

SYNTHESIS OF NANOPARTICLES BY LASER ABLATION IN LIQUID METHOD AND OPTICAL APPLICATIONS

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF ENGINEERING AND SCIENCE
OF BILKENT UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF
MASTER OF SCIENCE
IN
MATERIALS SCIENCE AND NANOTECHNOLOGY

By

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August 2023

I certify that I have read this thesis and that, in my opinion, it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

SYNTHESIS OF NANOPARTICLES BY LASER ABLATION IN LIQUID METHOD AND OPTICAL APPLICATIONS

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M.S. in Materials Science and Nanotechnology

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August 2023

Pulsed laser ablation in liquids (PLAL) method is a fast, green, and straightforward method that can be used to synthesize pure nanoparticles free of ligands, capping agents, and waste products. Several types of nanoparticles such as metals, oxides, alloys, semiconductors, composite and compound nanoparticles with spherical or complex morphologies can be synthesized with PLAL method. In this thesis, AuCu nanoparticles for photovoltaic application, AgCu nanoparticles for tunable optical properties, CuS/Cu_{1.8}S nanoparticles for photothermal and photoacoustic application, and (Y_{0.83}Yb_{0.16}Er_{0.01})₂O₃ nanoparticles for upconversion photoluminescence application are synthesized. The synthesized AuCu nanoparticles are used in organic solar cells and enhanced the photocurrent production, proven by the 21.4% increase in the power conversion efficiency. AgCu nanoparticles show composition and laser fragmentation dependent tunable surface plasmon resonance between 420 nm – 580 nm, giving 160 nm tunability. These nanoparticles also show complex morphologies with Janus nanoparticle and core-shell type configurations. Copper sulphide nanoparticles show a broad absorbance in the NIR region with absorbance peak at 1183 nm. Nanoparticles with 1 mg/mL concentration show a 52.2 °C

temperature increase in 3 minutes of 3.23 W/cm^2 1080 nm CW laser irradiation. Photoacoustic imaging experiments where copper sulphide nanoparticles are utilized show a significant contrast enhancement compared to ultrasonic imaging at 1 cm depth. The upconversion nanoparticles show an intense red emission at 651 nm from 980 nm laser irradiation and lowered green emission compared to the target material which shows nanoparticles produce more heat compared to the target which can be useful for photoluminescence – photothermal applications.



Keywords: Nanoparticles, Pulsed Laser Ablation in Liquids, Photothermal, Photovoltaic, Photoacoustic, Photoluminescence, Alloys, Localized Surface Plasmon Resonance, Copper Sulphide Nanoparticles, Rare Earth Oxides, Absorbance, Optical Characterization

ÖZET

SIVIDA LAZER ABLASYON İLE NANOPARÇACIK SENTEZİ VE OPTİK UYGULAMALAR

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Malzeme Bilimi ve Nanoteknoloji, Yüksek Lisans

Tez Danışmanı: Dr. Bülend Ortaç

Ağustos 2023

Sıvılarda darbeli lazer ablasyonu (PLAL) yöntemi, ligandlar, kaplama maddeleri ve atık ürünlerden arındırılmış saf nanoparçacıkları sentezlemek için kullanılabilecek hızlı, çevre dostu ve basit bir yöntemdir. Küresel veya karmaşık morfolojilere sahip metaller, oksitler, alaşımlar, yarı iletkenler, kompozit ve bileşik nanoparçacıklar gibi çeşitli nanoparçacık türleri sıvılarda darbeli lazer ablasyonu yöntemi ile sentezlenebilir. Bu tezde, fotovoltaiik uygulama için AuCu nanoparçacıkları, ayarlanabilir optik özellikler için AgCu nanoparçacıkları, fototermal ve fotoakustik uygulama için CuS/Cu_{1.8}S nanoparçacıkları ve yukarı dönüşüm fotolüminesans uygulaması için (Y_{0.83}Yb_{0.16}Er_{0.01})₂O₃ nanoparçacıkları sentezlendi. Sentezlenen AuCu nanoparçacıkları, organik güneş pillerinde kullanıldı ve güç dönüştürme verimliliğindeki %21,4'lük artışla kanıtlanan fotoakım üretimi artışı gerçekleştirildi. AgCu nanoparçacıkları, 420 nm - 580 nm arasında, bileşime ve lazer parçalanmasına bağımlı ayarlanabilir yüzey plazmon rezonansı göstererek 160 nm ayarlanabilirlik sağladı. Bu nanoparçacıklar ayrıca Janus nanoparçacıkları ve çekirdek-kabuk tipi konfigürasyonlar gibi karmaşık morfolojiler göstermektedir. Bakır sülfid nanoparçacıkları, 1183 nm'de absorbands zirvesi ile yakın kızılötesi bölgesinde geniş bir absorbands gösterir. 1 mg/mL konsantrasyonlu nanoparçacıklar, 3 dakikalık

3.23 W/cm² 1080 nm CW lazer ışınlamada 52.2 °C'lık sıcaklık artışı göstermektedir. Bakır sülfid nanoparçacıklarının kullanıldığı foto akustik görüntüleme deneyleri, 1 cm derinlikte ultrasonik görüntülemeye kıyasla önemli bir kontrast artışı göstermektedir. Yukarı dönüşüm nanoparçacıkları, 980 nm lazer ışınlamasından 651 nm'de yoğun bir kırmızı emisyon ve hedef malzemeye kıyasla daha düşük yeşil emisyon göstermektedir. Bu, nanoparçacıkların hedef malzemeye kıyasla daha fazla ısı ürettiğini gösterir ve nanoparçacıkların hedef malzemeye kıyasla fotoluminesans - fototermal uygulamalar için yararlı olabilecek daha fazla ısı ürettiğini gösterir.

Anahtar Kelimeler: Nanoparçacıklar, Sıvılarda Darbeli Lazer Ablasyon, Fototermal, Fotovoltaik, Fotoakustik, Fotoluminesans, Alaşımlar, Lokalize Yüzey Plazmon Rezonansı, Bakır Sülfid Nanoparçacıkları, Nadir Toprak Oksitleri, Absorbans, Optik Karakterizasyon

ACKNOWLEDGEMENT

I would like to thank my advisor Asst. Prof. Dr. Bülend Ortaç for being a mentor for me throughout my master's studies. Your energy and friendly demeanor towards us students allowed me to unlock the potential I had. Thanks to you, I completed my master's studies as a happy, stress-free, and successful student. You have been a role model to me that I aspire to be in my future.

I want to thank my thesis committee members Asst. Prof. Dr. Fatih İnci and Prof. Dr. Ali Çırpan for accepting to be my thesis committee members and for reading and evaluating my thesis. Since I have worked with both of their research groups in my thesis study, their contribution in my thesis is much valuable.

I would like to thank all Ortaç Research Group members for their contribution in my thesis and in my life. I want to thank Dr. Ali Karatutlu for being an unofficial second advisor to me and for all the things he taught me. I would like to thank Elif Yapar Yıldırım for being like a big sister for me and helping me throughout my master studies. I would like to thank Dr. Hamid Reza Bahari for introducing me to a new field and broadening my horizon with his project. I was lucky to work with you. I want to thank Dr. Esra Kendir for her ideas, advices, and her help in my study. I would like to thank Samet Akçimen and Gizem Mutlay for helping me in my studies, experiments and being a friend for me. I would like to thank Prof. Dr. Sevil Savaşkan Yılmaz, Assoc. Prof. Dr. Timuçin Emre Tabaru and Saliha Mutlu for introducing me a new field of study and bringing new ideas to our group during my studies.

I would like to thank Prof. Dr. Hayrettin Köymen and his students Çağatay Çelebi and Yasin Kumru for their collaboration and enriching our study.

I would like to thank Dr. İsmail Eş for his contribution in my study and being a mentor for me during my studies.

I would like thank my family for their support throughout my education. I want to thank my mother for always supporting me, praying for me and being my strength in my life. I want to thank my brother for always believing me even when I didn't believe in myself. Thank you for your support and for being like a brother, father and a friend at the same time.

I would like to thank my friend Güneş for bringing joy into my life. You were the source of happiness during my master's studies. I want to also thank Samet, Halit, Doğukan for their friendship. Our struggles together made it easy for me to overcome them. I want to also thank Eylül, Melis, Gün, Cansın, Pedram, Muhammadali and Elif for being a friend to me. You guys made it better and easier for me.

I would like to also acknowledge supports from UNAM and TÜBİTAK for financially supporting me in my studies.



For my brother and my mother.

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1 NANOTECHNOLOGY AND NANOPARTICLES

Nanotechnology is the branch of technology usually made in the scale of 1 to 100 nanometers. At this scale, many important biological, chemical, and physical phenomena happen. Nanotechnology and nanoscience study the control and manipulation of matter on the atomic, molecular and supramolecular scale. The study of nanotechnology includes the design and production of nanomaterials, devices that use these nanomaterials, or in general, new advanced systems with unique features.

In today's world, nanotechnology has found its place in many applications. One of the most important of these applications are in electronics technology. The microprocessors and the transistors of these microprocessors inside the electronic devices we use today have gotten smaller and smaller to the point where the quantum tunneling effect may occur [1]. This enabled to make compact, small electronics with high processing powers. Another important development is in the field of medicine. Drug delivery systems that make use of the nanoparticles are used to deliver drugs to specific places inside the body to increase their efficiencies [2]. Examples to other essential applications are such as sunscreens that use titanium oxide to block UV radiation [3], water purification systems that use silver nanoparticles to filter water at nanoscale [4], clothing industry that develop anti-wrinkle and anti-stain fabrics [5], energy production such as increased efficiency in solar cells with nanoparticles [6].

Nanoparticles usually ranging between 1 to 100 nanometers have found its place in many practical applications in nanotechnology due to their unique properties. They show these properties due to their high surface to volume ratio [7] and small size. Their small size allows them to show

properties that are different than their bulk counterparts without changing the composition. In addition, since their size is shorter than wavelength of visible and infrared light, they interact with light differently than bulk materials. This leads the path to materials and technologies that use light-matter interaction at nanoscale. Nanoparticles can be modified or engineered to control their properties by changing their size, shape or dimension, composition and surface properties. For instance, localized surface plasmon resonance (LSPR) wavelength of plasmonic nanoparticles redshift when their size gets bigger [8]. This effect is also known as quantum confinement effect. In addition, gold nanorods have 2 different LSPR peaks due to their rod-shape structure creating longitudinal and transverse plasmon bands [9]. Other than changing the wavelength of the absorbed light, small sizes of nanoparticles increase their reactivity, since they have much more surface that can react with reactants in the environment. This makes them the perfect candidate for catalysis to shorten the reaction times [10].

In conclusion, nanoparticles have a variety of properties that differ them from their bulk counterparts. Quantum effects are present in nanoparticles due to their small size and high surface-to-volume ratio. Nanoparticles show some properties due to these quantum effects that make them useful for their optical properties such as LSPR, magnetic properties as a result of existence of magnetic domains in magnetic nanoparticles or catalytic properties owing to their large surfaces with respect to their volumes that increase reactivity.

1.1 NANOPARTICLE SYNTHESIS METHODS

Nanoparticles are synthesized in many different ways. The two general methods for synthesis are called bottom-up and top-down methods. In bottom-up method, nanoparticles are

generated from smaller constituents such as atoms and molecules. In this method, usually chemical reactions are used with the help of chemical precursors to assemble the atoms into nanoparticles. In the top-down method, bulk materials are used to break down into nanoparticles with various physical and chemical techniques.

1.2 BOTTOM-UP NANOPARTICLE SYNTHESIS METHODS

There are several ways to synthesize nanoparticles with bottom-up method. In bottom up synthesis methods, nanoparticles are synthesized by the assembly of smaller constituents such as atoms, atom clusters and very small nanoparticles. Usually, precursor materials are used in a reduction reaction to form nanoparticles. Examples of these methods include hydrothermal synthesis, sol-gel synthesis from chemical precursors, self-assembly method by utilizing fundamental forces.

1.2.1 Hydrothermal Synthesis Method

Hydrothermal synthesis method makes use of precursor materials. These materials can be in the form of metal salts, organic compounds or combination of materials. In a sealed autoclave, which is an environment with high temperatures and pressures, precursor materials are reacted to form nanoparticles. The size, morphology, crystal structure can be controlled by changing the parameters of reaction time, temperature and pressure [11]. After synthesis, some post treatment is required such as washing, and drying. Advantages of this method include size and shape control by changing reaction conditions. However, procedures of the synthesis experiments must be known previously or discovered during the process to be able to control these parameters.

Hydrothermal synthesis also produces nanoparticles with high homogeneity, meaning narrow size distribution and same, well defined crystal structure. In addition, the amount of synthesized nanoparticles can be scaled, meaning they can be produced in large quantities. The main disadvantage of this method is that the optimization of the reaction parameters (time of reaction, precursor material concentration, temperature, pressure) are really complex to produce nanoparticles in the desired size, morphology and structure. Also, processes such as washing, purification and drying are needed to remove unwanted residual reactants.

1.2.2 Sol-Gel Synthesis Method

Sol-Gel is a wet chemical nanoparticle synthesis method through an inorganic polymerization process. It is mostly used for synthesizing metal oxide nanoparticles. This method makes use of metal salts. These metal salts are dissolved in some suitable solvent to prepare the solution (sol) and some catalyst materials to start the reaction between metal salts and the solvent to create the metal ions inside the solution. After dissolving, hydrolysis of the solvent is started to produce metal oxides/hydroxides. The hydrolysis process is followed by the condensation of metal oxides/hydroxides to form metal-oxygen-metal bonds. The condensation process allows the growth of nanoparticles inside the solution. Continuation of this process leads to the gelation (gel) of the solution where molecules with metal-oxygen-metal bonds are linked to each other to form a gel matrix. Inside this gel matrix, the nanoparticles are dispersed. For additional growth and organization of the matrix, an aging process is employed. After the completion of the aging process, the gel is dried to remove the gel matrix and obtain the nanoparticles inside the gel matrix. A post-treatment process such as sonication or grinding is used to extract nanoparticles.

The main advantages of this method include the ability to obtain specialized products like fibers [12], microspheres, films, or coatings, obtaining products with high purity and homogeneity, narrow size distribution of nanomaterials and production of nanomaterials with complex shapes . In addition, the sol-gel process is scalable. This advantage makes sol-gel process suitable for production in large quantities. However, there are some disadvantages of this process that makes it unsuitable in some situations. The first of these disadvantages is that the sol-gel process is a long, complex process that is prone to mistakes and problems. Optimizing all the parameters and process steps can be quite challenging and can take a long time [13]. From start to finish, obtaining nanoparticles can take several days which makes it hard to optimize the process and progress of the scientific work becomes harder. Also, there is still the possibility of aggregation of nanoparticles [14], synthesis of nanoparticles with irregular shapes [15] and inhomogeneous sized nanoparticles [16].

1.2.3 Self-Assembly Synthesis Method

In self-assembly synthesis method, nanoparticles are created by the aggregation of building blocks without external effects. The inherent properties of these building blocks are used to create nanoparticles through physical and chemical interactions. The self-assembly method excels at creating nanoparticles with complex structures since physical conditions or the chemical environment may favor the aggregation of building blocks in certain structures [17]. Main factors affecting the nanoparticle synthesis through self-assembly are the concentration and nature of building blocks, environmental conditions and the solvent used. The self-assembly process is made up of 3 main sub-processes, namely, nucleation, growth and assembly. First, small clusters are created through some weak molecular interactions such as Wan der Waals or hydrogen bonding

interactions. Then, more molecules stick onto these small clusters through aggregation and give rise to the growth of the nanoparticles. At last, during the assembly process, these nanoparticles and building blocks self-assemble themselves into complex structures.

Self-assembly is governed by thermodynamics and molecular interactions of building blocks. These interactions are;

kinetics and thermodynamics where the speed of the process and thermodynamical properties of the assembled structure balance each other [18],

entropic effects where the decrease of entropy in assembled structures needs to be compensated by solvent molecules [19],

intermolecular forces such as Van der Waals forces and hydrogen bonding forces in processes of nucleation and growth of nanoparticles [20].

Although self-assembly method has the advantage of structure control and tailored properties through incorporation of several modifications, it is time consuming and expensive to find optimum conditions to synthesize nanoparticles this way. Structure control of these nanoparticles would usually require transmission electron microscope characterization. Reproducibility of the process is also hard since the process depends on several parameters such as temperature, pH and concentration.

1.3 TOP-DOWN NANOPARTICLE SYNTHESIS METHODS

In top-down methods, nanoparticles are synthesized by breaking bulk materials apart by physical techniques. Compared to chemical precursors used in bottom-up methods, materials such as bulk

materials, powders, thin films are used in top-down methods as starting materials. There are several ways to synthesize nanoparticles with top-down method. Examples of these methods include mechanical milling, for mechanical force based method, chemical etching method for chemical based methods, and laser ablation method for laser and energy based methods.

1.3.1 Mechanical Milling Method

Mechanical milling is a widely used nanoparticle synthesis method. Mechanical milling makes use of high energy ball mills to create nanoparticles from bulk materials by intense mechanical forces. As a simple explanation, the grinding balls inside a hollow container mill the starting materials, causing the material to break apart to create nanoparticles gradually in the process. Although the starting materials are usually metallic, sometimes ceramic or organic materials are also used to synthesize nanoparticles with ball milling. In short, the procedure of synthesis with ball milling is as follows. After selecting the starting materials, they are mixed together for a homogenized milling process. The movement and rotation of the grinding media start to break down the bulk material. The continuation of the grinding of the balls into the mixture allows for a reduction in size to create the nanoparticle powder or suspension. At last, the resulting nanoparticle media are subjected to post-treatment to obtain nanoparticles such as centrifuge, washing, or filtration.

The ball milling process can be controlled with parameters such as grinding media, time of the milling, speed of rotation, the temperature of the process, milling atmosphere and others. Ball milling is a mechanical process and can produce several grams of nanoparticles in a few hours [21]. In addition, it is an easy and inexpensive process. These reasons make ball milling an enticing method for industrial applications where bulk production of nanoparticles might be needed.

However, there are also some disadvantages of ball milling synthesis that make this method undesirable. Since nanoparticles are produced with a mechanical force based method, the shape of the nanoparticles can be nonuniform, making the nanoparticles inapplicable for applications based on the shape of nanoparticles [22]. The high mechanical force also creates defects or changes the crystal structure of nanoparticles from the starting bulk material, altering the properties of nanoparticles compared to the bulk material [23]. The mechanical force can also wear down the grinding materials of the ball mill. This introduces contamination in fabricated nanoparticles, causing a change in the content of the nanoparticle [24].

1.3.2 Chemical Etching Method

Nanoparticle synthesis by chemical etching is a method that uses chemical etchant solutions to dissolve material from a substrate. Basically, nanoparticles are synthesized by dissolving a substrate material inside a chemical etchant solution by controlling parameters such as concentration, time and temperature. The most vital decision of the process is to choose a proper chemical etchant for the substrate material. Several different type of nanoparticles such as metal, semiconductor, oxides can be synthesized with this method. After selecting the substrate material which is desired to have nanoparticles, an etchant solution is selected according to the starting substrate material. For instance, metals are usually etched with acidic solutions whereas semiconductors require complex processes such as metal assisted chemical etching [25]. The reaction between substrate and etchant starts the etching process with methods such as spray coating or immersion depending on the scale of synthesis. After the synthesis is over, the solution is separated from nanoparticles. Post-treatment processes such as washing, filtration and centrifuge might be needed depending on the synthesis conditions. By controlling the abovementioned

parameters, nanoparticles with sophisticated shapes [26] and controllable sizes can be synthesized. This makes the chemical etching method a valuable method since the shapes of the nanoparticles can be controlled with suitable synthesis parameters. In addition, the chemical etching method offers the possibility of integration into fabrication processes such as lithography which can allow the creation of more advanced systems involving nanoparticles [27]. However, the limitations of this method prevent chemical etching method to become a widely used method for nanoparticle synthesis. First of all, the optimization of the parameters to synthesize desired nanoparticles can be challenging and time consuming. Also, these parameters and the condition of the starting materials can affect the uniformity of synthesized nanoparticles [28]. In addition, the chemical waste produced during synthesis is usually environmentally hazardous and requires appropriate disposal. Careful waste treatment is important with the chemical etching method.

1.3.3 Laser Ablation Method

Laser ablation method is an energy based novel technique to produce nanoparticles from bulk materials. Laser ablation refers to the removal of material from a starting bulk material by changing the physical phase of the material through focused pulsed laser light. This phase change may be in the form of melting, vaporizing and in the plasma phase. Since this is an energy based method, it does not require chemicals and it is an environmentally friendly method. Several types of nanoparticles can be synthesized with this method such as metallic, semiconductor, alloy, dielectric, oxide nanoparticles [29][30][31]. The popularity of the laser ablation method continues to grow since this method allows to synthesize pure nanoparticles which is required in applications of nanoparticles for optimal efficiency. A pulsed laser ablation setup is straightforward. A typical laser ablation setup requires a pulsed laser, ranging from millisecond pulse lasers to femtosecond

pulsed lasers, an optical lens to focus the incident light beam onto the target material to increase the light intensity on the target, a collection chamber or substrate to collect nanoparticles and a target material to synthesize nanoparticles. The medium of ablation can be vacuum, gas or liquid. Nanoparticles can be deposited onto a solid substrate when the environment is vacuum, can be synthesized inside a liquid and collected by techniques such as centrifugation, filtration and sedimentation, and when nanoparticles are synthesized in a gaseous environment, they can be collected by gas condensation or electrostatic precipitation depending on the nanoparticle properties. The advantages of laser ablation synthesis of nanoparticles can be described as follows:

1. Synthesized nanoparticles are highly pure since no chemical precursors or additives are needed in this method.
2. This is a nontoxic method since it does not require chemicals to synthesize nanoparticles. This advantage makes the laser ablation method a good candidate to produce nanoparticles for biomedical applications.
3. Laser ablation is a versatile method and can be applied to synthesize nanoparticles from lots of different types of materials. In addition, by choosing a suitable solvent, compounds, oxides, alloys and several other types of nanoparticles can be synthesized.
4. Stoichiometry of alloy nanoparticles can be controlled by choosing an appropriate target since alloy nanoparticles synthesized from alloy targets have the same composition [32] or by ablating pure targets of the desired alloy nanoparticle inside the same chamber and processing them with enough energy and time to become alloy nanoparticles [33]. If the ablated material mass and time are controlled, then alloy nanoparticle composition can also be controlled.

5. If large amounts are not required, with laser ablation, nanoparticles can be obtained within minutes. The moment focused laser light interacts the target material, the nanoparticle production starts. A suitable high power pulsed laser can shorten the amount of time for the needed time for synthesis.

However, there are also some disadvantages that prevent the laser ablation method from becoming a widely used nanoparticle synthesis method. The disadvantages of laser ablation method and how researchers overcome them are explained below:

1. The most important disadvantage of the laser ablation method is the aggregation of nanoparticles. Laser ablation method can produce nanoparticles without any chemical stabilizers agents but in most instances, this results in nanoparticles having high surface energy due to liquid not providing an adequate surface charge layer. A weak surface charge layer will result in a low zeta potential. In this situation, nanoparticles tend to aggregate or agglomerate to reduce surface area and energy. To overcome this, ablation environment can be chosen accordingly to reduce particle interactions [34] or stabilizing agents can be used to reduce the possibility of aggregation [35].
2. Laser ablation method usually produces nanoparticles with a broad size distribution [36]. This may be attributed to mechanisms such as differences in the growth processes of nanoparticles, particle coalescence during cooling and solidification of nanoparticles, and aggregation of nanoparticles during and after the synthesis. To overcome this problem, researchers are implementing several solutions. Using stabilizer agents, surfactants can help make the size distribution narrower and also increase the functionality of nanoparticles [37]. Physical and laser based post-treatment processes are also used to control the size and size distribution of nanoparticles. Physical treatments such as centrifuge or filtration are

used to remove nanoparticles with unwanted sizes. Laser based post processes such as laser melting and laser fragmentation are also used to alter the sizes of nanoparticles. Laser melting is used to increase the sizes of nanoparticles by melting the nanoparticles with long pulse width lasers (nanosecond, microsecond) and allowing them to solidify together, creating bigger sized nanoparticles [38]. Laser fragmentation is used to decrease the sizes of nanoparticles by breaking up the nanoparticles into smaller sizes through ultrashort (femtosecond) pulsed lasers [39].

Laser ablation method is a good way to process materials and also to synthesize nanoparticles. It is important to delve more into the physics and mechanisms of the laser ablation method.

1.4 LASER ABLATION

Laser ablation is the process of removal (ablation) of material from a solid target by using lasers. Thus, it is important to study the effects of different types of lasers on the laser ablation process and the physical phenomena during the laser ablation. Continuous wave (CW) and pulsed lasers can be used for laser ablation. However, the answer to the question of how material is removed during laser ablation differs with different types of lasers.

1.4.1 Laser Ablation by CW Lasers

CW lasers send photons by constant emission; thus, they do not have a peak power feature. CW lasers realize laser ablation by the absorbance of photons and heating up the target material during the process. The heated material first melts and then vaporizes, resulting in removal of material

from target surface. The thermal effect is the main mechanism of continuous wave laser ablation and results in a large heat affected zone when compared to pulsed lasers. This causes temperature increase in regions where laser processing is not wanted. This may lead to the deformation of the target material and lower precision on ablation. In nanoparticle synthesis by laser ablation, CW lasers are also not desirable for several reasons. CW lasers have lower production rate due to a slower heating rate. This also affects the size distribution of nanoparticles due to excessive heating and melting of nanoparticles during ablation. Target material degradation may also cause some problems such as unwanted reactions between the target and the ablation environment such as oxidation or byproducts of precursors.

