise renewable energy resources in almost all areas where fossil fuels have a usage. Renewable energy is able to be used in the production of electricity, in transportation and logistics as a fuel, in buildings and industrial processes as a heat release after conversion. Wind, flowing water, sunlight, the internal heat of the earth and biomass are natural resources of renewable energy.

Biomass is a significant renewable energy source because of its economic potential, easiness in production and functional usage in many areas. Biomass is defined as organic materials in total produced by a living organism like plants and animals in a stated time and place in the world. Biomass could be manufactured by almost all organic materials we know such as seed waste, wood, wastewater, paper waste, straw and manure. These days, better half of biomass production is produced by products of agriculture which are known as energy crops. That makes photosynthesis that underlies formation of food and fibre along with biomass-based biofuels quite an important process. Photosynthesis and the energy conversion required for the production of biomass are utterly related to each other.

In this thesis, quantum dots having three various structures were interacted with photosynthetic pigments which are responsible for light harvesting to increase and simplify biomes production by enhancing the efficacy of photosynthesis. In addition, photosynthetic pigments were extracted by spinach leaves that are easily provided and they are kept intact during the interactions. The compositions of quantum dots' structures were designated in accordance with the absorption wavelengths of photosynthetic pigments. The quantum dots interacted were oleic acid-capped CdSSe QDs, CdSTe QDs with the Te-riched core and CdSTe QDs with the outer S-enriched region. Also, all quantum dots were synthesis two-phase synthesis method which is one of the bottom-up approaches. The CdSSe QDs were synthesised as they have an emission in the same UV range in electromagnetic spectrum that photosynthetic pigments absorb light. The CdSTe QDs with the Te-riched core have a stated composition owing to the same reason and emission spectrum in the near IR region that pigments have also absorption. The CdSTe QDs with the outer S-enriched region have no emission of light in any common region with photosynthetic pigments that absorb radiation. Those quantum dots are synthesised to examine the quantum dot-photosynthetic pigment interaction when there is no possibility of energy transfer. The

results of the interactions were analysed by UV-Visible Spectrophotometer and Fluorescence Spectroscopy and experimental data was exhibited in the section of Results & Discussion in detail.

As a result of all experiments, the absorption intensity of the photosynthetic pigments interacted with the Te-enriched CdSTe QDs was increased by 50% at the excitation wavelength of 410 nm. Additionally, the light harvesting capacity of photosynthetic pigments was enhanced at 500-575 nm in the green-light range of spectrum in the presence of the CdSTe QDs with the Te-riched core.

İŞLENMEMİŞ FOTOSENTETİK PİGMENTLER İLE Cd-İÇEREN KALKOJENİT KUANTUM NOKTALARIN ETKİLEŞİMİ

ÖZET

Küresel ısınmanın gezegenimize zararlı etkileri yüksek miktarda tehlikeli gaz salınımı ve hızla tüketilen fosil yakıtlar sebebiyle her geçen gün artıyor. Bu zararlı etkileri azaltmak, çevreye zararı neredeyse yok denecek kadar az olan yenilenebilir enerji kaynakları ve çevresel sürdürebilirlik ile mümkün. Dahası, bilim adamlarına göre dünyanın neredeyse enerji üretiminin tamamını elde ettiği fosil yakıtlardan petrol 35, gaz 37, kömür ise 107 yıl sonra tükenecek. Bu durum daha yaşanılabilir bir dünya için çevresel sürdürülebilirlik ve temiz yenilenebilir enerji kaynaklarının önemini daha da artırıyor.

Temiz ve yenilenebilir enerji kaynakları sınırlı ve zararlı olan fosil yakıtların kullanıldığı her hemen hemen her alanda kullanılabilir. Bu alanlardan bazılarına örnek olarak elektrik üretimi, taşımacılık ve lojistik, binaların ısıtması ve endüstriyel süreçler verilebilir. İlaveten, temiz ve yenilenebilir enerji üretimi için doğal ve sürdürülebilir kaynakları olan rüzgar, akar sular, güneş ışığı, yerkürenin iç sıcaklığı ve biyokütle kullanılabilir.

Biyokütle son yıllarda üretim kolaylığı, geniş kullanım alanları ve ekonomik potansiyeli ile diğer yenilenebilir enerji kaynakları arasında öne çıkmıştır. Bilimsel tanım olarak, biyokütle dünyada belirli bir yer ve zamanda hayvan ya da bitki gibi organizmalardan üretilen toplam organik malzemedir. Biyokütle belki de hiç tahmin edilmeyecek neredeyse akla gelen tüm organik malzemelerden kolaylıkla elde edilebilir. Bu organik malzemelere örnekler atık çekirdekler, tahta, atık su, kağıt atıkları, saman ve hayvan gübreleri olabilir. Günümüzde biyokütle üretiminin büyük hacmi enerji mahsülü diye adlandırılan tarım yan ürünlerinden sağlanıyor. Tüm besin, lif ve biyokütleden elde edilen biyoyakıtın temeli olan fotosentez bu sebeple son derece mühim. Çünkü tarım kaynaklı biyokütle üretiminde verim fotosentez verimi ile doğrudan ilişkili. Fotosentez sürecinde ürün miktarını artıran etkiye sahip her değişim biyokütle miktarını da arttırır.

Bu tezde biyokütle üretimini kolaylaştırmak ve verimini artırmak amacıyla üç farklı yapıda sentezlenen kadmiyum içeren kalkojenit kuantum noktalar fotosentez mekanizmasında ışık emiliminden sorumlu olan pigmentler ile fotosentez verimini yükseltmek için etkinleştirildi. Etkileşimler süresince ıspanak yaprağından kolay bir yöntemle izole edilen fotosentetik pigmentler yapıları zarar görmeden korundu. Pigmentlerle etkileştirmek için seçilen kuantum nokta yapıları fotosentetik pigmentlerin ışığı soğurma dalga boylarına göre belirlendi. Etkileştirilen bütün kuantum noktalar, aşağıdan-yukarı sentez yaklaşımlarından biri olan çift faz sentez metodu kullanılarak sentezlendi. Kuantum noktaların yapısal karakterizasyonu X-Işını Difraksiyonu (XRD) ve Fourier Dönüşümlü Kızılötesi Spektroskopisi (FTIR) ile fotofiziksel karekterizasyonu ise UV-Görünür Bölge Spektroskopisi ve Floresan Spektroskopisi ile yapılmıştır. Kuantum noktalardan CdSSe, fotosentetik pigmentlerin

elektromanyetik spektrumun UV bölgesinde yaptıkları soğurma sebebiyle aynı aralıkta enerji salınımı yapacak şekilde sentezlenmiştir. Zengin teleryum miktarına sahip CdSTe kuantum noktalar ise, aynı sebepten pigmentlerin kızılötesi bölgesine yakın dalga boyu aralığında radyasyon soğurdukları için belirli bir kompozisyona ve ışık salınımı spektrumuna sahiptir. Dış kısmında zengin kükürt miktarı ile CdSTe kuantum noktalar ise pigmentlerin ışık soğurduğu herhangi bir dalga boyunda enerji salınımı yapamazlar. Bu kuantum noktalar, enerji transferi ihtimali olmadığındaki fotosentetik pigment-kuantum nokta etkileşimini incelemek için sentezlenmiştir. Gerçekleştirilen etkileşimler radyoaktif elektron geçişlerini aydınlatmak amacıyla V-Görünür Bölge Spektroskopisi ve Floresan Spektroskopisi kullanılarak incelenmiştir. Elde edilen tüm deneysel veriler ayrıntılarıyla birlikte Sonuçlar ve Tartışma kısmında sunulmuştur.

Oleik asit kaplı kadmiyum içeren kalkojenit kuantum noktalar ile ıspanak yapraklarından elde edilen fotosentetik pigmentlerin etkileşim sonuçları birkaç maddede özetlenebilir. Floresan Spektroskopi sonuçlarına göre fotosentetik pigmentlerin oleik asit kaplı CdSSe kuantum noktaları ile etkileşiminde, 620 nanometre (nm) ve üzeri uyarımlarda kuantum noktaların pigmentler üzerinde herhangi bir etkisi olmamış ve pigmentler etkileştirilmemiş hallerindeki emisyon spektrumunu korumuştur. Etkileşim 350 nm dalga boyu ile uyarıldığında etkileşitirilmiş pigmentlerin emisyon yoğunlukları tamamen sönümlenmiştir. Fakat 410 nm ve 460 nm dalga boyu tarımlarında, tamamen sönümlenme olmamıştır. Bu uyarımlarda oleik asit kaplı CdSSe ile etkileşen pigmentlerin emisyon yoğunlukları azalmıştır ve radyasyon yayan elektron geçişlerinin bir kısmı engellenmiştir.

