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Examination of Silver Nanoparticles Formation by Laser Ablation in Organic Liquids

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ABSTRACT

Silver Nanoparticles (NPs) were prepared via pulse laser ablation in different organic liquids such as acetone, toluene, and cyclohexane. Particle size, optical and stability properties of synthesized colloidal Nanoparticles were investigated by Atomic Force Microscope, UV-visible spectroscopy and Zeta potential measurements, respectively. In toluene and cyclohexane, results show that some parts of silver NPs with core-shell structure are evidently observable. Silver Nanoparticles in toluene did not have surface Plasmon resonance in their optical absorption spectrum like Nanoparticles in acetone and cyclohexane because of the existence of the non-crystalline carbon which it is covering them and inhibiting the Plasmon band of Ag NPs .Preparation in acetone results in shorter wavelength of (SPR) and stable solution in comparison with using cyclohexane. The results were discussed qualitatively by considering influences of polarity, viscosity and carbon chains of surrounding molecules on size, surface Plasmon resonance and stability of silver Nanoparticles.

Keywords: Atomic Force Microscope, Laser Ablation in Organic Liquids, Silver Nanoparticles, Surface Plasmon Resonance, Zeta Potential.

1. INTRODUCTION

Silver Nanoparticles (NPs) have received excessive attention because of high optical response in the visible and near infrared spectra [1]. In addition of the wavelength-selective absorption, the silver NPs have light scattering capability with molar extinction coefficient as high as $10^{11}M^{-1}cm^{-1}$ larger than organic dye molecules [2].Silver NPs have surface Plasmon resonance which is a collective oscillation of conduction electrons in phase with incident light [3]and their ability to convert the energy of incoming photons into a collective oscillation, therefore these Nanoparticle can be regarded as containers to the Plasmon surface. Surface Plasmon resonance of Nanoparticles is effect by their morphology, composition, surface chemistry, and surrounding environment [4]. The controlling of electrons oscillation is possible by varying the shape of Nanoparticles. Therefore, light absorbing and scattering can be handled which may enhance local electric fields at the surface of Nanoparticles [3]. As a result, silver NPs have found tremendous applications in a large range of topics, such as electro-optical and semiconducting materials [2], LSPR sensing, surface-enhanced Raman scattering, and plasmonic circuitry [1].

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Silver NPs are antibacterial agents without the toxic effects to human body such as antibiotics, thyroid deficiency medication of certain drugs [5], silver NPs have anti-inflammatory activity which make it have a great use in oncology [6]. In addition, one of the most applications of silver NPs is used as conductive –ink in the ink-jet printing technology for production of electrode or circuit patterns in plasma displays (PDP), radio frequency identification (RFID), and photovoltaic solar cells for example , silver NPs in toluene used as a conductive ink was demonstrated by Szczech *et al.* [7].

Silver colloidal NPs can be prepared by several methods for example arc discharge in liquid [8], electrochemical [9] and pulse laser ablation in liquid [10] etc., pulse laser ablation in liquid has received great research interest since an establishment of a novel Nanoparticles production technique [10]. It top-down approaches which involve the removal or reformation of atoms from bulk to get nano sized particle, its clean with no product or chemical remains. Compared to usual bottom–up approaches such as chemical synthesis, it is a fast and cheap production technique at room temperature [11].Also, possibility the control on the broadening of particle size distribution due to post ablation agglomeration by variation of laser parameters [12],adding surfactants such as HCL, NaOH or using organic liquid [13]. Therefore, the choice of liquid is very necessary during laser ablation process because of its influence on the aggregate growth, shape, solid phase, surface Plasmon resonance, particle size and particle size distribution of nanoparticles [13].

In general, it is necessary to understand the mechanism of particle production and growth for pulsed laser ablation of metal target in liquid according to Mafune model [14]. During laser irradiation, plasma plume is generating from ablated materials which extend in liquid medium. Nanoparticles can be generated by the collision between free atoms or clusters through van der Waals forces and their nucleate [15,16]. After laser ablation, the nucleation process stopped, but the aggregation and grain growth are continuous [15]. The rate of aggregation depends on many factors, such as interaction of liquid molecules with surface atoms of Nanoparticles, and the Nanoparticles- Nanoparticles interaction which occurs by collisions through Brownian motion [16]. Numerous studies have reported that the final size, size distribution, shape, of Nanoparticles by laser ablation depend on several factors, these factors depend on energy per pulse, ablation time, pulse duration, laser wavelength, target material and the nature of the liquid [17].