1.4.2 Laser Ablation by Pulsed Lasers

Pulsed lasers ranging from micro to femtosecond pulsed lasers have different mechanisms of ablation. Although other parameters also have an effect, the underlying mechanism that causes a difference in the ablation mechanism of pulsed lasers is their pulse duration. When electrons absorb the incident laser light, excitation of electrons occurs. Electrons transfer this energy by collisions to the lattice atoms of the material. This process creates phonons which are vibrational energy. Phonons increase the vibrational energy of lattice atoms, creating an increase in the temperature of the material by heat diffusion. Usually, the electron-phonon cooling time of materials is in the range of a few picoseconds [40]. This results in the two ablation mechanisms of pulsed lasers, namely, hot ablation for microsecond and nanosecond pulsed lasers and cold ablation for picosecond and femtosecond lasers.

During pulsed laser ablation, physical phenomena such as explosive boiling, spallation, material fragmentation, thermal ablation, and Coulomb explosion.

Explosive boiling or phase explosion occurs through the absorption of photons which causes a rapid heating and temperature increase in the target material. When the material absorbs a very high amount of energy in a short time, the temperature at the point of interaction rises rapidly. This results in rapid vaporization of the material at laser material interaction point, and the creation of vapor bubbles. These vapor bubbles then explode, creating shockwaves as a result. These shockwaves can also remove material from the target surface, enhancing laser ablation efficiency.

Spallation is the removal of material in laser ablation due to high intensity laser light creating cracks in the target material. When target material is rapidly heated due to the high intensity laser light, thermal stress can be generated. This stress then can cause formation of cracks on the surface of the target material. Due to the continuation of laser energy on the target and buildup of stress on the target, this crack can result in the fragmentation of the material. These fragments are usually large in size and are the reason for bimodal size distribution in nanoparticle synthesis by laser ablation [41].

Material fragmentation is a phenomenon similar to spallation. Rapid heating from a pulsed laser creates thermal stress on the material. Thermal stress inside the material generates stress waves which then trigger a crack formation. Continued stress on the material can start the fragmentation process of the material. The properties of the material such as strength, thermal conductivity and initial condition of the material also have an effect on the fragmentation mechanism. The difference between spallation and material fragmentation is that spallation is about material ejection from the target whereas material fragmentation is about cracking and breaking the material into smaller pieces.

In thermal ablation phenomenon, the material absorbs the incident laser light. This absorbed light energy is transformed into heat and a thermal gradient is formed at the irradiated region. The heat is conducted into nearby regions inside the material that create a heat affected zone in the material. As more laser light is absorbed, the energy of the material at the irradiation point reaches to the boiling point of the target. The vaporized material is then removed from the target. The vapor pressure from the vaporized material can also influence the material ablation from the target through shockwave generations of the vapor bubble explosions.

Lastly, coulomb explosion happens mostly with nanoparticles. When charged particles interact with incident laser light, particles ionize. The positively charged ions feel a repulsion from other positively charged ions. The repulsive forces from Coulomb interactions of the charged particles cause an explosive fragmentation of the particle due to expansion from the charged ions [42].

These are most of the effects that affect the material removal by the laser ablation process. However, their frequency in different types of pulsed lasers differs. Different lasers have differences in ablation efficiency and the impact of ablation on the target material. Most important of these effects are ablation threshold and heat affected zone. Ablation threshold is the minimum laser fluence required for laser ablation of target material. Ultrashort pulsed (ps, fs) lasers generally have much lower ablation thresholds compared to ns lasers [43][44]. This means ultrashort pulsed lasers can ablate materials with lower powers more efficiently. However, ns laser systems are much cheaper than their ultrashort pulsed counterparts and high power systems are more available. High power systems can easily surpass the ablation threshold and generate more ablation in shorter times, giving high productivity in laser ablation process. Heat affected zone is the thermally affected zone from laser pulses. Ns lasers have higher pulse duration than the electron phonon cooling time and they generate a large heat affected zone in the target material. Ultrashort pulsed

lasers produce very small HAZ, delivering efficient material removal. Ultrashort pulsed lasers are more suitable in terms of precise, shallower material removal and when surface quality is an important aspect of the application.

Other than laser material processing, pulsed laser ablation is an excellent way to synthesize nanoparticles. Nanoparticle synthesis by laser ablation is usually done inside liquids to collect nanoparticles inside and also make use of the liquid to control and change the properties of the nanoparticles. This thesis is about synthesizing nanoparticles by laser ablation method in liquids.

1.5 NANOPARTICLE SYNTHESIS BY LASER ABLATION IN LIQUIDS

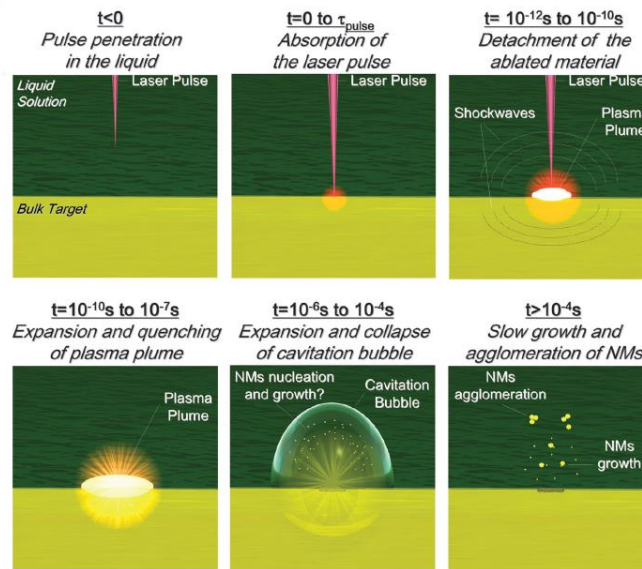


Figure 1: Sketch of the timeline of LASiS. Ablation with ns pulses has been considered in this example. Nucleation and growth of NMs are hypothesized in the 10^{-6} – 10^{-4} s time range, although precise information is lacking. Adapted from [45].

The physics of the nanoparticle synthesis by laser ablation in liquid should be understood well to increase the productivity of the synthesis and to understand the condition of the synthesized

nanoparticles. The mechanism of laser ablation in liquids (LAL) is explained below in the temporal domain. The short explanation in figure 1 is given in detail below.

Absorption of the laser pulse ($t = 0$ s)

The process starts with the absorption of laser light by the material. This absorption can be categorized into linear and nonlinear absorption. Nonlinear absorption such as two-photon absorption and multiphoton absorption occurs when the energies of two or more photons surpass the energy to excite an electron of the target material [46]. Nonlinear absorption usually happens with fs lasers due to having higher fluence per time compared to other longer pulsed lasers [47][48]. As mentioned before in pulsed laser subchapter of the laser ablation chapter, thermal and nonthermal effects occur according to the pulse length of the laser [49].

Removal of ablated material ($t = 10^{-12}$ s to $t = 10^{-10}$ s)

In ms and μ s laser ablation, ablation of material from the target surface usually happens with vaporization of the material. Basically, heating of the material by laser causes the material to reach a critical temperature where ablation of material from the surface occurs. This slow heating from long pulse durations causes a phase change where liquid and gas phase of the target are present. The material is then removed by vaporization. In ns pulsed laser ablation, material is ablated by explosive boiling. In ps and fs laser ablation, material is ablated from the target surface by fragmentation and other similar processes.

Due to its temperature ablated material becomes a plasma plume. The lifetime of the plasma plume is between 10^{-9} s to 10^{-6} s, depending on the properties of the liquid and laser parameters such as energy per pulse and pulse duration [50].

Expansion and shrinking of plasma plume ($t = 10^{-10}$ s to $t = 10^{-7}$ s)

The plasma plume expands due to its high temperature and high energy with respect to the surrounding environment. During this expansion of plasma plume, a shockwave is produced and sent into the liquid [51]. This plasma plume consists of ablated material, liquid solution species such as ionized liquid molecules or vapor of solution, and ions from target and liquid. After expansion, plasma plume reaches an equilibrium point and starts to shrink in size. This shrinking is due to the cooling of the plasma plume since energy is lost to expansion of the plume and the pressure on the plume by the liquid environment. Prolonged laser irradiation (longer pulses) at this stage might result in a longer lifetime for the plasma plume [52]. When plasma plume shrinks to its lowest size, it generates a shockwave and a cavitation bubble is created from the cooled plasma which turned into hot vapor.

Generation and collapse of cavitation bubble ($t = 10^{-6}$ s to $t = 10^{-4}$ s)

The cooled plasma turns into vapor and generates a cavitation bubble from this vapor. Due to the shockwave generated by the collapsed plasma plume, a region with low pressure inside the liquid is formed. Cavitation bubble starts to expand into the low-pressure region. It contains mostly ablated material and liquid vapor. This cavitation bubble expands much longer time than the plasma plume. Although it is not certain, it is believed that the nanoparticle formation takes place in this stage [53]. Cavitation bubble reaches the maximum size when pressure at the bubble liquid boundary comes to an equilibrium. The cavitation bubble then starts to shrink due to the pressure from the liquid. After some time, for example, 100 μ s according to figure 2 below, the cavitation

bubble collapses and generates a second shockwave. With this shockwave, the nanoparticles are released into the surrounding liquid.

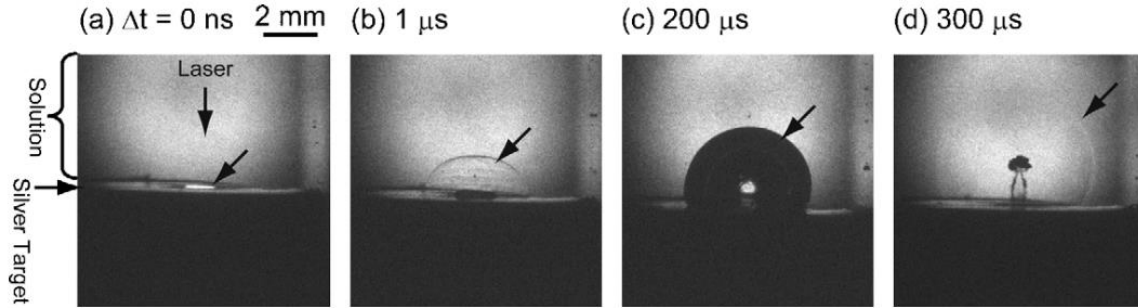


Figure 2: 10-ns resolved shadowgraph images of laser ablation phenomena observed for the 18 mM PVP solution. Some remarkable phenomena were selected: (a) optical emissions, (b) shockwave, (c) cavitation bubble and (d) secondary shockwave generated at the bubble collapse. Adapted from [54].

Agglomeration and slow growth of nanoparticles ($t > 10^{-4}$ s)

After nanoparticles are released to the liquid, they might grow in size by absorbing small atom clusters or small nanoparticles due to a process called Ostwald ripening [55]. Agglomeration of nanoparticles is another way for the growth of nanoparticles where nanoparticles come together and stick to each other to form a nanoparticle cluster. This situation mostly occurs when the colloid is not stable. If the layer of surface charge of nanoparticles is not enough to repulse them, nanoparticles start to agglomerate.

1.6 NANOPARTICLE SYNTHESIS BY PURE MATERIALS AND OPTICAL PROPERTIES

We can categorize the nanoparticles synthesized by LAL method into two categories by the

composition of nanoparticles. The first category would be same composition with the target material such as synthesizing metal nanoparticles such as Au, Ag, Cu, Sn etc., ceramic nanoparticles, carbon nanoparticles, alloy nanoparticles and several others would fall in this category. In this category, ablated materials do not react with the liquid environment. Liquid only affects the nucleation dynamics of the nanoparticles. The second category would be nanoparticles with different composition from the target material. Assuming that the only materials affected by the pulsed laser light are the target material and the liquid, meaning that there is no other material that can join the nucleation process of nanoparticles, liquid molecules can react with the ablated material due to very high temperatures achieved. Examples of these nanoparticles can be metal oxides [56] and nitrides [57], transition metal chalcogenides [58][59].

These nanoparticles have enhanced optical properties. For example, noble metal nanoparticles such as Au, Ag, Cu have plasmonic absorption properties that make them useful for plenty applications. This raises the question of what is optical absorption.

Optical absorption is the absorption of the incident light by a material. There are two general absorption of light: linear and nonlinear absorption. Linear absorption is the absorption of light that increases exponentially with the incident light which is explained by Beer-Lambert law as in Eq.1 below.

$$I(x) = I_0 * e^{-\varepsilon lc} \quad (\text{Eq.1})$$

Where $I(x)$ is the intensity of light after traveling distance x , I_0 is the incident light, ε is the molar absorption coefficient, l is the optical path length in the path of light, and c is concentration of light absorbing material. In linear absorption, the absorbed light increases linearly with the incident light power. The absorption is determined by the electronic structure of the materials. If incident

photon has higher energy than the energy required for an electronic transition in the target material, then the photon is absorbed. A sub-category of this absorption is plasmonic absorption by nanoparticles.

Plasmonic absorption by nanoparticles is a phenomenon that depends on the localized surface plasmon resonance. A plasmon is the oscillation of the free electrons of noble metal nanoparticles. In the surface of plasmonic nanomaterials, plasmons become localized surface plasmons due to much smaller size than the wavelength of incident light. Localized surface plasmons are standing waves that resonate usually in the frequency of UV, visible and near infrared light depending on the nanomaterial size [60] and shape [61] and the dielectric function [60] of the liquid environment. This means that at the resonance wavelength; nanomaterials will absorb light much more than other wavelengths.

Nonlinear absorption is the phenomenon where absorption coefficient changes with the intensity of the incident light, giving it its nonlinearity. Nonlinear absorption originates from high order optical nonlinearities and result in phenomena such as two photon absorption or multiphoton absorption. These phenomena occur with very high light intensities and materials can absorb light with a wavelength they normally do not absorb. Laser ablation with ps and fs laser pulses usually cause nonlinear absorption in the target materials.

Alloy nanoparticle synthesis is another sub-category for synthesis of nanoparticles from pure materials where nanoparticles have the same composition with the target materials. Alloy nanoparticles can be synthesized by an alloy target where nanoparticles would have the same composition with the target material or they can be synthesized by laser fragmentation or laser melting of two or more different metallic nanoparticles. During these types of laser processing of colloid processes, which will be explained in detail in the next chapter, nanoparticles can be melted

or turned into plasma to nucleate together which would form alloy nanoparticles. Alloy nanoparticles synthesized by LAL method are important since during nucleation process, core-shell nanoparticles, biphasic nanoparticles, Janus nanoparticles or hybrid nanoparticles can be synthesized.

Alloy nanoparticles can show tunable optical properties such as tunable LSPR peak [62] and tunable photoluminescence [63]. This makes them valuable for optical applications such that the optical property can be changed by changing the composition of the nanoparticles. In addition, structures such as core-shell nanoparticles or biphasic type Janus nanoparticles can be synthesized by LAL method [62][64].

Photoluminescence property is a vital optical property of nanoparticles. Photoluminescence can be categorized into two categories: down-conversion and up-conversion.

In down-conversion photoluminescence, materials absorb a photon with an energy higher than the electronic transition energy to higher levels. This absorption causes an electron to be excited into higher energy levels. Then excited electrons transfer their energy to neighboring electrons with lower energies. After energy transfer, electron in the conduction band recombines with a hole in the valence band, emitting a photon with lower energy and higher wavelength than the absorbed light [65].

In upconversion photoluminescence, nonlinear optical processes take place. For example, upconversion luminescence can be seen in rare earth ion doped ceramics such as Er^{+3} , Yb^{+3} [66]. Upconversion materials absorb photons such as near infrared light with low energy in a nonlinear absorption. Then, absorbed photons excite these rare earth ions to higher energy levels. These levels are usually are not stable and excited electrons do nonradiative relaxations to more stable

lower levels. At these levels, nonlinear optical processes start where excited ions interact with each other to transfer energy between them. This results in the return of the excited electrons to ground state accompanied by an emission of a photon with higher energy and lower wavelength than the incident light.

Down-conversion and upconversion photoluminescent nanoparticles have found themselves a great deal of use in applications such as bioimaging [67], biosensing, optoelectronics and anti-counterfeiting [68].

1.6.1 Nano-compound Synthesis by Laser Ablation in Liquid Method

The second category of synthesized nanoparticles by LAL method is compound synthesis where ablated materials react with the liquid environment by the impact of laser light. This method allows the synthesis of compounds of oxides [69], hydroxides [69], nitrides [57], sulfides [70] etc., with a suitable liquid that can react with the pure target material. The target can also be a compound or it can be a pure elemental target. It is important that the target should also be able to react with the liquid. For example, while laser ablation of Au target in DMSO yields Au nanoparticles [71] meaning no reaction with the liquid occurs, laser ablation of Cu target in DMSO yields copper sulfide nanoparticles [70]. The high temperature and pressure make it possible for the liquid and ablated material to react with each other.

The nano-compound nanoparticles have many applications. Photothermal therapy (PT) and photoacoustic imaging (PAI) are promising applications of nano-compound nanoparticles. Examples of these include iron oxide [72] for PT, and copper sulphide for PT [73] and PAI [74].

Photothermal therapy by nanoparticles is an emerging field of research with a promising future. As the name suggests, nanoparticles are used to absorb photons to generate thermal effect in living

cells, mostly tumors and cancer cells to kill them. Most of the cells die when their internal temperature rises above around 42°C. However, it is also important to keep live cells and tissues alive. Heating with lasers would cause the death of healthy cells too. As a solution to this, lasers with a wavelength that do not harm living cells should be chosen. This wavelength range is called second near infrared biological window of wavelengths which correspond to range of 1000 – 1350 nm. This range offers deep penetration depth, reduced tissue scattering and optical absorption by living cells as water absorb minimally in this range. PT works by localized heat generation so that nanoparticles must have a high absorbance in this window. In addition, nanoparticles themselves should be nontoxic so that only the combination of laser light and nanoparticle interaction would cause the death of unhealthy cells. Our work on copper sulphide nanoparticles (CSNP) shows great promise as a nontoxic PT agent. The results of our work are given in the results chapter.

Another promising application is photoacoustic imaging. In PAI, nanoparticles are used to enhance the acoustic imaging process. Like in PT, nanoparticles absorb the incident laser light. This causes a rapid heat generation by nanoparticles. Because of this rapid absorption of energy, nanoparticles experience a thermal expansion which causes the generation of acoustic waves. These acoustic waves then can be detected by an ultrasonic transducer and converted into an image. This would allow to image tissues by PAI. Like in PT, the laser light should be unarmful to the tissue so a proper wavelength and laser power should be chosen for imaging. CSNP are a great candidate also for PAI. Nanoparticles, especially CSNP, can improve contrast and resolution compared to ultrasound imaging.

1.7 POST TREATMENT OF NANOPARTICLES

Depending on the application, nanoparticles obtained by LAL method might be subject to a post treatment. These post treatments could be done to modify their size and size distribution, shape, increase colloidal stability, or to change the environment they are in. Physical separation methods are usually used in this step are centrifugation and drying. Centrifugation is used to separate nanoparticles from the liquid environment by a sedimentation process. By controlling the revolution of centrifugation device, size distribution control can also be achieved. Large aggregates and nanoparticles can be easily removed with a short centrifugation process. Drying can be performed on the colloid to obtain nanoparticles in a powder form. This is also used in a drop casting method to prepare solid samples for characterization purposes where drops from the colloid are dried on a solid substrate such as glass or silicon wafer by using a hot plate to evaporate the liquid.

To increase the colloidal stability of the nanoparticles and to protect the nanoparticles from aggregation and agglomeration, surface modification can be implemented. This can be done by adding chemical stabilizers into the colloid. This addition can be done before or after the synthesis of nanoparticles. For example, adding polyethylene glycol (PEG) which is a biocompatible polymer into gold colloid in water [75] can increase their colloidal stability and enhance their biocompatibility.

There are other methods which are done by pulsed lasers to control the size and shape of the nanoparticles. These methods are called Laser Melting in Liquids (LML) and Laser Fragmentation in Liquids (LFL) where the low intensity laser light and high intensity laser light are used respectively.

1.7.1 Laser Melting in Liquids

Laser melting in liquids (LML) [76] can be used as a post-treatment of nanoparticles synthesized by laser ablation. The attention of nanoparticle synthesis is usually on synthesizing smaller nanoparticles. However, bigger nanoparticles have some advantages that make them useful for several purposes. Submicrometer particles have enhanced blood circulation time, also known as enhanced permeability and retention effect, which is relevant for targeted drug delivery [77]. Large particles have also lower cytotoxicity [78], which is also important for therapeutic applications of nanoparticles. Large nanoparticles have also enhanced optical and magnetic properties due to stronger absorption of laser light. Thus, it is vital to understand the mechanisms of synthesizing larger nanoparticles by LML process.

LML process is used to increase the sizes of nanoparticles dispersed in liquid solution. The usual requirement for this process is that nanoparticles should be agglomerated for efficient LML process. When unfocused low intensity pulsed laser light (ns laser pulses) is used to irradiate a colloid with agglomerated particles, laser pulse melts the particles on the way of laser beam. The localized beam breaks up the agglomerated nanoparticles, melt them, and then the reassembly of these particles lead to the synthesis of submicrometer particles. In this process, it is important to have a low stability colloid to trigger agglomeration process. Tsuji et al. synthesized gold submicrospheres from gold nanoparticles stabilized by citrate solution. While 0.01 mM, and 0.005 mM result in the synthesis of submicrospheres of sizes around 200 nm, 1 mM, 0.05 mM concentration of citrate solutions do not allow the synthesis of submicrospheres [76].

Other than size increase, LML can be used to reshape nonspherical nanoparticles. Nanoparticles with different shapes can be melted with LML process with a lower laser intensity than size increase process and can be turned into spherical nanoparticles [40]. This could be important for

shape dependent applications such as plasmonic absorption.

Typical laser parameters for LML process requires low laser pulse fluence ($<150 \text{ mJ/cm}^2$), which allows to use unfocused pulsed laser light, ns pulse durations to heat nanoparticles. UV-Vis-NIR wavelengths can be used in LML process but UV wavelengths are more advantageous since most materials absorb UV light efficiently than visible or NIR light.

1.7.2 Laser Fragmentation in Liquid

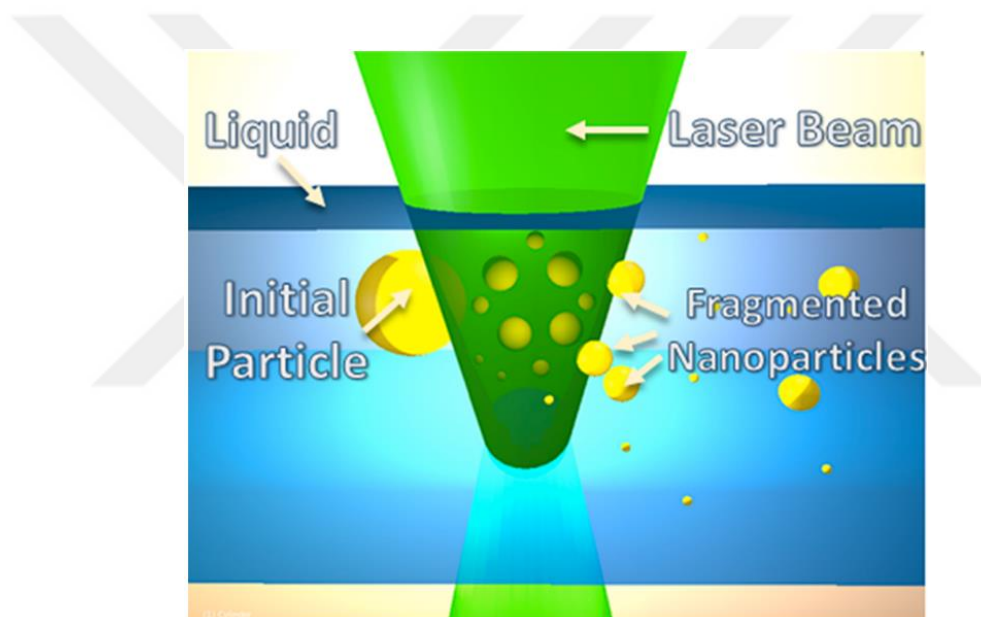


Figure 3: Scheme of LFL. An initially micrometer- or nanometer-sized (not necessarily spherical) particle suspension or colloid is fragmented by a laser beam into smaller NPs. Adapted from [40].

Laser fragmentation is the process of fragmenting powder particles or nanoparticles in a colloid to achieve smaller sized nanoparticles. Compared to low intensity laser irradiation of LML process, laser fragmentation in liquid (LFL) is a high intensity process due to the need of fragmenting larger particles. A typical LFL setup requires a pulsed laser (ranging from fs to ns pulse duration), from UV to NIR laser wavelengths and fluences above fragmentation threshold, focusing optics to

achieve high intensity at focal spot, and usually a stirrer to stir the nanoparticles inside liquid to the laser beam. Fs lasers have clear advantage due to high intensity power achieved by ultrashort pulse durations. The focusing lenses are usually chosen with long focal lengths such as 100 mm so that focused laser beam inside the liquid would have a nearly evenly intensity distribution. This is important to have a homogeneous fragmentation of particles. Other than size reduction, LFL process can also reshape the nanoparticles into spherical shape due to similar physics of the LAL process.

The mechanisms of size reduction in LFL process are photothermal vaporization [79] and Coulomb explosion [80]. In photothermal vaporization, nanoparticles experience very rapid heating and this causes a bubble formation around the nanoparticle due to liquid vaporization around the nanoparticle. Then, this bubble creates an environment for the nanoparticle which is also in vapor or plasma form to coagulate and solidify. These new solidified nanoparticles come out much smaller than the initial fragmented nanoparticle. This phenomenon is usually seen with ns pulsed lasers due to melting-evaporation process. In Coulomb explosion, pulsed laser light turns nanoparticles into highly charged nanoparticles due to electron ejection. Then, charged nanoparticle are fragmented from the inside by exploding due to becoming unstable by the Coulombic charge repulsion forces which prevail against cohesive forces that keep nanoparticle intact. This is usually seen with ultrashort pulsed lasers.

The efficiency of LFL process depends on parameters such as laser wavelength, laser pulse duration, laser fluence, pulse repetition rate, revolution rate or speed of the nanoparticles, nanoparticle concentration of the colloid, focal spot size, properties of the material such as boiling point and properties of the liquid.

