

SYNTHESIZATION OF NOBLE METAL NANOPARTICLES BY PULSED LASER ABLATION METHOD IN LIQUIDS AND THIN FILM APPLICATIONS

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By

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ABSTRACT

SYNTHESIZATION OF NOBLE METAL NANOPARTICLES BY PULSED LASER ABLATION METHOD IN LIQUIDS AND THIN FILM APPLICATIONS

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Pulsed Laser Ablation in Liquid (PLAL) is promising, alternative, easy, fast and free of agent method for synthesization of nanoparticles (NPs). Various kinds of NPs can be synthesized easily by PLAL, such as base metals, noble metals, semiconductors, nanoalloys, magnetic and core-shell nanostructures. Additionally, crystallized NPs can be easily obtained in one-step procedure by PLAL without subsequent heat-treatments. Synthesization of gold (Au), silver (Ag) and platinum (Pt) NPs with PLAL using Nd: YLF laser (Q-Switched Laser, 527 nm wavelength, 16 W average power, 110 ns pulse duration, and 16 mJ pulse energy for 1 kHz) in different liquid environments is reported. Firstly, Ag, Au and Pt NPs have been synthesized with pulsed Nd: YLF laser in deionized water. Secondly, these NPs have been synthesized in methanol under similar conditions. Colloidal NP solutions are then characterized with Transmission Electron Microscopy, Scanning Electron Microscopy, X-Ray Photoelectron Spectrophotometer, X-Ray Diffractometer and UV-Vis Photospectrometer analysis techniques.

In the second part, applications of noble metal nanoparticles have been investigated. Firstly, Au and Ag NPs have been synthesized in Polyvinylpyrrolidone solution in order to prepare nanofibrous composites. The Au and Ag NPs embedded in nanofibrous composites then characterized with UV-Vis Photospectrometer and Transmission Electron Microscopy. In addition, AuNPs have been synthesized with varying energies of laser (9,2 mJ, 12 mJ and 16 mJ for 1kHz) in order to understand the role of laser energy on PLAL. Finally, thin-film applications also presented: Pulsed Laser Deposition by PLAL and simple spin-coating deposition with AuNPs synthesized in methanol.

Keywords: Pulsed Laser Ablation Method, Gold, Silver and Platinum Nanoparticles, Pulsed Laser Deposition, Thin Film Deposition, Optical Characterization, Transmission Electron Microscopy, X-Ray Photoelectron Spectroscopy, X-Ray Diffractometer.

ÖZET

SOY METAL NANOPARÇACIKLARIN DARBELİ LAZER ABLASYON YÖNTEMİYLE SIVILARDA ÜRETİMİ VE İNCE FİLM UYGULAMALARI

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Sıvı içerisinde Darbeli Lazer Ablasyon gittikçe gelişen, diğer nanoparçacık üretim tekniklerine alternatif olabilecek, kolay, hızlı ve başka bir kimyasal ajan gerektirmeyen nanoparçacık üretim tekniklerinden biridir. Bu teknik ile baz metal, yarıiletken, manyetik nanoparçacıklar ile alaşım halinde veya çekirdek-kabuk şeklinde olan nano yapılar üretiler. Kristal nanoyapıları ısı işlemi gerektirmeden tek bir adım ile elde etmek mümkündür. Altın, gümüş ve platin nanoparçacıkların Nd: YLF lazer (Q-Anahtarlama, 527 nm dalga boyu, 16 W ortalama güç, 110 ns darbe süresi, ve 1 kHz için 16 mJ darbe enerjisi) sistemi kullanılarak deiyonize su ve metanol sıvıları içerisinde Darbeli Lazer Ablasyon yöntemi ile üretimi rapor edilmiştir. Geçirgen Elektron Mikroskobu, Taramalı Elektron Mikroskobu, X-Işınlı Fotoelektron Spektroskopisi, X-Işınlı Kırınım Ölçer ve Morötesi / Görünür Bölge Spektroskopisi ile oluşturulan koloidal nanoparçacık sıvıların karakterizasyonları sunulmuştur. Tezin ikinci bölümünde, soy metal nanoparçacıkların uygulamalarına örnek olarak ilk başta altın ve gümüş nanoparçacıklar polimer bir sıvı olan Polyvinylpyrrolidone

içinde nanofiber yapılarda kullanılmak için sentezlenmiştir. Elde edilen nanofiberler içerisine gömülü nanoparçacıklar Taramalı Elektron Mikroskobu ve Morötesi / Görünür Bölge Spektroskopisi ile karakterize edilmiştir. Lazer enerjisinin Darbeli Lazer Ablasyon'da ki rolünü anlamak için lazerin ortalama enerjisi 9,2mJ, 12 mJ ve 16 mJ olarak değiştirilerek deiyonize su içerisinde altın nanoparçacıklar elde edilmiş ve karakterize edilmiştir. Bu uygulamalara ek olarak, cam örnek üzerine sıvı içinde Darbeli Lazer Kaplama tekniği ile film büyütülmesi ve nanoparçacık sıvıdan ince film kaplama yapılması ele alınmıştır.

Anahtar Sözcükler: Darbeli Lazer Ablasyon, Altın, Gümüş ve Platin Nanoparçacıklar, Darbeli Lazer Kaplama, İnce Film, Optiksel Karakterizasyon, Geçirgen Elektron Mikroskobu, X-Işınlı Fotoelektron Spektroskopisi, X-Işınlı Kırınım Ölçer.

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Dedicated to my lovely Grandmother

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List of Symbols/Abbreviations/Acronyms

NP - Nanoparticle	SPR - Surface Plasmon Resonance
NPs - Nanoparticles	LSPR – Localized Surface Plasmon Resonance
NMNP - Noble Metal Nanoparticle	XPS - X-Ray Photoelectron Spectroscopy
NMNPs - Noble Metal Nanoparticles	XRD - X-Ray Diffractometer
PLA - Pulsed Laser Ablation	SEM - Scanning Electron Microscope
PLAL - Pulsed Laser Ablation in Liquids	EDX - Energy Dispersive X-Ray
Au – Gold	TEM - Transmission Electron Microscope
Ag – Silver	Nd: YLF - Neodymium-doped yttrium lithium fluoride (Nd: LiYF ₄)
Pt – Platinum	Nd: YAG - Neodymium-doped yttrium aluminum garnet (Nd:Y ₃ Al ₅ O ₁₂)
Cu - Copper	a.u. - arbitrary unit
AuNP - Gold Nanoparticle	fcc - face-centered cubic
AuNPs – Gold Nanoparticles	PVP - Polyvinylpyrrolidone
AgNP - Silver Nanoparticle	nm – nanometer
AgNPs – Silver Nanoparticles	cm - centimeter
PtNP - Platinum Nanoparticle	
PtNPs – Platinum Nanoparticles	
UV - Ultraviolet	
DVD - Digital Versatile Discs	
Vis - Visible	
NaBH₄ - Sodium Borohydride	
PLD - Pulsed Laser Deposition	

Chapter 1

1. Introduction

1.1 Nanotechnology & Nanomaterials

Basic advancements in science and technology may arise twice in a century and lead to a massive wealth creation. For instance, textile which left its place to railroads and automobiles in the 20th century, was the main technology in 19th century. Today, we use computer-oriented technology being estimated to last till 2025. Nanoscience and Nanotechnology will be one of the future possible dominant technologies in the 21st century and we are just at the beginning [1]. The new technology starts with the famous speech of Richard Feynman; “There is Plenty of Room at the Bottom”, claiming that 24 volumes of Encyclopedia Britannica can be written on the head of a pin. If Feynman had been justified, even all books in The Library of Congress, British Museum Library and National Library in France could have been as small as three square yards (two and a half meter square) [2]. Today, we experience that he is right! Recent technological devices such as, Digital Versatile Discs (DVDs), notebooks, smart phones, textile products and many other electronic devices use nanotechnology. These new advancements are the only visible part of an iceberg and the influence of nanotechnology will be felt more in all areas of our daily lives in the future. Basically, nanotechnology deals with processes taking place at the nanometer scale that is, approximately 1 to 100 nm. Nanoparticle (NP) is a particle whose three

dimensions are 1 to 100 nm exists in diverse shapes such as spherical, triangular, cubical, pentagonal, rod-shaped, shells, ellipsoidal and so forth [3]. Moreover, NP has a higher surface to volume ratio and increased percentage of atoms at the grain boundaries giving it distinctive features and enabling it to have unique optical, catalytic, and electrical properties [3]. These properties make NPs so important in nanotechnology that it is used in various applications such as surface-enhanced Raman spectroscopy [4], nanophotonics devices [5], drug delivery [6], solar cells [7], catalysis [8], sensor [9] and nanotextile [10].

1.2 The Synthesis of Nanoparticles

1.2.1 Top-down method

Top-down method is essentially the breaking down of a system into its subsystems. It can be exemplified as constructing a building or a statue by shaping a rock. The top-down approach often uses cutting, milling or drilling tools to get smaller components. Micropatterning techniques such as, photolithography, plasma etching and laser ablation can be classified under this method.

1.2.2 Bottom-up method

Bottom-up method is uniting of smaller components to comprise larger systems. It can be represented as constructing a building by uniting bricks or assembling the parts of a car engine. In biotechnology, bottom-up method is used to get biotechnological components by combining single molecules. In nanotechnology, it can be defined as self-assembly of atoms and molecules to form larger systems. Chemical vapour deposition (CVD) and sol-gel process can be classified under this method.

1.3 Nanoparticle Synthesis Techniques

A number of techniques can be used for NP preparation. Some examples are chemical reduction [11], photo-reduction [12], flame metal combustion [13], electrochemical reduction [14], solvothermal [15], electrolysis [16], chemical fluid deposition [17], and spray pyrolysis [18]. The standard method to obtain Noble Metal Nanoparticles (NMNPs) is chemical reduction of metal salts in the presence of stabilizing molecules [19]. The citrate reduction method in aqueous solution and the NaBH_4 reduction method are the most popular methods for synthesis of NMNPs [19]. In addition, the pulsed laser ablation in liquids (PLAL) has become an increasingly popular top-down approach for producing NPs. PLAL has been a relatively new method that was first introduced by Fojtik et al. in 1993 [20] and has become increasingly popular top-down approach method.

1.4 Pulsed Laser Ablation Method

Pulsed laser ablation (PLA) has been used since the invention of the pulsed ruby laser in 1960 by T.H.Maiman [21]. Soon after this invention, Brech and Cross used ruby maser to observe the scattering of light from metal surface and it was the first time of laser-material interaction [22]. First studies about PLA were performed in diluted gas and vacuum environments in the late 80s. The first study of PLA at the solid-liquid interface was reported by Patil and his co-workers in 1987 [23]. Patil and his co-workers synthesized metastable form of iron oxide using high power pulsed laser in liquid [23]. Basically, PLA has three alternative techniques according to its environment; vacuum, gas and liquid. Among them, liquid environment is the newest one

compared to the others and has received much attention as an original NP production technique.

PLAL has many individual advantages over other NP synthesization methods. First of all, it is chemically free of agents and the experimental set-up is cheap provided that laser is available and has easily controlled parameters. Secondly, various kinds of NPs can be synthesized easily by PLAL, such as metals [24], noble metals [10], semiconductors [25], nanoalloys [26], magnetic [27] and core-shell nanostructure [28]. Additionally, crystallized NPs can be easily obtained in one-step procedure by PLAL without subsequent heat-treatments [10]. These advantages allow a designer to use number of choices of different targets and liquids corresponding to the desired parameters of synthesis.

Solvents, pulse duration and power of a laser are parameters of PLAL. Provided that one of these parameters changed, the size and shape of nanoparticles could be changed. For instance, AuNPs synthesized in water consist of 8 nm diameter (64% standard deviation), if a 1064-nm wavelength, 9 nanosecond pulse duration and 10-20 Joule/cm⁻² fluence is used [19]. On the other hand, they have 4-130 nm diameters when 800 nm wavelength, 120 femtosecond pulse duration and 60-1000 Joule/cm⁻² fluence is used [19].

If the solvent changes, all thermodynamic relation between liquid and target changes as well. For instance, AgNPs have diameter of 7.8 nm (with 49% standard deviation) in Dimethylsulfoxide, 4.8 nm (with 46% standard deviation) in Tetrahydrofuran and 3.8 nm (with 79% standard deviation) in Acetonitrile when 1064 nm wavelength, 9 nanosecond pulse duration and 10 Joule/cm⁻² laser fluence is used [19].

1.5 Noble Metal Nanoparticles

Gold, Silver, Mercury, Platinum, Iridium, Palladium, Osmium, Rhodium, and Ruthenium are known as noble metals and show high resistivity to oxidation and corrosion even at high temperatures and these features make them precious metals. These metals show distinctive physical and chemical properties different from the most base metals and lead to use noble metals as a “nanoparticles” in nanotechnology. NMNPs are widely used and applicable in nanotechnology due to the existence of localized plasmonic modes in the visible–near infrared interval, the easy surface functionalization and the chemical and physical stability [19]. These features of NMNP have attracted great attention in the field of optoelectronics, biotechnology, chemical applications. The number of publications on NMNPs shows exponential growing and thus they are indispensable and the basis for the most of the applications on nanotechnology [3].

1.6 Optical, Thermal and Catalytic Properties of Noble Metal Nanoparticles

Optical properties, such as optical emission and absorption, purely depend on transition between valence band and conduction band. Noble metals, similar to other metals, do not have their electrons on bounded. There is a cloud around the atomic core and thus they become good conductors. This unique property also affects optical properties. When a photon with certain wavelength comes onto this cloud, photon can be absorbed and oscillations in the electron cloud are produced. This phenomenon is formed on the surface of metals thereby

it is called Surface Plasmon Resonance. Other photons with various wavelengths can be reflected and may not get in oscillation.

The penetration depth of Electromagnetic (EM) waves in metal is at the order of 30 nm [3]. Provided that the diameter of a NP is smaller than 30 nm, the EM waves can propagate through the particle. These EM waves drive conduction band electrons as a group according to the fixed positive lattice ions [3]. Eventually, a net charge difference occurs on the surface of nanoparticle [3]. These charges form an oscillating dipole and radiate EM waves. The radiated EM waves are known as Localized Surface Plasmon Resonance (LSPR). If some of the photons are released with the same frequency in all directions, this process is called scattering. If some of the photons are converted into phonons or vibrations of the lattice, this process is referred to as absorption [3].

If the diameter of a particle gets smaller the energy required to collectively excite motion of the surface plasmon electrons increases [29]. If the shape of the particles changes, same conditions occur. Thus, we observe changes in plasmon resonances causing a difference in absorption peaks. Moreover, on the condition that a surrounding medium changes, the surface plasmon resonance band changes as well due to the dielectric properties of the surrounding medium [30]. Surrounding medium with high refractive indices is much more polarizable and thus couples with the surface plasmon electrons more readily [31]. The energy required to excite the electrons collectively is decreased [31]. The technique for measurement of SPR can be performed with a standard ultraviolet-visible (UV-Vis) spectrometer. Figure 3-1 illustrates the absorption spectrum of AuNPs and the image of various sizes and shapes of AuNPs. As seen in the figure, the energy

required to excite the surface plasmon of Au NPs with diameters near 5 nm is comparable to the energy of visible light [31].

NMNPs are used for their LSPR in some fields. Here are some examples:

- The molecule-specific imaging and diagnosis of diseases such as cancer can be carried out by means of the strong LSPR scattering of AuNPs conjugated with specific targeting molecules [32].
- Nanorods or nanoshells of Au have LSPR is in the near-infrared region. Hence, they can be used in vivo imaging and therapy [32].
- Nonspherical plasmon resonant NMNPs offer favorable properties for their use as analytical tools, transport vehicles, as well as diagnostic and therapeutic agents [33].

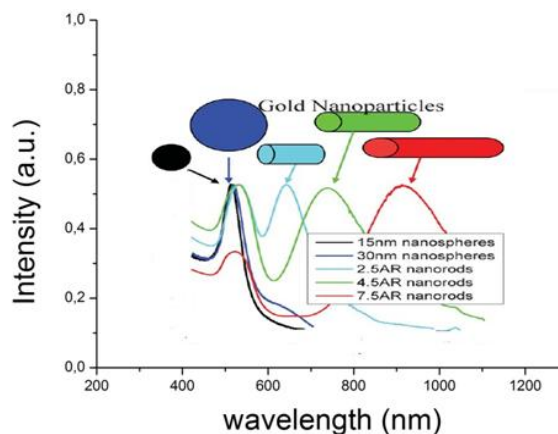


Figure 1-1. Absorption spectrum various sizes and shapes of AuNPs. Adopted from [34].