Tez kapsamında yapılan kükürt miktarı zengin oleik asit kaplı CdSTe kuantum ile olan etkileşimler, oleik asit kaplı CdSSe kuantum nokta-fotosentetik pigment etkileşimleriyle benzer sonuçlar vermiştir. Yine kuantum noktaların pigmentler üzerinde 620 nm ve 660 nm dalga boyu uyarımlarında herhangi bir etkisi olmamış ve pigmentlerin kuantum noktalar varlığında emisyon spekturumları değişmemiştir. İlaveten, 410 nm ve 460 nm uyarımlarında fotosentetik pigmentlerin emisyonları belli oranlarda azalmıştır ve radyasyon yayan elektron geçişlerinin azaldığı kanıtlanmıştır. Yalnız 350 nm dalga boyuna sahip ışık ile uyarılan etkileşimde pigment emisyonlarının sadece %95'i sönümleniştir.

Oleik asit kaplı zengin teleryum miktarına sahip CdSTe kuantum noktalar diğer iki kuantum nokta-fotosentetik pigment etkileşimlerinden farklı eğilimde spektroskopi sonuçları vermiştir. CdSTe kuantum nokta-fotosentetik pigment etkileşimi 350 nm dalgaboyu ile uyarıldığında pigment emisyon yoğunlukları üç kat azalmıştır, sönümlenmemiştir. Bir sonraki uyarı dalga boyu olan 410 nanometrede pigmentlerin ve kuantum noktaların emisyon yoğunlukları %50 oranında azalmıştır. Etkileşim 460 nanometrede uyarıldığında ise 685-720 nm aralığında ise etkileştirilmiş pigmentlerin emisyon yoğunlukları tam %15 artmıştır. Bu aralıkta radyasyon yayan elektron geçişleri fazlalaşmıştır. Ayrıca, bu kuantum noktaların varlığında fotosentetik pigmentlerin fotolüminesans uyarım spektrumunda 500-575 nm dalga boyu arasındaki yeşil ışık bölgesindeki ışığı soğurma kapasiteleri artırılmıştır. Bu etkileşimin diğer etkileşimlerle emisyon spektroskopisindeki tek ortak sonucu ise 620 nm ve 660 nm uyarımlarında görülmüştür. Diğer etkileşimlerdeki gibi bu dalga boylarındaki uyarımlarda CdSTe kuantum noktalarıyla etkileştirilmiş pigmentlerin etkileştirilmemiş olanlarla emisyon farkı yoktur.

Bu tez, bitki yapraklarından izole edilen işlenmemiş fotosentetik pigmentleri yapılarını koruyarak kadmiyum içeren kalkojenit kuantum noktalarla etkileştirmeyi ve bu sayede pigmentlerin yeşil ışık bölgesindeki ışığı soğurma kapasitesini artırmayı başararak özgün bir çalışma halini almıştır. Tüm spektroskopik veriler sonucu fotosentetik noktalar emisyon spektrumları ve fotolüminesans uyarım spektrumlarında karakteristik piklere sahip olarak oleik asit kaplı CdSSe, zengin teleryum miktarına sahip oleik asit kaplı CdSTe ve kükürt miktarı zengin olan oleik asit kaplı CdSTe kuantum noktalar ile etkileşimlerinde bozulmadıklarını göstermişlerdir. Tez kapsamında yapılan tüm kuantum nokta-fotosentetik pigment etkileşimlerinin, etkileştirilmemiş pigmentlerin ışığı soğurma ve emisyon spektrumları göz önüne alarak detaylı bir şekilde optik incelemesi yapılmıştır.

1. INTRODUCTION

1.1 Purpose of Thesis

According to scientists, energy crises and environmental sustainability are the main challenges that humanity has been dealing with because of their being almost fully-dependent on fossil fuels. The unaccountable consumption of those fuels has led to global warming since enormous greenhouse gas emissions to the atmosphere [1]. It has been estimated the current amount of fossil fuels is insufficient for the world's necessity and coal, oil and gas would respectively be over in 107, 35 and 37 years [2]. Thus, it is obvious that alternative clean energy resources must be primary for recent studies in science [1].

Clean and voluminous renewable energies are able to utilised for electricity production, transportation as a fuel, buildings and industrial processes as a heat beside they are produced from various self-renewing resources like wind, flowing water, sunlight, the internal heat of earth and biomass derived from energy crops, seed waste, wood, straw, wastewater, household and paper waste [3, 4].

Biomass is the quantity of organic material in total produced by living organisms of one animal or plant species in a specific area in a stated period of time [5]. Since biomass resources have an economic potential, their usage in many areas has become quite significant in time. Biomass has recently derived from by-products of agriculture in huge annual volumes and developed as energy crops [4]. That makes the process of photosynthesis a fundamental backstage of all food, fibre and biomass-based biofuels besides efficiency of photosynthesis is directly related to the energy conversion to produce biomass/biofuel [6].

There are plenty of environmental parameters to obtain photosynthesis efficiency such as temperature, CO_2 concentration of air and light. However, light is a crucial source and parameter for plant growth coordination and the most efficient performance of photosynthesis [7]. According to the paper of Zhu and his teammates, greenery does not show perfect absorption in photosynthetically-active radiation range which is 400-

740 nm due to chlorophyll's weak performance at absorbing in the green band of spectrum. That prevents absorption of 10% of photosynthetically-active radiation and reduces the photosynthetic conversion efficacy [6].

In my thesis, healing light harvesting capacity of photosynthetic pigments (PPs) in green spectrum which would directly increase photosynthesis efficiency was the main goal and that was achieved by exploiting the interaction between cadmium-based chalcogenide quantum dots (QDs) and raw photosynthetic pigments while long-term stability of pigments was succeeded outside their natural environment. Additionally, photosynthetic pigments were extracted from spinach leaves in a facile method which could be executed even in a kitchen.

Quantum dots' unique photophysical properties and potential of being energy/electron donor were reasons to particularly use quantum dots as a nano-structure for trials of modulating light harvesting capacity of photosynthetic pigments. The quantum dots interacted with photosynthetic pigments were ternary oleic acid-capped CdSSe QDs, CdSTe QDs with the Te-riched core and CdSTe QDs with the outer S-riched region. Quantum dots were synthesised by novel two-phase synthesis method to obtain high photoluminescence quantum yield under the mild synthesis conditions that are low temperature and less toxic heavy metal precursors.

1.2 Photosynthetic Pigments

Photosynthesis is the natural process converting sunlight to biochemical energy (carbohydrates) that is the fundamental source of life. Photosynthetic pigments are biomolecules in the photosynthetic system of organisms such as plants, algae and some bacteria. They are responsible to absorb radiation in a specific range in the electromagnetic spectrum and transfer the absorbed energy to the reaction centre of photochemical conversion. Photosynthetic pigments are a mixture of two water-insoluble pigment kinds: chlorophylls and carotenoids. Chlorophylls and carotenoids always exist together and they enable photosynthetic organisms an equilibrium for capturing light and conquering all habitats where the light is supplied [8, 9].

1.2.1 Chlorophylls

Chlorophylls are biomolecules having a basic porphyrin macrocycle and four pyrrole rings bound to a magnesium (Mg^{2+}) ion in the hole created by four nitrogens facing

inward (Figure 1.1). Also, chlorophylls have quasi-crystalline structure [8, 9]. Their responsibility is light harvesting and conversion of light to electrochemical potential for reducing carbon dioxeide in the atmosphere to carbohydrates [8].

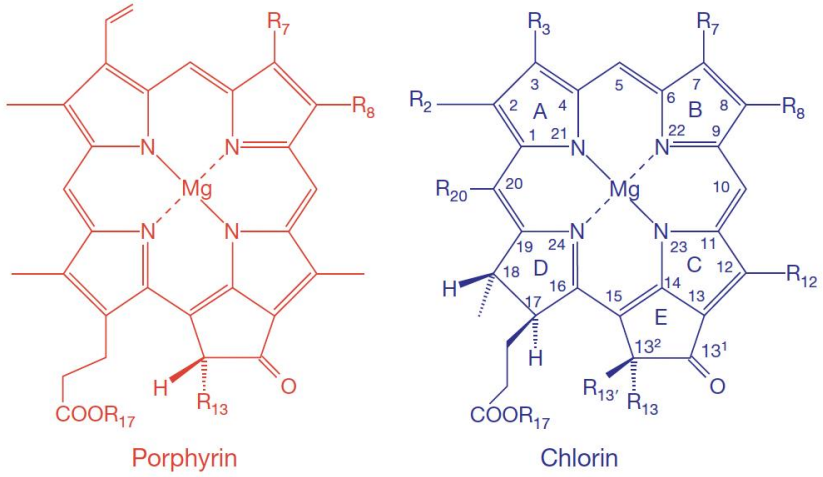

Figure 1.1 : Structure of common chlorophylls.

Chlorophylls have an oxidation-reduction potential as a part of reaction centre and antenna or light harvesting structures. It becomes quite negative after absorbing a photon. The negativity leads to an electron transfer to neighbour molecules, pheophytins. That process is the primary photochemical reaction and it happens in the reaction centre. By the way, the reaction centre is the place photochemical conversions are executed [9].

The optical properties of chlorophylls can be explained by the four-orbital models of porphyrins which cause four main absorptions in the near infrared, near-ultraviolet and visible regions of electromagnetic spectrum [8]. In particular, chlorophylls together with carotenoids have a UV light absorption at 200-350 nm due to their C=C and C=O bonds and near-infrared absorption between 620 and 720 nm. In organic solvents, chlorophyll has long-time excited states (~10^-8 sec), thus they are highly fluorescent biomolecules [8].