2 ALLOY NANOPARTICLE SYNTHESIS

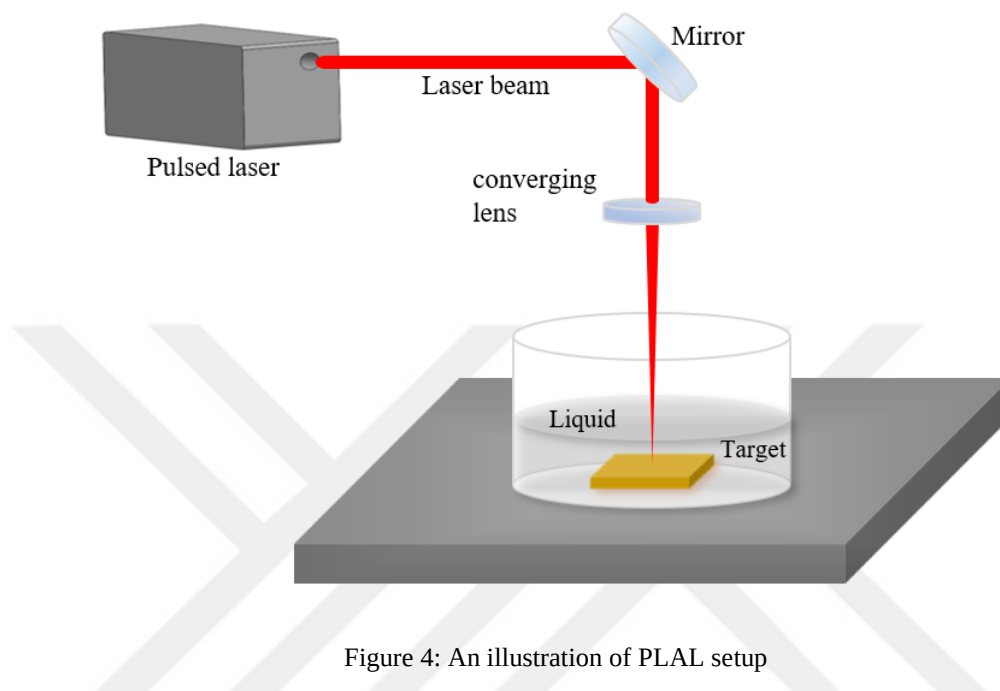


Figure 4: An illustration of PLAL setup

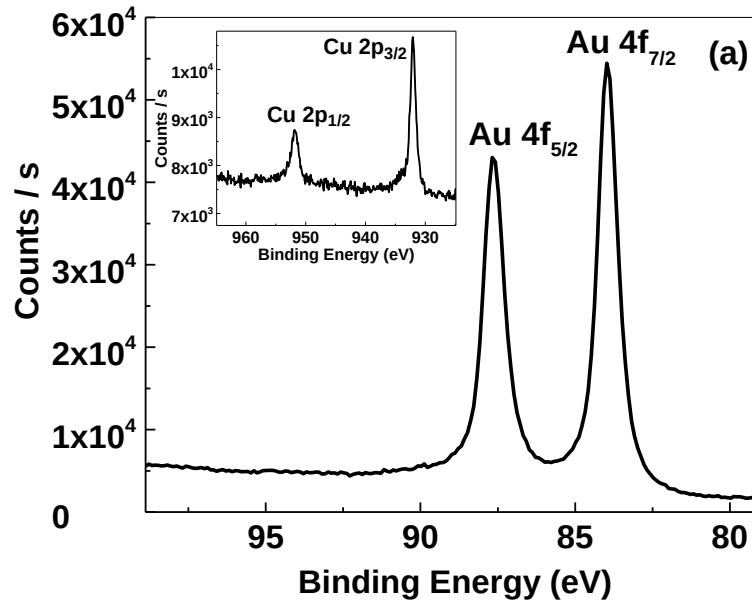
In this thesis, all nanoparticles are synthesized by pulsed laser ablation in liquid (PLAL) method. There are two projects regarding alloy nanoparticles synthesis. First, AuCu alloy nanoparticles were synthesized by PLAL method in methanol for photovoltaic applications. Second, AgCu nanoparticles were synthesized in ethanol for tunable optical properties.

2.1 AuCu ALLOY NANOPARTICLE SYNTHESIS

The experimental setup for AuCu nanoparticles (NP) synthesis consist of a Q-switched nanosecond pulsed laser, a converging lens for focusing, the AuCu target, the cuvette for liquid, and methanol. All materials are bought commercially and used without further treatments. The pulsed laser (Empower, Q-switched laser, Spectra Physics) has parameters of 527 nm wavelength from a Nd:YLF crystal, 100 ns pulse duration, 1 kHz repetition rate. The laser was operated at 15 W average power which corresponds to 15 mJ energy per pulse. The laser beam was focused with

a 50 mm plano-convex lens onto the target which is immersed inside the methanol and placed at the bottom of the quartz cuvette. The AuCu target was bought commercially and has 90% Au and 10% Cu. The ablation process is carried out for 5 minutes. The target and the cuvette were cleaned with acetone and then in distilled water ultrasonic bath for 3 minutes. A colloidal solution with 0.512 mg/mL concentration of NP was synthesized in 10 mL of methanol. The resulting colloid had dark purple color. Due to high concentration of NP, the synthesized colloid was used immediately after synthesis in solar cell fabrication.

The characterization of AuCu NP was done with X-Ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscope (SEM), High Resolution Transmission Electron Microscope (HRTEM) and UV-Vis-NIR Spectrophotometer. The elemental composition of the gold target and the synthesized NP was done by XPS measurements. The XPS instrument K-Alpha (Thermo Scientific) operated at 12 kV and 2.5 mA. The XPS sample was prepared by drop casting on a Silicon (Si) wafer substrate.



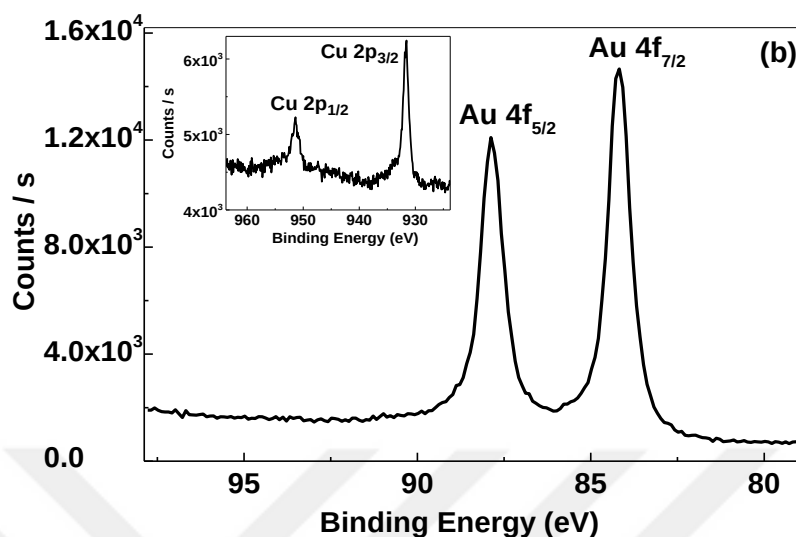


Figure 5: XPS spectrums of (a) the target sample and (b) colloidal NP solution

Fig.5(a) shows the XPS spectrum of Au element of the target sample and Fig.5(b) shows the XPS spectrum of Cu element of the synthesized NP. The target sample and nanoparticles are scanned for Au and Cu peaks due to their composition. The target sample have peaks at 84.15 eV and 87.65 eV for Au. These peaks correspond to $4f_{7/2}$ peak and $4f_{5/2}$ peaks respectively. The inset of Fig.5(a) show XPS spectrum of Cu element. The peaks are at 932.2 eV and 951.9 eV. These peaks correspond to $2p_{3/2}$ and $2p_{1/2}$ peaks respectively. The areas of XPS spectrum for Au and Cu elements are calculated and the result shows that the target sample have 90% Au and 10% Cu. Therefore, it was determined that this target can be used for its plasmonic feature in photovoltaic applications. Fig.5(b) shows the values for binding energies of Au and Cu for synthesized NP from the target sample in methanol. Au has two peaks at 84.35 eV and 87.85 eV. These values correspond to $4f_{7/2}$ peak and $4f_{5/2}$ peak respectively. The inset of Fig.5(b) shows the Cu spectrum for synthesized nanoparticles. The peaks are at 931.5 eV and 951.2 eV. These peaks correspond to $2p_{3/2}$ and $2p_{1/2}$ peaks respectively. The integrated areas also show 90% Au and 10% Cu elemental

composition for nanoparticles. This shows that the target and nanoparticles have same elemental composition.

The synthesized nanoparticles are imaged by SEM and TEM. FEI-Quanta 200 FEG model was used for SEM images, while FEI Technai G2 F30 TEM was used for the TEM images.

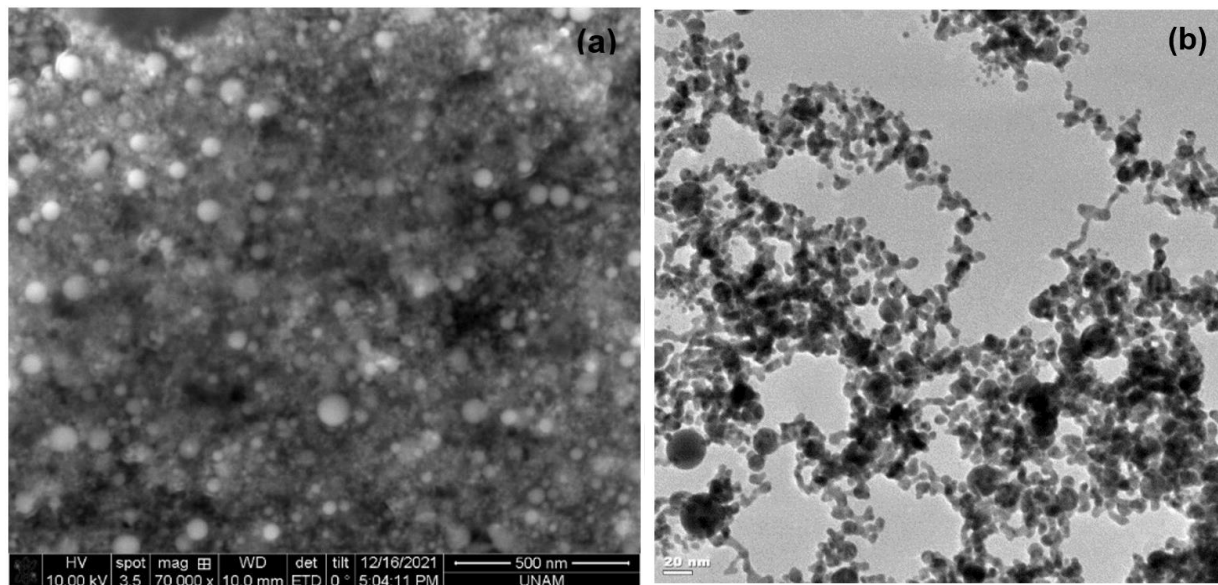


Figure 6: SEM (a) and TEM (b) images of AuCu nanoparticle colloid generated by pulsed laser ablation in methanol.

Figure 6(a) shows the image of nanoparticles taken by SEM, and Figure 6(b) shows the image taken by TEM. The SEM image is taken at secondary electron mode with 10 kV voltage, 3.5 spot size, 70000x magnification, and 10.0 mm working distance. The scale bar is at 500 nm. The SEM image shows that most of the nanoparticles are below 50 nm in diameter and have spherical shapes. Most of the nanoparticles are so small that SEM cannot image them properly and they are seen as grainy layers of gold. However, there are also some bigger particles, showing two ablation mechanisms from the PLAL method resulting in bimodal size distribution [41]. The TEM image in Figure 6(b) shows AuCu nanoparticles. The nanoparticles have spherical shapes and some of

the nanoparticles show a chainlike formation. There is a visible aggregation of nanoparticles. However, Au nanoparticles are known for their colloidal stability due to their high surface charge [81]. This could be attributed to the incorporation of Cu in Au nanoparticles, lowering the surface charge, thus reducing surface potential, causing aggregation and agglomeration. The absence of stabilizers and high concentration of the colloid also contributes to the aggregation of nanoparticles. This means high concentration would result in higher collisions of nanoparticles inside the liquid, leading to a higher probability of aggregated and agglomerated cluster formation.

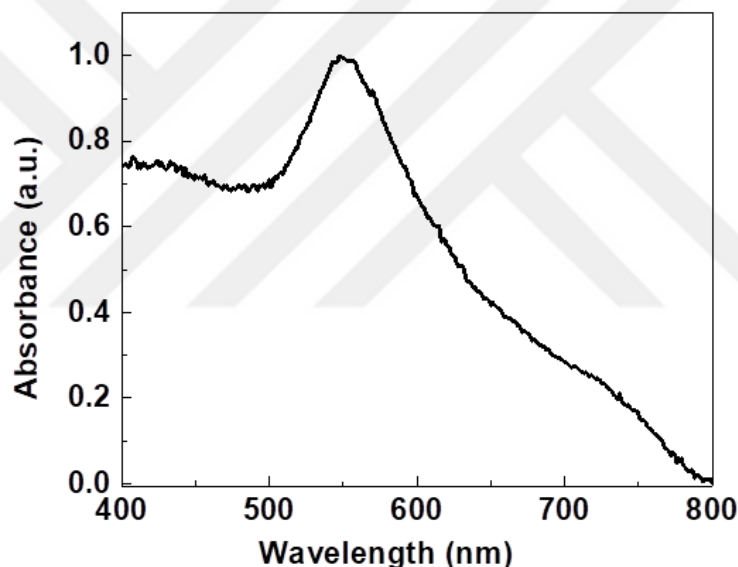


Figure 7: Visible absorbance graph of synthesized nanoparticles

Figure 7 shows the absorbance graph of synthesized nanoparticles in the visible range (400-800 nm). The Cary 5000 UV-Vis-NIR Spectrophotometer was used to measure the solution's absorption spectra. Double beam mode was utilized after baseline correction. Between two observations at the same wavelength, there was an average delay of 0.100 seconds. The LSPR peak of nanoparticles is at 548 nm. In our situation, the incorporation of Cu in Au increased the peak wavelength from around 520-525 nm for Au nanoparticles to 548 nm. The absence of a peak

around 600 nm, the LSPR wavelength of Cu nanoparticles, shows that the concentration may not be enough for this peak to be visible in the graph or that these nanoparticles might be incorporated inside gold nanoparticles.

2.1.1 Photovoltaic Characterizations of Solar Cells

This work is done by Çirpan Research Group at Middle East Technical University. All designs, measurements, and characterizations stated in this subchapter belong to those who worked on this project. These results are published in the Journal of Dyes and Pigments. The figures and data are adapted from this article. [82]

The synthesized AuCu nanoparticles show LSPR effect similar to Au nanoparticles. Thus, it was determined that these nanoparticles could be used as Au nanoparticles in solar cells. After the synthesis and characterization of nanoparticles, they are used to boost the efficiency of organic solar cells. This is done by embedding the synthesized nanoparticles into the active layer of the solar cells without changing the thickness of this layer to achieve higher photocurrent production. The active layer of the organic solar cells (OSCs) contains a polymeric p-type donor material and a fullerene-based n-type acceptor material (PC₇₁BM). This will be achieved by the localized surface plasmon resonance effect of the AuCu nanoparticles. These photovoltaic characterizations are done to 5 different OSCs. These are benzoxadiazole bearing polymer (POxT), its bromine (POxT-Br) and thiol (POxT-SH) comprising derivatives, POxT-SH: %0.171 AuCu nanoparticles by mass and POxT-SH: methanol.

Figure 7 in [82] shows these OSCs' current density (J) versus voltage (V) curves. From this graph, parameters such as open circuit voltage V_{oc} , short circuit current density J_{sc} , and fill factor FF are calculated. From the values of these parameters, power conversion efficiency (PCE) can be calculated. Table 1 shows the summary of these values for the five different OSCs.

	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)
POxT: PC ₇₁ BM	0.70	3.49	52.8	1.29
POxT-Br: PC ₇₁ BM	0.65	3.30	36.5	0.78
POxT-SH: PC ₇₁ BM	0.80	5.57	60.9	2.71
POxT-SH: PC ₇₁ BM, %0.171 AuCu NPs	0.78	6.52	64.5	3.29
POxT-SH: PC ₇₁ BM, methanol	0.80	4.17	54.3	1.82

Table 1: Summary of photovoltaic parameters V_{OC} , J_{SC} , FF, and PCE

As table 1 shows, POxT-SH shows better results than other OSCs that does include gold NPs. This is due to well defined active layer morphology with aligned polymer domains of this OSC.

Due to its enhanced photovoltaic performance, nanoparticles are embedded in POxT-SH OSC. The design of thiol incorporated molecular design of POxT-SH is expected to reverse the NP assisted recombination in the active layer which would result in lower PCE. This way, the LSPR effect of our nanoparticles can be utilized. %0.171 AuCu NPs by mass is determined to be utilized due to showing higher photovoltaic performance. The addition of our nanoparticles enhanced the charge carrier generation and transport by LSPR effect and improvement in morphology. In addition, the effect of the liquid where nanoparticles are synthesized should be determined. Pure methanol treatment of POxT-SH OSCs showed quite lower PCE value than NP-incorporated OSC. This indicates that enhanced photovoltaic performance could be attributed to the plasmonic effect of our nanoparticles and their interaction with the polymer.

Figure 8 in [82] shows produced OSCs' external quantum efficiency (EQE) versus wavelength graph to verify J_{SC} values. EQE is the value of produced electrons by the impact of incident photons on the solar cell. As it can be seen from the graph, thiol-modified gold NP incorporated OSCs have the highest EQE value.

2.2 AgCu ALLOY NANOPARTICLE SYNTHESIS

Alloy targets and their EDS analysis are produced by Can Okuyucu at Structure and Dynamics Metals Laboratory at Metallurgical and Materials Engineering department, Middle East Technical University led by Prof. Dr. Yunus Eren Kalay.

Nanoparticles have attracted great attention with the emergence of nanotechnology and the increase in their usability in different areas such as electronics [83], solar cells [82], targeted drug delivery [84] and many other areas and continue to increase. One of the reasons for this increased attention to nanoparticles is their changing optical properties concerning their bulk counterparts. The optical properties of nanoparticles may change depending on their size and shape. Laser ablation in liquid technique can be utilized to synthesize and realize the potential use of alloy nanoparticles in optical applications [60]. The post treatment by the laser fragmentation technique on nanoparticles colloids present the opportunity to shift optical absorption behavior due to the particle size change, composition change and morphology transformation effects [85][86][64]. This is achieved by changing the average size of the nanoparticles resulting in change of the peak wavelength of LSPR effect, changing the composition of the nanoparticles resulting in a change of the alloy LSPR behavior.

In this study, alloy nanoparticles of AgCu alloys were synthesized by femtosecond pulsed laser ablation method in ethanol. Ag and Cu alloy targets ($\text{Ag}_{1-x}\text{Cu}_x$, $x = 0.15, 0.30, 0.50, 0.70, 0.85$) were produced using pure Ag and Cu targets by arc melting method. Compositions of targets were chosen accordingly to control the nature of the resulting nanoparticles. Laser ablation and laser fragmentation processes are done by 1 kHz, 150 fs laser at 500 mW and 250 mW power and stirring at 100 rpm.

2.2.1 Laser Ablation of Alloy Targets

Nanoparticles are synthesized by immersing alloy targets ($\text{Ag}_{1-x}\text{Cu}_x$, $x = 0.15, 0.30, 0.50, 0.70, 0.85$) into 2.5 mL ethanol. 2.5 mL ethanol was used to decrease the length between the surface of the liquid and the surface of the target which increases the productivity of laser ablation process [87]. The laser has 150 fs pulse width, 1 kHz repetition rate. An average power of 500 mW was used for ablating alloy targets. This corresponds to 500 μJ pulse energy per pulse. Targets were cleaned with ethanol and distilled water before using in PLAL process. The ablation process takes about 15 minutes. Fig. 10 shows an illustration of the PLAL setup for nanoparticle synthesis from alloy targets. The laser beam from fs laser is directed with a mirror and focused with a 50 mm converging lens onto the target. Synthesis of targets high in copper gives a brown color while targets high in silver gives a yellow colored colloid. Figure 9 and figure 10 shows photographs of colloids of alloy nanoparticles with high Cu content and high Ag content respectively.

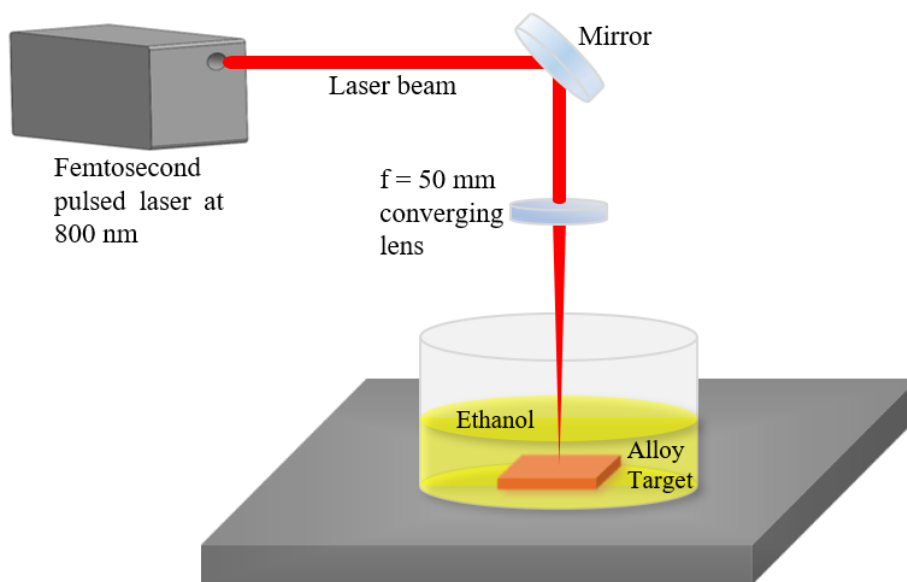


Figure 8: Illustration of the PLAL experimental setup for alloy targets

The crystal structure of the alloy targets are identified by X-ray diffraction analysis (Panalytical X'Pert PRO Multipurpose Diffractometer). The radiation source for the X-rays is $\text{CuK}\alpha$, the operating voltage was 45 kV and the used current was at 40 mA. The targets are placed on XRD analysis dough and the top surface of the target is pressed with a glass slide to even out the height of the target and the analysis plate to collect optimum XRD signal. The images of the nanoparticles were taken by using a scanning electron microscope (SEM). The operation voltage was varied between 5 kV to 30 kV. The samples were prepared by drop casting the nanocolloid prepared by laser ablation to a Si wafer for SEM imaging. The Energy Dispersive X-Ray Spectroscopy (EDS) measurements are taken at 20.0 kV, using the EDS mode of SEM. The optical absorption spectra were taken by using the synthesized nanocolloid. The spectra of the nanocolloid were recorded in a quartz cuvette using a spectrophotometer (Varian Cary 5000 UV/Vis/NIR spectrophotometer).



Figure 9: Alloy nanoparticles with high Cu content



Figure 10: Alloy nanoparticles with high Ag content

2.2.2 Characterization of Alloy Targets

After the production of alloy targets from pure Ag and Cu metals, EDS measurements are taken at 20.0 kV. The results in Fig. 11 show that atomic composition of the alloy targets are (15.15 % Ag, 84.85% Cu), (30.53% Ag, 69.47% Cu), (50.65% Ag, 49.35 Cu), (70.25% Ag, 29.75 Cu), (86.33 Ag, 13.67 Cu). Since Cu and Ag are not fully immiscible together, a small variation of target

composition in different regions of the target is expected. Nevertheless, all the targets are compositionally close to their assigned composition values. The target photographs in Figure 12 show that high Ag content targets look grayish like a pure silver target and high Cu content targets start to look browner colored.