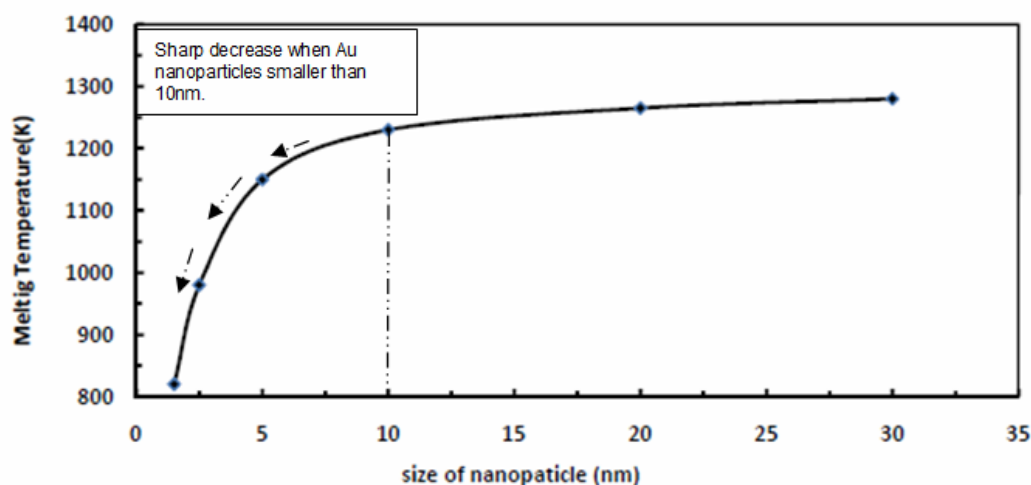


Figure 1-2. Relation of melting point and radius of Au Nanoparticles [36].

A large increase in the surface area of NPs has a significant effect on material properties as well. For instance, the melting point of AuNPs can decrease significantly for particle sizes less than 10 nm [35]. Figure 1-2 shows the relation of melting point and radius of AuNPs. It is clear from the figure that the melting point of AuNPs with smaller sizes than 10 nm decreases sharply.

The exposed surface is the only active area for catalytic properties of any materials because inner atoms do not interact with substrates [37]. Therefore, NPs can be better candidates for catalytic reactions instead of bulk ones. Noble metals, especially Pt, are known as good catalysts and they are deeply studied and used for catalytic applications. Although they are very efficient for speeding up reactions, they are very expensive and the price of Pt limits the use of these materials as a catalyst. Therefore, smaller particles are required for cost efficiency. For instance, a Au particle with 20 nm diameter contains 384.000

atoms, while a 3-nanometer particle contains 300 times fewer atoms almost 1.300 atoms [37]. Assuming the both AuNP as a sphere, we can calculate their surface area. A 20-nm AuNP has 1256 nm² surface area on the other hand a 3-nm AuNP has 28.27 nm² surface area. We realize 300 times fewer atoms at a 3-nm AuNP but the surface area is about 44 times less. The smaller particles we get the more efficient catalysts we obtain. Therefore, more effective and low-cost catalyst can be generated by increasing active area interacting with substrate and decreasing the volume of the catalyst. Although smaller NPs are more effective and cheaper as a catalyst, it is inevitable to face some drawbacks. For instance, a PtNP with 2 nm produces water for the synthesis of hydrogen peroxide and limits our cost-efficiency problem [37]. As a result, the controlling size of NPs eliminates the waste and supply for only desired products.

NMNPs are used for their catalytic properties. Here are some examples:

- Bulk Au is inert and has often been thought as poorly active for catalytic reactions. However, when AuNPs diameters are below 10 nm, it turns out to be surprisingly active for many reactions, such as CO oxidation and propylene epoxidation [38].
- AgNPs located at a graphene edge catalyze oxidation of neighboring carbon atoms [39].
- Well-dispersed PtNPs are an important catalyst for fuel-cell reactions [40].

Chapter 2

2. The Formation Mechanism of Nanoparticles

When the laser beam reaches the surface of target, the energy of the photons in the laser beam is transferred into electrons and then into the lattice, diffusing the energy into the material afterwards [3]. Laser beam focusing on the surface of the material may be in the order of micron levels which heat the surface in a way that it reaches a critical temperature and causes rapid vaporization process [3]. This rapid vaporization forms ionized atoms and electrons i.e.; plasma on the target. On the condition that plasma has more energy with more laser power, it can expand and then cool therefore particles on the order of nanometer and micrometer begin to form.

Plasma is confined when it occurs in liquid environment apart from vacuum and gas phases. As a result, a lot of different mechanisms including generation, transformation, and condensation of plasma plume in liquid are formed. These mechanisms are still not fully understood. Some authors [41-45] have tried to explain these mechanisms using thermodynamics rules and generalized them for all particles using carbon-phase diagram.

.

2.1 Pulsed Laser Ablation Method in Gas

The products of PLA in gas directly come from the condensation of the plasma [41]. Thus, PLA in gas environment needs special gas chamber component and a wafer where synthesized particles are collected. This technique is the main mechanism for Pulsed Laser Deposition (PLD) and has opened new ways for both NP generation and thin film deposition.

PLA in gas has important chemical reactions in the transformation and condensation of the plasma plume for formation of NPs and thin-films. There are two chemical reactions that may happen at the gas-solid interface region. In the first case there are ion-ion interactions from plasma plume and ambient gas. The molecules of the ambient gas might turn into ions owing to the excitation by the high temperature of the plume [41]. Then ions of the ambient gas and plasma plume can interact and form molecules. In the second case, there are ion-molecule reactions. Formed ions of the plasma disperse into the ambient gas where they can collide with the molecules of the gas in order to cause the chemical reactions and form new molecules [41].

2.2 Pulsed Laser Ablation Method in Liquid

Pulsed laser ablation method in liquid is basically simple, does not require any vacuum system and is cheap. It requires a liquid, target and a laser system. However, the mechanism of NP formation and thin film deposition is rather complex and has still not been fully understood. In this part, the steps and thermodynamic aspect of the mechanism of PLAL are briefly explained.

2.2.1 The evolution of pulsed laser ablation in liquid

When a laser beam counters with the surface of a solid target in liquid, plasma is generated. Then the surface of target is heated in a way that it reaches critical temperature where causes rapid vaporization process [3]. This rapid vaporization forms ionized atoms and electrons i.e.; plasma on the target [3]. After plasma is formed, it initiates to react with liquid and it is schematically illustrated in Figure 2-1 . The figure shows us the evolution of the laser ablation in liquid. First formed plasma by laser beam is called "laser-induced plasma" and this is illustrated in Figure 2-1.a. If the plasma is enlarged by laser-induced plasma due to more energy provided by laser, it is called the plasma-induced plasma [41]. In other words, firstly, laser causes plasma at interface of liquid and solid then the formed plasma grow out and larger plasma occurs. (Please see Figure 2-1.b.) After plasma-induced plasma occurs, four chemical reactions arise inside the plasma and interface layer of plasma and liquid, at nanoscale time range [41]. In first stage, metastable phase can be formed by high temperature chemical reactions inside the plasma [41]. Next, the second set of reactions play a role where reactant species from target and liquid begin to contact and affect each other. At the third part, these formed reactant species get into high temperature chemical reactions with molecules in liquid [41]. High pressure inside the plasma induced plasma push the ablated species into liquid and this process is named as the fourth phase [41]. After these four kinds of processes are completed, cooling down and condensation in the confining liquid starts and NPs begin to form.

The mechanisms involved in the nucleation, phase transition, and growth of nanocrystals upon laser ablation in liquids are not fully understood. A few papers have been reported to explain the nucleation,

phase transition, and growth of stable and metastable phases at the nanometer scale using the thermodynamic method [41-45].

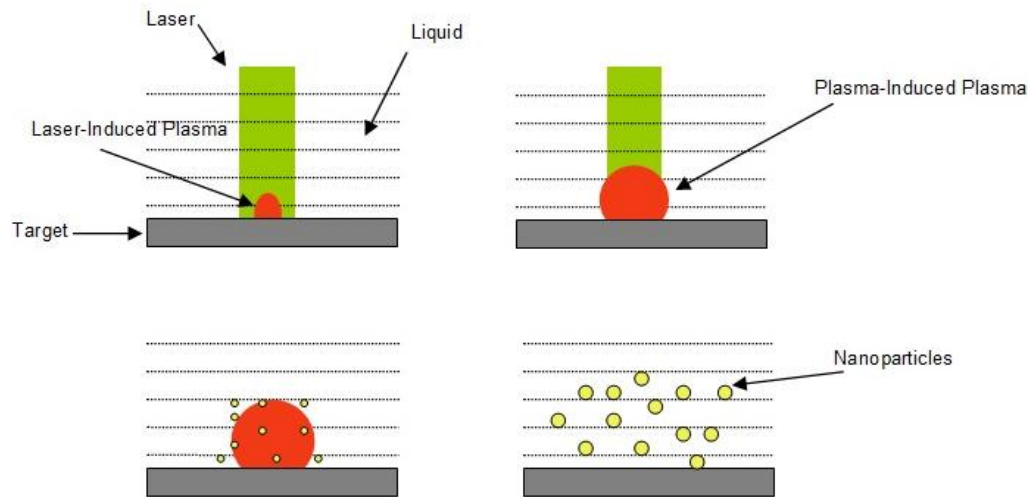


Figure 2-1. The evolution of PLA mechanism in liquid.

2.2.2 Nucleation thermodynamics

Nucleation thermodynamics of laser ablation aims to explain how nuclei behave and form. Yang and his coworkers [41-45] use and establish this theory according to the carbon phase diagram, and try to generalize it for other NPs.

First of all, nucleation thermodynamics of laser ablation is based on several assumptions [42]. First, formed nuclei from laser ablation are perfectly spherical and they are mutually non-interactive [42]. Nucleation thermodynamics of laser ablation is founded on carbon phase diagram where the Gibbs free energy is a measure of the energy

of a state in the phase transformation among competing phases. According to this theory, both diamond and graphite phases can simultaneously exist at given thermodynamic conditions but only one phase with the minimum free energy can be stable. Other phases can be metastable.

Under the assumption of perfectly spherical and mutually non-interactive nuclei, Laplace-Young equation gives the size-induced additional pressure ΔP of nuclei. The phase stability of the nucleation stage of an atom cluster in the gases or liquid is quite different from that of the phase diagram that is determined at atmospheric pressure [44]. The nuclei are under high-pressure and called “capillarity” [44]. This additional pressure is expressed by the Laplace-Young equation [44]. The equation is $\Delta P = 2\gamma/r$, where γ is the surface energy density of plasma and equals to $\gamma = 3.7 \text{ J/m}^2$ and r is the size of nuclei [44]. The equilibrium phase boundary between graphite and diamond in the carbon phase diagram is expressed by $P^e = 2.01 \times 10^6 T + 2.02 \times 10^9$ where T is the temperature [41] [44]. Thus, we can obtain the size-dependent equilibrium phase by uniting these two formulas and get $P^e = 2.01 \times 10^6 T + 2.02 \times 10^9 - 2\gamma/r$ [44]. When the pressure-temperature conditions are on the equilibrium line, the Gibbs free energy difference of the phase transition from graphite to diamond is, $\Delta g_{T,P}^d = \Delta V(P - 2.01 \times 10^6 T - 2.02 \times 10^9) + 2\gamma/r$, in which ΔV is the molar volume difference between diamond and graphite [41]. Then, the Gibbs free energy difference of the phase transition from graphite to diamond for nuclei formation expressed as [44];

$$\Delta G(r) = \frac{4}{3}\pi r^3 \Delta V \times (P - 2.01 \times 10^6 T - 2.02 \times 10^9 + 2\gamma/r) / V_m + 4\pi r^2 \gamma$$

where V_m is the molar volume of diamond.

When $\frac{\partial \Delta G(r)}{\partial r} = 0$, the critical size of diamond nuclei can be calculated as follows [41]:

$$r^* = 2\gamma \left(\frac{2}{3} + \frac{V_m}{\Delta V} \right) / \left(2.73 \times 10^6 T + 7.23 \times 10^8 - P \right)$$

This established thermodynamic nucleation theory might be a general approach for nanoparticle formation in laser ablation of solids in liquids [41].

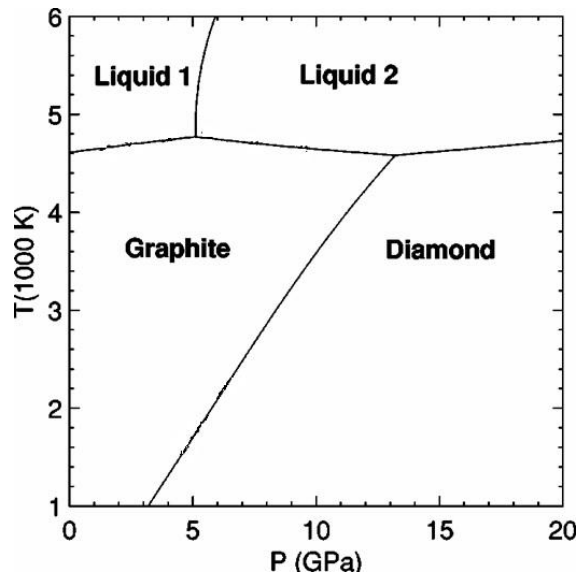


Figure 2-2. Carbon-phase diagram . The measurements of graphite melting done by Togaya and the graphite-diamond phase boundary measured by Bundy et al. Adopted from [46].

2.2.3 Kinetic growth

After laser beam reaches the target, a dense plasma plume is formed at the solid-liquid interface. Temperature and pressure of plasma reach their maximum values and then they start to decrease. This decline in

the process is called as condensation of plasma which leads to the formation of nanocrystals via growth of nuclei [41].

Assume the clusters and the surrounding plasma have the same temperature T , then isothermal nucleation time is given by [41].

$$\tau = \sqrt{2\pi mkT} \frac{kT\gamma}{p_s(T)(\Delta\mu)^2} \quad \text{eqn. (2.1)}$$

where $m, k, T, \gamma, p_s(T), \Delta\mu$ denote the mass of a single atom, the Boltzmann's constant, the absolute temperature, the surface energy density of diamond, saturated vapor pressure of nuclei at the temperature of T and atom chemical potential difference respectively. Figure 2-3 shows the relation between pressure/temperature and nucleation time. It is clear that nucleation time decreases with increment in pressure. However, increment in temperature adversely affect the nucleation time due to effect of saturated vapor pressure of nuclei. Moreover, based on Wilson–Frenkel growth law, generally, the growth velocity V of the crystalline nucleus can be expressed as [41].

$$V = hv \exp(-E_a / RT) [1 - \exp(-|\Delta g_m| / RT)] \quad \text{eqn. (2.2)}$$

where h, m, E_a, R , and T are the lattice constant of diamond nuclei in the growth direction, the thermal vibration frequency, the mole adsorption energy of atoms attached at surface sites, the gas constant, and the temperature [41]. Consequently, the diameter of nanodiamonds could be expressed as: $d = V(2\tau_d - \tau) + 2r^*$, where τ_d and r^* are the laser pulse duration and the size of critical nuclei of diamond, respectively [41]. The size of nanodiamond prepared by laser ablation with Nd: YAG laser with wavelength $\lambda=532$ nm, pulse width $\tau = 10$ ns, repetition frequency $\nu= 5$ Hz and power density $P=10^{10}$ W cm⁻² are in

the range of 40 to 200 nm and this is perfectly fit with formula $d = V(2\tau_d - \tau) + 2r^*$ [45]. Therefore, these theoretical results are in well agreement with experimental cases and can be employed to control the size of nanocrystals synthesized by laser ablation in liquids [41].

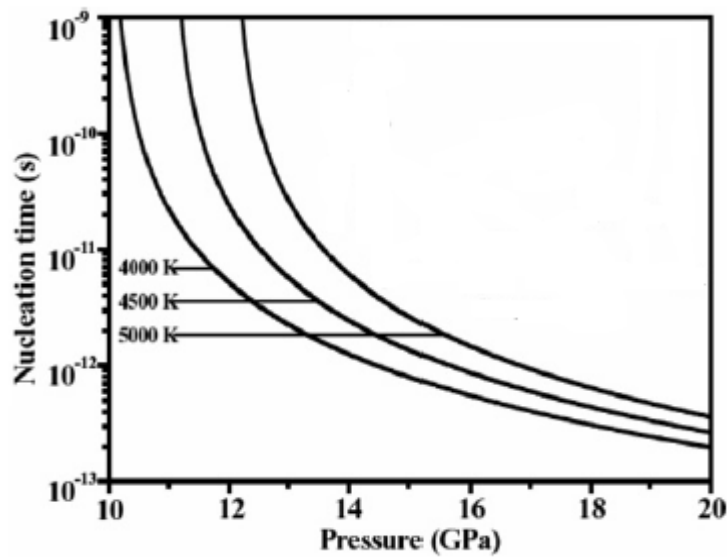


Figure 2-3. The Relation between nucleation time and pressure. Adopted from [41].

Chapter 3

3. Experimental Results and Discussions

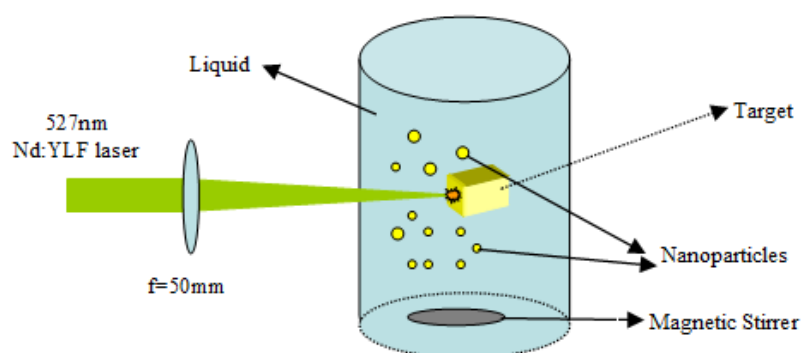


Figure 3-1. Experimental scheme of PLAL.