1.2.2 Carotenoids

Carotenoids are not only light harvesting photosynthetic pigments but also the biomolecules which have a wider functionality than chlorophylls. It is known that there are more than 800 kinds of carotenoids. Carotenoids are kinds of tetraterpenes which have two C20-units bound tail-to-tail to a chain of 32 carbon atoms owing eight methyl side chains (Figure 1.2). They have a rod-shaped structure; hence they display a similar

absorption with linear polyenes. Most carotenoids have a yellow-orange colour that is in charge of their maximum absorption being overlapped in the blue region of 450–530 nm whereas chlorophylls have a very low absorption intensity [8].

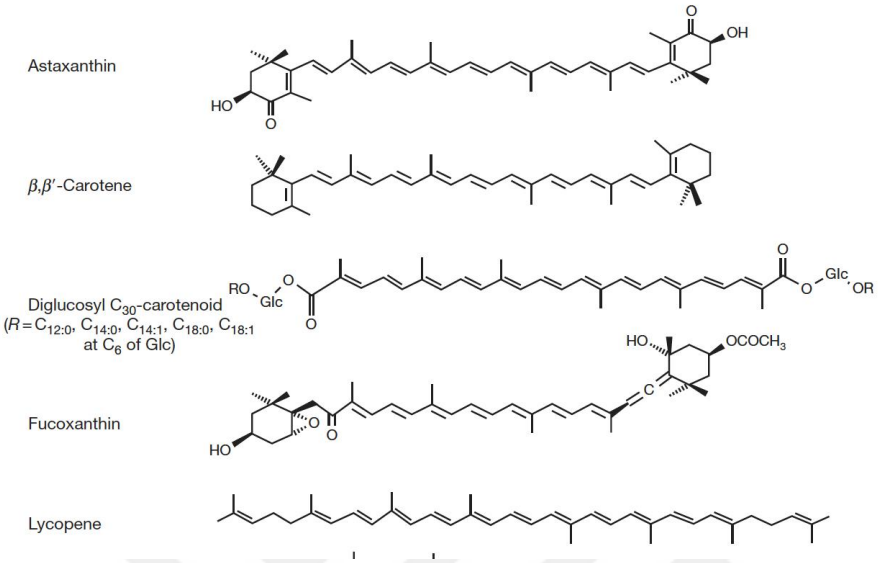

Figure 1.2 : Example structures of carotenoids.

The crucial duty of carotenoids in photosynthesis is conservation of photosynthetic complexes under the overexposure of light. In that condition, the reaction centre becomes nonoperative to catch the absorbed photon coming from the light harvesting complex. Then, chlorophylls having long-lived-excited states start to spread a hazard to the organism because of their potential of forming reactive oxygen species. In that point, carotenoids are able to emit excess energy and quench triplets of chlorophyll by triplet energy transfer to their own low-lying forbidden triplets. During the transfer, an amount of heat is dissipated. In the end, they could prevent formation of reactive oxygen species [8,9].

1.2.3 Protection system of photosynthetic pigments

Ultraviolet (UV) radiation has unfortunately hazardous effects on many photosynthetic structures like photosynthetic pigments, and most light harvesting protein complexes beside electron transfer rate (ETR) [10]. Within the scope of photosynthetic pigments, UV radiation brings on poorness of light harvesting system by uncoupling of chlorophylls and decreases efficacy of photosynthesis. As a result, some doses of UV light cause decline in leaf development and finally in biomass production [11].

The UV radiation in the electromagnetic spectrum consists of three particular wavelength range swhich are UV-A (320–400 nm), UV-B (280–320 nm) and UV-C (100–280 nm [12]. It was proven that the UV-A radiation is specifically impairing for Photosystem II in the study of Eniko and Imre [13]. Although the UV-B light is a little percentage of the total solar energy, it puts down the rate of photosynthesis. Recent studies show that the UV-B radiation between 280-315 nm and 100-280 nm of the UV-C light affects photosynthetic pigments and breaks their C=C and C=O bonds [12, 14, 15]. In the analysis of Piccini's study, it was obtained that the UV-B radiation leads to stress for olive trees which is directly effective for growth of leaves and photosynthetic activity [16].

Plants and algae have a protection system to deal with overexposure of UV radiation and harmful effects of reactive oxygen species. Also, that protection brings on inhibition of biomolecule degradation organisms have. That protection system is triplet energy transfer operated by carotenoids as it was mentioned in the subtitle of carotenoids. That is why protection system could not operate when photosynthetic pigments are isolated and tried to be used in ex vivo applications such as LED, solar cells and biosensors [8, 12, 16].

1.3 Quantum Dots

Quantum dots are zero-dimensional nanostructures and they are semiconductor nanocrystals with unique optical and electronic properties. In semiconductor bulk materials, electrons are continuously able to move without any restriction. However, electrons of quantum dots have discrete energy levels and as they are quantised in three dimensions. That is the reason of quantum dots' being called zero-dimensional [17, 18]. Quantum dots usually contain 100-1000 atoms in their structure which have a high surface-volume ratio and these atoms are III-V or II-VI elements most of the time [19].

High photostability, wide absorption and narrow emission are some of the optical properties of quantum dots [20]. Quantum dots could emit radiation in a wide range from infrared to visible region and that absorption range is up to their size and composition [21]. Due to their configurable optical and electrical properties, quantum dots are significant nanostructures in many areas such as bio-imaging, light emitting diodes (LEDs), solar cells, photovoltaic and quantum computing [17].

1.3.1 Quantum confinement effect

Quantum confinement effect in quantum dots could be understood easily by perceiving the term: excitons which are technically electron-hole pairs. Bands in semiconductor materials are formed by energy levels. There are valence band and conduction band and they are separated by an energy gap which is called 'bandgap'. The bandgap is an intrinsic property for semiconducting and conducting materials. An electron in the valence band could come through the bandgap by receiving an adequate energy from light absorption or thermal excitation and reach the conduction band as it left a hole behind. After a stated time, the excited electron generates a charge carrier movement or recouples with a hole by means of energy release. In that stage of quantum dots, the excited electron is disposed to weakly bond to its hole by electrostatic Coulomb force since the diameter or the size of quantum dots is less than the material's characteristic 'Bohr radius'. Bohr radius is the distance between electron and its hole or the interval in electron-hole exciton in the other words [Figure 1.3]. Then, quantum confinement effect which converts the bands to discrete energy levels in quantum dots comes into insight [17].

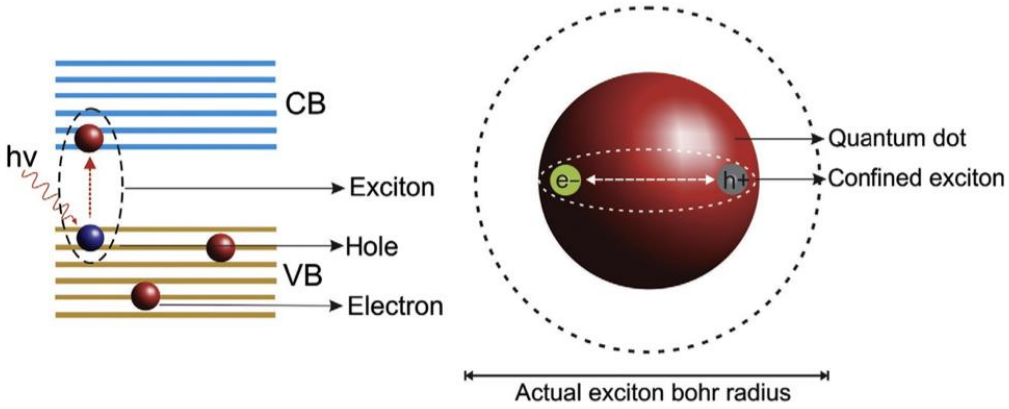

Figure 1.3 : Exciton formation in energy band of quantum dots and comparison of exciton radius with quantum dots size [17].

The quantum confinement effect has an impact on the optical and electrical properties of quantum dots due to the relation between the bandgap and the size of the dots. Below the Bohr radius, the bandgap energy increases as the particle radius of semiconductor decreases [22]. That relation makes quantum dots amazing nano materials to be specifically synthesised for stated problems in many research fields.

1.3.2 Optical properties of quantum dots

Quantum dots are highly photo-luminescent nanomaterials. Thus, photoluminescence must be explained to understand the optical properties of quantum dots [19]. Photoluminescence is a kind of energy release process as a radiation. An electron is not able to protect its stability in the valence band when an external source supplies the sufficient energy to be transferred to the conduction band. The amount of sufficient energy is the bandgap energy. Electron transits to the conduction band and leaves a hole behind. Then, the electron comes back to the valence band to be stable again by emitting radiation at a particular wavelength. That circle of the electron is called photoluminescence [23,24,25].

Quantum dots have various fascinating optical properties because of the quantum confinement effect as it was mentioned before. Also, those properties could be adjusted by the size and the composition of quantum dots [26]. For electron excitation in quantum dots, the energy which is needed to increase with the decrease of diameter beside the electron emits higher energy during the photoluminescence. That means quantum dots with a larger size have shorter bandgap and the need of less energy to excite their electrons [27].