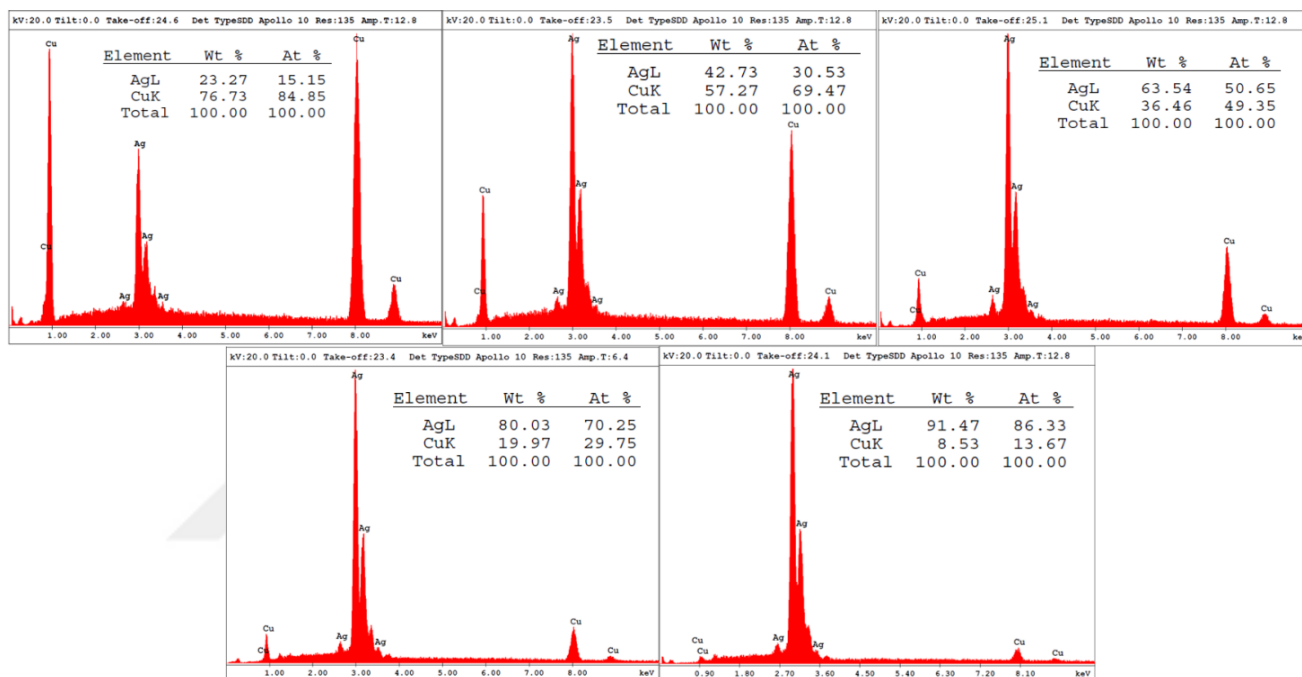


Figure 11: EDS measurements of alloy (Ag_{1-x}Cu_x, X = 0.85, 0.70, 0.50, 0.30, 0.15) targets

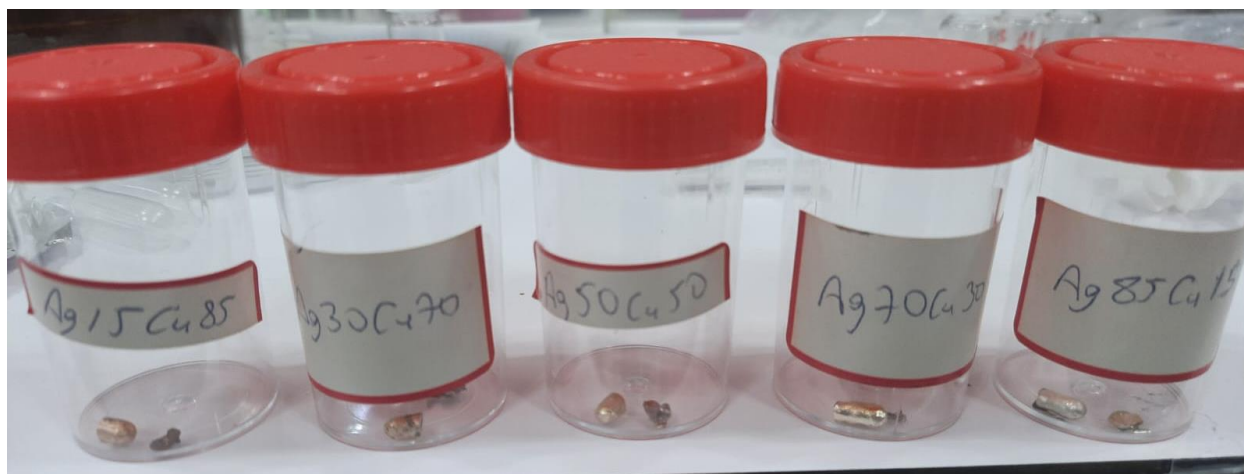


Figure 12: Photograph of alloy targets

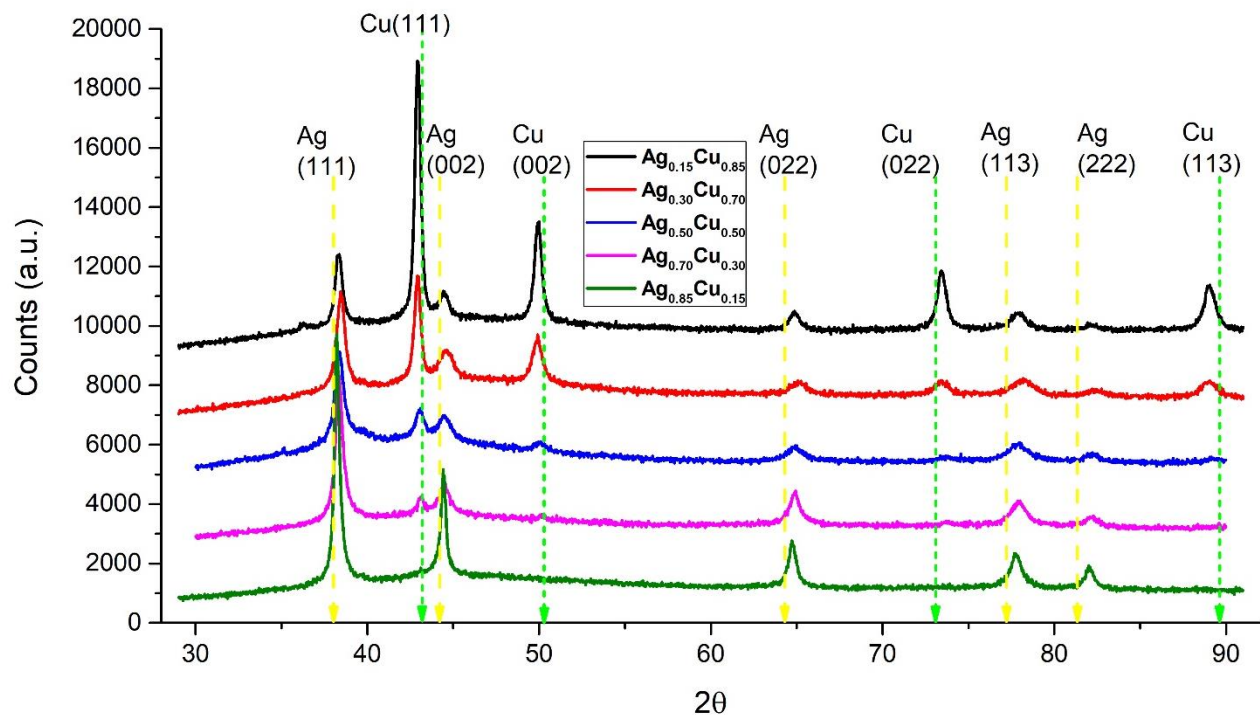


Figure 13: XRD patterns of alloy targets

	Ag (111)	Cu (111)	Ag (002)	Cu (002)	Ag (022)	Cu (022)	Ag (113)	Ag (222)	Cu (113)
Ag_{0.15}Cu_{0.85}	38.306	42.906	44.442	49.917	64.852	73.370	77.882	82.022	88.950
Ag_{0.30}Cu_{0.70}	38.441	42.902	44.540	49.873	65.081	73.370	78.094	82.366	88.935
Ag_{0.50}Cu_{0.50}	38.340	43.041	44.443	50.024	64.886	73.643	77.829	82.189	89.076
Ag_{0.70}Cu_{0.30}	38.339	43.086	44.482	50.142	64.844	73.681	77.876	82.099	--
Ag_{0.85}Cu_{0.15}	38.197	43.220	44.404	51.599	64.691	--	77.706	81.978	--
Cu ref		43.191		50.300		73.888			89.622
Ag ref	38.039		44.210		64.305		77.223	81.352	

Table 2: Peak positions of all alloy targets and indices

The crystal structure of the alloy targets was first confirmed by an XRD study and presented in Figure 13. Count values were increased by 2000 counts between each target for better visualization. This means the increase of count value in $\text{Ag}_{0.15}\text{Cu}_{0.85}$ by 8000, $\text{Ag}_{0.30}\text{Cu}_{0.70}$ by 6000, $\text{Ag}_{0.50}\text{Cu}_{0.50}$ by 4000, $\text{Ag}_{0.70}\text{Cu}_{0.30}$ by 2000. The reference lines for Ag are shown with yellow lines, and for Cu are shown with light green lines in the graph. The 2θ values of the peaks of all alloy targets are given in Table 2. These values can be indexed as Ag (111) at 38.039, Cu (111) at 43.191, Ag (002) at 44.210, Cu (002) at 50.300, Ag (022) at 64.305, Cu (022) at 73.888, Ag (113) at 77.223, Ag (222) at 81.352, and Cu (113) at 89.622 degrees according to ICDD 98-018-0878 for silver and ICDD 98-005-3246 respectively. According to references, Ag and Cu have cubic crystals and belong to the Fm-3m space group, 225 space group number. Reference pure silver has $a=b=c=4.0940 \text{ \AA}$, while reference copper has $a=b=c=3.6250 \text{ \AA}$. Ag peaks show a shift to higher angles while Cu peaks show a shift to lower angles. In the case of Ag, this means the interatomic spacing has decreased due to alloying with Cu, a smaller element than Ag. This causes tighter packing of atoms in the crystal which causes the interatomic distance to decrease and the angle shifts to the right. In the case of Cu, we can see a shift to lower angles which means interatomic spacing has increased due to alloying with Ag, a larger element than Cu. Alloying Cu with Ag causes the lattice of the crystal to expand and increases the interatomic distances. This causes the XRD peaks to shift to left.

2.2.3 Laser Ablation of Alloy Targets

Nanoparticles are synthesized in ethanol with all of these alloy targets. The first characterization method is measuring their absorbance properties due to their plasmonic properties. Figure 13 gives the normalized absorbances of the PLAL synthesized nanoparticles in the range of 300-800 nm.

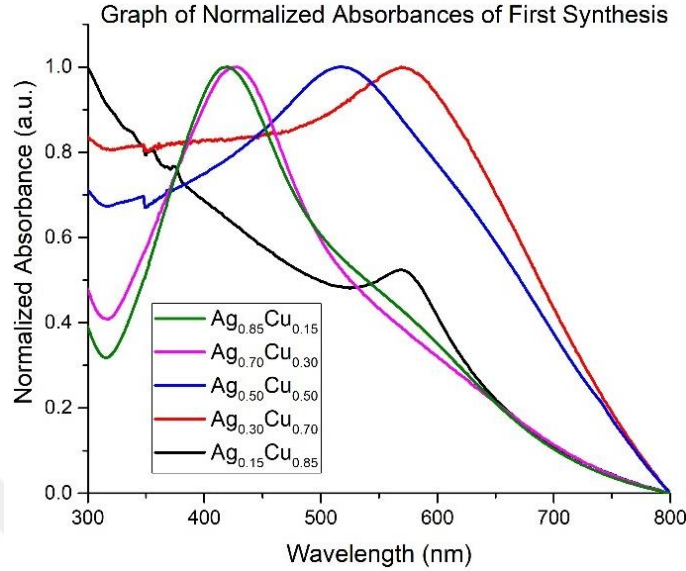


Figure 14: Graph of normalized absorbances of laser ablated alloy nanoparticles

The absorbance graph shows the plasmonic properties of Ag, Cu, and AgCu alloy nanoparticles. $\text{Ag}_{0.85}\text{Cu}_{0.15}$ has its plasmonic peak at 419 nm, $\text{Ag}_{0.70}\text{Cu}_{0.30}$ has its peak at 428 nm, $\text{Ag}_{0.50}\text{Cu}_{0.50}$ has its peak at 519 nm, $\text{Ag}_{0.30}\text{Cu}_{0.70}$ has its peak at 569 nm, and $\text{Ag}_{0.15}\text{Cu}_{0.85}$ has its peak at 569 nm. It is apparent that by changing the composition of the alloy target, the LSPR wavelength can be tuned. In our case, this tunability is roughly between 400 nm to 600 nm, corresponding to 200 nm tunability since plasmonic peak of Ag is around 400 nm and the plasmonic peak of Cu is approximately 600 nm. Increasing Cu content creates a redshift of the plasmonic peak, while increased Ag content creates a blue shift. Other than plasmonic peak wavelength change, the shapes of the peak also change with the composition of the nanoparticles. $\text{Ag}_{0.50}\text{Cu}_{0.50}$ and $\text{Ag}_{0.30}\text{Cu}_{0.70}$ have broad absorbances between 300 nm to 700 nm, giving a broad absorption in visible wavelengths.

The SEM images of nanoparticles prepared by laser ablation are also taken for morphological analysis. The nanoparticles show core-shell type and biphasic type configurations in the images.

Ablation time, target composition and concentration of nanoparticles affects the resulting images of nanoparticles.

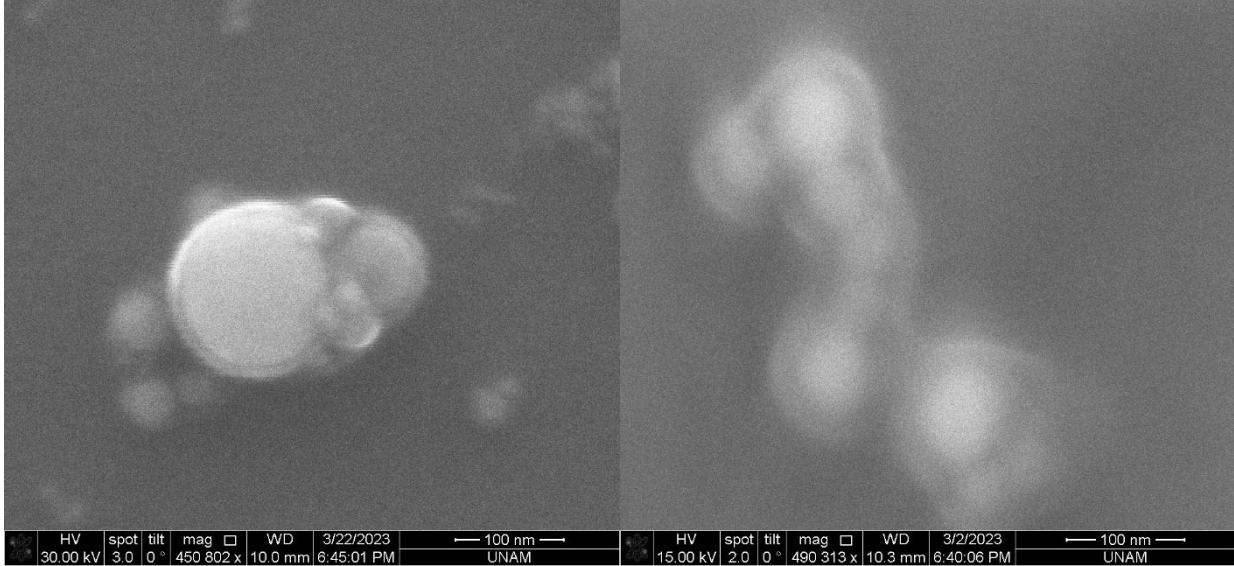


Figure 15: Core-shell type $\text{Ag}_{0.15}\text{Cu}_{0.85}$ and $\text{Ag}_{0.30}\text{Cu}_{0.70}$ alloy nanoparticles

The literature also confirms [64] that when Cu content is higher in AgCu alloy nanoparticles, the resulting nanoparticles have a core-shell type configuration. The SEM images also show that the shell thickness of the nanoparticles increase, which results from increased Ag in the composition. In this configuration, Cu forms the core and Ag forms the shell of the nanoparticles. This is also evident since melting point of Cu is 1085 °C, while melting point of Ag is 962 °C. We know that while nanoparticles are formed in PLAL method, they transform from solid into vapor or plasma phase and then cool into solid temperatures, meanwhile forming the nanoparticles. This would result in Cu solidifying before Ag, giving solid core Ag in melted Ag pool. When Ag also solidifies, they form the shell of the nanoparticles. Although SEM cannot image the smallest particles, the sizes of the nanoparticles that are distinguishable are small enough.

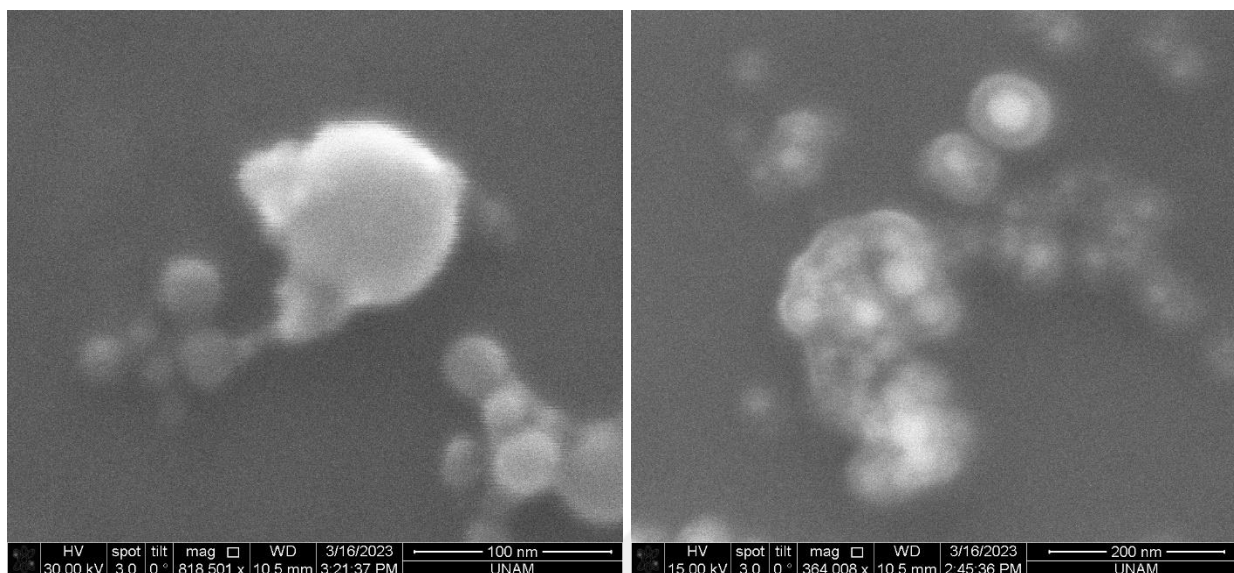


Figure 16: SEM images of $\text{Ag}_{0.85}\text{Cu}_{0.15}$ alloy nanoparticles (biphasic type and core-shell type)

When Ag content is higher in AgCu alloy nanoparticles, the expected morphology is biphasic type nanoparticles. In first image of Figure 16, we can see snowman and dumbbell type biphasic Janus nanoparticles. However, the second image shows core-shell type $\text{Ag}_{0.85}\text{Cu}_{0.15}$ alloy nanoparticles. This is different from the literature since high Ag containing AgCu alloy nanoparticles show single phase or biphasic type configurations [64]. We understood that an oxide shell is formed due to ablation in ethanol. Although not as oxidizer as water, ethanol can also cause nanoparticles to form an oxide layer or fully oxide the nanoparticles as we will see in the fragmentation chapter by the change in the absorbance of the nanoparticles. This means the resulting particles can be AgCu dumbbell or snowman type biphasic Janus nanoparticles or they can be single phase AgCu nanoparticles with an oxide layer. We believe this oxide layer is composed of copper oxide shell since the plasmonic property of Ag is protected in this configuration. We can conclude that the oxide layer is an oxide compound of Cu, due to absorbance data and SEM images.

2.2.4 Laser Fragmentation of Alloy Nanoparticles

After laser ablation of alloy targets in ethanol and producing alloy nanoparticles, we implemented a laser fragmentation process. The optical absorbance data and SEM images are recorded from this process. Fragmentation time was used as a parameter to control the absorbance of alloy nanoparticles. Figure 17 shows an illustration of the laser fragmentation process where alloy nanoparticles are stirred with a magnetic stirrer and 800 nm fs laser light is focused in the middle of the liquid to fragment the nanoparticles in the liquid.

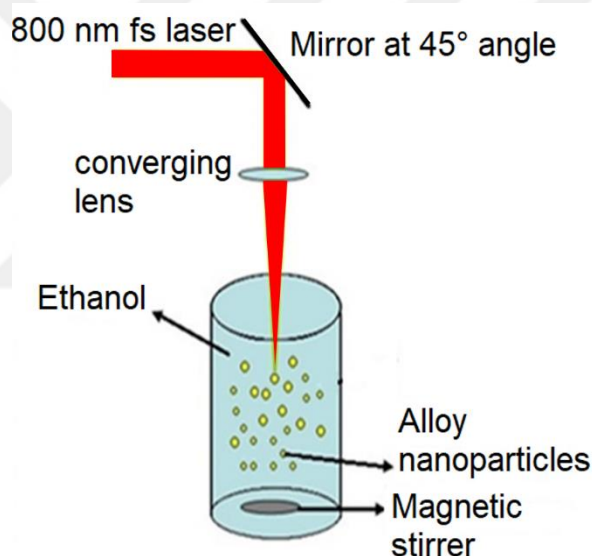


Figure 17: Experimental setup for laser fragmentation process by PLFL method

After laser ablation process in 2.5 mL ethanol for 10 – 15 minutes, PLFL process is started. An additional 2.5 mL of ethanol is added to increase the liquid content of nanocolloid. This is needed to decrease the concentration of the nanoparticles that would join the fragmentation process and for a proper PLFL process since the laser light would be focused into the middle of the liquid. The average power of the laser was 500 mW for the duration of PLFL. 50 mm lens was used to focus the laser light.

Absorbance study and SEM study is done for laser fragmented nanoparticles. Absorbance study of laser fragmented alloy nanoparticles show a great promise in tunability of plasmonic absorbance of alloy nanoparticles.

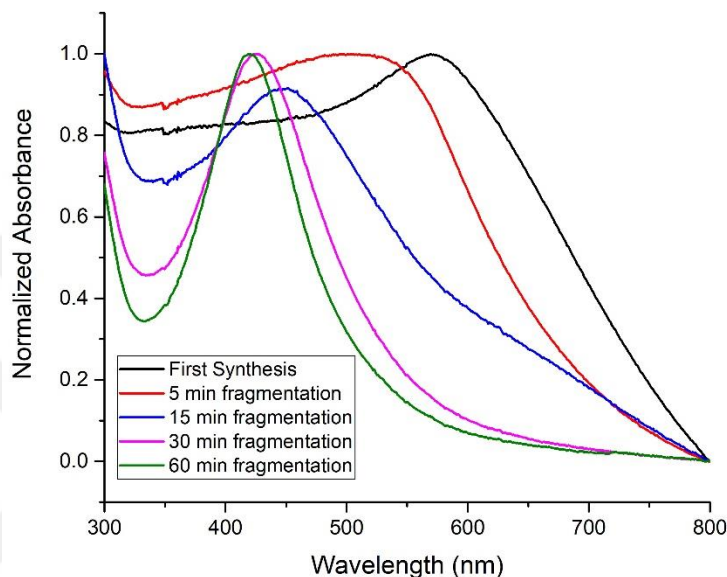


Figure 18: Normalized absorbance graph of fragmentation of $\text{Ag}_{0.30}\text{Cu}_{0.70}$ alloy nanoparticles

Figure 18 shows the normalized absorbance graph of laser fragmentation of $\text{Ag}_{0.30}\text{Cu}_{0.70}$ alloy nanoparticles in 60 minutes. The first synthesis from laser ablation has a peak at 569 nm. The other peaks are at 504 nm for 5 minutes of fragmentation, 452 nm for 15 minutes of fragmentation, 426 nm for 30 minutes of fragmentation, and 420 nm for 60 minutes of fragmentation. Laser fragmentation process in ethanol causes the oxidation of the copper in $\text{Ag}_{0.30}\text{Cu}_{0.70}$ alloy nanoparticles. Then, LSPR peak of these nanoparticles gradually shifts to the LSPR region of spherical Ag nanoparticles. By adjusting the concentration of the nanocolloid, laser power and fragmentation duration, the LSPR peak can be tuned between about 580 nm to 420 nm in AgCu alloy nanoparticles in ethanol. This tunability comes from oxidizing the Cu in AgCu nanoparticles. The peak shifts to Ag region by increased fragmentation time. This is caused by the gradual

oxidation of Cu and the plasmonic effect changes with decreased Cu percentage in AgCu alloy nanoparticles. When all of the Cu is oxidized, the LSPR behaves like a pure Ag nanoparticle since copper oxide does not have a plasmonic behavior.

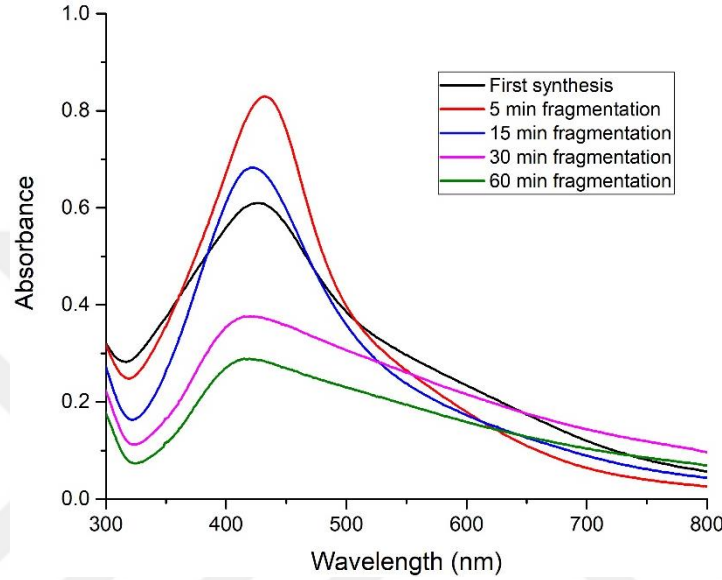


Figure 19: Absorbance graph of fragmentation of $\text{Ag}_{0.70}\text{Cu}_{0.30}$ alloy nanoparticles

In another target, we can see other effects of laser fragmentation process. The $\text{Ag}_{0.70}\text{Cu}_{0.30}$ target does not show much tunability since it has only 30% of Cu content. However, in figure 19, we can see that 5 min fragmentation process increases the absorbance compared to first synthesis by laser ablation. This can be attributed to achieving narrower size distribution by laser fragmentation process. In further fragmentation times, we see that the peak wavelength also shifts to the left, meaning nanoparticles containing Ag are getting smaller in size. However, there is also decrease in absorbance with increased laser fragmentation time after 5 minutes of fragmentation. The peak wavelength blueshifts but this is also accompanied by the decrease and broadening of the absorbance peak. We know that absorbance gets broadened when size distribution is also broader. When the laser light is focused by a 50 mm lens, the laser light away from focal point will have

greater intensity difference compared to focal point. In addition, these alloy nanoparticles are synthesized without any stabilizers or ligands. This results in a low colloidal stability where nanoparticles aggregate and sediment in very short amount of time (e.g. 1 day). These nanoparticles aggregate and form clusters of nanoparticles inside the colloid. So, when out of focus laser light interacts with these aggregated clusters, the process called laser melting in liquid (LML) can occur. This process in PLFL is also called concentration driven coalescence where large amount of aggregated small nanoparticles form a large nanoparticle from the interaction with the out of focus laser light during PLFL. I have encountered this effect is in my study often times because these nanoparticles had low colloidal stability, high concentration and my setup has a 50 mm lens which is a short focal length for PLFL purposes.