This work aims to prepare of silver NPs by pulse laser ablation in different organic liquids, and study the effect of liquid on the optical, structural and stability properties of silver Nanoparticles.

2. EXPERIMENTAL WORK

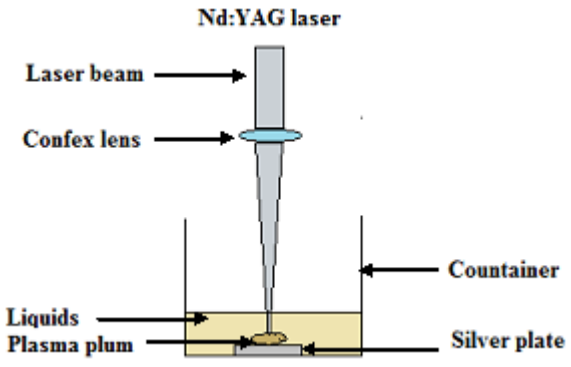
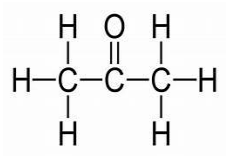
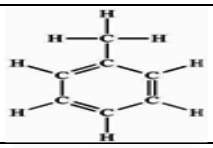
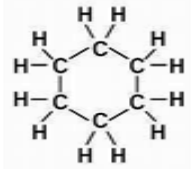


Figure 1. Schematic diagram of laser ablation in liquid.

Pulsed laser ablation (PLA) in liquids was performed using Q-switched Nd:YAG with output energy of 800 mJ/pulse for 1.06 μm wavelength. The PLA pulse width was 7 ns and the repetition rate was 10 Hz. Silver plate with (99.99%) purity from Blaybil Company in Al-Naher Street/ Baghdad was used, silver plate placed at the bottom of the beaker filled with 3 ml liquid. The height of liquid above the target surface was 5 mm in order to reduce the light absorption. A Gaussian laser beam was normal incident and focused by optical lens with 10 cm focal length on the target surface, the effective diameter of 1 mm and laser fluence of 101 J/cm^2. During the laser ablation, the target was moving for each pulse shot. This step increases uniform ablation of silver surface and escalates material removal process. After 100 laser pulses, the color of the solution became light orange due to the formation of silver NPs. The schematic diagram of laser ablation in liquids is shown in Figure 1. The chemical formula, relative polarity, viscosity and refractive index of the liquids are given in Table 1 below.

Table 1 Chemical formula, Relative polarity, viscosity and refractive index of the liquids

Liquids	Chemical formula		Relative polarity	Viscosity (Mp)	Refractive index
Acetone	C_3H_6O		0.355	0.36	1.359[18]
Toluene	C_7H_8		0.099	0.950	1.497[18]
Cyclohexane	C_6H_{12}		0.006	1.02	1.4266[18]

UV–VIS absorption spectra of the silver solution were obtained by Shimadzu spectrophotometer. Morphology and particle size distribution were characterized by Atomic Force Microscope (AFM), using a JEOL JEM1010 microscope, at 100kV. In addition, zeta potential and stability were analyzed by Zeta Potential analyzer Ver.572, Brookhaven Instruments.

2. RESULTS AND DISCUSSION

The topography and particle size distribution of silver NPs was characterized by Atomic Force Microscope (AFM). After remaining the samples in ultrasonic bath for 15mins, AFM test was prepared by drying a drop of colloidal silver particles onto glass substrate at room temperature. Figure 2 display AFM images with histogram size distribution of silver NPs observed in acetone, toluene and cyclohexane respectively.