Experimental scheme of PLAL is illustrated in Figure 3-1. Target is placed in liquid and the laser is focused on the target. A magnetic stirrer is used for dispersing nanoparticles and not shielding the laser.

Gold Piece (99.999% Kurt J.Lesker), silver piece (99.999%, Kurt J.Lesker), Platinum piece (99.999%, Kurt J.Lesker), methanol (99%, Aldrich) were purchased commercially. The water is deionized water purified using the Millipore Milli-Q Ultrapure Water System.

The laser of the system is Nd: YLF (Empower, Q-switched laser, Spectra Physics) solid state laser. Laser wavelength is 527 nm and power can be selectively changed. A 50-mm lens has been used for all experiments.

First, Au, Ag and Pt NPs were synthesized in deionized water. Secondly, these NPs were synthesized in methanol. Applications of NMNPs, such as NMNP synthesization in polymeric solution for nanofibers, effects of varying average powers, thin film deposition has also been studied. Firstly, Au and Ag NPs were synthesized in Polyvinylpyrrolidone (PVP) for obtaining nanofibrous composites. Secondly, AuNPs synthesized with varying average power of laser were studied in order to understand the effect of average laser power on NP synthesis. Lastly, thin film deposition of glass in liquid and colloidal thin film application of NPs with spin coating was investigated.

3.1 Gold, Silver and Platinum Nanoparticle Synthesis in Water

Au, Ag and Pt NPs were synthesized in water by using pulsed Nd:YLF laser (Empower, Q-Switched Laser, Spectra Physics, USA) with 527 nm wavelength, 16 W average power, 110 ns pulse duration, and 16 mJ pulse energy for 1 kHz. The ablation was carried out for 5 min for each synthesis. The laser was focused on the Au, Ag and Pt targets by a lens with focal length of 50 mm. The intensity of color of Ag, Au and Pt NPs increased with irradiation time and the energy density of the laser beam. Ablation of AgNPs immersed in water is yellow, AuNPs is red and PtNPs is dark grey (Figure 3-2).

Scanning Electron Microscope (SEM) is a type of electron microscope that scans the surfaces of samples by electron beams and receives images. The electrons interact with atoms on surface of the sample and

produce signals which can be measured with special detectors inside SEM. The types of signals that can be generated from the surface of the samples are secondary electrons, back scattered electrons and characteristic X-Rays.

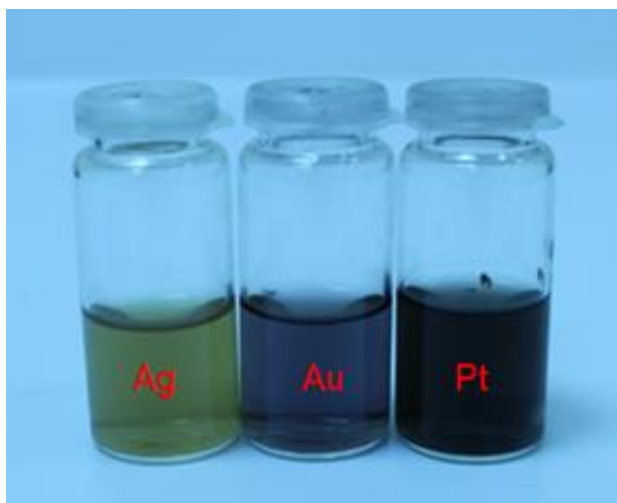
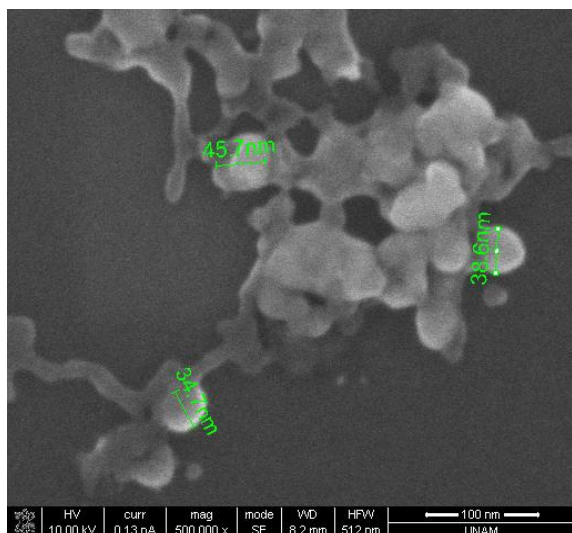


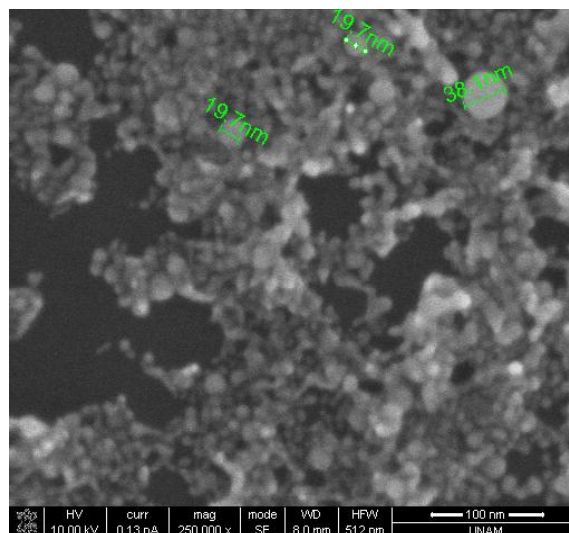
Figure 3-2. Picture Ag, Au, and Pt NPs synthesized in water.

SEM gives detailed information about sample surface and topography, chemical composition, electrical conductivity and image that optical microscopes cannot resolve. FEI-Quanta 200 FEG model was used for measurements. Figure 3-3 shows SEM pictures of Au, Ag and PtNPs. We can understand from the SEM images whether NPs aggregate or not. All of them were prepared on silicon wafer and dried on hot plate at 150 °C for 1-2 min. Figure 3-3.a shows AgNPs with sizes 25 nm - 45 nm. Figure 3-3.b shows AuNPs with sizes 2nm - 40 nm and Figure 3-3.c shows PtNPs with smaller sizes 2 - 20 nm. These images have been taken in 2 days after synthesis and it is clear that they have just started to aggregate.

a)



b)



c)

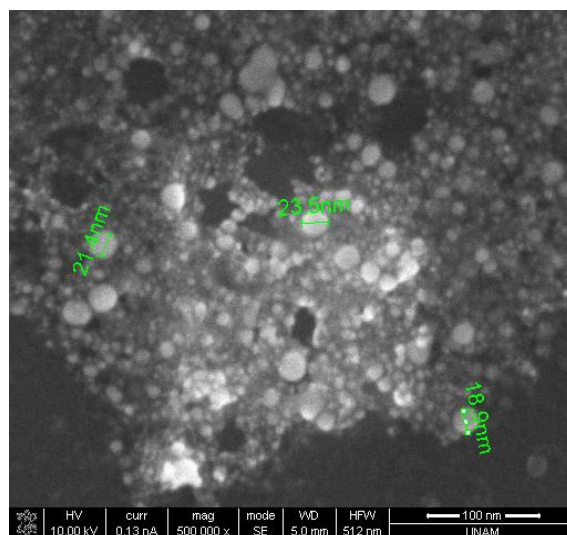


Figure 3-3. SEM pictures of Au, Ag, PtNPs in Water a) AgNPs, b) AuNPs, c) PtNPs.

X-Ray Photoelectron Spectroscopy (XPS) is a widely used and powerful characterization tool for surface properties of samples. The spectrum achieved with XPS allows us to determine the chemical state of the elements such as oxidation number and the electronic interactions with neighboring elements from the first coordination shells [47]. The XPS method also provides us additional information about oxide layers on the surface of the crystallites. Figure 4.3 shows XPS studies of Au, Ag and PtNPs. Thermo Scientific X-Ray Photoelectron Spectroscopy K-alpha was used for measurements. All of them are prepared on silicon wafer and dried on hot plate at 150 °C for 1-2 min. The argon gas was used to etch the surface for 2-5 nm to supply us better results without oxidation. Figure 3-4.a shows XPS spectrum of AgNPs. The 3d line of AgNP is split due to the spin orbit coupling. The spectrum shows us that 3d_{5/2} and 3d_{3/2} peak of Ag nanoparticles are nearly 368,3 eV and 374,4 eV respectively. These values exactly match with literature [48]. Figure 3-4.b shows XPS spectrum of AuNPs. The spectrum indicates that 4f_{7/2} peak of AuNPs is located on almost 84,0 eV and 4f_{5/2} peak located on 87,7 eV and they are in well agreement with literature [47]. Lastly, PtNPs show Pt4f_{7/2} peak a in the range of 71.2 eV and Pt4f_{5/2} peak at 74.5 eV. XPS spectrums of PtNPs completely fit to literature [49]. All samples etched with Argon gas before measurement thus oxidized state was not observed. This suggests that the oxidation state of NMNPs is present only on the surface of the crystallites.

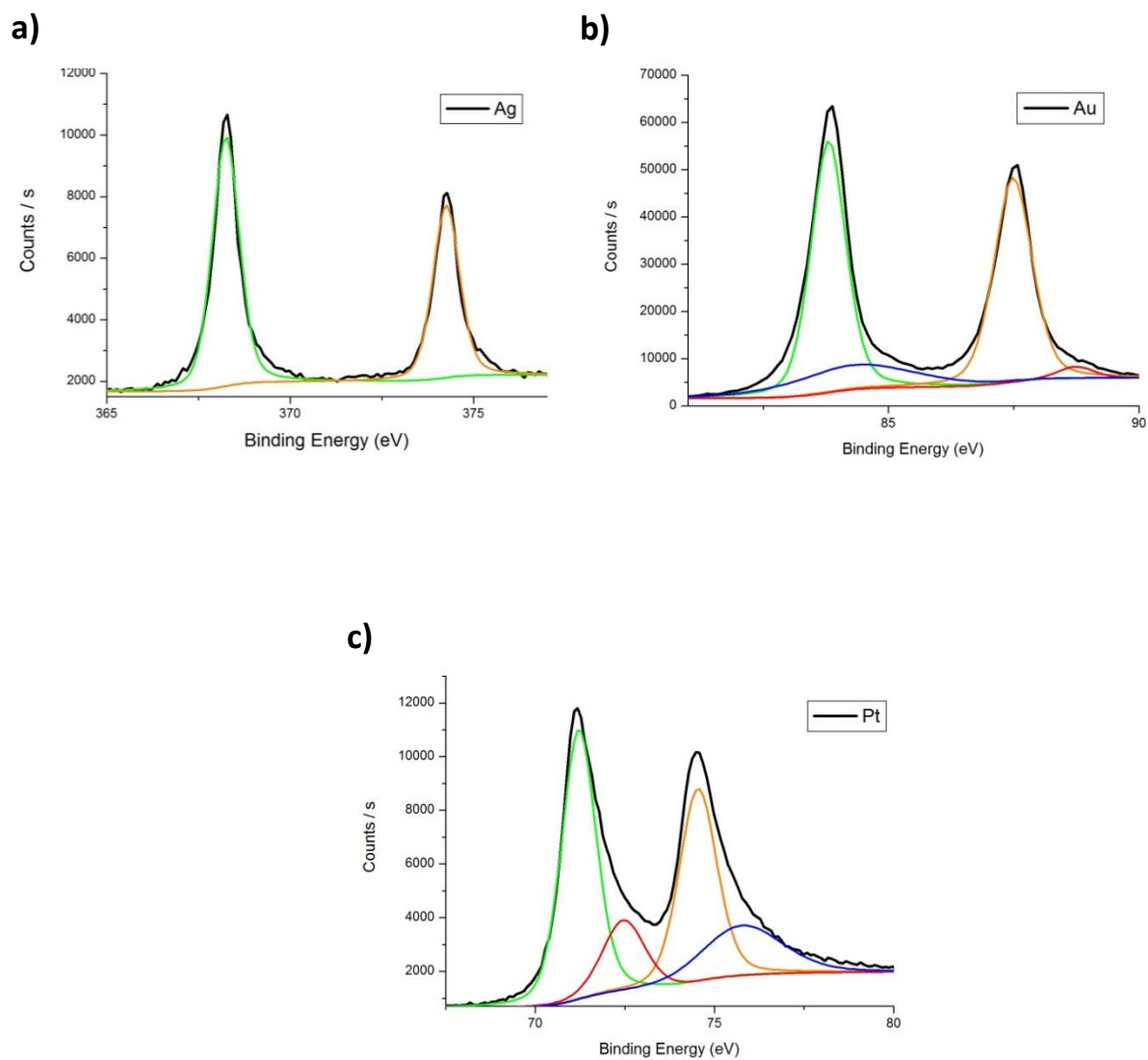


Figure 3-4. XPS studies of Ag, Au, Pt NPs on Silicon Wafer. a) XPS Spectrum of AgNPs after etching b) XPS Spectrum of AuNPs after etching c) XPS Spectrum of PtNPs after etching.

The crystalline nature and facets of samples can be easily understood by X-Ray Diffraction (XRD). XRD is a technique to measure the interference pattern of atom layers so a wavelength similar to the distance between atomic structures of interest should be used. The formed interference patterns by X-Rays scattered from crystals are described by Bragg's law, explaining why special oriented faces of crystals reflect X-Ray beams at certain angles of incidence. The formula is $n\lambda = 2d \sin \theta$, where n is the integer, d is the distance between atomic layers and θ is the angle of incidence. Figure 3-5 demonstrates the XRD spectrums of Au, Ag and PtNPs. PANalytical X'Pert PRO X-ray Diffraction (XRD) equipment was used for these measurements. The detector is solid state PIXcel detector with 255 channels. The source is Copper with 1.54 Å at 45kV and 40mA. All samples were dried on a special silicon wafer of the XRD equipment with hot plate at 150 °C for 1-2 min. The diffractogram for AgNP (a) indicates four distinct diffraction peaks at 38.11, 44.37, 64.57 and 77.56 respectively, which correspond to the (111), (200), (220) and (311) crystalline planes of the face-centered cubic (fcc) Ag reported on JCPDS cards 4-0783 [50]. The diffractogram for AuNP (b) has diffraction peak values of 38.11, 44.36, 64.57 and 77.54, which can be assigned to the (111), (200), (220) and (311) reflections of the fcc Au corresponding to JCPDS file No.040784 [50]. The diffractogram for PtNP (a) indicates four distinct diffraction peaks at 39.68, 46.13, 67.47 and 81.23 respectively, which correspond to (111), (200), (220) and (311) fcc Pt [51]. These measurements, verify that the NPs synthesized in water are crystal and fcc orientation.

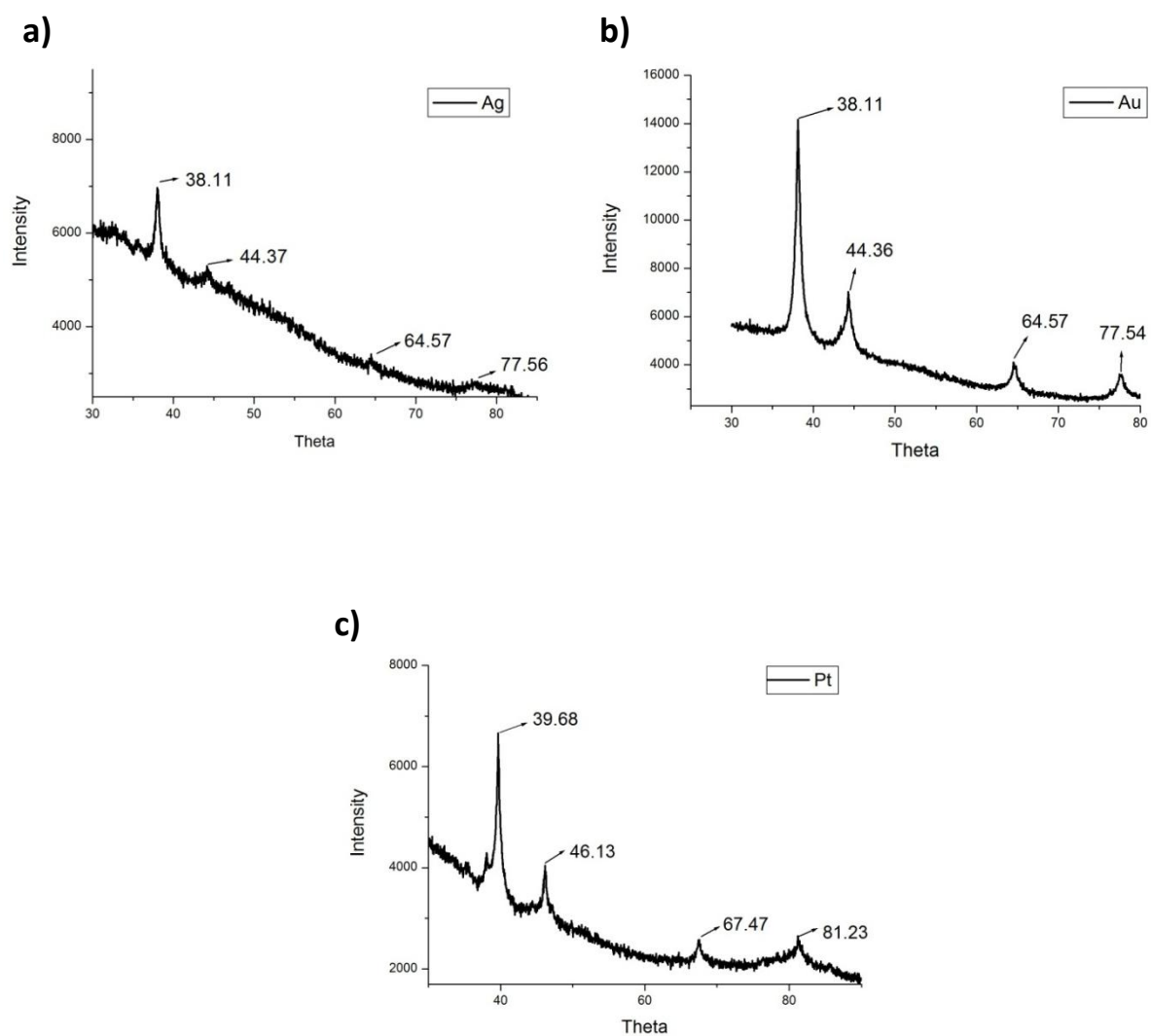


Figure 3-5. XRD studies of Ag, Au and Pt NPs. a) Ag NPs, b) Au NPs, c) Pt NPs.