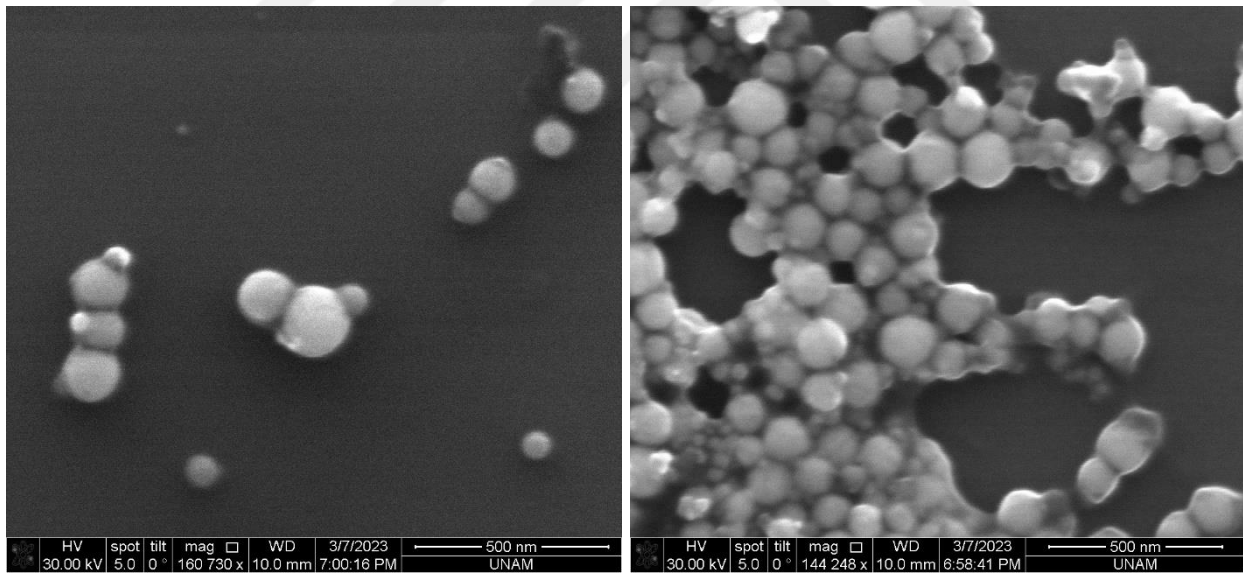


Figure 20: SEM images of $\text{Ag}_{0.70}\text{Cu}_{0.30}$ alloy nanoparticles after 30 minutes of laser fragmentation

Figure 20 shows the alloy nanoparticles from $\text{Ag}_{0.70}\text{Cu}_{0.30}$ target, laser fragmented for 30 minutes. In first image, we can see dumbbell and snowman type biphasic Janus nanoparticles. This is consistent with the literature since Ag content is higher than Cu content. These particles were not visible in laser ablation samples. After laser fragmentation, their amount increases. We can also

confirm the decreased absorbance effect since nanoparticles have much larger diameter. In images after laser ablation, we would see a size distribution ranging from a few nanometers to a few hundred nanometers. Other than biphasic particles, single phase nanoparticles have spherical shapes.

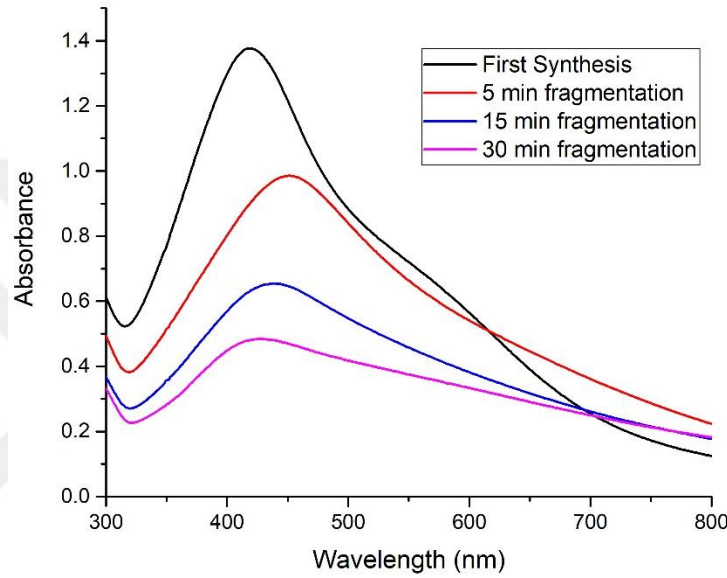


Figure 21: Absorbance graph of $\text{Ag}_{0.85}\text{Cu}_{0.15}$ alloy nanoparticles from first synthesis to 30 minutes laser fragmentation

Figure 21 shows the absorbance graph of laser fragmented $\text{Ag}_{0.85}\text{Cu}_{0.15}$ alloy nanoparticles. We do not see absorbance tuning in this composition since only 15% Cu does not offer much tunability. However, we again see a decrease in absorbance after laser fragmentation. First of the possible reasons is the deposition of nanoparticles on the quartz cuvette during stirring. We have noticed that nanoparticles stick to the quartz cuvette and this can reduce the absorbance value. In addition, although not as much as copper, silver can also get oxidized during laser fragmentation process. This would reduce the silver content and LSPR absorbance of the silver.

Furthermore, in figure 21 and figure 19, in absorbance graphs of $\text{Ag}_{0.85}\text{Cu}_{0.15}$ and $\text{Ag}_{0.70}\text{Cu}_{0.30}$ alloy nanoparticles, the first synthesis data which is the data taken after laser ablation process, show a

shoulder in the region around 550-600 nm which is the region of plasmonic absorbance of spherical Cu nanoparticles. Our dumbbell and snowman type biphasic AgCu nanoparticles might be able to achieve separate plasmonic resonance, thus we may be able to see this in the absorbance graph. After laser fragmentation, this shoulder is lost. This may mean that Cu is oxidized in this process which happens much easier and quicker than oxidizing Ag in ethanol.

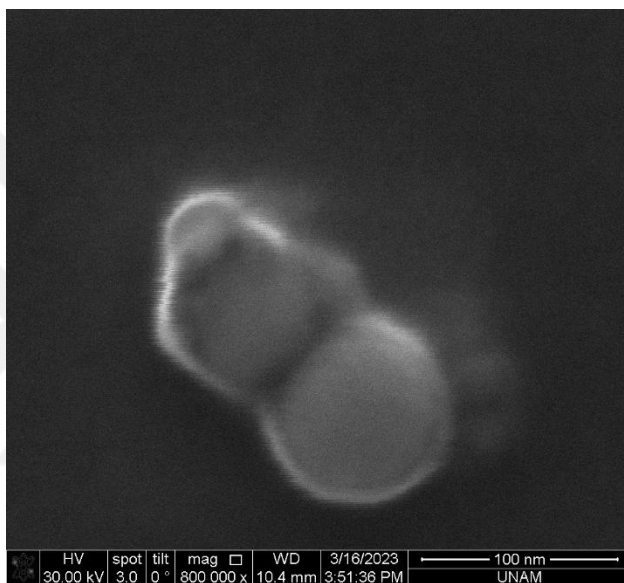


Figure 22: SEM image of $\text{Ag}_{0.85}\text{Cu}_{0.15}$ alloy nanoparticle after 5 minutes of laser fragmentation

In figure 22, we have the SEM image of $\text{Ag}_{0.85}\text{Cu}_{0.15}$ alloy nanoparticle after 5 minutes of laser fragmentation. This nanoparticle shows a snowman type configuration on the upper part and dumbbell type configuration on the lower part. In addition, this nanoparticle is covered with a shell. This shows that 3 different type of biphasic configuration can be seen in one nanoparticle cluster with the effect of laser fragmentation process. This image also supports the creation of oxide shell since the initial nanoparticles are in biphasic Janus nanoparticle form.

In this study, we have synthesized 5 different composition $\text{Ag}_{1-x}\text{Cu}_x$, ($x = 0.85, 0.70, 0.50, 0.30, 0.15$) alloy nanoparticles and studied their optical absorbance properties and their size and

morphology in SEM. These nanoparticles show a great promise in plasmonic absorbance tunability of metallic nanoparticles and the laser fragmentation process can be used to create an oxide layer in metallic nanoparticles in an oxidizing liquid. This type of core-shell nanoparticles can be used in various applications owing to their unique composition and structure.



3 COPPER SULPHIDE NANOPARTICLE SYNTHESIS AND OPTICAL APPLICATIONS

The photoacoustic imaging experiments in this chapter are done in collaboration with Köymen Research Group, BASTA, Bilkent University. The cell studies and DLS measurements in this chapter are done by Dr. İsmail Eş from İncilab, UNAM and in vitro photothermal application on MCF-7 cells are done in collaboration.

3.1 SYNTHESIS OF NANOPARTICLES

A copper plate with high purity is immersed in 5 mL of dimethyl sulfoxide (DMSO) and ablated with a nanosecond pulsed laser (Empower, Spectra-Physics) for 4 minutes. The pulsed laser operates with 100 ns pulse duration, 1 kHz repetition rate, and has a wavelength of 527 nm. The average power from the laser was 15 W which results in 15 mJ energy per pulse. Before ablation, copper targets were cleaned with distilled water and isopropyl alcohol. The focusing of the laser beam on the surface of the target was done with a 50 mm focusing lens.

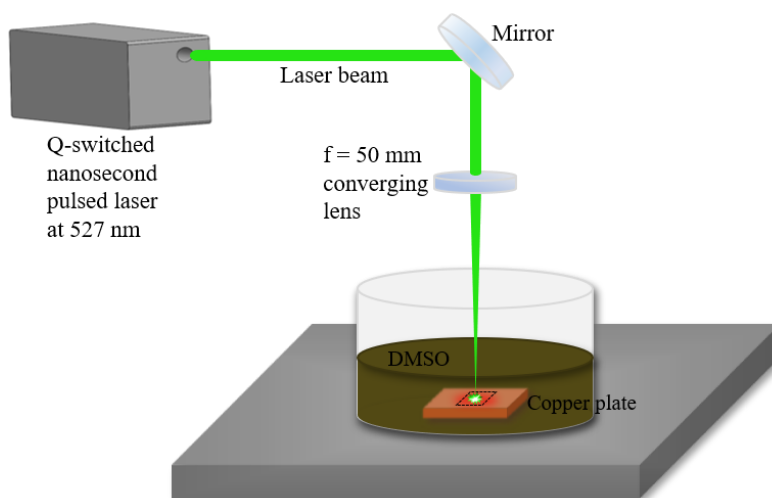


Figure 23: Illustration of the experimental setup of nanoparticle synthesis by laser ablation

At the end of the ablation process, a concentration equal to 1 mg/mL Cu reacting with S atoms of DMSO molecules was prepared. The exact concentration could not be calculated because the resulting compounds had two different stoichiometries after laser ablation. Other concentrations lower than 1 mg/mL are prepared by diluting the highest concentration. An illustration of the PLAL setup for nanoparticle synthesis can be seen in Figure 23.

3.2 CHARACTERIZATION OF NANOPARTICLES

The characterization of synthesized nanoparticles is done by X-ray diffraction (XRD) analysis, TEM imaging, Energy Dispersive X-Ray Spectroscopy (EDX) measurement, Dynamic Light Scattering (DLS), zeta potential measurement, absorbance measurement, and photoluminescence measurement. To determine crystalline structure of the nanoparticles an XRD analysis is done by Panalytical X'Pert PRO Multipurpose Diffractometer operating at 45 kV and 40 mA. The XRD sample is prepared by drop casting the synthesized colloid onto quartz substrate on a hot plate at 200 °C. Before drop casting, the colloid is centrifuged at 10000 rpm for 2 minutes to precipitate the nanoparticles. This is done to shorten the sample preparation time to minimize the oxidation of the sample. It was observed that long sample preparation times caused the oxidation of the nanoparticles which transformed copper sulphide into copper sulphate. The TEM image is taken with HR-TEM, FEI-Tecnai G2F30 operating at 300 kV voltage. The TEM samples prepared by taking one drop from the colloid and drop casting onto carbon coated Cu TEM grid. The absorbance spectrum is recorded with Varian Cary 5000 UV/Vis/NIR spectrophotometer by putting the synthesized colloid inside a quartz cuvette. The photoluminescence behavior of the nanoparticles is determined with Horiba Scientific Jobin Yvon, Fluorolog, FL-1073 with the excitation wavelength at 320 nm. The sample for photoluminescence characterization is prepared same way as the XRD measurement.

Figure 24 shows the XRD pattern of the synthesized Copper Sulphide nanoparticles (CSNP). The 2θ values of peaks and their corresponding Miller indices are given in Table 3. The resulting XRD pattern shows that the synthesized nanoparticles have two different stoichiometries. These are Covellite (CuS) and Digenite (Cu_{1.8}S), respectively. These indices are assigned according to CuS (ICDD No 03-065-3556) and Cu_{1.8}S (ICDD No 04-003-4437). This suggests that CuS crystal has a hexagonal shape, the lengths of the unit cell are at $a=b=3.7960 \text{ \AA}$, $c=16.3600 \text{ \AA}$, and belongs to

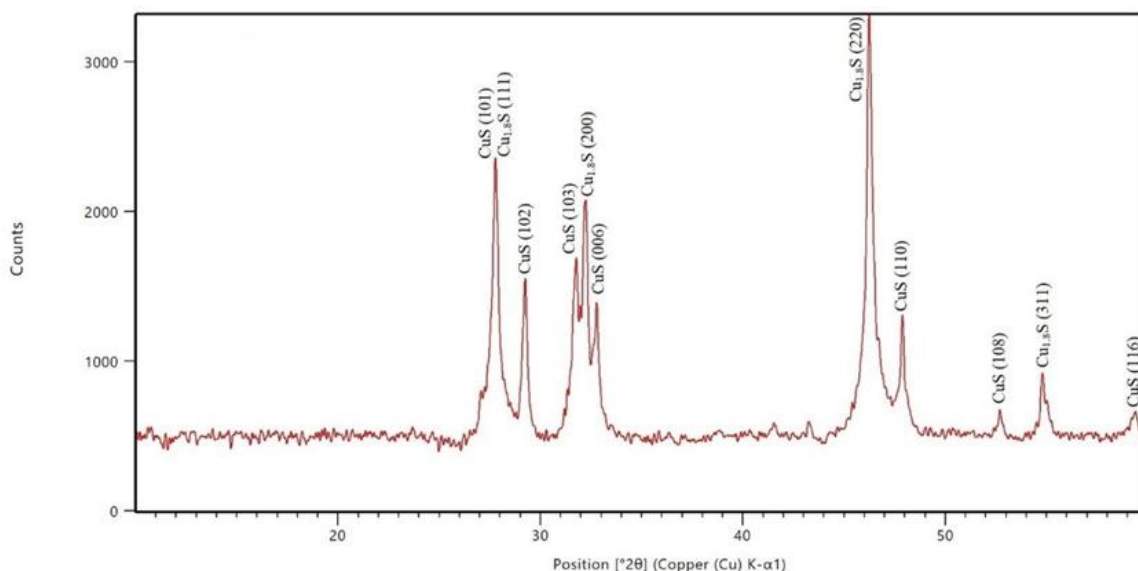


Figure 24: XRD pattern of the synthesized CSNP

2θ values	Indices
27.79	CuS (101) and Cu _{1.8} S (111)
29.24	CuS (102)
31.69	CuS (103)
32.22	Cu _{1.8} S (200)
32.79	CuS (006)
46.24	Cu _{1.8} S (220)
47.89	CuS (110)
52.70	CuS (108)
54.80	Cu _{1.8} S (311)
59.40	CuS (116)

Table 3: 2θ values and corresponding indexes of synthesized nanoparticles

space group P63/mmc. $\text{Cu}_{1.8}\text{S}$ crystal has cubic shape, the lengths of the unit cell are at $a=b=c=5.5640 \text{ \AA}$, and belongs to space group Fm-3m. To the best of our knowledge, this is the first synthesis of $\text{Cu}_{1.8}\text{S}$ nanoparticles with the PLAL method. We believe the reason for double stoichiometry may result from the rapid sulphurization of the Cu target surface during the laser ablation process. The change of color of the target surface after laser ablation in DMSO also supports this hypothesis. During high temperature ablation process, the target surface may be affected and laser beam interacting with this thin layer of sulphurized Cu may give different stoichiometry. This may be caused from high energy of the pulses and long pulse duration (100 ns) of the laser.

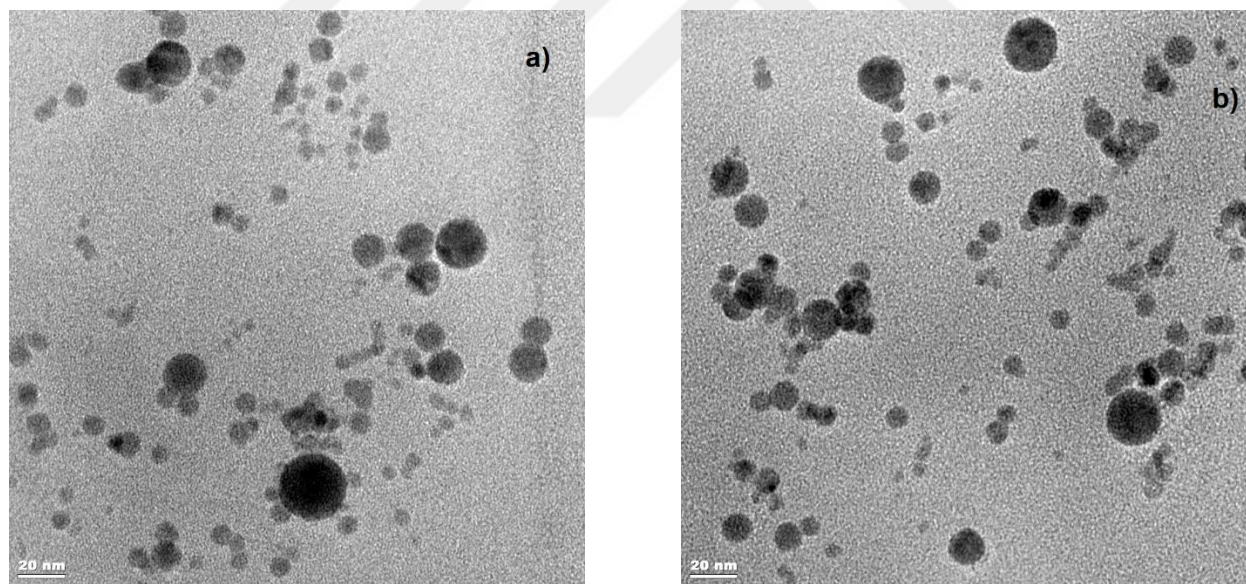


Figure 25(a, b): TEM images of CSNPs. Scale bar is 20 nm.

In our study, we used TEM and DLS techniques to examine the CSNPs. Synthesized CSNPs are imaged via TEM and their size, shape and elemental composition are identified. Figure 25a and 25b shows the CSNP synthesized in DMSO. As the images show, the nanoparticles have spherical

shapes and their sizes are below 30 nm. Figure 26 shows a TEM image of a CSNP and crystal planes can be seen clearly. This image also proves that the synthesized nanoparticles are

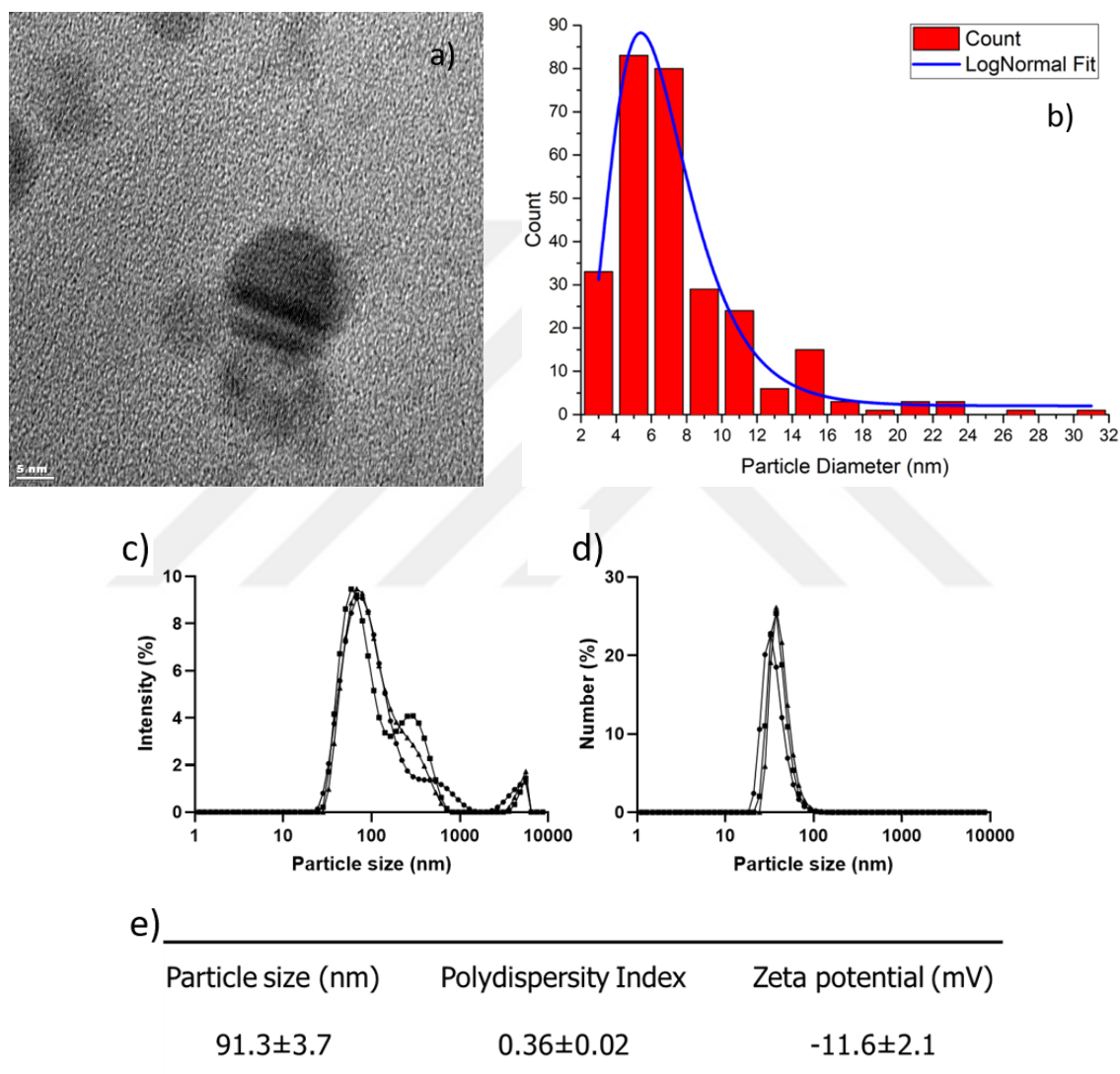


Figure 26: a) TEM image of a CSNP with visible crystallinity, b) nanoparticle size distribution histogram and lognormal fit, c) Intensity and d) number-weighted particle size of CSNPs, e) Physicochemical properties of synthesized CSNPs

crystalline. The size distribution histogram is created by counting more than 250 nanoparticles from several TEM images. The sizes are measured by using the ImageJ software. The histogram

shows that most of the nanoparticles are smaller than 10 nm but sizes reach up to around 30 nm. This result also shows that these sizes of nanoparticles synthesized in our work are smaller than the ones in the literature [58][70]. The size distribution has a log-normal distribution, as expected from PLAL synthesized nanoparticles [88].

According to the DLS results (see Figure 26 c-e), the average size of the CSNPs, based on intensity-weighting, was 91.3 ± 3.7 nm, and the polydispersity index (PDI) ranged from 0.3 to 0.4. Intensity-weighted size refers to the distribution of sizes based on the intensity of scattered light, providing information about the relative abundance of particles of different sizes. On the other hand, the number-weighted size distribution gives insights into the relative population of particles with different sizes or PDI. The number-weighted particle size was approximately 30 nm, which closely matched the results obtained from the TEM images.

The outer layer of metal sulfide particles usually consists of two types of functional groups: sulfido-groups ($>SH$) and hydroxo-groups ($>OH$) [89]. Consequently, the electrical charge present on the surface of a metal sulfide particle relies on the concentration and individual electric charge of these respective sulfido- and hydroxo-groups. The surface charge strictly depends on how the atoms are arranged in the crystal lattice structure and how the metal (Cu in this study) and sulfide ions interact with each other. The threshold zeta potential value differs significantly among other metal sulfide systems due to variations in the Hamaker constant, which is the coefficient accounting for the Van der Waals interaction between two materials [90]. As a result, the solid fraction of metal-sulfide nanoparticles varies, impacting their colloidal stability. In our study, the CSNPs displayed a zeta potential of -11.6 ± 2.12 mV (Figure 26e). A continuous aggregation of CSNPs followed by sedimentation was observed. Colloidal stability is directly associated with the zeta potential of the nanoparticle system. For instance, previous studies have suggested that

aggregation tends to dominate within a zeta potential range of -15 mV to +15 mV [91]. Furthermore, it has been established that the colloidal stability of a suspension containing CSNPs can be attributed to a highly negative zeta potential of approximately -38 mV at a pH of 6 [92].