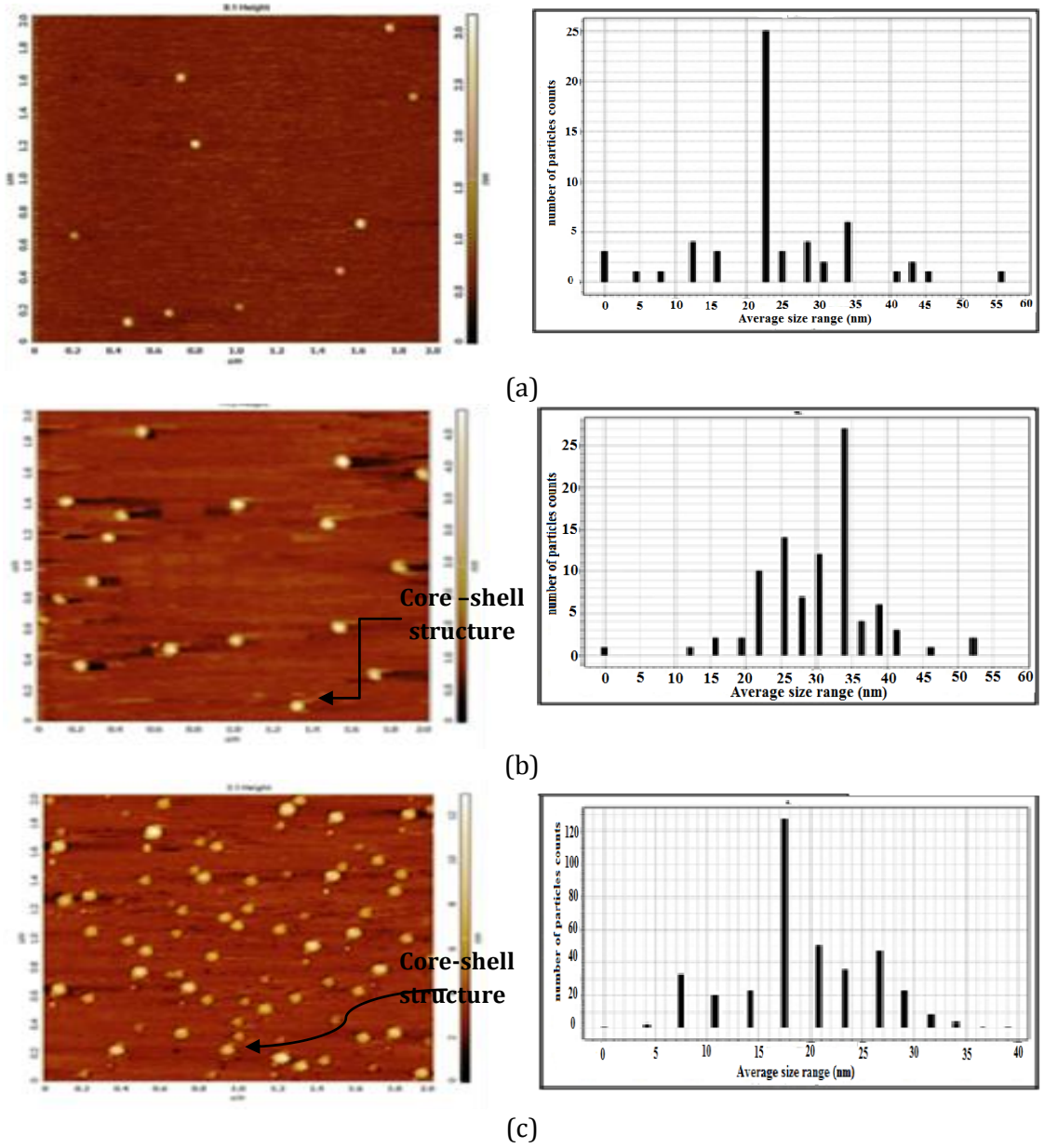


Figure 2. AFM images and histograms of size distribution of silver NPs in: a) Acetone, (b) Toluene, and (c) Cyclohexane.

AFM images show spherical shapes NPs for all solvents. Figure 2(a) exhibits silver NPs were well dispersed in acetone with no noticeable aggregation, compared to that of nanoparticles shown in Figure 2(b&c). This result was attributed to the properties of acetone. Acetone has high polar molecules due to contain bonds between oxygen and hydrogen with different electronegative charges. It generates a stronger electric double layer on the Nanoparticles surface. Therefore, the repulsive force between nanoparticles increased, prevented their growth, and aggregation.

On the other hand, toluene and cyclohexane are non–polar solvents, it have bonds between atoms with similar electro negativity charges, such as carbon and hydrogen. In general, Low polarity of liquid lead to weaker bonds between the nanoparticles and permits the further growth in liquid [19]. Preparation in toluene and cyclohexane as is evident from figures of AFM, A halo rings around some particles carbon shell or carbon matrix. The core shell structure is due to dissociation of toluene and cyclohexane during laser ablation [20], because of high plasma

temperature during laser ablation which cause to a graphitization of the hydrocarbon in toluene and cyclohexane that forms a carbon shell enclosing the silver NP [21].