UV-Vis Spectroscopy or Absorption Spectroscopy is a spectroscopy technique for absorption or reflectance measurements for solid and liquid samples. Basically, the spectrophotometer sends white light to the monochromator which transmits specific wavelengths. Then, the selected wavelength of light reaches the sample and spectrophotometer behind sample detects remaining photons by its detector. Figure 3-6 specifies absorption studies of Ag, Au and Pt NPs. The absorption spectrum of the solution has been measured by Cary 5000 UV-Vis-NIR Spectrophotometer. Baseline correction and double beam mode are used. The average time between two single measurements for single wavelength is 0.100 sec. There are little effects of source change at 350 nm. The data has been taken from 200 nm to 800 nm. All measurements had been performed in 2 days after synthesization. The AgNP spectrum exhibits a characteristic peak at 402 nm, the well-known surface plasmon resonance of spherical particles for AgNP [52]. AuNP has peak at 520 nm. The 520 nm peak of Au NPs is well-known. It shows that AuNPs has elongated shape [53]. The PtNP spectrum exhibits a broad band extending UV range and this is well agreement with literature [54].

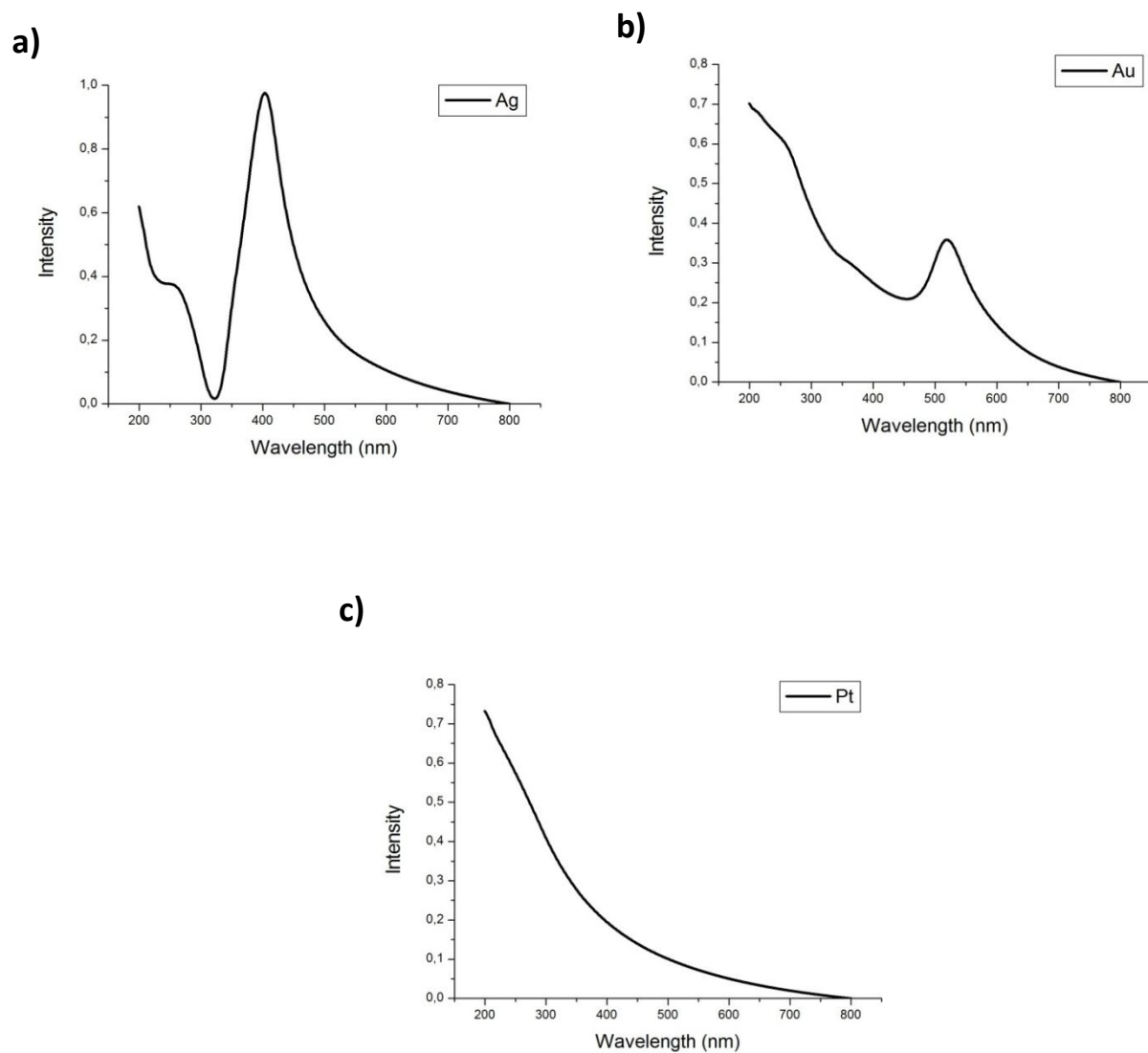


Figure 3-6. Absorption studies of Au, Ag, and Pt NPs. a) Ag NPs, b) Au NPs, c) Pt NPs.

Transmission Electron Microscope (TEM) is basically a type of electron microscope that sends electron beams to the sample and detects it with CCD detectors. Thank to de Broglie wavelength of electrons, it supplies super resolution, even one can detect a column of atoms. It plays a significant role for detecting NPs. One can measure size distribution of NPs, gather information about whether they are crystal. FEI Technai G2 F30 TEM was used for the measurements. All samples were prepared immediately after laser ablation synthesis. Size distributions of particles were carried out by calculation over 200 nanoparticles. Figure 3-7.a shows TEM image of AuNP. AuNP size distribution changes from 2.5nm to 25 nm. The HRTEM images (see Figure 4-7.b) of AuNP clearly state that lattice fringe separation is 0.232 nm [55]. This separation indicates that AuNP has (111) orientation. Ag NP sizes vary from 2.5 to 20 nm. Indeed, they are mostly in the range of 1-7.5 nm. Much bigger nanoparticles also were detected as seen in Figure 3-8.a. The lattice fringe separation is 0.233 nm. This value shows that AgNP has (111) orientation [56]. PtNP sizes are in the range of 1-32 nm and mostly are smaller than 20nm. The lattice fringe separation of PtNP is 0.237nm. This separation indicates that PtNP has (111) orientation [57].

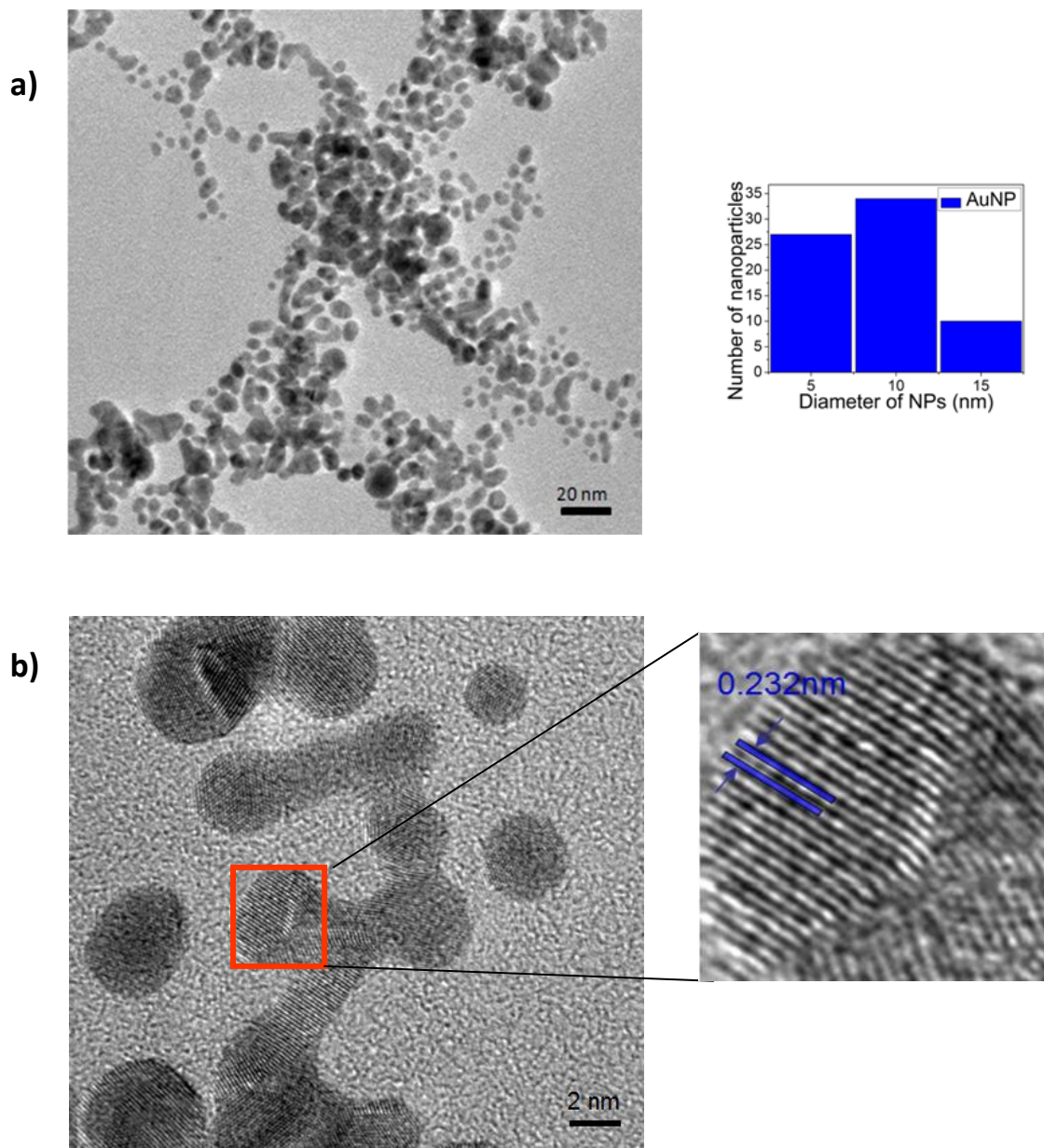


Figure 3-7. TEM studies of Au NPs. a) General image and size distribution. b) HRTEM image of Au NP: Atomic planes of Au NP.

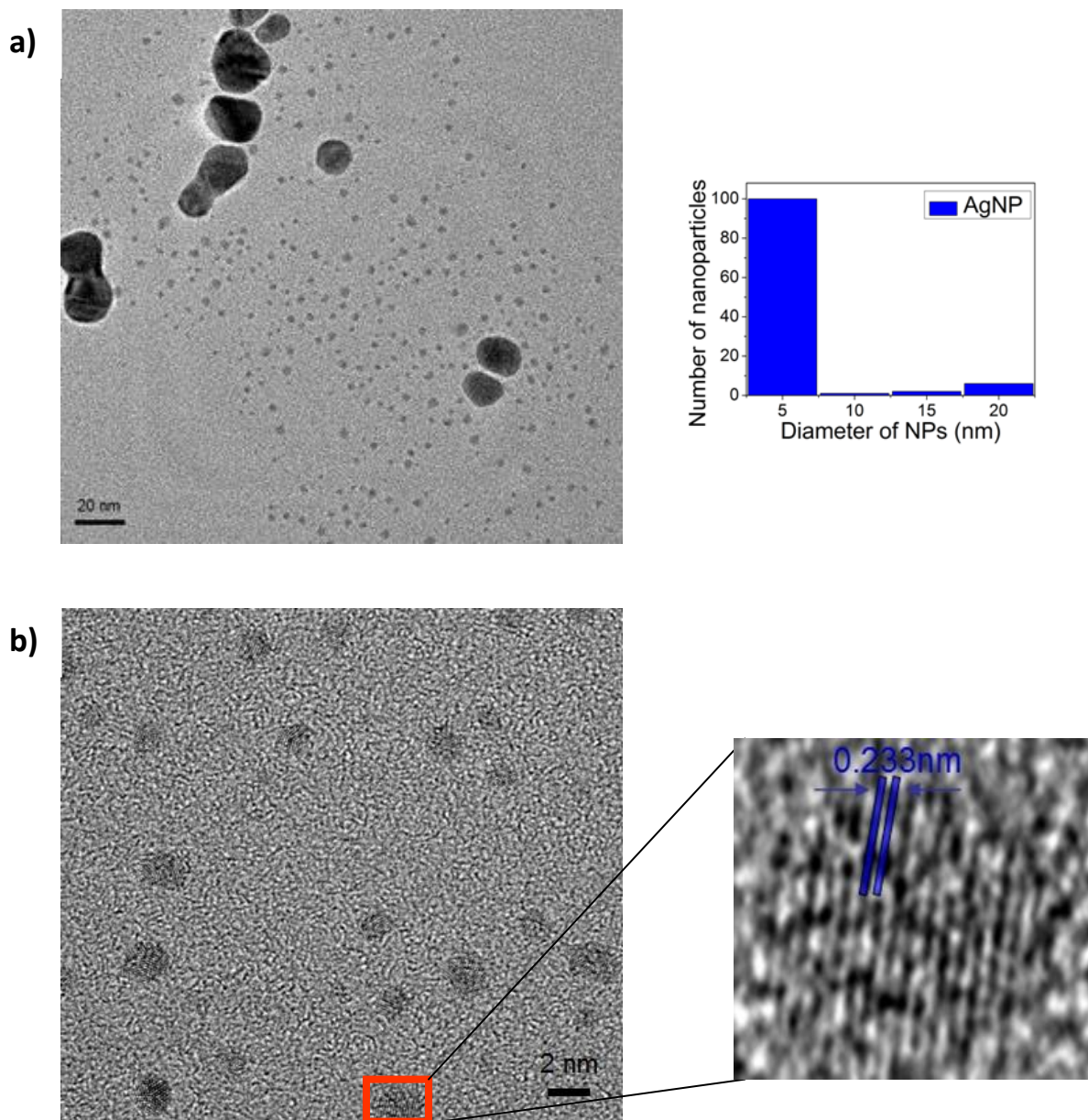


Figure 3-8. TEM studies of Ag NPs. a) General image and size distribution. b) HRTEM image of Ag NP: Atomic planes of Ag NP.