The Stokes shift and brightness are the other optical properties of quantum dots. The difference between the maximum absorption and the maximum emission of quantum dots is called Stokes shift [28]. Quantum dots have Stokes shift since they have an absorption at much lower wavelengths compared to their emission wavelengths and that is a great feature to sensitively detect in sensing systems [29]. Brightness in high densities is caused by overlap of excitation curve with the scattering curve and some quantum dots are brighter 20 times than a common fluorescent material [30, 31].

1.3.3 Methods for synthesise quantum dots

There are two fundamental methodologies to synthesise quantum dots which are top-down and bottom-up methods. In top-down methods, the synthesis process is based on carving bulk materials into structures into nanoscale [17, 20]. Ball milling and lithography are the top-down approaches and they are kinds of slicing and cutting methods. The ball mill is a grinder and it drops near the top of a rotating hallow cylindrical shell. Here, corrosion is the point to have nanostructures. Also, ball size, ball material, rotation speed and the bulk material chosen are factors of nanostructure

size. On the other side, lithography is a fabrication method to form one- or two-dimensional nanostructures having one material dimension in nanoscale at least. There are many types of lithography and some of them are X-Ray and extreme UV lithography, photolithography, focused ion beam, electron beam lithography and neutral atomic beam lithography [17].

1.3.3.1 Bottom-up approaches

The basis of bottom-up approaches is assembly of small units such as atoms or molecules into the ambitioned structures. The strategy of small unit assembly predicts forming nanostructures with proper shape together with structural design and it is called nano building blocks.

Bottom-up approaches are categorised into two main methods: physical and chemical methods. Inert gas condensation, physical vapour deposition, sputtering, arc discharge, laser ablation and laser pyrolysis are the physical synthesis methods. All those methods are based on condensation, sublimation, vaporisation and sputtering [17]. The method which is used in this thesis is a two-phase synthesis method and it is one of chemical bottom-up approaches. That is why chemical bottom-up methods are just explained in detail.

Chemical bottom-up methods which are wet chemical methods in other words are chemical vapour deposition (CVD), atomic layer deposition, spray pyrolysis, colloidal synthesis, sol-gel method, sonochemical synthesis, microwave assisted synthesis and lab-on-chip technique. Also, the two-phase method is a kind of colloidal synthesis.

There are many advantages of chemical bottom-up methods. First of all, chemical methods are quite simple and they require only a few instruments. It is not similar to the physical bottom-up methods. Secondly, synthesis of quantum dots is executed under mild conditions in the chemical methods. Also, doping of different atoms into the structures is possible while the synthesis is executing. As a final advantage, very large amounts of nanostructures with various sizes and shapes can be synthesised as a product of a chemical method [17].

1.3.3.2 Methodology of two-phase synthesis

Two-phase synthesis method was firstly reported by Brust et al. in 1994 and they prepared alkanethiol-capped Au nanocrystals by means of toluene/water interface. The

team enhanced that method and synthesised semiconducting nanocrystals, noble metal crystals and oxide nanocrystals [32]. Then, CdSe QDs with high quantum yield was successfully synthesised by this method.

Recently, liquid/liquid systems have a great importance for synthesis of colloidal nano materials [34]. The number of studies in which toluene/water was used as a liquid/liquid phase was sharply increased and became outstanding among other two-phase options such as chloroform/water, cyclohexane/water, and benzene/water [34]. The crucial process shown in Figure 1.4 is that the system consists of two immiscible liquids to form a liquid interphase between polar and non polar phases. The reaction of assembly of quantum dots happens at the interphase and hydrophobic nanocrystals which are synthesised were transferred to the non-polar phase [33].

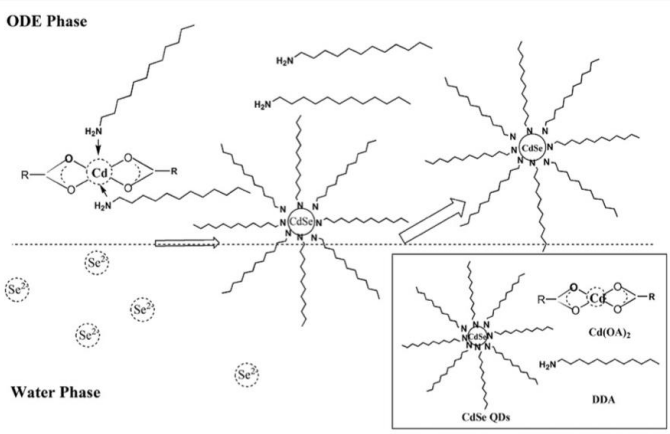

Figure 1.4 : Schematic illustration of CdSe QDs in ODE/water systems as an example [34].

Two-phase synthesis approach is executed under mild conditions that the process is controllable, reactions happen at low temperatures and precursors are less toxic compared to former organometallic methods. In addition, organometallic processes that have tough conditions are so complex and they have restricted biological incompatibility [32, 33, 34].

1.4 Energy Transfer between Quantum Dots and Photosynthetic Pigments

Many scientists are highly motivated to study the interaction quantum dots with biomolecules because of quantum dots' high quantum efficiency and absorption capacity. Many types of quantum dots such as Cd-based chalcogenide quantum dots and graphitic quantum dots possess a potential for energy transfer in biomolecules

owing to their being little hazardous and great biocompatibility. Similarly, hybrid systems composed of proteins and quantum dots enable development of nano systems for different purposes [36, 37].

There are plenty of work which investigated any interaction and energy transfer between photosynthetic structures and quantum dots. Here, some of those studies were summarised below and lightened with their underlying details.

In the study of Budak et al., carbon dopped-boron nitride quantum dots (C-BN) and boron-nitride-carbon quantum dots (BCN) achieved to increase 20% of fluorescence emission pf photosynthetic pigments isolated from spinach leaves and became a part of artificial antenna in photosynthesis [36]. That study was an example for the interaction between graphitic quantum dots and photosynthetic pigments and have the most details being similar with the study of this thesis.

According to the Erker and his team, energy transfer from oleic acid-capped CdTe/CdS quantum dots to light harvesting complex II b (LHCIIb) was obtained. Oleic acid-capped CdTe/CdS quantum dots were synthesised by a phase transfer method and interacted with the complexes through two different binding sites [37].

In 2012, Maksimov et al. discussed Forster's inductive resonance mechanism when an energy transfer was achieved between quantum dots and Photosystem II (PSII) as a donor-acceptor pair. They formed a QD-PSII complex and displayed data that shows a energy migration from the CdSe/ZnS quantum dots to Photosystem II. The energy migration led to enhancement of fluorescence emission of PSII and increase 60% in the rate of QA reduction by helping light absorption of PSII in the UV and visible region [38].

It was stated that when carbon quantum dots (CQDs) which have a sufficiently high quantum yield interacted with chloroplasts and rice plants, quantum dots convert the radiation in the UV range of 300-370 nm to photosynthetically active radiation (PAR) between 370-500 nm. Through this interaction, CQDs with 46.42% of quantum yield enhanced the photosynthesis. Nevertheless, any energy transfer inside of chloroplast did not happen [39].

The final example study from the literature is investigation of interacting CdTe QDs and reaction centre of photosynthesis. Highly-luminescent CdTe QDs efficiently absorbed light in a wide range of spectrum by acting as an artificial antenna. Then,

quantum dots transferred the energy that was harvested to the reaction centre of Rb. sphaeroides. The reason of choice of that particular quantum dots was their photoluminescence emission to make them coupled with the chromophore (acceptor pigment) in the reaction centre [40].

2. MATERIALS AND METHOD

2.1 Synthesis of Precursors

There are three precursors which must be prepared before synthesising quantum dots: cadmium myristate (Cd-Mry), NaHTe for CdSTe QDs or NaHSe for CdSSe QDs.

To synthesise cadmium myristate, cadmium acetate and myristic acid are dissolved in methanol and respectively mixed with 1:3 mole ratio at the room temperature (21℃). In the experiments for my thesis, 0.001 mmol cadmium acetate together with 2.500 mmol NaOH were dissolved in 5 mL methanol and 0.003 mmol myristic acid was dissolved in 100 mL methanol. Then, cadmium acetate solution was added to myristic acid solution drop-by-drop in an erlenmeyer flask after observing that both solutions became utterly homogeneous. Speed for that addition was about 1 drop/sec. The product needs to be filtered via filter paper and dried at the room temperature in the last step.

NaHTe was utilised as a tellurium precursor and synthesised by means of the method in reference **[**41]. In the N_2 atmosphere, 0.4 mol NaBH4 was dissolved in 10 mL distilled water. That saturated distilled water was added to 0.008 mmol Te powder via a glass syringe which had been degassed with N_2 gas for 15 mins. The dark solution we had was heated at 60℃ for 15 mins and colour of the solution was changed to lilac at the end.

The same method in the reference [41] was exploited to synthesise NaHSe. 0.134 mmol Se powder was placed in a flask and waited in N_2 atmosphere for 15 mins. 0.4 mol NaBH4 was dissolved in 10 mL distilled water on the other side. Then, it is carefully transferred to the Se flask via a glass syringe. NaBH4 solution must be degassed with N_2 gas before the transfer. Being heated to 60℃ for 15 mins, it was observed that the solution had a colour change.