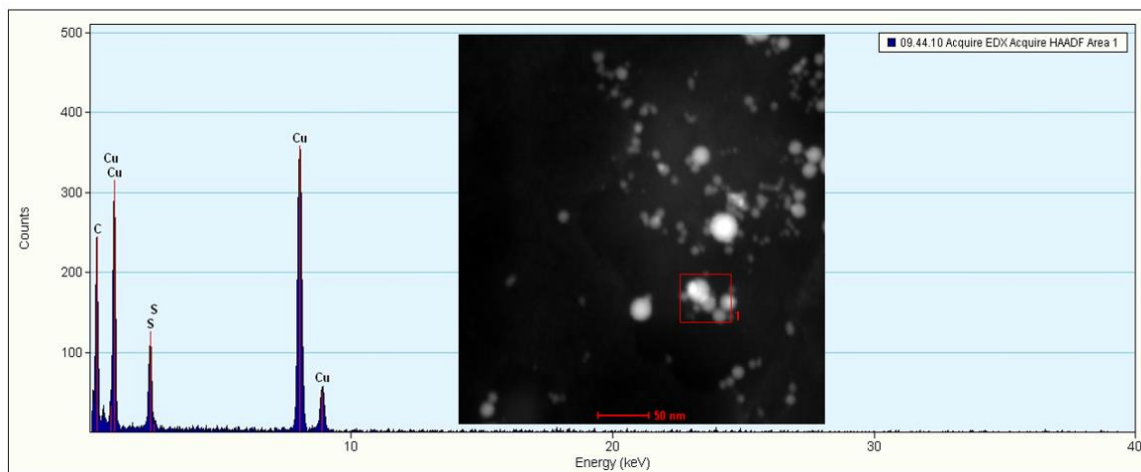


Figure 27: EDX spectrum of the CSNP (red square shows the EDX scanned area)

Figure 27 shows the EDX spectrum of the CSNP and the inset is an image taken in the high-angle annular dark field image mode. The elements from this spectrum are Cu, S and C. Cu and S are components of CSNPs. C peak comes from carbon coating of the TEM grid.

The absorbance spectrum of the CSNP colloid in DMSO is recorded between 230 – 1600 nm. Figure 28 shows the absorbance spectrum from 400 nm to 1600 nm while inset graph shows the full spectrum from 230 nm to 1600 nm. The red dashed area between 1000 – 1350 nm shows the near infrared second bioimaging window (NIR-II) where NIR-II light have enhanced spatial resolution, increased tissue penetration, reduced autofluorescence from tissues and lower phototoxicity [93]. The absorbance spectrum shows a broad absorbing region between 1000 nm to 1600 nm. The absorption peak is at 1183 nm and has a wide absorption range in the NIR region. Absorbance at 1080 nm, which is the wavelength for our photothermal study, is at 92.7% of the peak at 1183 nm and absorbance at 1064 nm is at 90.8% of the peak absorption in the NIR region,

which is the wavelength of common and a majority of near-infrared lasers. Also, most of the high absorbance is in the second near-infrared region (1000- 1700 nm) where biological tissues have low absorption and scattering of photons [93]. This suggests that CSNPs can be used for the

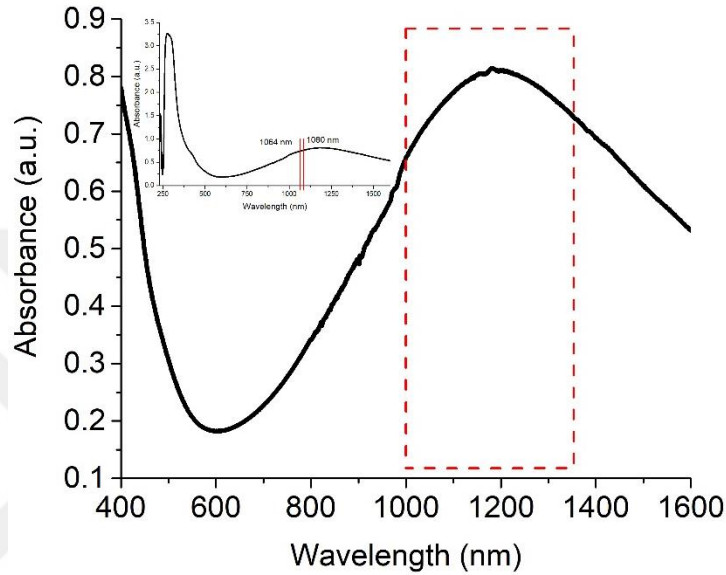


Figure 28: Absorbance spectrum of CSNPs in DMSO. (the inset shows the full range spectrum)

absorption of the light of NIR lasers and CSNPs can image deeper in live tissues than commonly used gold nanostructures [94] or carbon-based nanomaterials [95] which they have their absorption peaks in the first near-infrared region (700-1000 nm). The incorporation of $\text{Cu}_{1.8}\text{S}$ NPs seems to increase the peak wavelength of the LSPR since the LSPR of CuS NPs is around 900 – 1000 nm [96][97]. To study the bandgap of the nanoparticles the Tauc plot is drawn from the absorbance graph. The corresponding Tauc plot for bandgap estimation is shown in Figure 29. Tauc relation is used to estimate the bandgap value, which is given by [98]

$$(\alpha h\nu)^n = K(h\nu - E_g) \quad (\text{Eq.2})$$

where α is the absorption coefficient, h is Planck's constant, ν is the frequency of light, $n=2$, for direct and $n = \frac{1}{2}$ for indirect transitions, K is a constant and E_g is the bandgap. Using this relation, the bandgap is found to be 3.64 eV for direct transitions.

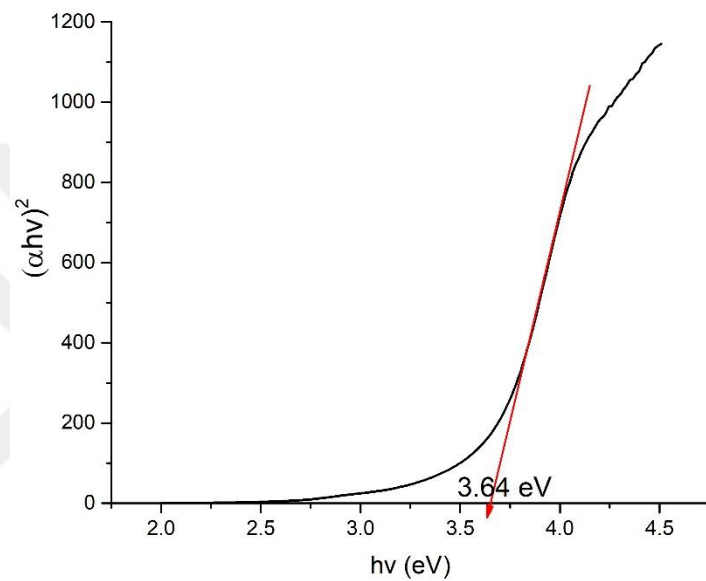


Figure 29: Corresponding Tauc plot of the inset absorbance graph in figure 28

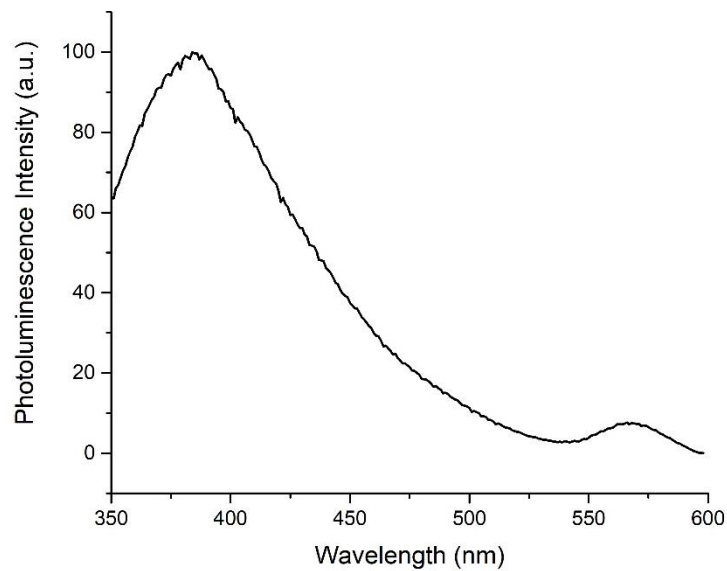


Figure 30: Graph of photoluminescence intensity of CSNPs excited at 320 nm

Due to the substantial usability of CSNPs in photo-applications, photoluminescence behavior is studied. In addition, the laser ablation process can produce deficiencies in the crystalline structure of the nanoparticles [99]. On account of these, the photoluminescence properties of the NPs are recorded. Figure 30 depicts the photoluminescence (PL) behavior of the synthesized CSNPs. The PL spectra are recorded between 350–600 nm and NPs are excited at 320 nm wavelength from the xenon lamp of the spectrophotometer.

The spectrum has 2 peaks, the first at 383 nm and the second at 570 nm wavelengths. The first peak at 383 nm might be coming from defects and vacancies in the crystal structure or electron-hole recombination in the surface states [100][101][102]. The second peak at 570 nm may be attributed to the recombination of sulfur vacancy of the Cu^{2+} ion [103]. Both emissions in the blue region and the green region are compatible with the literature [100][101][102][103][104]. Considering these results, we can also say that these nanoparticles may be used for photo imaging for their photoluminescence response in the blue and green regions.

3.3 PHOTOTHERMAL EXPERIMENTS

Fiber-coupled diode (LD-1080-FBG-400) continuous wave laser was used for the photothermal excitations at 1080 nm and a thermal camera (FLIR Systems, Thermovision A40) was used to observe and record the change of temperature of nanocolloids. To investigate the photothermal response of the sample to the laser beam, we exposed a 4 mm-spot-sized laser beam of 1080 nm wavelength to the top surface of the colloidal sample. The power of the laser was adjusted by using Thorlabs driver through 1 W/cm² to 3.23 W/cm². Temperature was recorded for 300 s for every 5 s. Temperature values are recorded for concentrations from 1mg/mL to 0.0078125 mg/mL.

Concentrations lower than 1 mg/mL are prepared by diluting the 1 mg/mL batch. Concentration values are calculated by the decrease in the mass of the Cu target in the ablation process. This means that the 1 mg/mL sample is prepared by 1 mg of Cu reacting in liquid to produce copper sulphide nanoparticles. Nanocolloids are used inside 2 mL Eppendorf tubes. An illustration of the experimental setup is shown in figure 31.

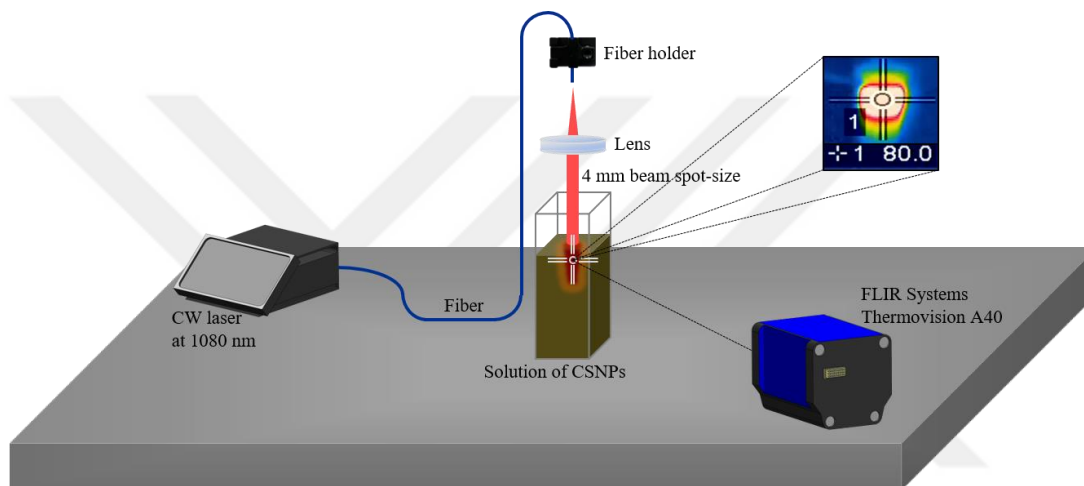


Figure 31: Illustration of the photothermal experiment setup

3.3.1 Photothermal Properties of Nanoparticles

To investigate the photothermal response of the sample to the laser beam, we subjected the sample's top surface to a 4 mm-spot-sized laser beam of 1080 nm wavelength with a laser power intensity of 3.23 W/cm^2 and a laser power of 406 mW, as shown in the representative images in Figure 32a. The temperature was measured every 5 s for 300 s. The heat expansion became apparent throughout the laser exposure duration. The scope of the NIR thermal camera was adjusted to capture the region of the sample with the highest temperature. Significant temperature increases were reported where the initial temperature was $28.4 \text{ }^\circ\text{C}$ and reached $80.6 \text{ }^\circ\text{C}$ in 300 s

resulting in a 52.2 °C temperature change. At various laser intensities, 1mg/mL of CSNPs were irradiated with a 4 mm laser spot of 1080 nm wavelength and a spot size of 4 mm (varies from 1 to 3.23 W/cm²). In the process of the laser intensity-dependent temperature change of 1mg/mL of CSNPs, the initial temperature of the CSNPs was maintained at room temperature (28.4 °C) before the application of each laser intensity. Under the laser irradiation with different intensities of 1 W/cm², 2 W/cm², 3 W/cm², and 3.23 W/cm², the latest temperatures reached were recorded as 45 °C, 61.3 °C, 77 °C, and 80.6 °C respectively. Therefore, it can be deduced that the maximum heat release occurred when the highest laser intensity was applied as provided in Figure 32b where temperature increased with an increase in the laser intensity. To demonstrate the concentration-dependent temperature change of 1 mg/mL of CSNPs, the laser intensity was set to 3.23 W/cm² and irradiated in all concentrations (from 1 to 0.0078125 mg/mL). As presented in Figure 32c, the photothermal response of nanoparticles displays a progressive/gradual increase in temperature between each concentration as the illumination is initiated. The latest temperature reached for the least dense (0.0078125 mg/mL) of CSNPs with the highest irradiation laser intensity was 41.1 °C while the temperature for the highest dense solution reached 80.6 °C. It is clear that the denser sample has not only more of the CSNPs exposed to the laser beam but also a higher light absorption intensity. In this way, the CSNPs confirm a concentration-dependent temperature increase at a constant laser intensity. In addition, we also confirmed that CSNPs have photothermal stability. As shown in Figure 32d, five consecutive heating-cooling cycles under repeated laser ON/OFF actions were performed. The sample with 1mg/mL concentration was under excitation at 1080 nm wavelength with the 4 mm-spot-sized laser beams for 300 s and is kept cooling down at room temperature. Since there was no discernible change in behavior between repeated cycles and CSNPs could reach the same maximum temperature (about 80 °C) for each repeated cycle, it can

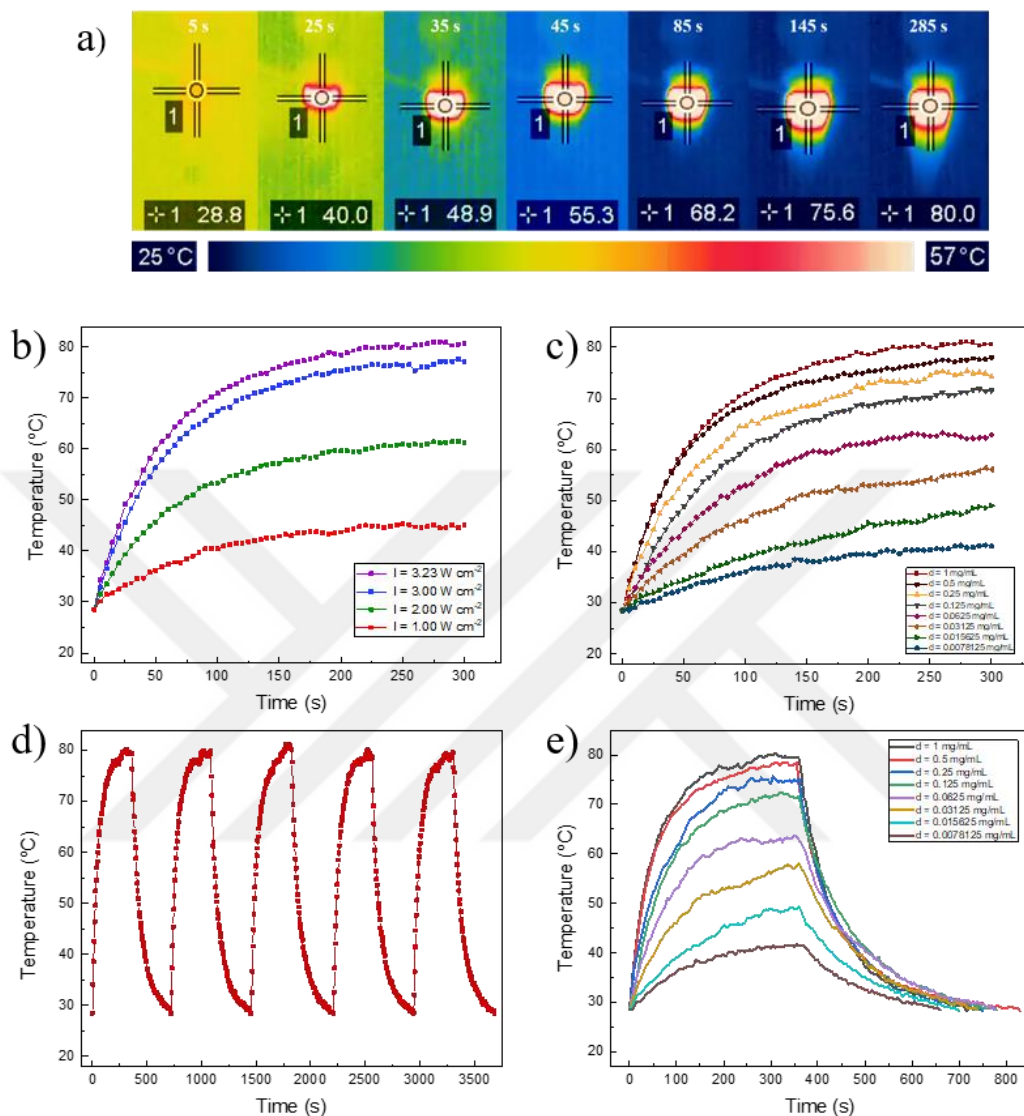


Figure 32: a) Time-dependent IR thermal camera captures of CSNPs placed into a micro centrifuge tube where the center region of the sample is exposed to the laser beam. The initial temperature was 28 °C. b) The temperature of CSNPs recorded under a continuous laser beam irradiation with 4 mm-spot sized at different laser power intensities. c) The temperature of CSNPs with different concentrations measured every 5 s for 300 s under exposure to the 4 mm-spot sized at an intensity of 3.23 W cm^{-2} . d) Five heating-cooling consecutive cycles for photothermal stability of CSNPs measured for 300 s under exposure to the 4 mm-spot-sized laser beams with a concentration of CSNPs of 1mg/mL at an intensity of 3.23 W cm^{-2} . e) Concentration-dependent temperature change of 1mg/mL of CSNPs with cooling curves.

be concluded that CSNPs preserve their reversible photothermal properties. Besides the heating response of all concentrations with a laser intensity of 3.23 W/cm^2 , cooling behaviors reflect consistency and are presented in Figure 32e. In conclusion, the synthesized CSNPs show that with even low concentrations, large temperature changes can be achieved and the NPs can be used repeatably. It can be seen that CSNPs show great promise for photothermal applications.

3.4 EFFECT OF CSNPS ON CELL VIABILITY

The MCF-7 breast cancer cell line was cultured in DMEM medium supplemented with 10% FBS and 1% penicillin and streptomycin under a humid atmosphere at 37°C and 5% CO_2 . For the cytotoxicity assay, the MTT (3-(4,5-Dimethylthiazol-2-yl)-2,5-Diphenyltetrazolium Bromide) agent from ThermoFisher was used. Cells were seeded at a concentration of 5×10^4 cells/well in 200 μL of culture medium in 96-well microplates with a flat bottom and incubated for 24 hours at 37°C and 5% CO_2 to allow attachment. CSNP nanoparticles were then added at varying concentrations 0.0625 mg/mL, 0.03125 mg/mL, 0.015625 mg/mL, 0.00625 mg/mL, 0.003125 mg/mL while maintaining a DMSO concentration of 0.5%. After the incubation period, 5 mg of MTT was dissolved in 1 mL of PBS. 10 μL of the MTT labeling reagent (final concentration of 0.5 mg/mL) was added to each well, and the microplates were incubated for an additional 5 hours in a humidified atmosphere at 37°C and 5% CO_2 . Finally, 100 μL of the biological grade DMSO was added to each well to facilitate the solubilization of formazan crystals and enable the measurement of assay results and the absorbance values were measured using a plate reader at 570 nm.

3.5 IN VITRO PHOTOTHERMAL APPLICATION OF CSNPS

Polydimethylsiloxane (PDMS) was prepared by thoroughly mixing the base polymer and curing agent at a ratio of 10:1 to obtain a homogeneous mixture. The mixture was then degassed to remove any air bubbles and poured into microplates with 24 wells and a flat bottom, creating a thin layer of PDMS on each well. To enhance temporary hydrophilicity and facilitate the attachment of mammalian cells, the PDMS layers were treated with O₂ plasma using parameters of 50 sccm O₂, RF power of 100 W, chamber temperature of 20°C, and a cycle time of 2 minutes. Once the PDMS surface became hydrophilic, the cells were seeded onto the PDMS layers and allowed to reach 70% confluency. Subsequently, the cells were treated with CSNPs at concentrations of 0.0625 mg/mL, 0.03125 mg/mL, 0.015625 mg/mL, 0.00625 mg/mL, 0.003125 mg/mL (in a 10% DMSO solution), followed by a 20-minute sedimentation period. After removing the medium, fresh medium was gently added to the wells to avoid disturbing the CSNPs. Subsequently, the cells were exposed to a CW laser operating at 1080 nm at a power density of 3.23 W/cm² at a 4 mm beam diameter for 5 minutes, and cell viability was confirmed using a live/dead viability assay.

3.6 CELL VIABILITY FOLLOWING PHOTOTHERMAL TREATMENT USING LIVE/DEAD ASSAY

The protocol involves staining the cells with a combination of two fluorescent dyes: calcein-AM and ethidium homodimer-1 (EthD-1). Calcein-AM is a cell-permeant dye that labels live cells with green fluorescence, indicating their viability. EthD-1, on the other hand, is a cell-impermeant dye that enters only cells with compromised membranes, such as dead or dying cells, and labels them with red fluorescence, indicating cytotoxicity. To perform the protocol, the cells were first

prepared by washing and suspending them in DMEM. The cell suspension was then treated with a working solution of the calcein-AM and EthD-1 dyes (1:4), followed by incubation for 30 min at room temperature. After the incubation, the cells were observed under fluorescence and confocal microscopes.

The taken images were further processed in Fiji using live dead quantification macro. First, to quantify the signal in the green (live cells) and red channels (dead cells), the images were split and treated separately. It was ensured that the images were in 8-bit space. To reduce background noise, the brightness and contrast were adjusted. Next, the grayscale image was converted into a binary black and white image. The green channel was selected, and the threshold was adjusted. Selecting the correct threshold was crucial, as setting it too high would result in signal loss, while setting it too low would cause fusion of cells close to each other, making counting more difficult. To separate the individual cells that appeared as one, the image was selected and it was processed using “watershed” command. This created thin separation lines between the objects detected as separate by the software. Finally, the prepared image was subjected to automatic counting by selecting "Analyze Particles" from the analyze menu. The percentage of live cells was computed by dividing the number of spots detected in the green channel by the total number of green and red cells. This quotient was then multiplied by 100% to express the result as a percentage.

3.7 CYTOTOXICITY ASSAY OF CSNPS

We investigated the cytotoxicity effect of CSNPs on MCF-7 cancer cells (Figure 33). The experiment included six groups, namely: 1) untreated cells, 2) cells treated with 0.250 mg/mL concentration, 3) cells treated with concentration of 50% diluted sample of 0.250 mg/mL CSNP,

4) cells treated with concentration of 25% diluted sample of 0.250 mg/mL CSNP, and 5) cells treated with concentration of 10% diluted sample of 0.250 mg/mL CSNP, 6) cells treated with concentration of 5% diluted sample of 0.250 mg/mL CSNP. To assess the cytotoxicity, we measured cell viability in each group after the respective CSNP treatments. Our results showed that cell viability was there was no statistically significant difference in cell viability among the groups for each CSNP treated and non-treated MCF-7 cells. The lack of statistical significance suggests that the cytotoxic effect of CSNPs on MCF-7 cancer cells was not observed within the range of concentrations tested in this study. It is important to note that the absence of statistical significance does not necessarily imply the absence of any biological effect. Other factors such as the exposure duration, nanoparticle size, and cell type may influence the observed cytotoxicity. The absence of statistical significance doesn't guarantee the absence of biological effects as other factors, such as exposure duration, laser intensity, and cell type, can influence observed cytotoxicity. CuS nanoparticles have been reported to be safe to use in vivo in previous studies [97]. However, the cytotoxicity of these nanoparticles may vary depending on the specific cancer cell line, concentration, and experimental conditions employed. In our study, the MCF-7 cell line might have demonstrated resistance to the cytotoxic effects of CSNPs at the tested concentrations. Further investigations are warranted to explore the underlying mechanisms behind the observed lack of cytotoxicity in MCF-7 cells treated with CSNPs. Additionally, expanding the concentration range and exploring longer exposure durations could provide valuable insights into the potential cytotoxic effects of CSNPs on MCF-7 cells.

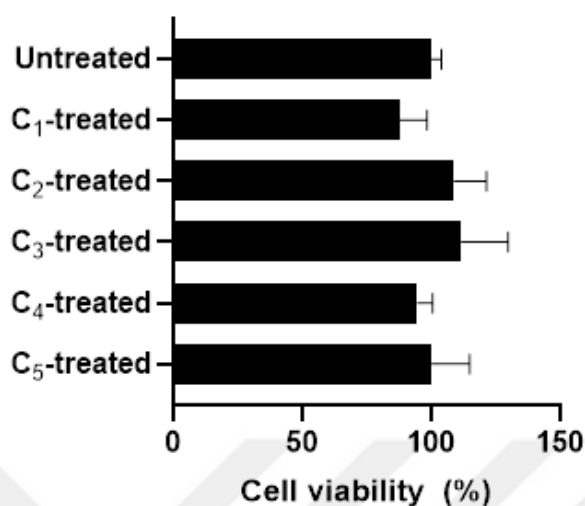


Figure 33: The viability of CSNPs-treated MCF-7 cells. C₁, C₂, C₃, C₄, and C₅ concentrations are 0.250 mg/mL CSNP, 50% diluted, 25% diluted, 10% diluted, and 5% diluted from 0.250 mg/mL sample of the synthesized CSNPs, respectively.