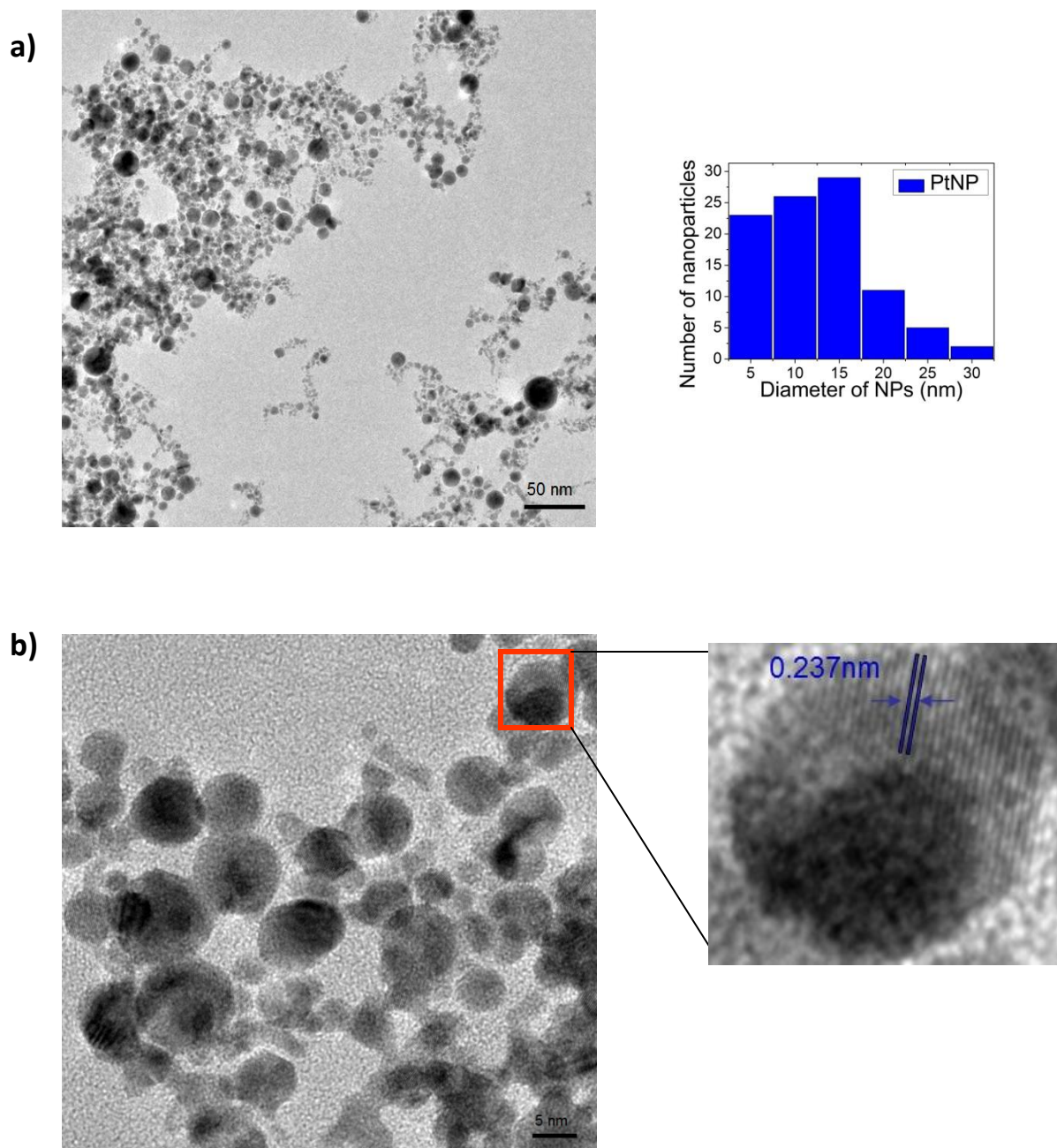


Figure 3-9. TEM studies of Pt NPs. a) General image and size distribution. b) HRTEM image of Pt NP: Atomic planes of Pt NP.

3.2 Gold, Silver and Platinum Nanoparticle Synthesis in Methanol

The polarity of the liquid environment plays an important role on nucleation, growth and aggregation mechanisms [52]. High polar molecules prevent growth, aggregation and precipitation because they give a strong surrounding electrical double layer [52]. Therefore, changing the liquid can be classified as one way for controlling the size of NPs in PLAL [52]. For instance, methanol's polarity is lower than water and therefore it gives us a good chance to observe how important role the liquid play in PLAL. Crystal properties, absorption, TEM, XPS studies of Au, Ag and Pt NPs in methanol have been studied.

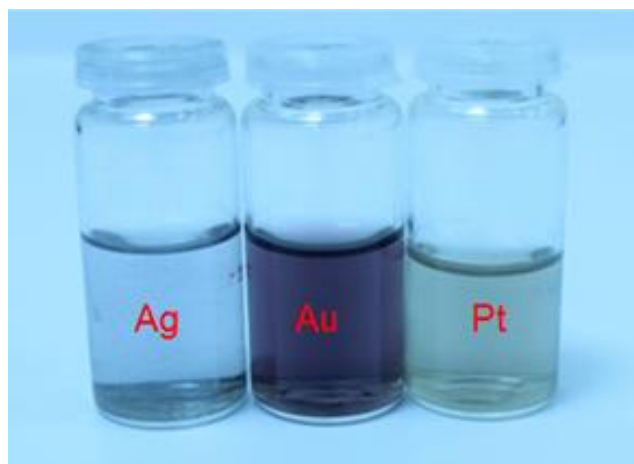


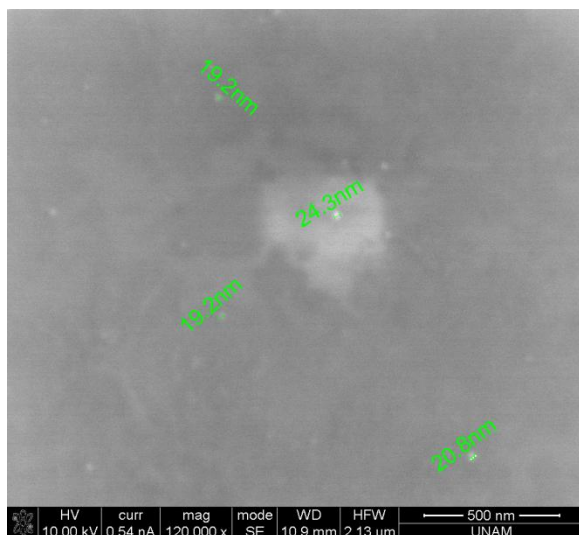
Figure 3-10. Picture of Ag, Au and Pt NPs.

Au, Ag and Pt NPs were synthesized in methanol by using pulsed Nd:YLF laser (Empower, Q-Switched Laser, Spectra Physics, USA) with 527 nm wavelength, 16 W average power, 110 ns pulse duration, and 16 mJ pulse energy for 1 kHz. The ablation was carried out for 5-10 min for each synthesis.

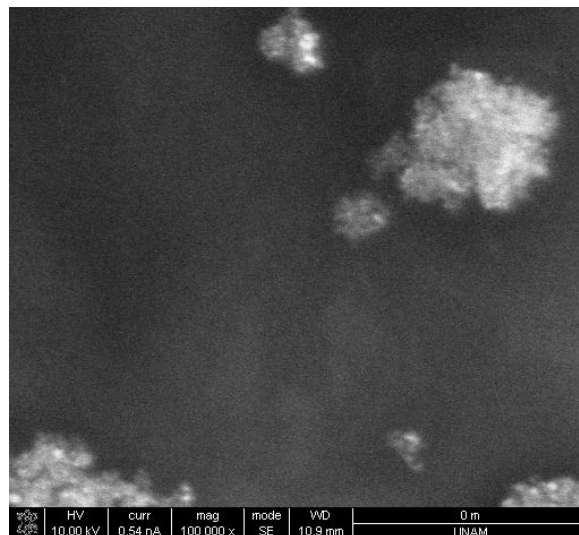
In methanol, since the polarity is decreased with regard to water, precipitation occurs in two or three days. Therefore, all measurements and preparation of samples have been performed immediately after laser ablation synthesis of Ag, Au and Pt NPs in liquid achieved.

SEM images of Au, Ag and Pt NPs are not so clear but they give estimation about the sizes of nanoparticles and how they spread. All of the samples are prepared on silicon wafer and dried on hot plate at 100 °C for 1-2 min. The samples of Au, Ag, and Pt NPs for SEM were taken immediately after laser ablation synthesis. SEM images show that AgNPs sizes are 19-25 nm and they are dispersed. Some aggregations were also observed. AuNPs sizes are small and united. PtNPs are well dispersed and there is no aggregation.

a)



b)



c)

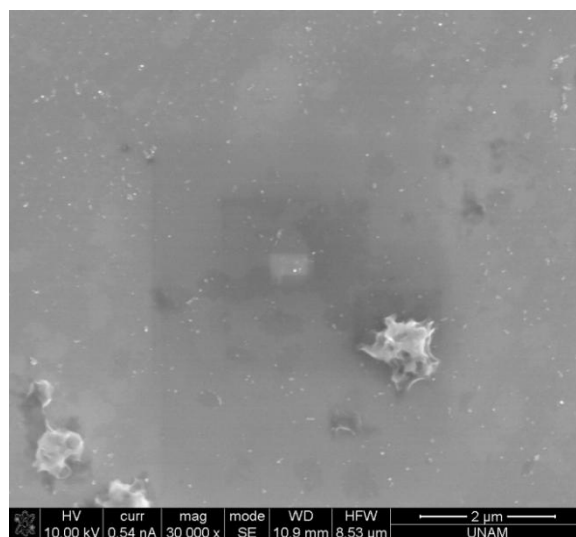


Figure 3-11. SEM pictures of Au, Ag, Pt NPs in Methanol a) Ag NPs, b) Au NPs, c) Pt NPs.

Figure 3-12 shows XPS studies of Au, Ag and Pt NPs in methanol. Thermo Scientific X-Ray Photoelectron Spectroscopy K-alpha has been used for the measurements. All of them are prepared on silicon wafer and dried on hot plate at 100 °C for 1-2 min. The argon gas was used to etch the surface for 2-5 nm to supply us better results without oxidation. Figure 3-12.a shows XPS spectrum of AgNPs. The 3d line of AgNP is split due to the spin orbit coupling. The spectrum shows us that 3d_{5/2} and 3d_{3/2} peak of Ag NPs are nearly 368.4 eV and 374.5 eV respectively. The XPS values of AgNPs in methanol exactly match with literature [48]. Figure 3-12.b shows XPS spectrum of AuNPs. The spectrum indicates that 4f_{7/2} peak of AuNPs are located on almost 84.2 eV and 4f_{5/2} peak located on 87.9 eV and they are well agreement with literature as well [47]. Lastly, PtNPs states that Pt4f_{7/2} peak is in the range of 71.6 eV and Pt 4f_{5/2} peak is 74.9 eV. XPS spectrum of PtNPs almost exactly fit with literature [49]. All samples etched with Argon gas before measurement thus oxidized state was not observed except PtNPs. PtNPs are in a bit oxidized state. If more argon gas etching had been applied on the surface of it, it would have been removed as well. These considerations suggest that the oxidation state is present only on the surface of the crystallites.

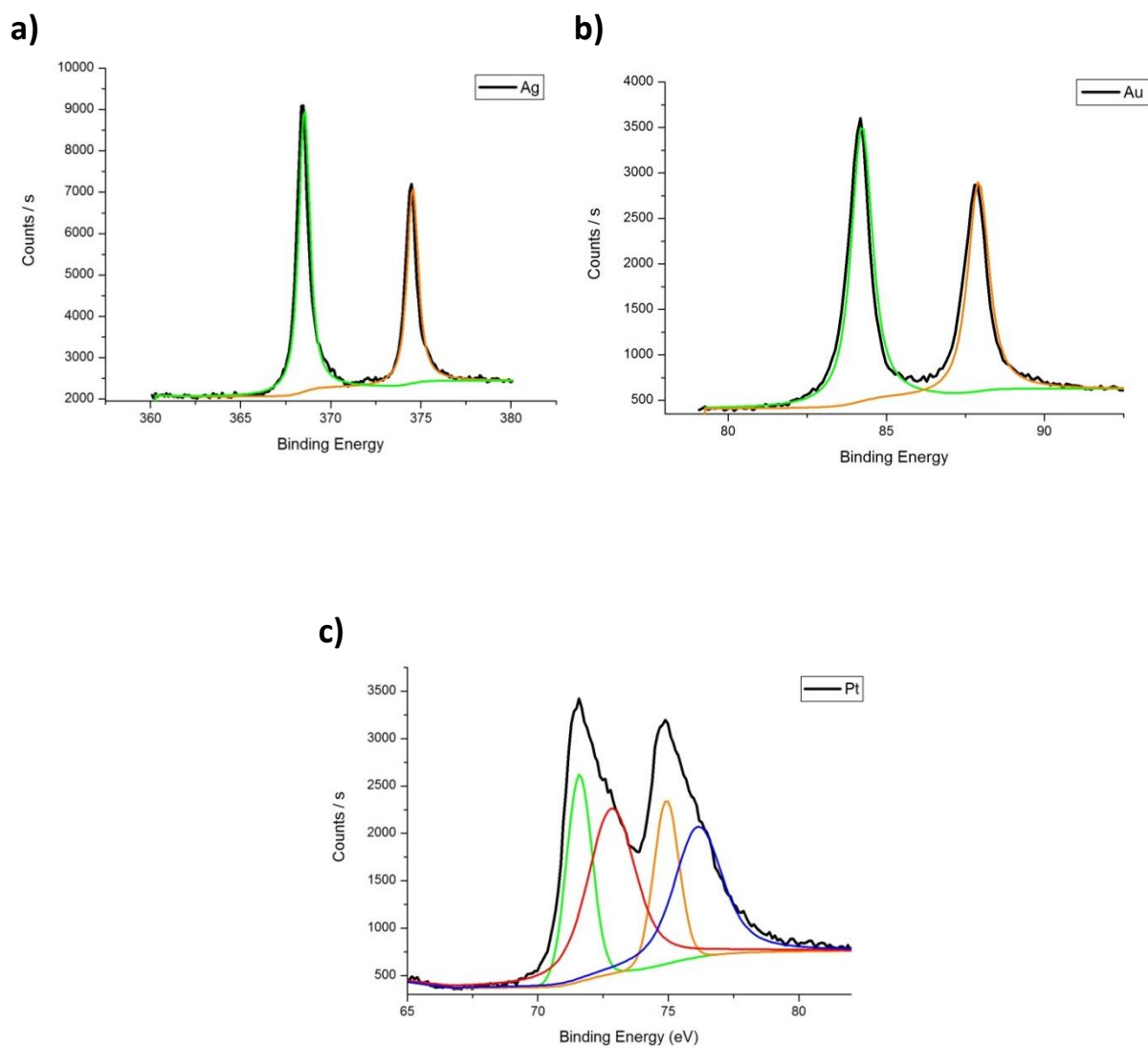


Figure 3-12. XPS studies of Au, Ag, Pt NPs in Methanol a) Ag NPs, b) Au NPs, c) Pt NPs.

Figure 3-13 demonstrates the XRD spectrums of Au, Ag and PtNPs in methanol. PANalytical X'Pert PRO X-ray Diffraction equipment was used for these measurements. All samples were dried on a special silicon wafer of the equipment with hot plate at 90 °C for 1-2 min. The diffractogram for AgNP indicates two distinct diffraction peaks at 38.11, 44.43 which correspond to the (111), (200) crystalline planes of the Ag reported on JCPDS cards 4-0783 [50]. The diffractogram for AuNP has diffraction peak values of 38.09, 44.31, 64.53 and 77.67, which can be assigned to the (111), (200), (220) and (311) reflections of the fcc Au corresponding to JCPDS file No.040784 [50]. The diffractogram for PtNP (a) indicates two distinct diffraction peaks at 39.70, 46.07 respectively, which correspond to (111) and (200) crystalline planes of the Pt. These measurements verify that the NMNPs synthesized in methanol are crystal. However, it was surprising that (220) and (311) crystal planes of Ag and PtNPs were not observed.

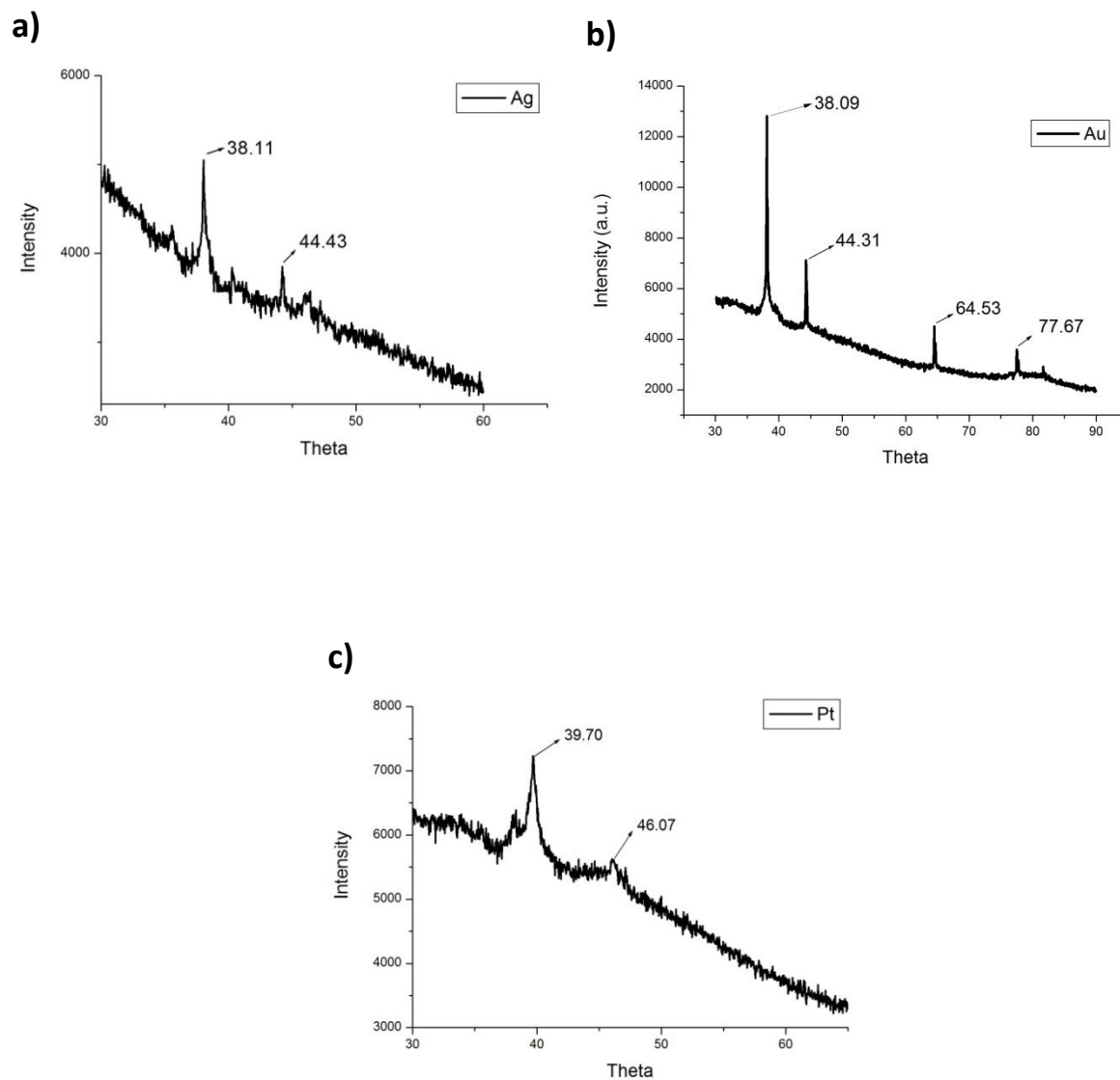


Figure 3-13. XRD graphs of Au, Ag, Pt NPs in Methanol a) Ag NPs, b) Au NPs, c) Pt NPs.