Histogram of size distribution demonstrates of created silver NPs in different liquids media. The histogram was normalized in order to represent the particles with average sizes ranging from 1-60 nm which depend on the nature of liquid. It is clear that the predominant average sizes of particles are obtained in acetone; toluene and cyclohexane were 23, 33 and 18 nm, respectively. However, the average size of silver NPs obtained in cyclohexane is smaller than other liquids, because of the viscosity of cyclohexane is higher than toluene and acetone (cyclohexane > toluene>acetone) due to that the plasma plume generated during laser ablation is confine in small region and it became stronger with increase of solvent viscosity [22], UV-Vis spectra of silver Nps obtained in different liquids are shown in Figure 3.

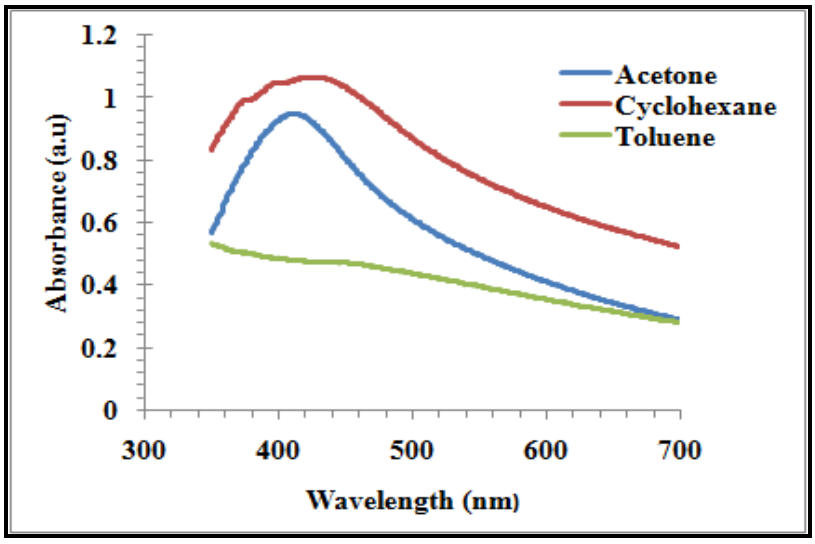


Figure 3. UV-Vis spectra of silver Nps obtained in different liquids.

As one can clearly see, no SPR was recorded in toluene. The absent of Plasmon band can be related to the existence of the non-crystalline carbon, graphite molecules which prevents the nanoparticles from growing in size, covering them and inhibit the plasmonic band of Ag NPs[23].While silver NPs in acetone and cyclohexane, it can be seen that a Plasmon band for silver NPs. In cyclohexane liquid, it is possible to note that the surface Plasmon resonance peak is wider, and a small red shift to longer wavelength; it is most likely due to an aggregation of silver nanoparticles as shown in figure 2(c). In addition the intensity of absorption peak in cyclohexane is higher than in acetone due to the number of generated NPs (formation efficiency) was increased. The increase of formation efficiency is due to the increment of the density and viscosity of solvent [24].

Stability of suspension depend on the compete between the Vander Waals attractive force and electrical double layer repulsive force that exist between particles due to Brownian motion, therefore the colloidal will be stable, If the repulsive force of the particles become dominate on the attractive force. Zeta potential(ζ-potential) is a potential of national boundary inside the diffuse layer of the liquid layer surrounding the particle, the magnitude of zeta potential gives as indication of the stability of the colloidal, if zeta potential more than ±30 mV ,the particles are normally stable because of theirs repulsive force prevent them from coming together and flocculating [19,20].Zeta potential is very important parameter for many applications including description of biomedical polymers, electro kinetic transfer of particles or blood cells, biocompatibility tests for medical devices or the description of clothing material properties in

the textile industry, medicinal drugs, water treatment, and refining to remove impurities [27]. In general, ζ-potential depends on various factors such as solvent types (polar or non-polar) and also the viscosity of the dispersion medium, these parameters are obtainable from Smoluchowski's coagulation equation [28].

$$\upsilon_E = 4\pi\varepsilon_\circ\varepsilon_r\frac{\zeta}{6\pi\mu}(1+kr) \quad (1)$$

Where υ_E is the electrophoretic mobility of particle in a unit electric field, $\varepsilon_r$and $\varepsilon_\circ$ are the relative dielectric constant and the electrical permittivity of a vacum respectively, μ is the solution viscosity, r is the particle radius and $\kappa=(2n_0z^2e2/\varepsilon_r\varepsilon_0k_BT\ )^{1/2}$ is the Debye–Hückel parameter, n_0 is the bulk ionic concentration, z is the valence of the ion, e is the charge of an electron, k_B is the Boltzmann constant, and T is the absolute temperature. It is can be seen that the mobility of silver nps is inversely depending on viscosity of liquid. Figure 4 illustrates the zeta potential of silver NPs in organic liquids.