2.2 Synthesis of Oleic Acid Capped-Quantum Dots

All quantum dots mentioned in the thesis were synthesised by means of liquid-liquid interphase method. In the liquid-liquid interphase synthesis method, quantum dots were formed at the water/toluene interphase by a reaction of cadmium precursor with NaHSe or NaHTe and sulphur precursor. Additionally, oleic acid exists in the toluene phase as a capping ligand [42].

2.2.1 Synthesis of CdSTe I and CdSTe II quantum dots

First of all, 5 mmol oleic acid was added to 0.111 g cadmium myristate (Cd-Mry) drop-by-drop in 50 mL toluene and stirred for 15 mins at 90℃ in the presence of N_2 gas to prepare the toluene phase. Secondly, 0.8 mmol thiourea was dissolved in 45 mL distilled water in a three-necked flask in the N_2 atmosphere for the water phase. The next step was adding 0.8 mmol NaHTe solution to thiourea solution absolutely saturated with N_2 gas by using a glass syringe. The reason for usage of a glass syringe was inhibiting oxidation of tellurium precursor. After all, CdSTe QDs started to be formed as toluene phase was added to the water phase at 100℃ under the N_2 gas. Then, amount of 1-2 mL of toluene phase was collected at certain intervals to observe the growth of quantum dots by means of UV light. The synthesis of CdSTe I QDs was terminated at the 40th hour. Quantum dots must be kept at 0-2℃ after precipitation in methanol (50% in volume) for analysis and characterisation.

S-riched CdSTe II QDs was synthesised by following the same instructions in the synthesis procedure of CdSTe I QDs. However, quantity of sulphur precursor was increased for CdSTe II QDs and the synthesis was terminated at the 24th hour, diversely.

2.2.2 Synthesis of CdSSe quantum dots

Likewise, the synthesis of CdSTe QDs, 50 mL-toluene phase had 5 mmol oleic acid and 0.111 g cadmium myristate (Cd-Mry) and was heated at 90℃ for 15 mins under gas for CdSSe QDs. Also, water phase of the synthesis was prepared in the same way with CdSTe QDs except adding NaHTe solution. Instead of NaHTe solution, 2 mL of NaHSe solution was added to the 0.8 mmol thiourea dissolved in 45 mL distilled water. After two phases got together to initiate formation of quantum dots, small amounts of toluene phase was periodically examined under UV light a few times to determine

termination time. The CdSSe QDs pictured with other quantum dots in Figure 2.1 were synthesised in 24 hours.

Figure 2.1 : CdSTe I QDs, CdSTe II QDS and CdSSe QDs under the UV light (336 nm), respectively.

2.3 Extraction of Photosynthetic Pigments

A facile extraction method was utilised for raw photosynthetic pigments. About 2.200 g of spinach leaves was respectively washed with tap and distilled water before being submerged in 40 mL absolute ethanol for 48 hours under 0-2℃. Then, a filter paper was used for filtration and the extraction was spilled into glass petri dish. In the end, we replaced that petri dish into a fume to make photosynthetic pigments dried. Pigments became a sort of powder which sticked to walls of the petri dish. Having a raw photosynthetic pigment in a powder form enable us to solve those pigments in any suitable solvent.

2.4 Interaction of Quantum Dots with Photosynthetic Pigments

Chloroform was chosen as a medium of the interaction between quantum dots with raw photosynthetic pigments. That is why all quantum dots and raw pigments were solved in chloroform. Photosynthetic pigments in a petri dish were solved in 10 mL chloroform. On the other side, each quantum dot samples were centrifuged at 14000 rpm for 2 mins for being able to be dissolved in chloroform. The amount of quantum dots in 3.0 mL chloroform were 9.5 mg of CdSTe I QDs, ~6.0 mg of CdSTe II QDs and ~5.0 mg of CdSSe QDs.

The interaction was executed in seven different erlenmeyer flasks which was detailed in the table below [Table 2.1]. Each erlenmeyer flask has 3 mL volume in total. The erlenmeyer flask with number 1 was a check sample and contained only raw photosynthetic pigments in chloroform (PPs). Erlenmeyer flasks with number 2-4 had a kind of quantum dots with the pigments (QDs+PPs). Also, 5-7th erlenmeyer flasks owned only a kind of quantum dots to examine the quantum dots' impact on the raw pigments' fluorescence emissions (QDs). Quantum dots and raw photosynthetic pigments were interacted by shaking flasks at 400 rpm for 1 hour. That shaking progress was made in the dark to prevent excitation of raw photosynthetic pigments by sunlight.

Table 2.1 : The details of each interaction mixture.

Erlenmeyer Flask	Chlorophyll	CdSTe I QDs	CdSTe II QDs	CdSSe QDs	Solvent [Chloroform]
1	1.5 mL	-	-	-	1.5 mL
2	1.5 mL	1.5 mL	-	-	-
3	1.5 mL	-	1.5 mL	-	-
4	1.5 mL	-	-	1.5 mL	-
5	-	1.5 mL	-	-	1.5 mL
6	-	-	1.5 mL	-	1.5 mL
7	-	-	-	1.5 mL	1.5 mL

2.5 Examination of the Interaction Between Quantum Dots and Photosynthetic Pigments

There are three main analysis stages for the thesis. To investigate any interactions occurred between quantum dots and raw photosynthetic pigments, structural and optical characterisation for both is required. Also, the interaction samples of quantum dots and the pigments was optically analysed by means of Fluorescence Spectroscopy.

For characterisation of quantum dots, X-Ray Diffraction (XRD) was used to examine compositions and structures of CdSSe QDs, CdSTe QDs beside S-riched CdSTe QDs. The diffractometer was Rigaku Smartlab X-Ray Diffractometer with CuKα radiation ($\lambda = 1.5406°$ A). The angle range was from 15° to 60° (2-theta, deg) and the data was collected in a step scanning mode. XRD data was also utilised to calculate size of quantum dots by Scherrer Rule. In addition, Fourier Transform Infrared Spectrometer

(FTIR) analysis was performed to prove that all oleic acid-capped quantum dots had the similar organic group on their surfaces.

In details of Fluorescence Spectroscopy, whole set of interaction samples (PPs, QDs+PPs and QDs) was analysed with excitation wavelength of 350, 410, 460, 620 and 660 nm. Then, Photoluminescence Excitation Spectrum (PLE) of photosynthetic pigments and quantum dots-interacted-pigments was recorded at 685 nm and 720 nm. The reason of choosing these specific wavelengths was explained under the subtitle 'Purpose of Thesis'.

To obtain absorption spectra of raw photosynthetic pigments, UV-Visible Spectrophotometer ATO-N4 was used. Scanning range was 300-800 nanometer for interaction samples containing only quantum dots and the range was 350-750 nm for other interaction solutions having photosynthetic pigments inside.

3. RESULTS AND DISCUSSION

3.1 Structural and Photophysical Characterisation of Quantum Dots

For structural characterisation of ternary chalcogenide quantum dots, X-Ray Diffraction (XRD) measurements were executed to obtain composition and crystal structures. XRD data is shown in Figure 3.1. and it was proven that all quantum dots presented a cubic crystal structure owing to three prominent broad peaks which correspond to the Miller indices [111], [220] and [311] according to the standard JCPDS data (JCPDS No. 15-0770 for CdTe and JCPDS No. 10-0454 for CdS) [43]. Positions of the XRD peaks were obtained as [111]: 25.63°, [220]: 43.14°, [311]: 50.80° for CdSSe QDs, [111]: 25.86, [220]: 43.30, [311]: 51.45 for CdSTe I QDs and [111]: 26.23, [220]: 43.90, [311]: 51.69 for CdSTe II (S-riched) QDs. These angles measured in the XRD data was utilised to lighten nanoscale of structures and size of quantum dots were calculated by Scherrer Rule. As a result of the calculations, CdSSe QDs has 2.4 nm in size, meanwhile CdSTe I QDs had 2.7 nm and CdSTe II QDs had 3.2 nm. Also, chemical compositions of quantum dots were obtained as CdSe(0.18)S(0.82) for CdSSe QDs, CdTe(0.19)S(0.81) for CdSTe I QDs and CdTe(0.07)S(0.93) for CdSTe II QDs. It was a fact that amount of sulphur is higher than Se or Te amount in the core of quantum dots because sulphur precursor had higher concentration than Se or Te precursor.