Figure 3-14 specifies that absorption studies of Ag, Au and Pt NPs in methanol. The absorption spectrum of the solution was measured by Cary 5000 UV-Vis-NIR Spectrophotometer. Baseline correction was done and double beam mode used. The average time between two single measurements for single wavelength was 0.100 sec. The data was taken 200 nm to 800 nm. All measurements have performed in 2 days of synthesization. The AgNP spectrum exhibits a characteristic peak at 399 nm the well-known surface plasmon resonance of spherical particles for Ag. The FWHM of the curve of surface plasmon resonance of AgNP in methanol (163 nm) is larger than AgNP (68 nm) in water. This indicates that NP size distribution is broader than AgNP in water. TEM images and size distribution also proves this. AuNP has peak at 524 nm. The SRP peak of AuNP is 524 nm which show us that the diameters were also increased compared to water. The 520 nm peak of AuNPs is well-known. It shows that AuNPs has elongated shape [53]. There is a little shift (~4nm) toward to red due to increase in diameter of AuNPs. As for the PtNP spectrum, it exhibits a broad band extending UV range and this is well agreement with literature [54].

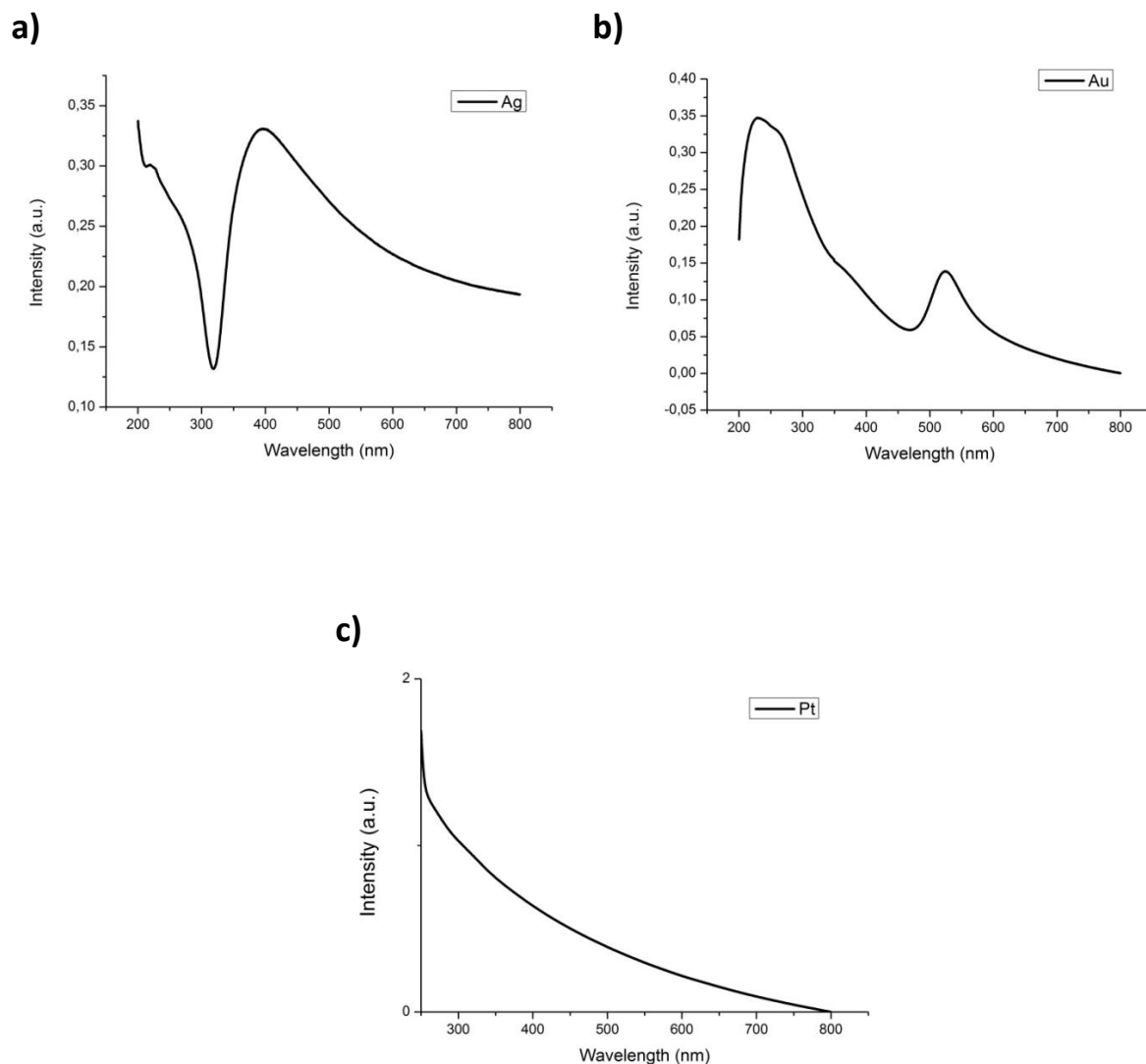


Figure 3-14. Absorption studies of Au, Ag, and Pt NPs. a) Ag NPs, b) Au NPs, c) Pt NPs.

FEI Technai G2 F30 TEM was used for the measurements. All samples were prepared immediately after laser ablation synthesis. Size distributions of NPs were done by calculation over 200 nanoparticles. Figure 3-15 shows TEM image of AuNP in methanol. AuNP size distribution changes from 2.5 nm to 20 nm. The TEM images of AuNP clearly state that lattice fringe separation is $2.32 \text{ \AA}$ [55]. This separation indicates that AuNP has (111) orientation. AgNP sizes vary from 2.5 to 20 nm. However, they are mostly in the range of 1-7.5 nm. Much bigger nanoparticles also were detected as seen in Figure 3-16. AgNPs lattice fringe $2.29 \text{ \AA}$ corresponds to (111) orientation [56]. PtNP sizes are in the range of 1-32 nm and mostly are smaller than 20nm. HRTEM image of PtNPs shows that the crystalline structures can be identified by their typical lattice fringes (see Figure 3-17). A large number of the particles can be viewed with clear (111) lattice fringes with a lattice spacing of $2.35 \text{ \AA}$ [57].

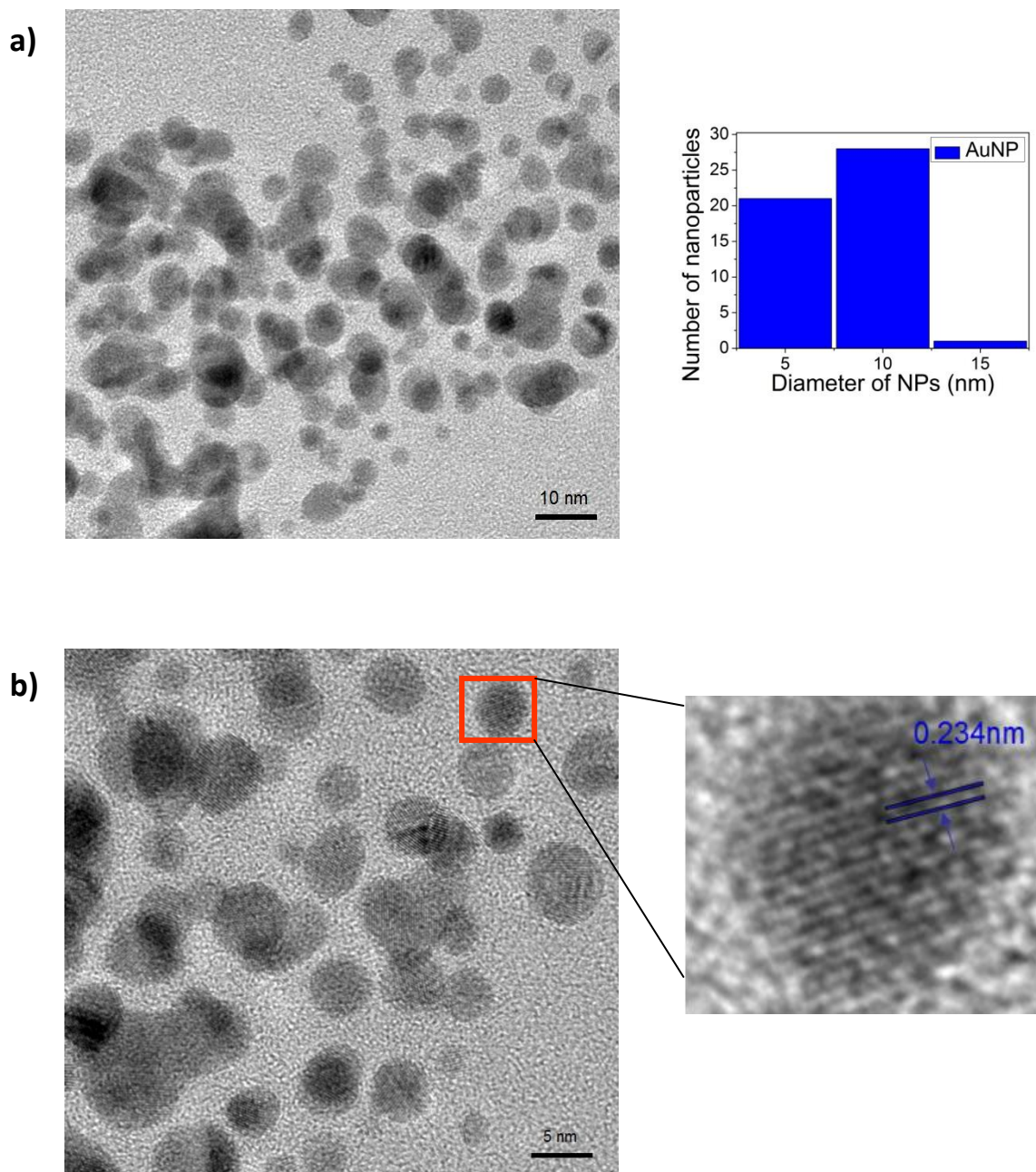


Figure 3-15. TEM studies of Au NPs in methanol. a) General image and size distribution. b) HRTEM image of Au NP: Atomic planes of Au NP.

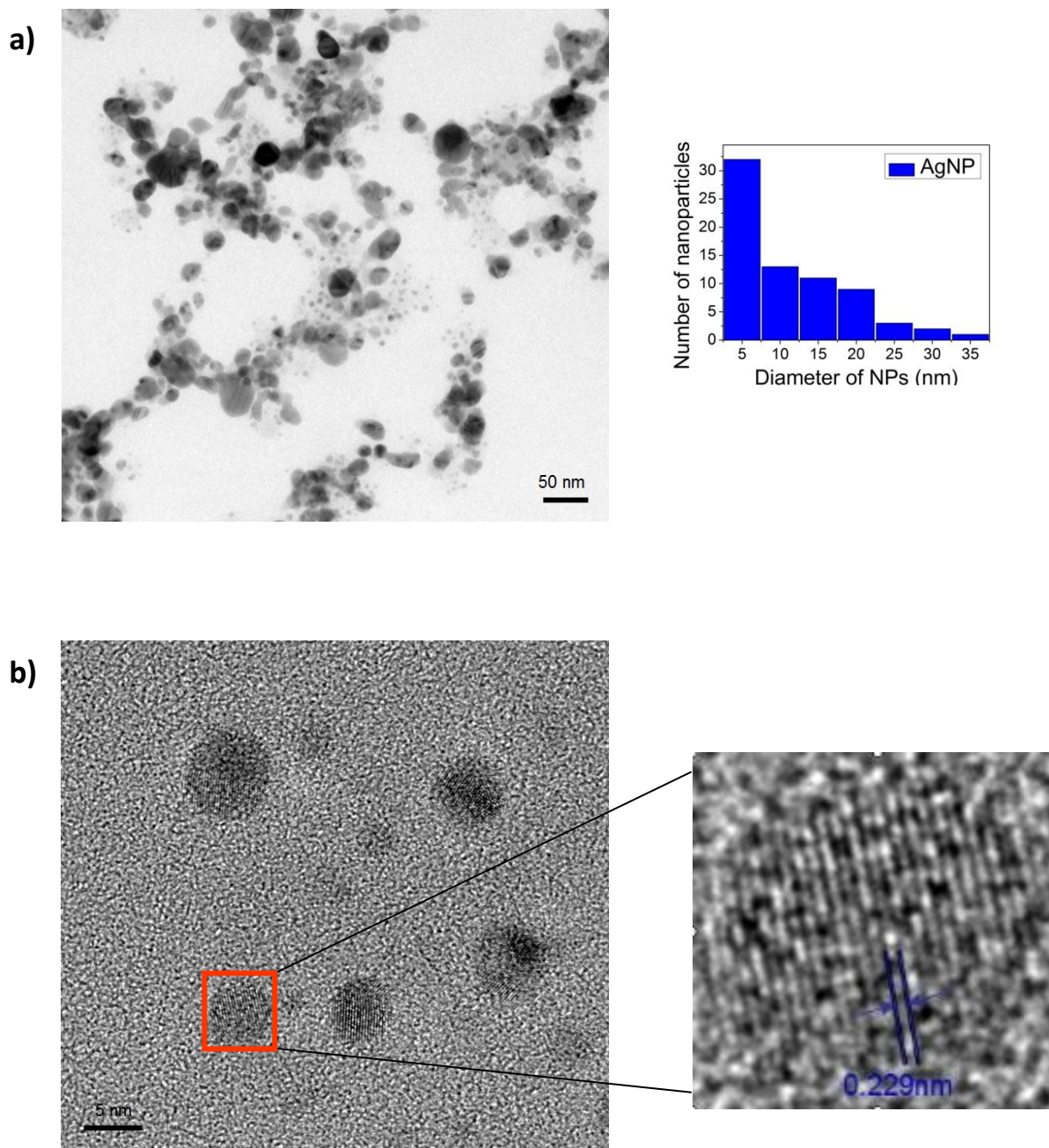


Figure 3-16. TEM studies of Ag nanoparticles in methanol. a) General image and size distribution. b) HRTEM image of Ag NP: Atomic planes of Ag NP.