3.8 IN VITRO PHOTOTHERMAL APPLICATION OF CSNPS ON MCF-7 CELLS

In this study, we investigated the in vitro photothermal application of CSNPs on MCF-7 cells (Figure 34). The cells were treated with different concentrations of CSNPs, followed by exposure to nanosecond laser ablation. The four concentrations used were: 1) 0.250 mg/mL CSNPs, 2) 50% diluted sample of 0.250 mg/mL CSNPs, 3) 25% diluted sample of 0.250 mg/mL CSNPs, and 4) 10% diluted sample of 0.250 mg/mL CSNPs. Each laser treatment lasted for 5 minutes. Our results revealed a substantial effect of the CSNPs in inducing cell death when combined with laser ablation. In all treated populations, a significant number of dead cells were observed, indicating the potential of the photothermal therapy approach using CSNPs. According to the live dead cell analysis using ImageJ, the cell viabilities were 22.5%, 34.5%, 34.9%, and 42.8% for CSNPs concentration of 100%, 50%, 25%, and 10% from the 0.250 mg/mL sample, respectively. Notably,

the highest concentration of CSNPs, 0.250 mg/mL, exhibited a particularly potent effect, resulting in a significantly low number of live cells (22.5% cell viability). This finding suggests that higher concentrations of CSNPs may enhance the photothermal ablation efficacy against MCF-7 cells. The remarkable cell death observed in this group indicates the promising therapeutic potential of CSNPs in combination with laser ablation for cancer treatment. Furthermore, our results demonstrated that the 10% diluted sample of CSNPs treated group exhibited a lower number of dead cells compared to the other three groups. Although not as pronounced as the 0.250 mg/mL CSNPs concentration, the observed decrease in cell death indicates that lower concentrations of CSNPs can still contribute to the photothermal therapy's efficacy. This finding suggests that the optimal concentration of CSNPs for photothermal treatment of MCF-7 cells may lie within the range of 0.025 mg/mL to 0.250 mg/mL.

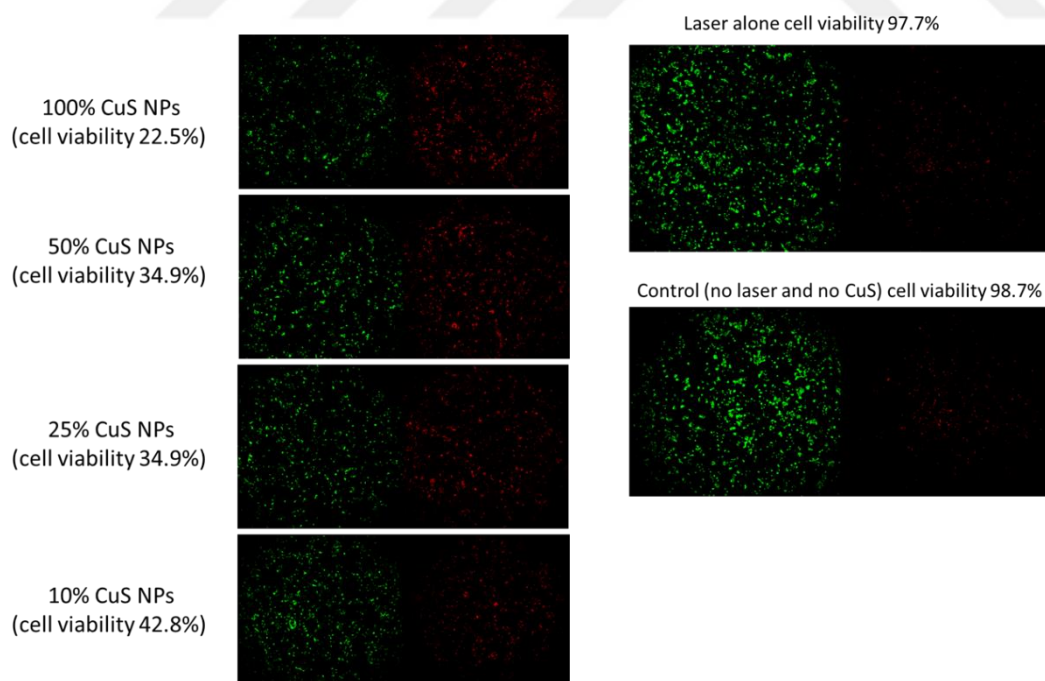


Figure 34: The cells treated with CSNPs with the concentration of 0.250 mg/mL, 50% diluted sample, 25% diluted sample, and 10% diluted sample of 0.250 mg/mL initial sample of total produced CSNPs. In addition, cell treated laser alone and control group (no laser and no CSNPs)

To better understand the specific fatal effect of laser treatment alone, we compared the results with two additional groups: "Laser irradiated cells without CSNPs treatment" and "cells without laser and CSNPs treatments". The laser irradiated cells had a cell viability of 97.7% while control group (cells without laser and CSNPs treatments) had a cell viability of 98.7%. Remarkably, both of these control groups demonstrated cell viability, indicating that the cells remained unaffected in laser treatment alone. Statistical analysis revealed no significant difference between the two control groups, indicating that the absence of laser treatment had a comparable effect to the absence of both laser treatment and CSNPs treatment. This suggests that laser irradiation on cells did not induce substantial (cytotoxicity) phototoxicity in MCF-7 cells. These findings contribute to the understanding of the in vitro photothermal application CSNPs and provide insights for the development of novel approaches in cancer treatment.

3.9 PHOTOACOUSTIC IMAGING EXPERIMENTS

The imaging setup consists of a pulsed laser source, a phased array system, an ultrasound transducer, and a photoacoustic phantom. A pulsed laser (Ekspla-NT350) system was used to expose the materials as seen in Figure 35. In the system, the pulsed laser light was at the wavelength of 1064 nm, and its energy was 5 mJ with a frequency of 10 Hz and pulse width of 5 ns. The laser light was collimated and coupled to the optical fiber. Digital Phased Array System (DiPhAS, Fraunhofer IBMT, Frankfurt, Germany) is used to collect data.

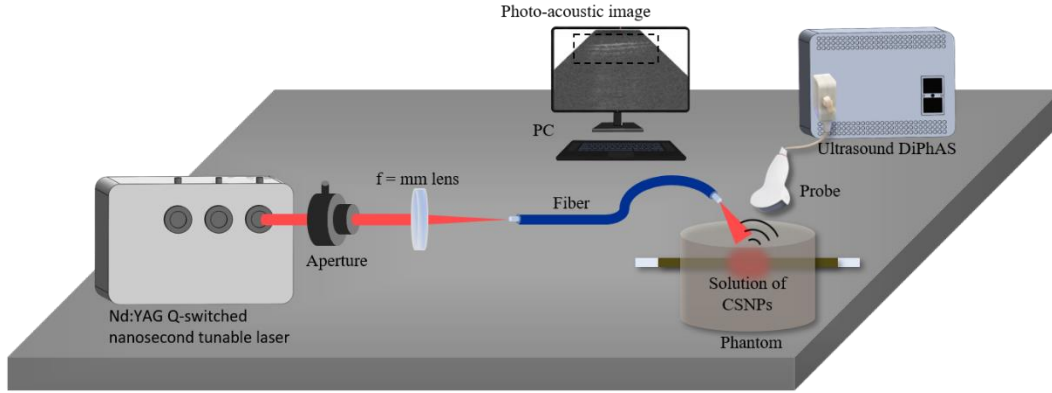


Figure 35: Illustration of photoacoustic experiment setup

A phased array ultrasonic transducer operating at 7.5 MHz center frequency is used in the experiments where the output end of the optical fiber is mounted at a 45° angle to the ultrasonic transducer. The transducer has 70% fractional bandwidth [105]. The transducer is equipped with 128 elements with a 0.1 mm element pitch. DiPhAS sends an external trigger signal to the laser system. After the laser system is triggered, optical pulses are initiated, and PA waves are generated inside the phantom. Using the ultrasound transducer and DiPhAS, samples of the PA waves are acquired at 80 MHz sampling frequency for 95 μ s record length. In the optoacoustic phantom, a 1 mm diameter polymer tube was filled with CSNP in DMSO, which we prepared in two different molarities of 0.25 and 1.00 mg/mL, was positioned at a depth of 1 cm. The outer diameter of the polymer tube we use here is 1.5 mm, and the inner diameter is 0.8 mm. The experiments were carried out for two configurations. For the first configuration, the transducer is positioned such that its axis is perpendicular to the axis of the acoustic wave propagation. The other configuration is parallel to the axis of the acoustic wave propagation.

3.9.1 Photoacoustic Properties of Nanoparticles

In photoacoustic imaging, a pulsed laser illuminates the region of interest, and the absorbed energy induces a thermo-elastic expansion, which generates acoustic waves. These acoustic waves are then received by an ultrasound phantom and post-processed to construct a photoacoustic image.

In this study, the acoustic waves generated due to the thermo-elastic expansion of the tube in response to the firing from the pulsed laser are received by a phased array transducer. The received signals are then beamformed using a delay-and-sum receive beamformer, a commonly used technique in literature, to form the image scan lines. Next, we employed the Hilbert transform-based envelope detection on the scan line data to obtain the envelope information, which was subsequently used for image construction.

To understand the motion of the tube caused by the thermo-elastic expansion, we first examined the beamformed signal along the axis of the wave propagation. Figure 36a presents the beamformed signal when the transducer is positioned such that its axis is perpendicular to the wave propagation axis. We obtained this beamformed signal in the case of 0.250 mg/mL concentration of CSNPs, 1064 nm excitation wavelength, and 5 mJ average energy. As seen in Figure 36a, thermo-elastic expansion of the tube volume results in two signals being formed. It is observed that the former signal comes from a depth of 0.95 cm as expected since the depth of the tube is approximately 1 cm. The acoustic waves generated due to the motion of the upper wall of the tube cause this signal to appear at the beamformer output. It is also observed that the acoustic waves generated due to the motion of the bottom wall of the tube cause the latter signal with a polarity opposite to that of the

former signal. This latter signal comes from a depth of 1.05 cm, which is compatible with the depth of the bottom wall of the tube.

When the ultrasound probe orientation is changed such that its axis is parallel to the wave propagation axis, the amplitude of the beamformed signal decreases significantly, and they become barely visible as shown in Figure 36b. It is also obvious that the two signals coming from the upper and bottom walls of the tube cannot be easily distinguished from each other when compared to those shown in Figure 36a. The reason is that the volume of the tube subjected to the optical firing of the laser increases in this orientation.

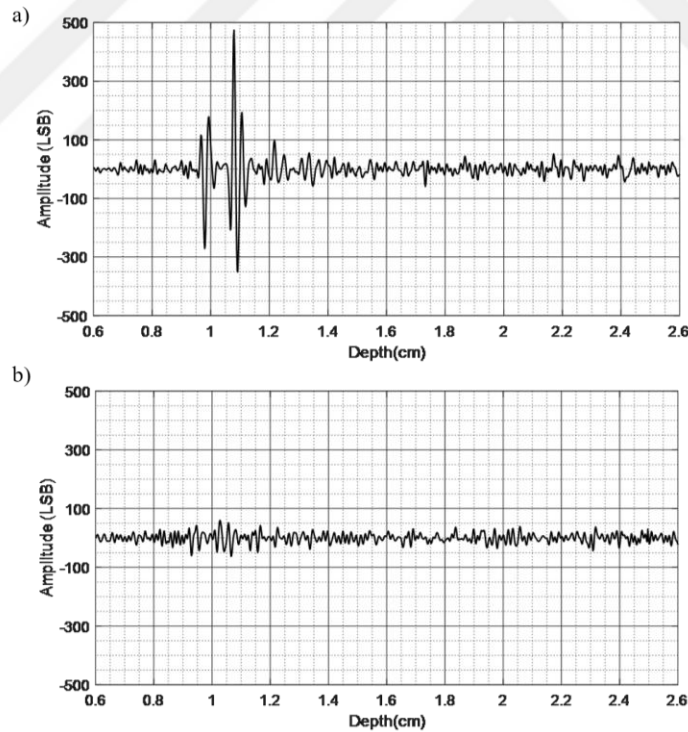


Figure 36: Beamformed Signals a) The transducer is positioned such that its axis is perpendicular to the wave propagation axis. b) The transducer is positioned such that its axis is parallel to the wave propagation axis. The amplitude unit is the least significant bit (LSB) of the analog-to-digital converter in DiPhAS.

In this case, the thermal expansion results in acoustic wave generation over an increased volume, in which the acoustic waves are destructively added up during their propagation toward the ultrasound probe. This destructive addition causes a significant decrease in the amplitude of the beamformed signal.

To gain a better understanding of the tube motion due to the thermo-elastic expansion, we also benefitted from the correlation. For this purpose, we correlated the beamformed signals shown in Figure 36 with the beamformed signal generated due to the motion of the upper wall of the tube. Note that the energy of the beamformed signal generated due to the motion of the upper wall of the tube is normalized to unit energy, which means that the correlator gain is unity. Figure 37 compares the correlator outputs for the perpendicular and parallel orientation of the probe as a function of depth. The two signals generated due to the motions of the upper and bottom walls are again distinguishable in Figure 37a, and the latter signal has an opposite polarity compared to the former signal. The correlator output shown in Figure 37a has a higher amplitude than that shown in Figure 37b, which confirms the adverse effect of the destructive addition of the propagating waves in the case of parallel probe orientation. The correlator output shown in Figure 37 is in good agreement with the results obtained from beamformed signals shown in Figure 36. Consequently, the beamformed signals and the correlator outputs well describe the motion of the tube under the laser excitation.

Next, we presented the photoacoustic images of the target, a polymer tube filled with 0.250 mg/mL CSNPs, positioned approximately at 1 cm depth in Figures 38a and 38b for different transducer orientations. These images are obtained with 1064 nm excitation

wavelength and 5.0 mJ average energy. For comparison purposes, we also constructed ultrasound images for different transducer orientations, shown in Figures 38c and 38d, as reference images. We used these images for both subjective evaluations, and to examine whether or not the results derived from the beamformed signals and correlator outputs are also observable in images. The photoacoustic image when the transducer is positioned such that its axis is perpendicular to the wave propagation axis is shown in Figure 38a. It can be easily seen from Figure 38a that the target is detected and clearly visible, while it is barely visible in the ultrasound image shown in Figure 38c.

The received acoustic waves generated from the expansion of the upper and bottom walls of the tube manifest themselves in Figure 38a, as two separate point-like targets at approximately 1.0 cm and 1.1 cm depths due to the transducer orientation. The distance between these two point-like targets, shown in dashed rectangular in Figure 38a, was measured as 1 mm, which is compatible with the distance between the upper and bottom walls of the tube. In addition, Figure 38a shows more detail compared to Figure 38c, such that the effects of the acoustic waves generated during the damping of the expansion of the tube are also visible, which are shown with arrows in Figure 38a. These effects are observed in the deeper region as expected, 1.2 and 1.4 cm depths, compared to point-like targets. These results shown in Figure 38 confirm that the quality of the photoacoustic images is better than that of the ultrasound images.

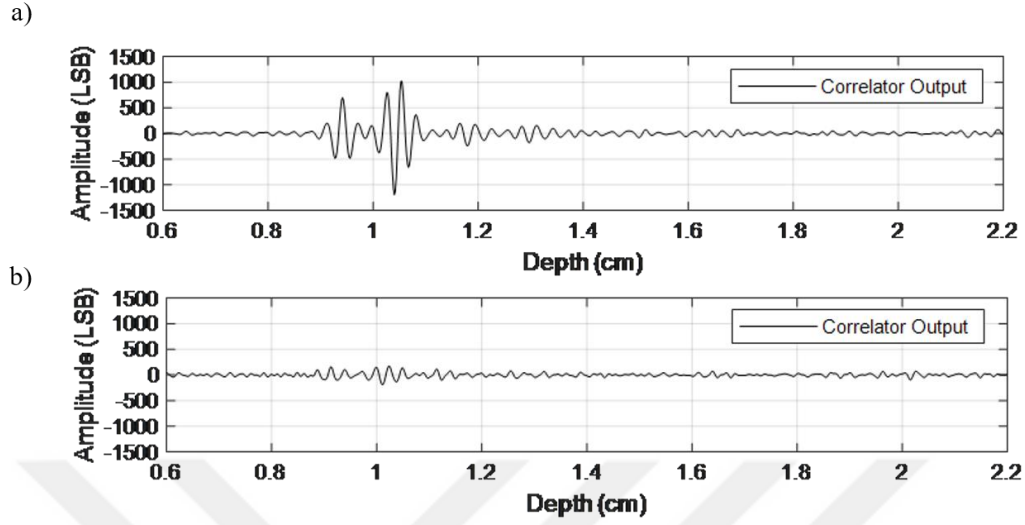
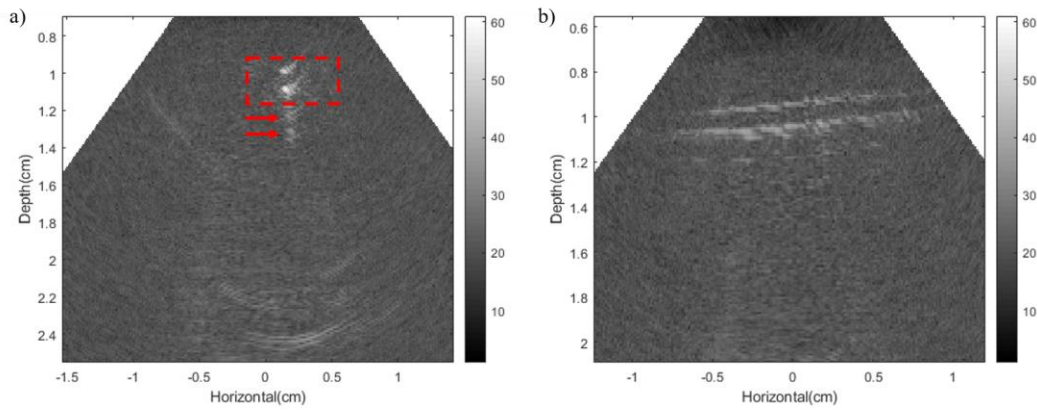


Figure 37: Correlator Outputs. The beamformed signals shown in Figure 36 are correlated with the beamformed signal generated due to the motion of the upper wall of the tube. a) The transducer is positioned such that its axis is perpendicular to the wave propagation axis. b) The transducer is positioned such that its axis is parallel to the wave propagation axis. The amplitude unit is the least significant bit (LSB) of the analog-to-digital converter in DiPhAS.



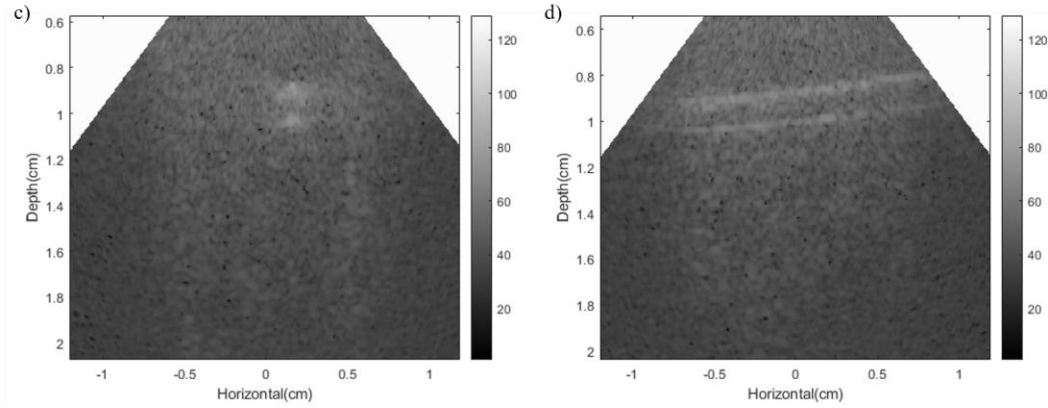


Figure 38: Perpendicular (a) and parallel (b) photoacoustic images with perpendicular (c) and parallel (d) ultrasound images. Photoacoustic images were taken at the concentration of 0.250 mg/mL, the excitation wavelength of 1064 nm, and the average energy of 5.0 mJ.

When the ultrasound probe orientation is changed such that its axis is parallel to the wave propagation axis, the quality of the photoacoustic image decreases significantly, as shown in Figure 39b, compared to the Figure 38a. The reason is the destructive addition of the acoustic waves in this probe orientation during their propagation toward the ultrasound probe. The significant decrease in the beamformed signal shown in Figure 38b manifests itself as poor quality in the photoacoustic image. Moreover, the parallel orientation of the transducer leads to the detection of the target as a line target instead of a point-like target. This is because, in this parallel orientation, the laser illuminates a longer section of the tube along its length. Despite this, the photoacoustic image shown in Figure 38b has a better image quality than the ultrasound image shown in Figure 38d in the case of parallel transducer orientations as well.

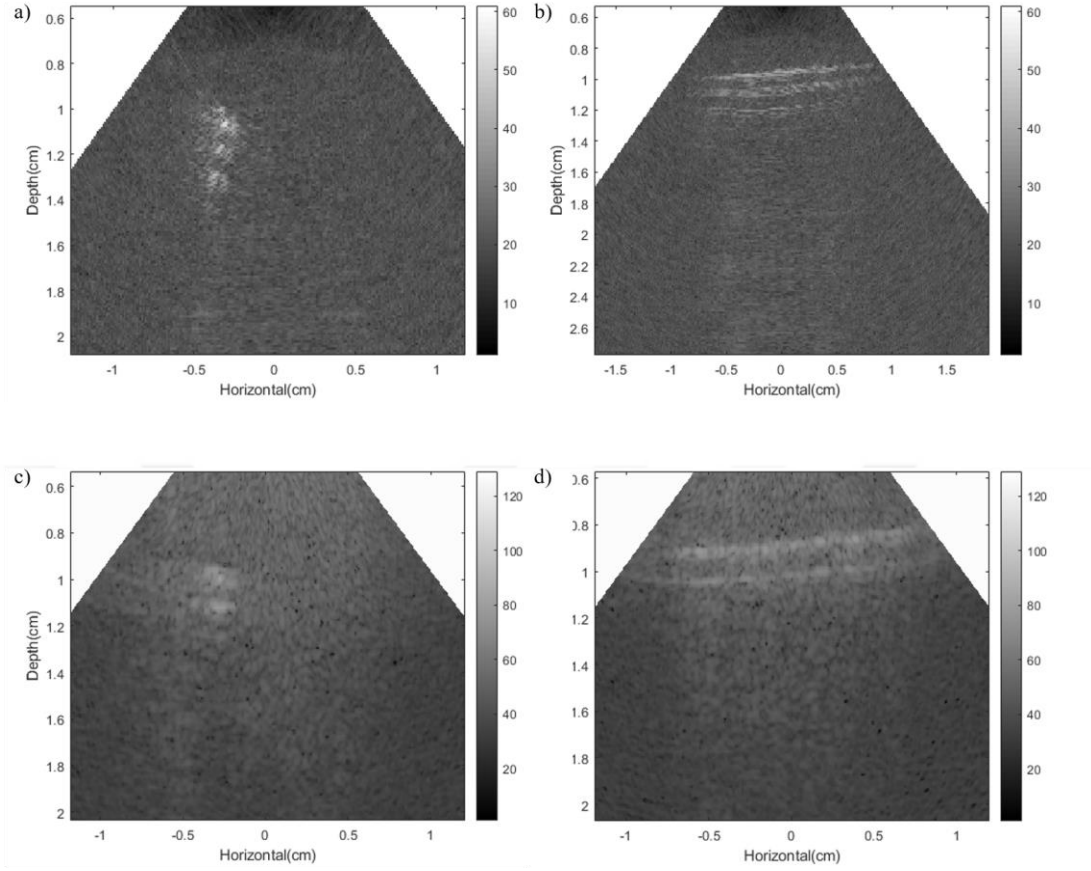


Figure 39: Perpendicular (a) and parallel (b) photoacoustic images with perpendicular (c) and parallel (d) ultrasound images. Photoacoustic images were taken at the concentration of 1.0 mg/mL, the excitation wavelength of 1064 nm, and the average energy of 5.0 mJ.

Figure 39 presents the photoacoustic and ultrasound images of the same polymer tube but with a different concentration of CSNPs, which is 1 mg/mL. We observed that the images shown in Figure 38 and Figure 39 have similar image qualities. However, the increased concentration causes an increased brightness around the surface and the bottom of the detected target in both Figures 39a and 39b compared to Figures 38a and 38b. As in Figure 38, the quality of the ultrasound images is significantly low compared to the photoacoustic images illustrated in Figure 39. Moreover, the transducer orientation has the same effect on both photoacoustic and ultrasound images in Figure 39 and Figure 38.

In conclusion, we demonstrated the synthesis of copper sulphide nanoparticles by nanosecond pulsed laser ablation in DMSO liquid in two different stoichiometries, namely Covellite (CuS) and Digenite ($\text{Cu}_{1.8}\text{S}$), in hexagonal and cubic orientations, respectively. We proposed that the rapid sulphurization of the target surface during long ablation times may have caused this dual synthesis.

The synthesized nanoparticles are characterized by XRD, TEM, UV-Vis-NIR spectroscopy and photoluminescence measurements. The synthesized nanoparticles are below 30 nm in size, mostly around 5-10 nm, have high absorbance in second near-infrared window, have a wide bandgap energy corresponding to 3.64 eV and two photoluminescence peaks at 383 nm and 570 nm when excited at 320 nm. In photothermal experiments, we achieved rapid local heating in laser irradiation regions, power and concentration-dependent heating, and photothermal stability upon heating-cooling cycles. In photoacoustic imaging experiments, we achieved significant contrast enhancement in perpendicular transducer placement and lesser contrast enhancement in parallel transducer placement due to increased volume and destructive addition of acoustic waves. These results are also verified with correlator outputs. With these results, we can deduce that photoacoustic imaging from deeper depths are within possibility with appropriate nanoparticle concentration and laser pulse energy.