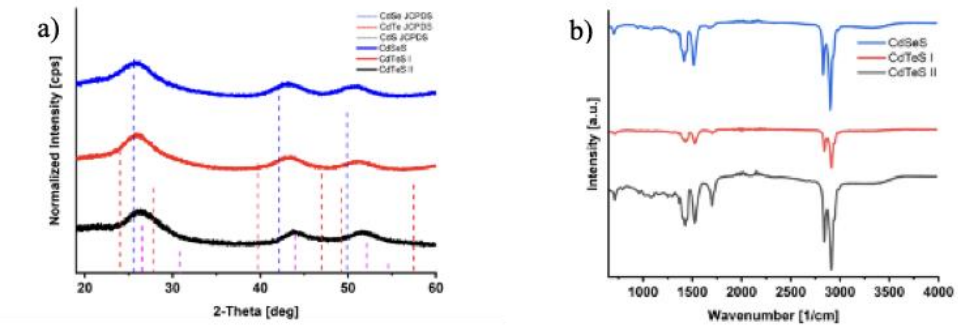

Figure 3.1 : a) XRD data and b) FTIR spectrum of CdSSe QDs, CdSTe I QDs and CdCdSTe II QDs

In addition, full-width at half maximum (FWHM) of the XRD peak of [111] for each quantum dot was determined (Figure 3.1.). The FWHM was 3.50° for CdSSe QDs. For CdSTe I QDs, the FWHM was 3.20° whereas it was 2.65° for S-riched CdSTe QDs (CdSTe II QDs).

To be sure of eliminating the impact of variety on the quantum dots' surfaces and obtain the effect of quantum dots' core structure, Fouirer Transform Infrared Spectrophotometer (FTIR) analysis was the most operative characterisation method. The FTIR data was shown in the Figure 3.1 and indicated that all quantum dots had the similar organic groups on their surfaces. Each quantum dot surface had been covered by carbon-hydrogen chains. Additionally, the FTIR peak which is belonged to -OH groups of oleic acid and typically obtained at 3400^{-1}-3600^{-1} was not observed in the FTIR spectrum of oleic acid-capped quantum dots. That means oleic acid was bonded to all kinds of quantum dots through -OH groups.

For photophysical characterisation of quantum dots, absorption spectrum by UV-Vis Spectrophotometer and emission spectrum by Fluorescence Spectrophotometer (Varian Cary Eclipse Fluorescence Spectrofluorometer) were obtained for each quantum dot and exhibited in Figure 3.2. For absorption spectra, the spectral range was between 400-750 nm. CdSSe QDs had a well-defined narrow peak centred around 475 nm. On the other hand, CdSTe I QDs had a slight and broad peak at ~600 nm beside CdSTe II QDs had and only outstanding decrease between 400-475 nm. In Figure 3.2.b, all quantum dots were excited with 350 nm-light and CdSSe QDs had a single peak centred at 505 nm with FWHM of 40 nm. CdSTe I QDs showed a single peak at 635 nm with the FWHM of 40 nm and CdSTe II QDs' single peak was positioned at 740 nm with the FWHM of 90 nm.

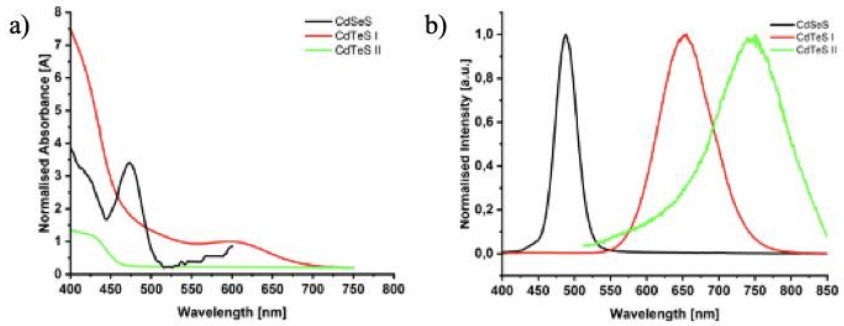

Figure 3.2 : a) Normalised absorption spectra of CdSSe QDs, CdSTe I QDs and CdSTe II QDs b) Normalised emission spectra of CdSSe QDs, CdSTe I QDs and CdSTe II QDs when excitation wavelength was 350 nm.

To characterise oleic acid-capped quantum dots in detail, each quantum dot was examined by exciting different wavelengths via Fluorescence Spectroscopy. Excitation wavelengths were 350, 410, 430, 460, 620, 660 and 666 nm for each structure. At the end of measurements, wavelength-dependent emission spectra of CdSSe QDs, CdSTe I QDs and CdSTe II QDs were provided with photoluminescence quantum yields (Figure 3.3). Photoluminescence quantum yield (PQY)of CdSSe QDs was 85% resulting an efficient fluorescence emission. CdSTe I QDs' PQY was 54% and CdSTe II QDs' PQY was calculated by 29%.

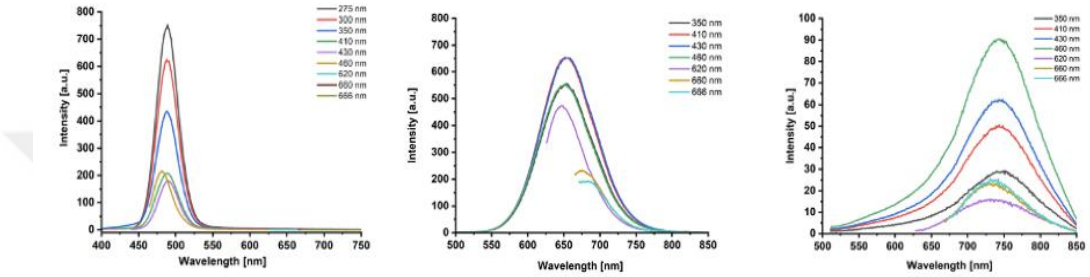

Figure 3.3 : Wavelength dependent emission spectra of a) CdSeS QDs b) CdSTe I QDs c) CdSTe II QD.

Raw photosynthetic pigments It is required to explain determination of the core structure and composition of these particular quantum dots. Photosynthetic pigments have a stated absorption band in the UV and near IR region which could be observed in the Figure 3.4. In set of quantum dots used in the thesis studies, CdSSe QDs were synthesised as they could emit a light in a spectrum matching the pigments' absorption in the UV region. CdSTe I QDs were able to emit a light in the near IR spectrum for the same reason. As a final, CdSTe II QDs (S-riched CdSTe QDs) were synthesised to examine the case when there is no possibility of energy transfer between quantum dots and photosynthetic pigments.

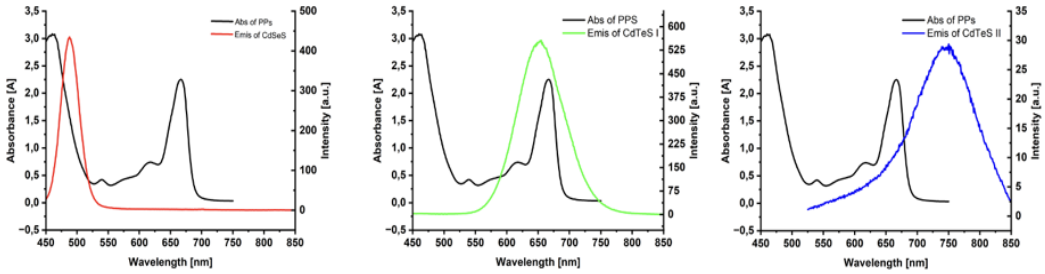

Figure 3.4 : Absorption of photosynthetic pigments overlapping with a) CdSeS QDs b) CdSTe I QDs c) CdSTe II QDs.

3.2 Optical Characterisation of Photosynthetic Pigments

Raw photosynthetic pigments extracted from spinach leaves were analysed by using UV-Vis Spectrophotometer and Fluorescence Spectrophotometer. In absorption spectrum, pigments exhibited a typical three intrinsic peaks: a broad peak at 435 nm with 140 nm of FWHM and two minor peaks at 620 and 660 nm, as shown in Figure 3.5.

The emission of photosynthetic pigments was varied by excitation wavelength. When the excitation wavelength was 350 nm, 410 nm or 660 nm, pigments had two overlapping peaks at 685 nm and 720 nm. Pigments additionally had a peak at 650 nm when they excited with 460 nm- and 620 nm-light. Nevertheless, photoluminescence excitation (PLE) spectrum was obtained and two major bands were recorded at an emission wavelength of 685 nm. First band observed between 225 nm and 470 nm. The other one was positioned from 500 nm to 700 nm.

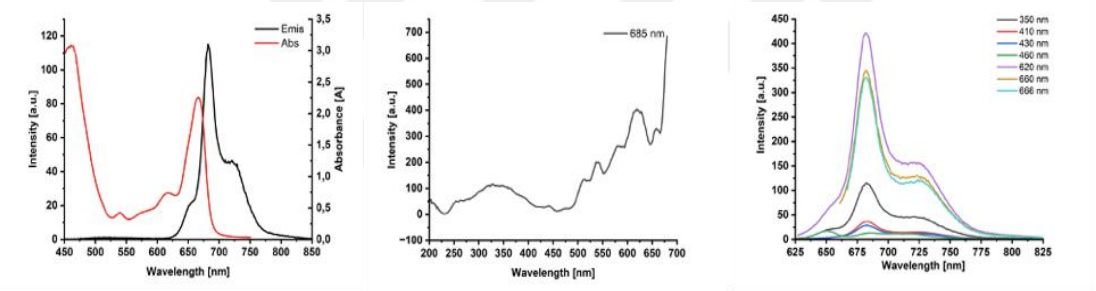

Figure 3.5 : a) Absorption and emission spectrum (excitation wavelength: 350 nm) of photosynthetic pigments b) PLE spectrum of photosynthetic pigments at a emission of 685 nm c) Wavelength dependent emission spectrum of photosynthetic pigments

3.3 Analysis of the Interaction Between Quantum Dots and Photosynthetic Pigments

For lightening the interaction between CdSSe QDs, CdSTe I QDs and CdSTe II QDs, each quantum dot-photosynthetic pigment mixture (PP-QDs) was analysed via Fluorescence Spectrophotometer and emission spectra of each PP-QDs were obtained at the excitation wavelength of 350, 410, 460, 620 and 660 nm. Reason of choosing these particular wavelengths was based on absorption spectra of photosynthetic pigments and emission spectra of quantum dots. At 350 nm, all Cd-based ternary oleic acid-capped quantum dots absorb light and convert it to fluorescence emission with high quantum yield. Photosynthetic pigments also have a fluorescence emission at this

wavelength. 410 nm and 660 nm were chosen as excitation wavelengths due to absorption spectrum of chlorophyll a. 430 nm and 620 nm were chosen by considering the absorption spectrum of chlorophyll b. These are the specific wavelengths for examining any change of chlorophyll a and chlorophyll b emission intensity which quantum dots leaded. Also, photosynthetic pigments were utterly unperished during the analysis at 350, 410, 460, 620 and 660 nm.