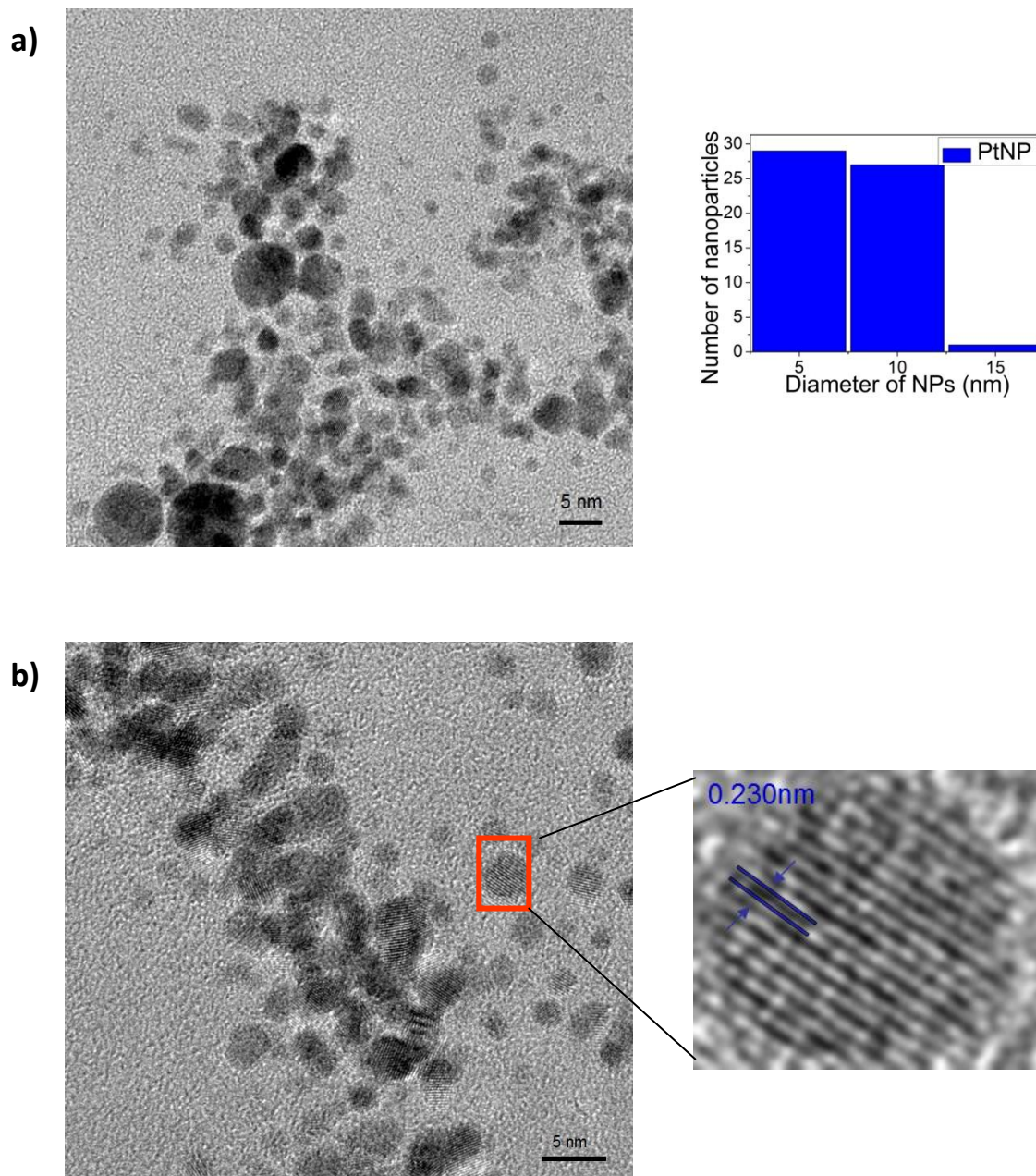


Figure 3-17. TEM studies of Pt nanoparticles in methanol. a) General image and size distribution. b) HRTEM image of Pt NP: Atomic planes of Pt NP.

3.3 Gold and Silver Nanoparticles Synthesis in Polymeric Solution

AuNPs and AgNPs were synthesized in PVP by using pulsed Nd: YLF laser (Empower, Q-Switched Laser, Spectra Physics, USA) with 527 nm wavelength, 16 W average power, 110 ns pulse duration, and 16 mJ pulse energy for 1 kHz. The ablation was carried out for 15 min for synthesis.

PVP is a water soluble polymer having a hydrophilic nature and it is widely used as a stabilizer and capping agent for AuNPs and AgNPs. Therefore, PVP can protect the NPs from agglomeration in the medium [10].

After AuNPs and AgNPs are prepared in PVP, the electrospinning of PVP/AuNPs and AgNPs solution was carried out for obtaining nanofibrous composites by Uyar Research Group at UNAM, Bilkent University.

UV-Vis-NIR Spectrophotometer and TEM studies were done from Au and Ag NPs embedded in nanofibers. FEI Technai G2 F30 TEM was used for the measurements. The AuNPs were in spherical form having average diameter in the range of 5 to 20 nm. They were mostly dispersed homogeneously in the PVP matrix, however, some aggregations of the AuNPs were also observed (Please see Figure 3-18.b). As for Ag NPs, their sizes change from 5 to 25 nm. Aggregations of Ag NPs were also observed. The dispersion of AgNPs on the surface of nanofibers is not as successful as AuNPs dispersion. (Please see Figure 3-18.b.)

Figure 3-18.a shows absorption spectrum of PVP/Au-NPs nanofibrous composite. The absorption spectrum of the nanofibrous composites was measured by Cary 5000 UV-Vis-NIR Spectrophotometer. Baseline correction was done and double beam mode used. The average time between two single measurements for single wavelength was 0.100 sec. The data was taken 200 nm to 800 nm. The absorption peak of 536 nm was clearly observed due to the SPR of Au-NPs. Also, this peak shifts to red if compared with SPR peak of AuNPs in water which shows us that the effects of material in SPR. Moreover, AuNPs sizes have been increased in PVP and this also caused shifting of spectrum to the red. The absorption peaks of 432 nm were clearly observed due to the SPR of AgNPs. , this peak shifts to red if compared with SPR peak of AuNPs in water. It shows us that the effects of material in SPR. These values are in agreement with literature [58].

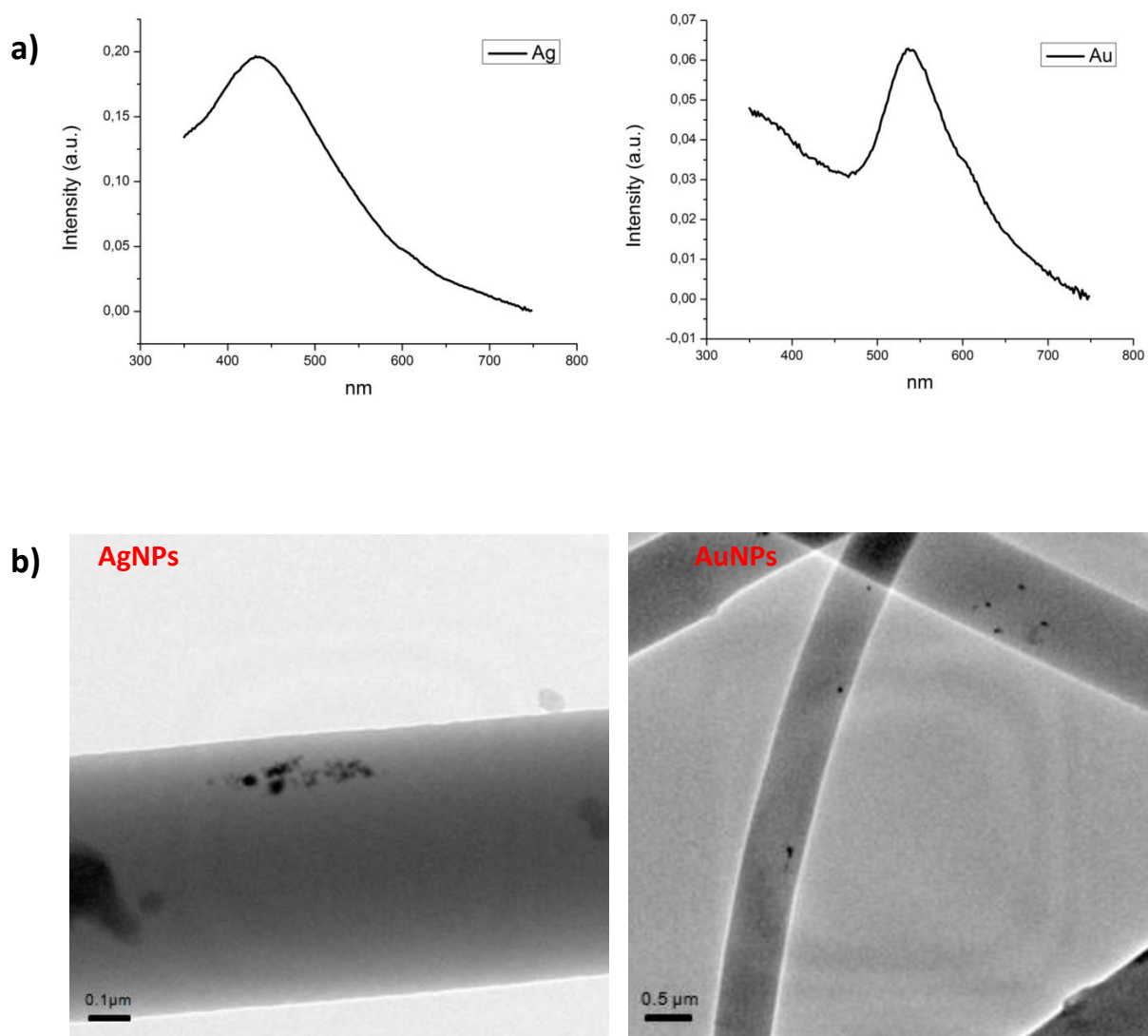


Figure 3-18. Absorption and TEM studies of Au and AgNPs embedded in nanofibers [10]. The Au-NPs were directly synthesized in PVP solution by laser ablation and then, the electrospinning of PVP/Au-NPs solution was carried out for obtaining nanofibrous composites [10]. a) Absorption study of of Au and AgNPs embedded nanofibers. b) TEM studies of of Ag and AuNPs embedded nanofibers.

3.4 Gold Nanoparticle Synthesis in Water with Different Average Powers

AuNPs were synthesized with Nd: YLF laser with different average power of the laser. If one of the main parameters of laser ablation, such as energy, wavelength and solvent changes, NP sizes and shapes may change. In order to control this dependency, AuNPs were synthesized with different average powers.

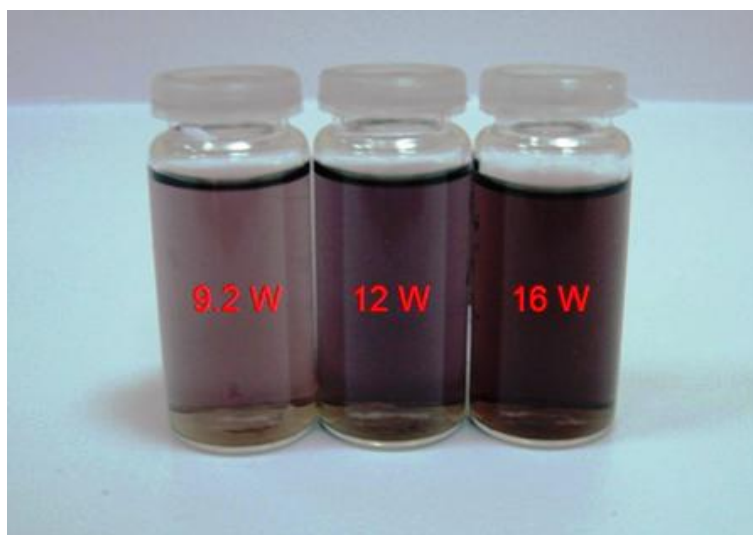


Figure 3-19. Image of AuNPs in water synthesized in different average powers.

Figure 3-20 demonstrates the absorption study of AuNP synthesized in different average powers. The laser is Nd: YLF laser (Empower, Q-Switched Laser, Spectra Physics, USA) with 527 nm wavelength. Red line indicates AuNPs synthesized in deionized water with the condition of 9.2 W average power, 150 ns pulse duration, and 9.2 mJ pulse

energy for 1 kHz for Nd: YLF laser. Green line represents the laser parameters as 12 W average power, 130 ns pulse duration, and 12 mJ pulse energy for 1 kHz. Blue line corresponds to 16 W average power, 110 ns pulse duration and 16 mJ pulse energy for 1 kHz laser parameters.

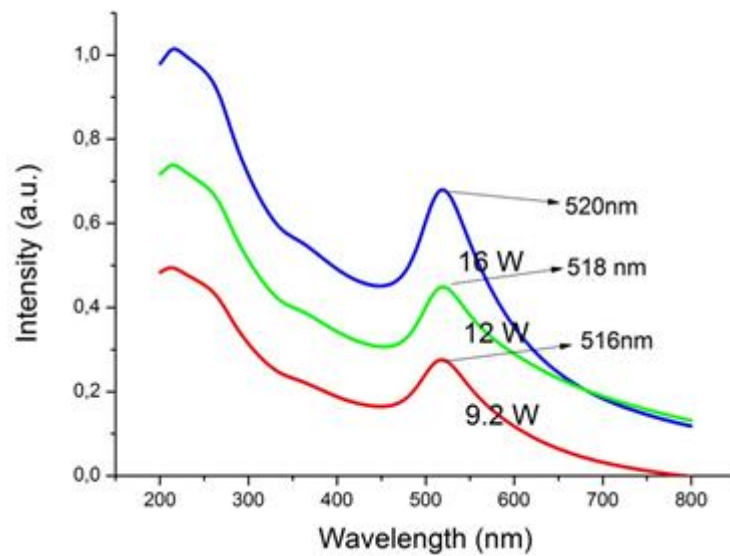


Figure 3-20. Absorption study of AuNP synthesized in different average powers. Blue line 16W, green line 12W and red line indicates 9.2W average powers. Their peak values change. Blue line has peak at 520nm, green line 518nm and red line 516nm peak values.

Absorption study of AuNP synthesized in different average powers specifies that there occurs shift toward to red if average power of laser is increased. Red line has peak value at 516 nm, green line has 518 nm and blue line has at 520 nm. This shift arises from size of nanoparticles. Each has different NP sizes and this causes the shift in surface plasmon resonances. TEM gives clear results about the sizes for 9.2W, 12W and 16W average power generation of AuNPs.

Each size distribution was obtained by measuring the diameters of more than 150 particles in sight on the given micrograph. Figure 3-21 shows the AuNP synthesized in water by using pulsed 9.2 W average power, 150 ns pulse duration, and 9.2 mJ pulse energy for 1 kHz. The ablation was carried out for 10 min. Size distribution changes from 2.5nm to 17.5 nm and most of NPs are smaller than 12.5nm. Figure 3-22 shows the AuNP synthesized in water by using 12 W average power, 130 ns pulse duration, and 12 mJ pulse energy for 1 kHz. The ablation was carried out for 7 min. Size distribution changes from 2.5 nm to 22.5 nm and most of NPs are in the range of 7.5 nm to 17.5 nm. Figure 3-23 shows the AuNP synthesized in water by 16 W average power, 110 ns pulse duration, and 16 mJ pulse energy for 1 kHz. The ablation was carried out for 5 min. The broadest distribution obtained with these parameters. Nanoparticles change from 1 nm to 30 nm. As expected from SPR measurement of AuNPs, the size distribution gets larger if more average power is applied.

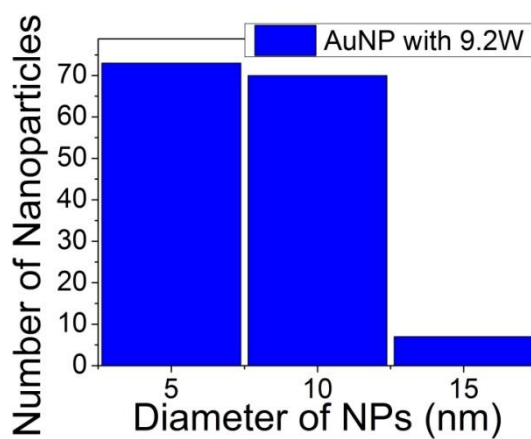
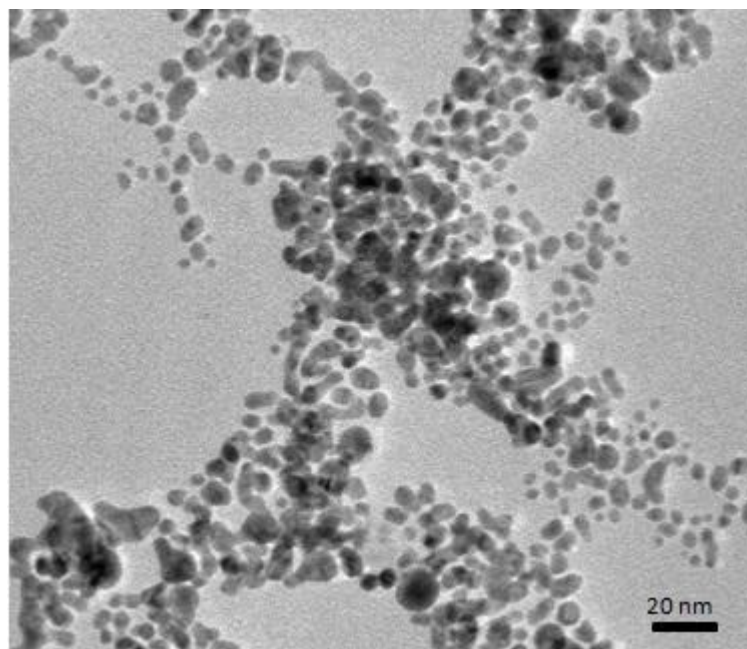


Figure 3-21. TEM studies of AuNPs synthesized in 527nm, 9.2 W, 150 ns Nd:YLF laser in water. General image and size distribution corresponding to the image.