4 SYNTHESIS OF UPCONVERSION NANOPARTICLES

4.1 Target Preparation

The target material is prepared by the invited scientist Dr. Hamid Reza Bahari-Poor in Ortaç Research Group.

The target is composed of Y_2O_3 at 83%, Yb_2O_3 at 16%, and Er_2O_3 at 1% in weight. The target will be referred as YYB. To prepare the YYB target, the powders of these rare-earth oxides are mixed and grounded. Following up, a calcination process of the grounded powder was done at 1200 °C for 8 hours in ambient atmosphere. Then, a sintering process of the pressed pallet was done at 1400 °C for 8 hours in ambient atmosphere to solidify the target. This target is then characterized with XRD, SEM imaging, absorbance spectrometer, and photoluminescence spectrophotometer. The YYB target is then used to synthesize nanoparticles.

4.2 Target Properties

The YYB target is first characterized by XRD analysis. The analysis is done by Panalytical X'Pert PRO Multipurpose Diffractometer operating at 45 kV and 40 mA. The sample is fixed on the analysis plate with a dough and flattened with a glass slide for proper data acquisition. XRD analysis is done between 2θ angles from 10 to 100. Figure 40 shows the XRD pattern of the YYB target material. According to XRD reference (ICDD No: 01-071-0099) the compound is yttrium oxide (Y_2O_3), has cubic crystal system and it is in space group Ia-3 with space group number 206. Y_2O_3 has 48 peaks between angles 10 to 100. For the sake of readability, only the ones above 10%

of the highest intensity are examined. The peak at 20.716° corresponds to (211), the peak at 29.369° corresponds to (222), the peak at 34.017° corresponds to (400), the peak at 48.750° corresponds to (440), and the peak at 57.836° corresponds to (622).

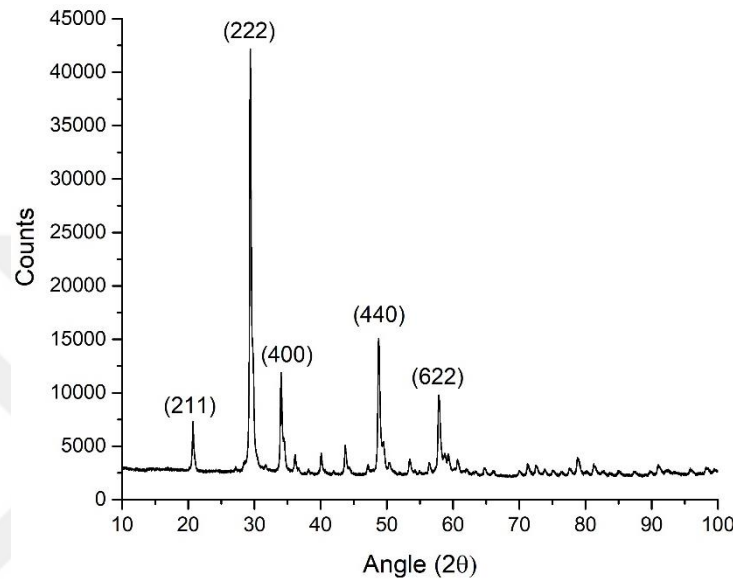


Figure 40: XRD pattern of the YYB target material

After XRD analysis, an SEM study is done to analyze the morphology of YYB target. A small

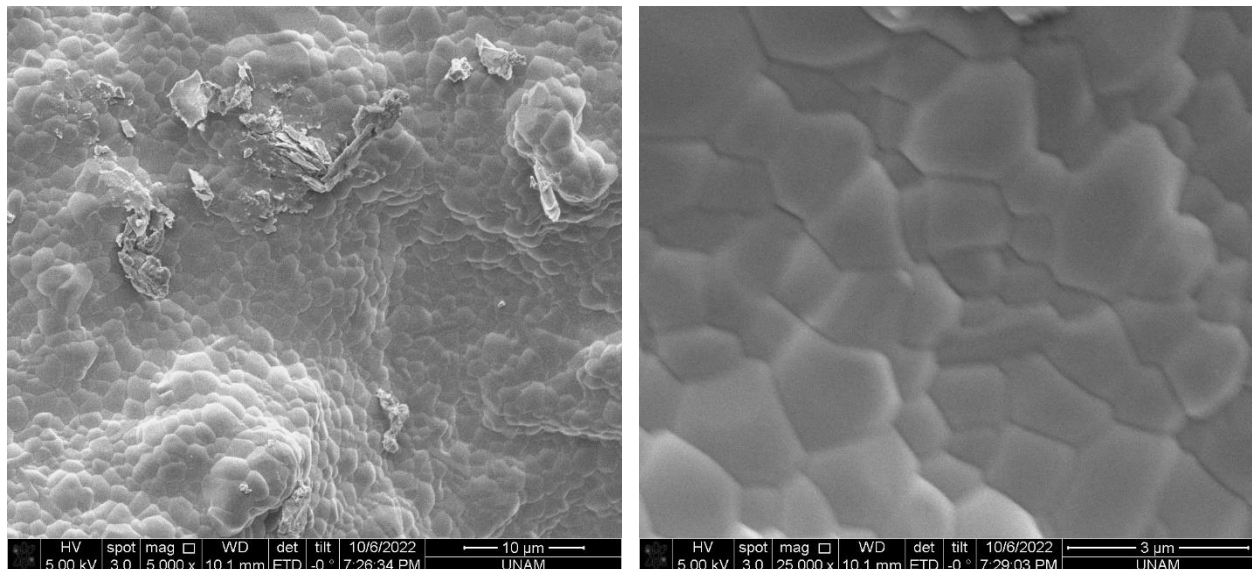


Figure 41: SEM images of sintered YYB target at 5000x and 25000x magnification

Piece from the target is removed and coated with 10 nm of gold/palladium. The images are taken at 5.00 kV with a 3.0 spot size. The images confirm that crystalline phase is well diffused and it's fully compact. The grains have grown into bubble shapes in a 1.0 – 1.5 microns of sizes. The boundaries of the grains show that there are not void spaces between the grains.

4.2.1 Optical Properties of the YYB Target

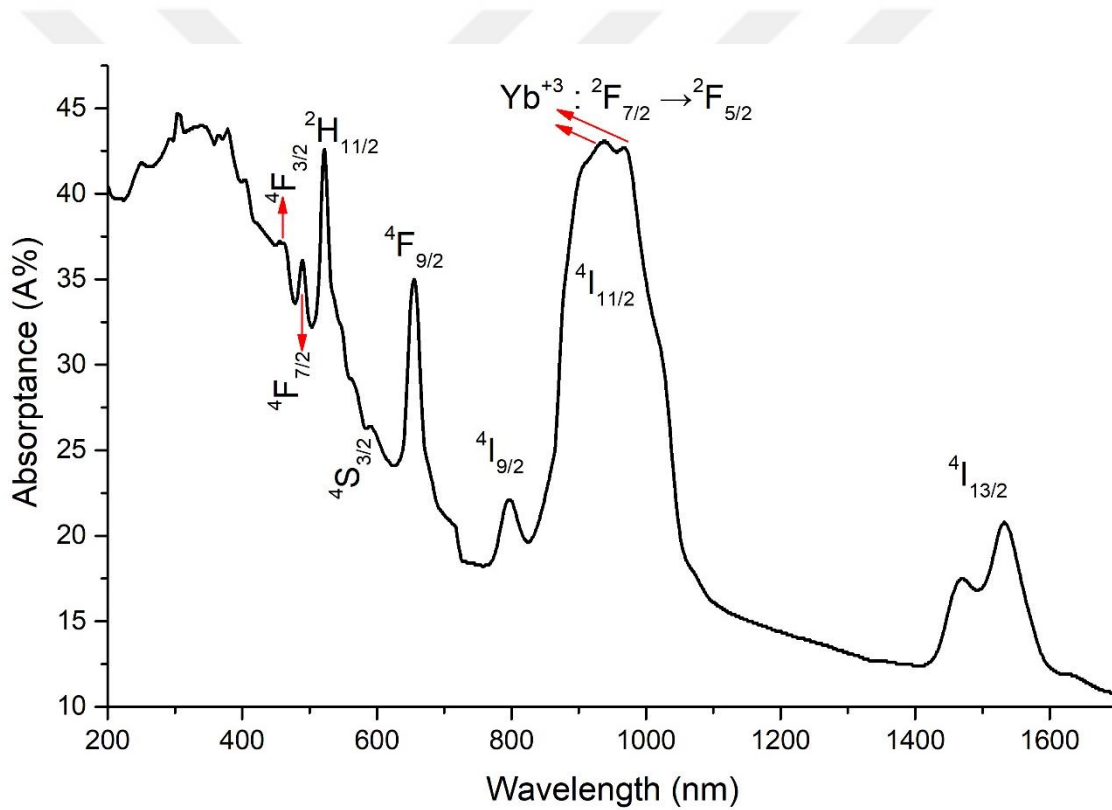


Figure 42: Absorbance graph of the YYB target

Absorbance properties of the YYB target is shown in Figure 42. The data is recorded with the diffuse reflection spectroscopy setup. Some of the absorbance levels and the corresponding regions of wavelength of the Yb³⁺ and Er³⁺ ion is shown in the figure. The envelope at 975 nm also includes the excitation of Er³⁺: $4I_{15/2} \rightarrow 4I_{11/2}$ so this envelope is important for our work.

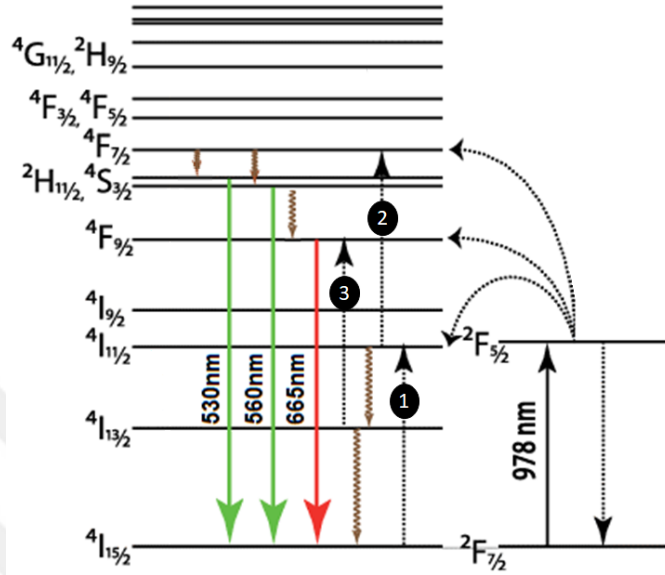


Figure 43: Simplified photoluminescence diagram of excitation of Yb^{+3} and emission from Er^{+3}

Figure 43 shows the photoluminescence diagram of Er^{+3} ion on the left and Yb^{+3} ion excitation on the right. The YYB target is composed of both Yb and Er because Yb^{+3} ions are used as a synthesizer to pump Er^{+3} ions for upconversion process.

Two phenomena occur during this upconversion photoluminescence process. First, Yb^{+3} ions absorb the incident light at 978 nm. This is ground state absorption and electrons in $2\text{F}_{7/2}$ level of Yb^{+3} ions are excited into the $2\text{F}_{5/2}$ level. Then, this is followed by an energy transfer process from the $2\text{F}_{5/2}$ level of Yb^{+3} to $4\text{F}_{11/2}$ level of Er^{+3} ion. Electrons in Er^{+3} are now in excited level of $4\text{F}_{11/2}$. The second process which is excited state absorption occurs at this stage. The photons with 978 nm wavelength excite these electrons into upper levels. This is shown by arrow with 2 in the figure. Electrons are excited into $4\text{F}_{7/2}$ level with excited state absorption process. Non-radiative relaxation processes can occur at this stage. If the electron relaxes into $2\text{H}_{11/2}$ level (shown with the leftmost brown relaxation arrow) a photon is emitted with 530 nm of wavelength. If the relaxation occurs

into the $^4S_{3/2}$ level, shown by second relaxation arrow, a photon would be emitted with 560 nm wavelength. These two emissions form the green emission from the YYB target [106].

The red emission occurs via a different excitation process. From $^4S_{3/2}$ level, electrons can further relax into $^4F_{9/2}$ level. The photons emitted from this level would have 665 nm wavelength. In addition, after the first excitation from Yb^{+3} pump, the electron can also relax into a lower level without getting excited into upper levels. If this happens, the electrons would relax into $^4I_{13/2}$ level. From this level, the excited state emission process can still occur. This is shown by the 3rd excitation process in the figure. When excited from this level, electrons go up to $^4F_{9/2}$ level. Again, the photons emitted from this level have 665 nm wavelength. These two processes make up the red emission of the YYB target.

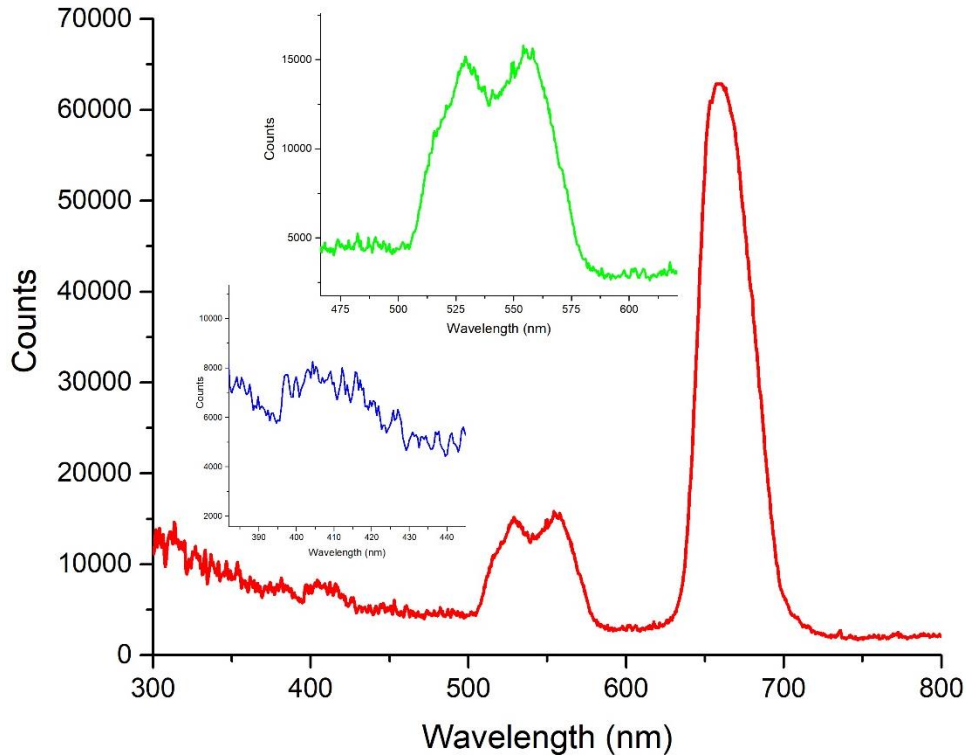


Figure 44: Photoluminescence graph of YYB target

The photoluminescence property of the YYB target is recorded and shown in Figure 44. The spectrum is recorded by using OceanView spectrometer which uses a fiber optic cable to capture the light which is placed at a 45° angle to the target. The target is irradiated by a 980 nm laser light. Figure 44 shows the photoluminescence graph of the YYB target. The target shows a small peak around 410 nm for the fourth excitation process Er^{+3} ion. The second peak comes from the green region. This region contains two peaks as described before in the text. The first peak is at 529 nm and second peak is at 558 nm which are consistent with the theory. The last peak comes from the red emitting region. The wavelength of the peak is at 660 nm. Overall, the target shows a strong red emission and an emission of green which is about a quarter of the intensity of the red emission.

4.3 Nanoparticle Synthesis from YYB Target and its Properties

YYB target is immersed in 2 mL of ethanol and ablated with a femtosecond pulsed laser (Spitfire, Spectra Physics) for 1 hour. 2 mL of ethanol was used to lower the distance between surface of the target and surface of the liquid to increase laser ablation productivity. The pulsed laser operates at 150 fs pulse duration, 1 kHz repetition rate, and has a wavelength of 800 nm. The average power of the laser was 500 mW which corresponds to 500 μJ energy per pulse. The YYB target was cleaned with acetone and ethanol before the ablation process. The laser beam was focused onto the surface of the target with a 60 mm planoconvex focusing lens.

The characterization of synthesized nanoparticles is done by TEM imaging, and photoluminescence measurement. The TEM image is taken with HR-TEM, FEI-Tecnai G2F30

operating at 300 kV voltage. The TEM samples prepared by taking one drop from the colloid and drop casting onto carbon coated Cu TEM grid. The photoluminescence spectrum of the nanoparticles is recorded with Horiba Scientific Jobin Yvon, Fluorolog, FL-1073 with the excitation wavelength at 978 nm.

Figure 45 shows the TEM image of the YYB upconversion nanoparticles (YYB-UCNP). The scale bar is at 50 nm length. The image shows that the nanoparticles are smaller than 50 nm and they have spherical shapes. It is visible that although there are some nanoparticles with diameters close to 50 nm, most of the nanoparticles have very small sizes.

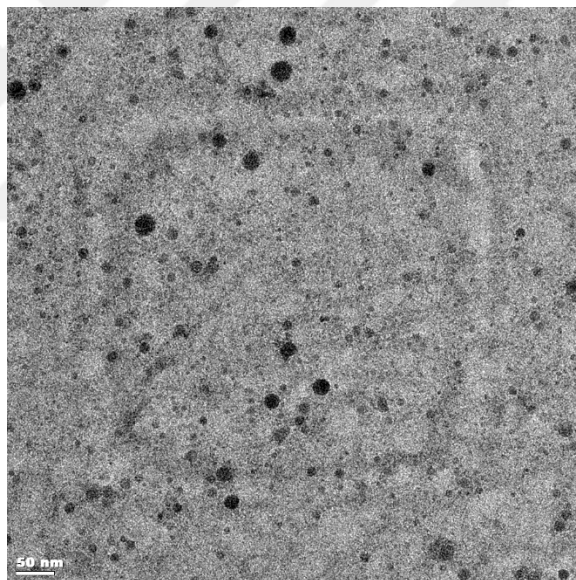


Figure 45: TEM image of YYB UCNP

Figure 46 shows the photoluminescence spectrum of the synthesized upconversion nanoparticles from YYB target in ethanol and the inset of the graph shows the zoomed in green emission and the photo shows a 980 nm laser excitation from our photoluminescence setup. UCNPs show a peak at 651 nm and a very small emission in green region which is between 560 - 575 nm. The YYB

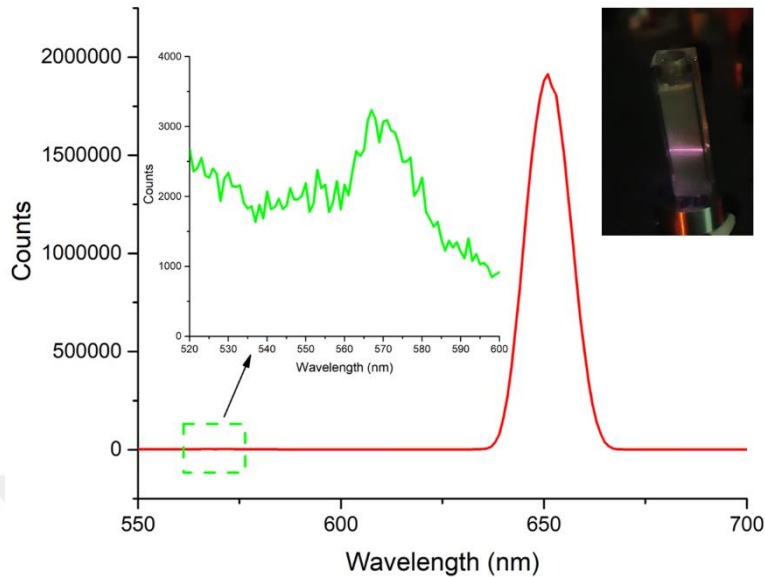


Figure 46: Photoluminescence spectrum of YYB-UCNPs (inset shows a photograph from our photoluminescence setup with 980 nm laser excitation)

target has a green emission which was around one fourth of the red emission in terms of count number. The UCNPs show a very dramatic change in the intensity of the red and green emissions. The count for red emission is around 2,000,000 while green emission count is around 3000. The ratios of photoluminescence intensity of red and green emissions between the YYB target and synthesized YYB-UCNPs are 0.25 for the target and 0.0015 for the nanoparticles. The green emission drops to 166 times lower intensity. This might be happening from the defects in the crystal from the laser ablation process. These defects might be increasing the chance of non-radiative decay from $^4F_{7/2}$ level to $^4F_{9/2}$ level and $^4I_{11/2}$ to $^4I_{13/2}$ level. These decays increase the chance of red emission and also increase the heat production from the nanoparticles. This property can be useful for photoluminescence - photothermal applications.

5 CONCLUSION

In this thesis, several nanoparticles are synthesized with pulsed laser ablation in liquids method. Gold nanoparticles are synthesized by nanosecond pulsed laser ablation in methanol and characterized by XPS, TEM, SEM and absorbance spectrophotometer. The nanoparticles have spherical shape and have diameters smaller than 50 nm. The optical absorbance data show that nanoparticles have a LSPR peak at 548 nm. After the synthesis and characterization of nanoparticles, they are used to boost the efficiency of organic solar cells. This is done by embedding the synthesized nanoparticles into the active layer of the solar cells without changing the thickness of this layer to achieve higher photocurrent production. Organic solar cells with nanoparticle incorporated at 0.129% in mass have shown the highest power conversion efficiency and thiol-modified nanoparticle incorporated organic solar cells have the highest external quantum efficiency value.

Secondly, AgCu alloy nanoparticles are synthesized by femtosecond pulsed laser ablation in ethanol. The targets were produced by arc melting method with atomic percentages of $\text{Ag}_{1-x}\text{Cu}_x$ where ($x = 0.15, 0.30, 0.50, 0.70, 0.85$). These nanoparticles are then characterized with absorbance spectrophotometer and scanning electron microscope. After laser ablation, alloy nanoparticles show tunable LSPR effect in relation to their composition. The peak wavelength changes between 420 – 580 nm, resulting in a 160 nm tunability of plasmonic absorbance peak. The nanoparticles show biphasic type Janus nanoparticle and core-shell type configurations. When these nanoparticles are laser fragmented, the LSPR peak could be shifted to Ag region of plasmonic absorbance. It was concluded that laser fragmentation in ethanol caused the Cu atoms to oxidize

and lose their plasmonic absorbance property. The fragmentation time, nanoparticle concentration and laser power allowed us to control the oxidation level of the nanoparticles, giving us another tunability of the plasmonic absorbance behavior. In addition, nanoparticles with complex morphology could be synthesized with this way. Snowman and dumbbell type AgCu Janus nanoparticles covered by copper oxide shell were seen in the SEM images. PLAL and PLFL methods may be used to synthesize alloy nanoparticles with complex morphologies and tunable optical properties.

Third, copper sulphide nanoparticles (CSNPs) were synthesized by nanosecond laser ablation in DMSO. These nanoparticles are then characterized by TEM, absorbance spectrophotometer, photoluminescence spectrometer, XRD, EDX, and zeta potential-size measurements. The nanoparticles have spherical shapes and smaller than 30 nm, and most of them have sizes smaller than 10 nm. CSNPs show a wide absorbance region between 1000 – 1600 nm with the peak wavelength at 1183 nm. XRD results showed that the CSNPs have two different crystals with CuS and Cu_{1.8}S appearing in the XRD result. To the best of our knowledge, this is the first synthesis of Cu_{1.8}S nanoparticles with PLAL method. Zeta potential measurements show that CSNPs are not stable and they have -11 mV of zeta potential which is below the ± 30 mV threshold for stable colloids. After synthesis and characterization, photothermal and photoacoustic properties of the CSNPs are investigated. Our results show that CSNPs synthesized with 1 mg/mL concentration of Cu can result in a 52.2 °C increase when irradiated with a CW laser with 1080 nm wavelength. They are photothermally stable as shown with the cycle experiments. Even, a few micrograms per milliliter showed a great potential in photothermal measurements. In addition, photoacoustic imaging experiments showed that 0.250 mg/mL concentration nanoparticles show a signal to noise ratio better than ultrasonic imaging measurements. Cell studies of our CSNPs on MCF-7 cells

showed that CSNPs have low cytotoxicity and irradiation with 1080 nm CW laser for 5 minutes with different concentrations show a concentration dependent cell viability. This proves that CSNPs have great potential in photothermal therapy.

Lastly, upconversion nanoparticles are synthesized by femtosecond laser ablation in ethanol. The target material and synthesized nanoparticles are characterized with TEM, XRD, UV-Vis-NIR absorbance spectrophotometer, and photoluminescence spectrophotometer. A target with Y_2O_3 at 83%, Yb_2O_3 at 16%, and Er_2O_3 at 1% in weight was prepared by calcination of powders and sintering of pressed pellet. Nanoparticles are synthesized in ethanol from this target. TEM image shows that nanoparticles have spherical shape and have diameters smaller than 50 nm. Photoluminescence measurements of the target and the synthesized nanoparticles show that our UCNPs show a great red emission from 980 nm laser irradiation. In addition, nanoparticles show much lower green emission compared to the target material, which gives rise to increased heat production from nanoparticles, increasing the potential use in photothermal – photoluminescence applications.

In conclusion, several nanoparticles have been synthesized by pulsed laser ablation in liquid method and their optical applications have been realized. PLAL is a promising method to synthesize nanoparticles with fast production rate, small sizes, spherical shapes or complex morphologies. Compounds can be synthesized by the interaction of the liquid and target material from basic pure targets. PLAL also is a green method that can synthesize chemical free, pure nanoparticles. In the future, it is expected that PLAL method will become a more common method with the availability of high-power pulsed lasers.

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