In Figure 3.6, emission spectra of interactions belonged to the PP-CdSSe QDs were compared with pure raw photosynthetic pigments' emission results. Emission of photosynthetic pigments was quenched in the presence of CdSSe QDs and emission intensity of CdSSe QDs was decreased at 350 nm. When the PP-CdSSe QDs were excited at 410 nm, the pigments emission was decreased to 1/5 and quantum dots emission intensity dropped to 1/20. At 460 nm pf excitation wavelength, emission of the pigments was quarter of the pure pigment emission while the CdSSe QDs intensity of emission was decreased to 1/20. There was no any emission change between the pure photosynthetic pigments and PP-CdSSe QDs for excitation wavelength of 620 nm and 660 nm. Here, quantum dots did not make any emission upon these wavelengths.

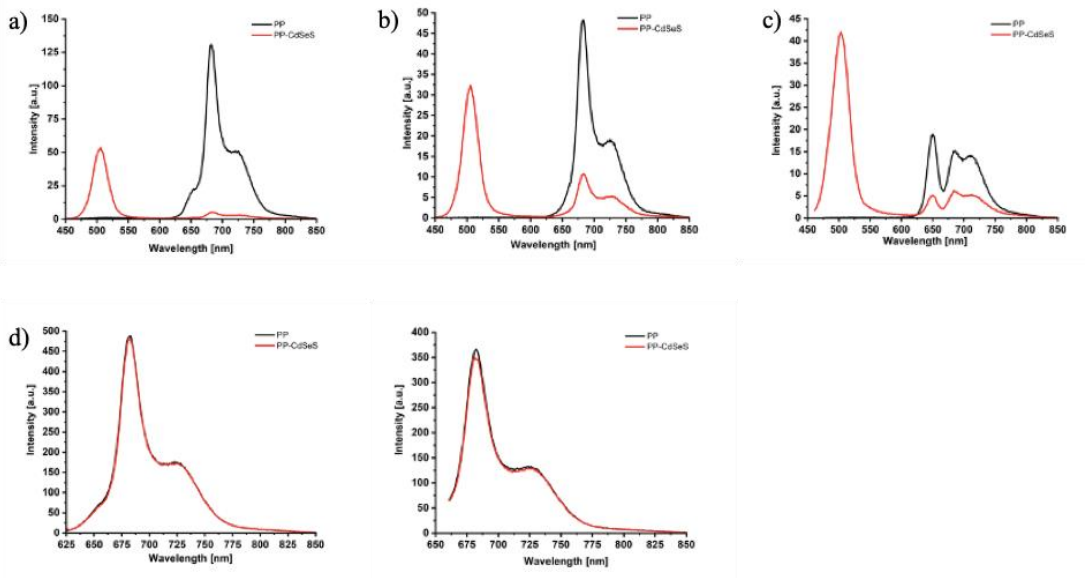

Figure 3.6 : Emission spectra comparision of interactions is belonged to PP-CdSSe QDs with pure raw photosynthetic pigments at a) 350 nm, b) 410 nm, c) 460 nm, d) 620 nm and e) 660 nm.

Emission spectra of interactions of PP-CdSTe I QDs were compared with pure raw photosynthetic pigments' emission spectra in the Figure 3.7. When the PP-CdSTe I

QDs were excited at 350 nm, the pigments emission was decreased by factor of 3 and quantum dots emission spectrum was overlapped with pigments emission at 625-700 nm. At the excitation with 410 nm, emission intensity of both pigments and quantum dots were decreased 50%. Emission of photosynthetic pigments did not change for excitation wavelength of 460 nm at the first peak around 650 nm yet it was declined 15% at the second peak at 685-720 nm. CdSTe I QDs' emission intensity was decreased by factor of 20. Any difference between emission spectra of pigments and CdSTe I QDs was not observed when excitation wavelength were 620 nm and 660 nm.

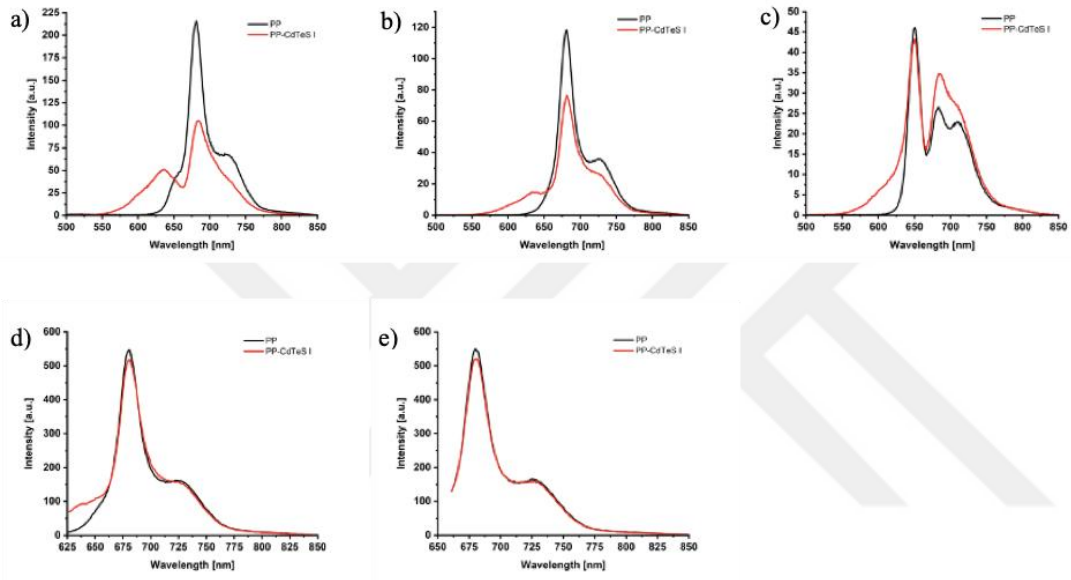

Figure 3.7 : Emission spectra comparison of interactions belonged to PP-CdSTe I QDs with pure raw photosynthetic pigments at a) 350 nm b) 410 nm c) 460 nm d) 620 nm e) 660 nm.

Comparison of PP-CdSTe II QDs' emission spectra with pure raw photosynthetic pigments was showed ins the Figure 3.8 and 95% of pigment emission was quenched as a result of the interaction at 350 nm. However, 1/3 of emission of CdSTe II QDs between 750-850 nm was kept. At 410 nm of excitation wavelength, emission intensity of pigments was decreased to 1/4 while emission of CdSTe II QDs was dropped to 1/8. Similarly, photosynthetic pigments had an emission dropped by factor of 3 and CdSTe II QDs had an only 10% emission of the initial fluorescence intensity. For the last two excitation wavelengths which are 620 nm and 660 nm, both intensity of CdSTe II QDS and pigments did not have any difference.

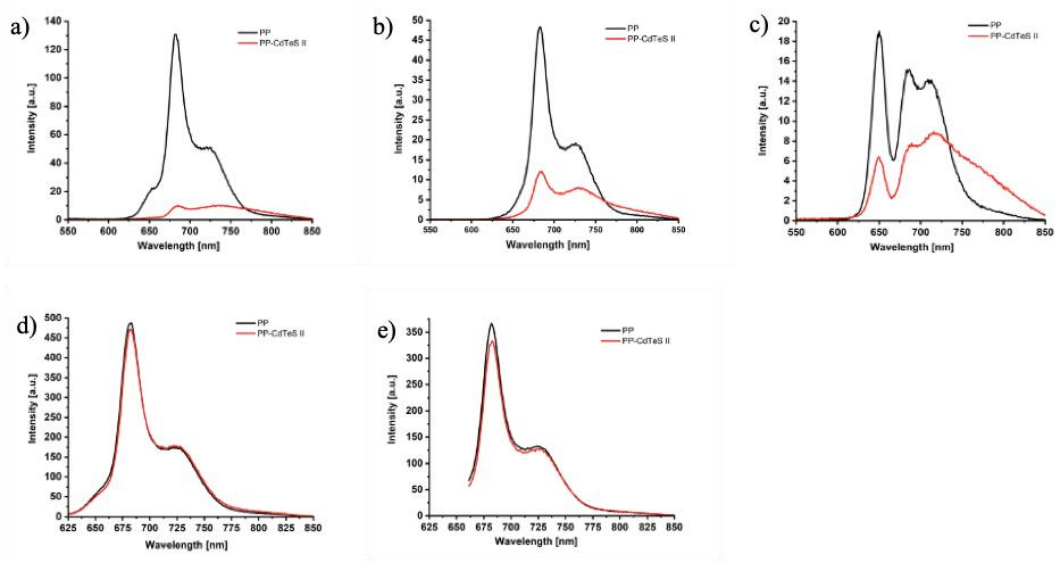

Figure 3.8 : Emission spectra comparison of interactions belonged to PP-CdSTe II QDs with pure raw photosynthetic pigments at a) 350 nm b) 410 nm c) 460 nm d) 620 nm e) 660 nm.