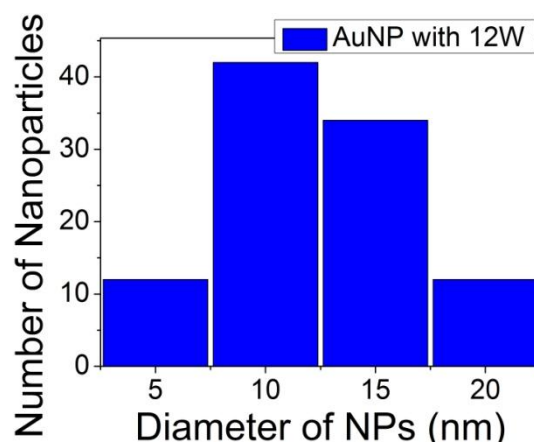
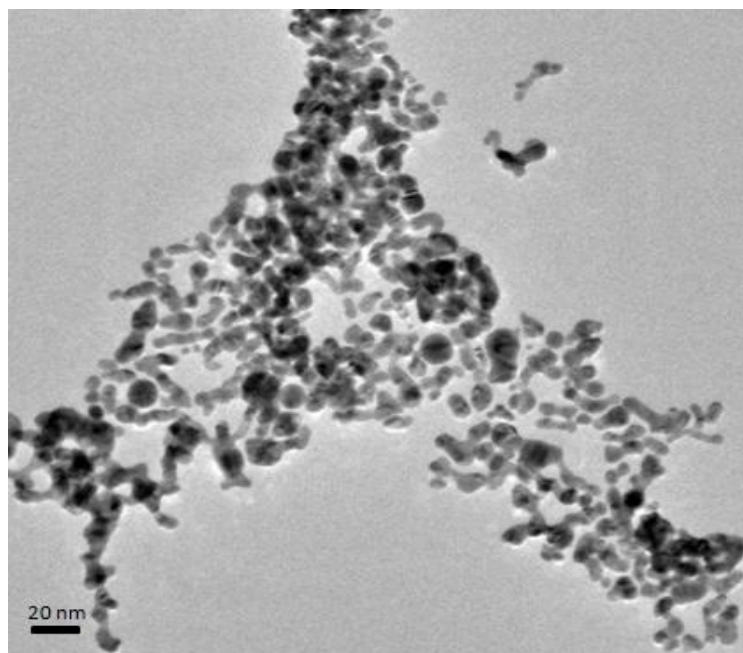


Figure 3-22. TEM studies of AuNPs synthesized in 527nm, 12 W, 130 ns Nd:YLF laser in water. General image and size distribution corresponding to the image.

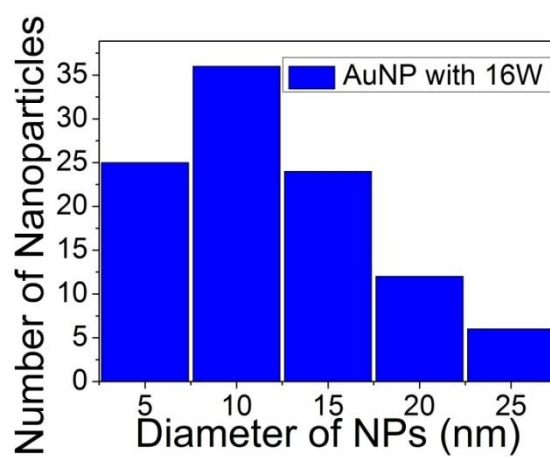
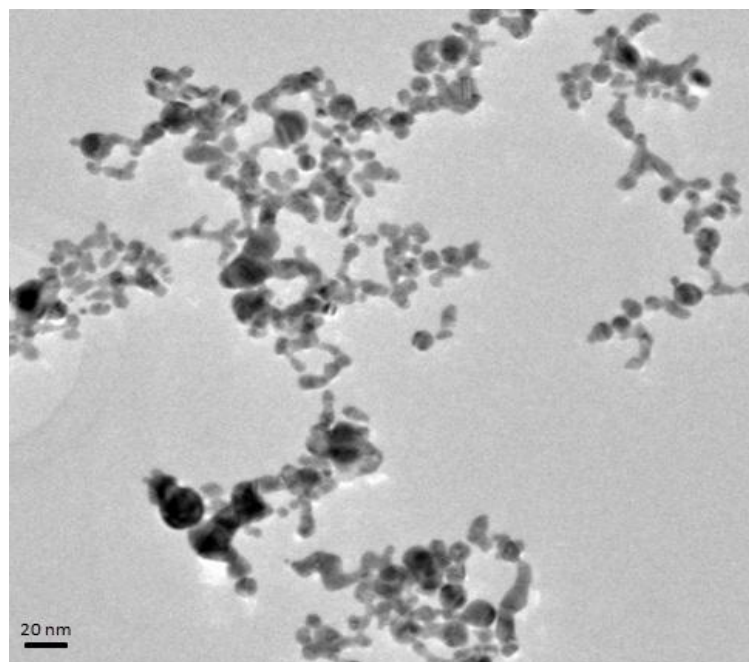


Figure 3-23. TEM studies of AuNPs synthesized in 527nm, 16 W, 110 ns Nd:YLF laser in water. General image and size distribution corresponding to the image.

3.5 Gold Thin Film Deposition on Glass Substrate

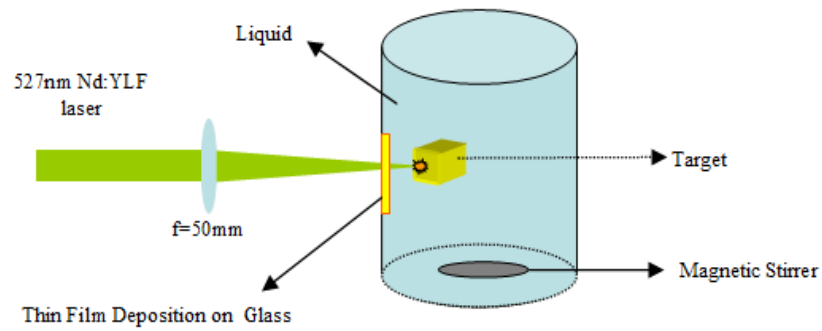


Figure 3-24. Schematic view of gold thin film deposition on glass by pulsed laser ablation in liquid technique

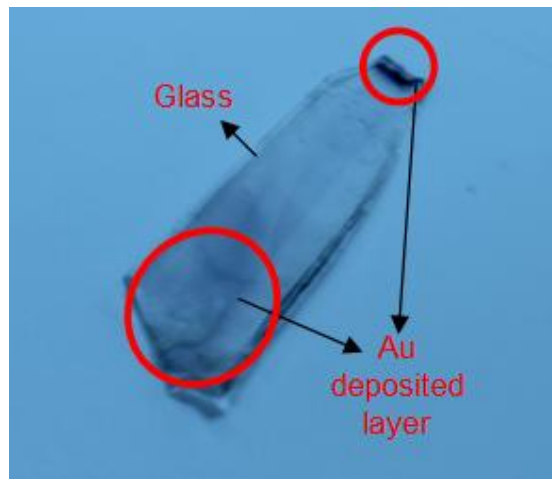


Figure 3-25. Picture of Au deposited glass substrate.

The mechanism behind gold thin film deposition in liquid on glass substrate is almost same with PLD. The formed plasma on substrate interacts with liquid instead of gas and constitutes a thin film Au layer

on the front face of the tube. The deposition of Au layer on glass has been carried out by Nd: YLF laser (Empower, Q-Switched Laser, Spectra Physics, USA) with 527 nm wavelength, 16 W average power, 110 ns pulse duration, and 16 mJ pulse energy for 1 kHz. Figure 3-24 indicates the schematic view of Au thin film deposition technique. Figure 3-25 shows the pictures of Au deposited on glass substrate.

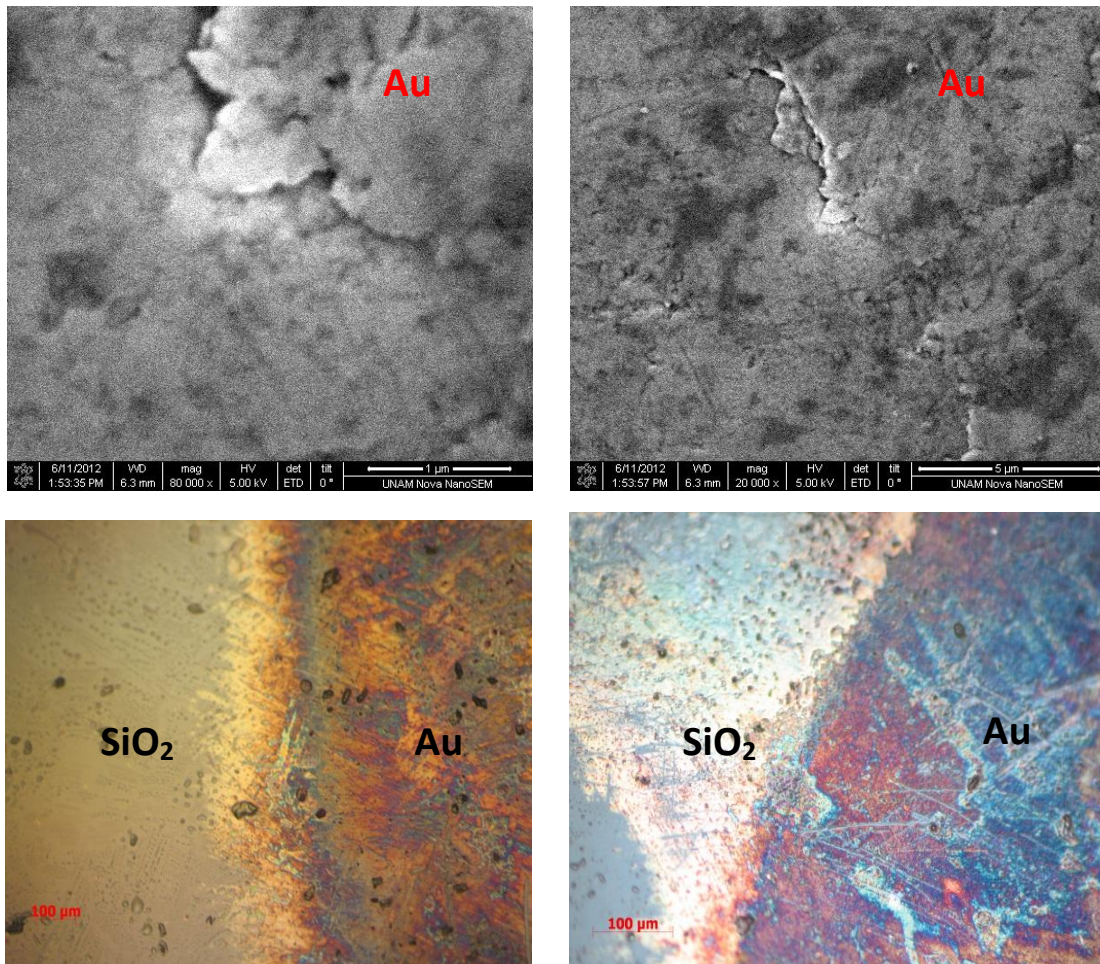


Figure 3-26. SEM and Optical pictures of Au deposited glass substrates.

Figure 3-26 shows SEM and optical pictures of Au deposited film. One of the disadvantages of this process is obvious. The layer is not homogenous and this technique cannot be applied on the fields where homogenous layer is needed. Figure 3-27 shows XPS studies of the film. Thermo Scientific X-Ray Photoelectron Spectroscopy K-alpha was used for measurement. Film was etched before measurement with Argon gas about 1-2 min. The spectrum indicates that $4f_{7/2}$ peak of AuNPs is located at almost 82,6 eV and $4f_{5/2}$ peak located at 86,3 eV. Oxidization of Au affects and lead to shift of XPS spectrum [47].

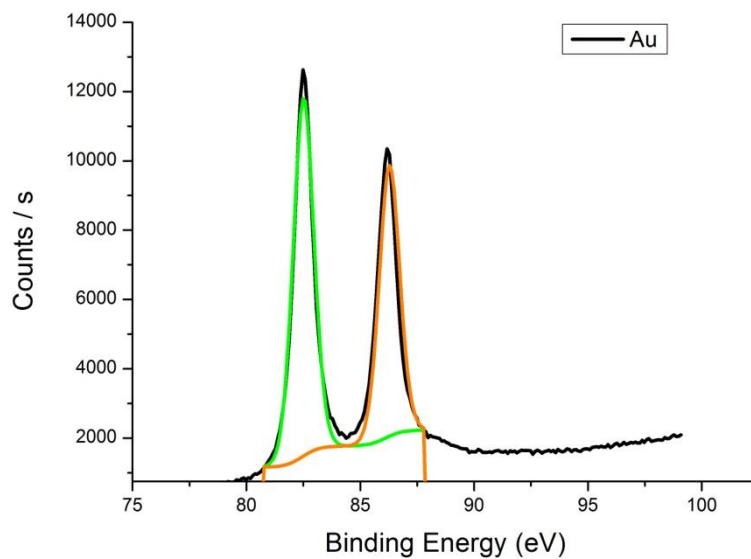


Figure 3-27. XPS Studies of Au deposited glass substrate.

3.6 Gold thin film deposition with spin coating

AuNP was synthesized in methanol by Nd: YLF laser 16 W average power, 110 ns pulse duration, and 16 mJ pulse energy for 1 kHz. After AuNP was synthesized in methanol, they were deposited on silicon wafer by spin coating with 1000 rpm and 2 min. Figure 3-28 shows SEM picture and EDX analysis. The more homogenous layer has been achieved by this method compared with Gold Thin Film Deposition in liquid. However, it is still not perfect and some corruption and aggregation have been detected as seen in Figure 3-28. Energy Dispersive X-Ray (EDX) analysis states the Au existence on the layer. The cross section SEM image states the thickness of the layer. According to images, the thickness is almost 40 nm.

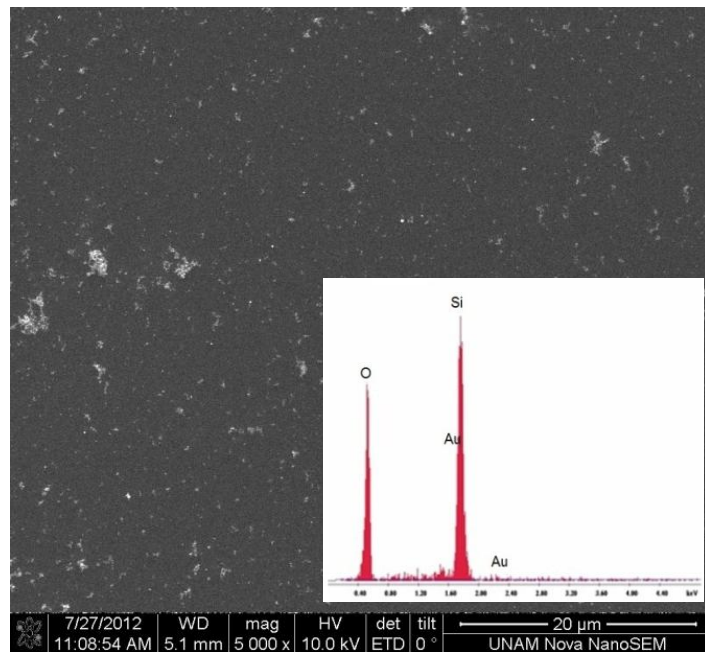


Figure 3-28. SEM picture and EDX analysis of Au deposited thin film.

Chapter 4

4. Conclusion

PLAL is a new and promising nanoparticle synthesization technique. It is also free of chemical agents, ligands or stabilizers and relatively cheap. It allows user to synthesize numerous type of nanoparticles from semiconductors to magnetic materials only by a one process. Different solvents or average power / pulse duration of laser change all mechanism and lead to different sizes/shapes/crystallites of same material. The synthesized nanoparticles with PLAL are mostly crystal and the size distributions are not large. Therefore, they are good candidates for many technological applications. An extensive work of NMNp synthesization by PLAL has been presented. Beside theoretical work of how nuclei and nanoparticles form with plasma, experimental results were discussed in detail.

Firstly, Au, Ag and Pt NPs were synthesized in deionized water with Nd: YLF laser (Q-Switched Laser, 527 nm wavelength, 16 W average power, 110 ns pulse duration, and 16 mJ pulse energy for 1 kHz). They were characterized with SEM, XPS, XRD, TEM, and UV-Vis Spectroscopy. In addition, AuNPs in deionized water have been synthesized with varying energies of laser (9,2 mJ, 12 mJ and 16 mJ for 1kHz) in order to understand the role of laser energy on PLAL. Secondly, these noble metals were synthesized in methanol with Nd: YLF laser (Q-Switched Laser, 527 nm wavelength, 16 W average power, 110 ns pulse duration, and 16 mJ pulse energy for 1 kHz).

Then, they were characterized with SEM, XPS, XRD, TEM, and UV-Vis Spectroscopy. NPs obtained in deionized water are more stable than in methanol. Also, small change in SPR and sizes of Ag, Au and Pt NPs in deionized water and methanol was observed. These differences were characterized with UV-Vis Spectroscopy and TEM. Crystal properties and chemical compositions of NMNPs in deionized water and methanol were same. Lastly, Au and Ag NPs were synthesized in PVP for nanofibrous composites. The characterization of Au and AgNPs in PVP was investigated by means of TEM and UV-Vis Spectroscopy. Thin-film applications were also presented: PLD-like deposition by PLAL and simple spin-coating deposition with AuNPs synthesized in methanol. The films were not homogenous. However, these two techniques of thin film deposition are an alternative, easy and cheap method.

For future work, PLAL of different materials can be performed such as semiconductors and metals. Also, NPs obtained by different lasers and different wavelength liquid environments can be studied. Moreover, synthesized NPs with PLAL can be investigated in applications, namely, solar cell, optical sensors, and cancer treatment.

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