Effect of quantum dots on the light harvesting capacity of raw photosynthetic pigments were also investigated by comparing photoluminescence excitation (PLE) spectra of PP-QDs mixtures at 685 nm and 720 nm with the one of pigments. Wavelengths of 685 nm and 720 nm in the fluorescence spectrum of the pigments comply typical the main absorption band Qy (0,0) and its satellite band Qy (1,0) for chlorophyll of chlorophyll a and chlorophyll b, respectively. Figure 3.9 presents those comparisons for each PP-QDs mixtures. For PP-CdSSe QDs interaction, PLE band covering the soret bands between 225-500 nm was completely quenched at both wavelengths and the band from 500 nm to 700 nm was intrinsic for photosynthetic pigments and the PP-CdSSe QDs mixture [Figure 3.9 a and b]. Photosynthetic pigments in the PP-CdSTe II QDs interaction had the similar PLE band with PP-CdSSe QDs. The PLE band of PP-CdSTe II QDs was wholly quenched at 225-470 nm and displayed the same character with photosynthetic pigments between 575 nm and 700 nm [Figure 3.9 e and f].

There is an exceptional result for the interaction of PP-CdSTe I QDs [Figure 3.9 c and d]. The PLE band of the mixture at both wavelengths was decreased at 225-470 nm yet it was not utterly disappeared like PP-CdSSe QDs interaction. Also, prominent enhancement in the in the intensity of the PLE band between 500-575 nm which is a green colour-range in spectrum when photosynthetic pigments interacting with CdSTe

I QDs. At last, photosynthetic pigments in the mixture of PP-CdSTe I QD exhibited an identical behaviour in the range of 575nm and 660 nm.

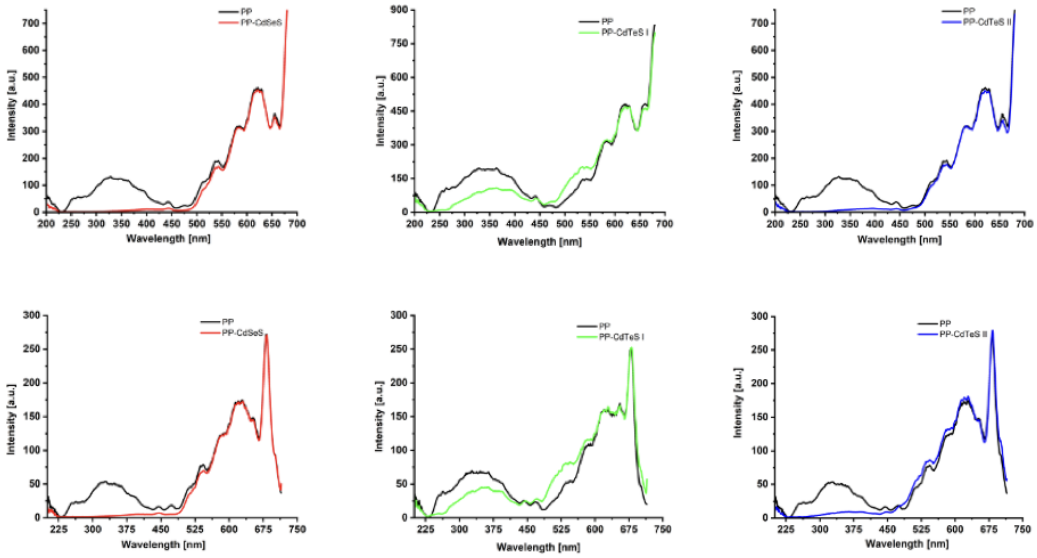

Figure 3.9 : Photoluminescence excitation (PLE) spectra of quantum dot-photosynthetic pigment interactions and pure pigments at emission wavelength of 685 nm and 720 nm.

4. CONCLUSION

In the scope of the thesis, the convenient solution was sought to increase photosynthesis efficiency for higher amounts of biomass production [50, 51]. By exploiting former studies which have a similar goal [46-49], it was decided to study on enhancement of light harvesting capacity of photosynthetic pigments by interacting them with Cd-based chalcogenide oleic acid capped-quantum dots. Oleic acid-capped CdSSe QDs, CdSTe QDs with the Te-riched core and CdSTe QDs with the outer S-riched region were synthesised by two-phase synthesis method. Then, all quantum dots were interacted with raw photosynthetic pigments that are isolated from spinach leaves by a facile extraction method.

In conclusion, the experimental data could be summarised in three parts. In the interaction between oleic acid-capped CdSSe QDs and photosynthetic pigments, pigments displayed radiative electron transition as a result of decrease in quantum dots' and their emission intensity. It proves reduction of radiative electron transition for both pigments and quantum dots upon their interaction. By the way, the CdSSe QDs were used in these experiments due to their ability to emit light in the specific UV region that photosynthetic pigments can absorb.

For examining the interaction between a nanostructure which emits radiation in the near IR region photosynthetic pigments can absorb, oleic acid-capped CdSTe QDs with the Te-riched core were synthesised. According to the experiments, photosynthetic pigments were able to harvest light at 410 nm with the high intensity. That excitation wavelength belonged to chlorophyll a. Also, utterly quenching in the emission spectra of CdSTe I QDs-PP interaction mixtures. Thus, quantum dots did not inhibit the radioactive electron transition. Transitions were just influenced slightly.

The CdSTe II QDs with the outer S-riched region were the quantum dots have no possibility to transfer energy to the photosynthetic pigments due to their optical properties like absorption and emission spectra. Raw photosynthetic pigments were stable and unperished during the interaction yet their light harvesting capacity was substantially dropped. The emission intensity of the pigments in the presence of oleic

acid-capped CdSTe II QDs was almost disappeared at all. The radiative electron transitions were restricted in the CdSTe II QDs-PP mixture due to quantum dots' low amount of Te in the structure. And thickness S-riched outer surface.

Emission spectra of photosynthetic pigments for all interactions had no difference compared to the pure pigments when they are excited at the wavelength of 660 nm. In other words, quantum dots have no impact on the photosynthetic pigments at that excitation wavelength. It is obvious that the interaction with quantum dots is not hazardous for photosynthetic pigments and light harvesting capacity of them is not affected by quantum dots at excitation wavelengths above 600 nm which quantum dots do not absorb radiation.

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CURRICULUM VITAE

Name Surname **:** Sümeyye AYKUT

EDUCATION **:**

- **B.Sc.** **:** 2021, Istanbul Technical University, Faculty of Science and Letter, Department of Chemistry
- **Summer School** **:** 2014, University of Minnesota-Twin Cities, MELP, *Intensive English Program*

RESEARCH EXPERIENCE:

- Sept 2021-June 2023, Istanbul Technical University, *BeeDot Research Group*, Graduate Researcher
- June-Sept 2023, ETH Zurich, D-MATL, *Complex Materials Research Group*, Invited Visiting Student
- 2018-Feb 2021, Istanbul Technical University, *BeeDot Research Group*, Undergraduate Researcher

PRESENTATIONS, PUBLICATIONS AND PROJECTS:

- **Demirors, A. F**., Aykut, S., Ganzeboom, S., Meier, Y. A., & Poloni, E. (2021). Programmable droplet manipulation and wetting with soft magnetic carpets. *Proceedings of the National Academy of Sciences of the United States of America*, *118*(46). https://doi.org/10.1073/pnas.2111291118
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- **Aykut, S.,** Ünlü, C. Spectroscopic Examination of The Interaction between Quantum Dost and Photosynthetic Pigments, *34th National Chemistry Congress, Yalova, September 1-6,* Turkey
- **Aykut, S.,** Ünlü, C. Microwave-assisted Synthesis of Carbon-Nitride Quantum Dots and Their Photophysical Characterisation, *31st National Chemistry Congress, Istanbul, September 10-13,* Turkey
- **TUBITAK 1001 (2022-2025)** Project titled as '*Investigation of the Interactions between quantum dots and photosynthetic protein complexes and increasing algae biomass – a renewable energy source – by using quantum dots'* [Grant Number: 221Z152]
- **TUBITAK 3501 (2019-2021)** Project titled as '*Developing water soluble boron nitride quantum dots and investigating them in vitro interactions'* [Grant Number: 118Z259]