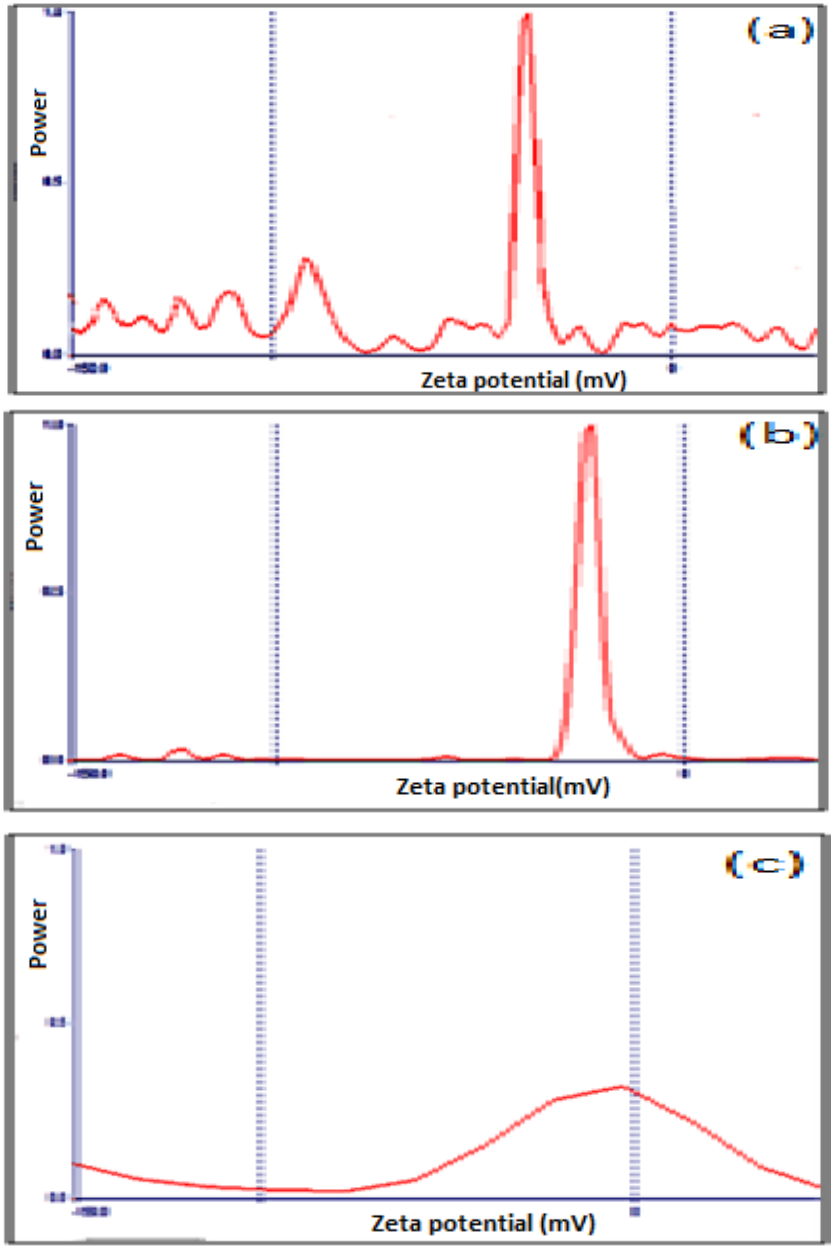


Figure 4. ζ-potential of silver NPs prepared by laser ablation in acetone, toluene, and cyclohexane, respectively.

The results of ζ-potential are given in table 2 below. The negative symbol of the ζ-potential is related to negative ions like enolates, hydroxide anions or carboxylated anion adsorbed which is deriving from the surfactant that surrounds the particles [29]

Table 2 ζ-potential results

Liquids	Electrophoresis Mobility(μm cm/V s)	ζ-potential (m V)	State of stability
Acetone	2.29	-37	stable
Toluene	1.76	-22	unstable
Cyclohexane	0.26	-10	unstable

In the case of acetone, it has been found that the ζ-potential have larger value because of the molecular polarity of acetone. Polar molecules generate a strong electrical repulsion the nanoparticles, the electric repulsion can separated the particle from each other and prevent them from aggregation [29].silver colloid obtained in toluene and cyclohexane are unstable if we compared the zeta potential of nanoparticles produced in acetone, because of non polar molecules for toluene and cyclohexane unable to create an adsorbed anionic species, It cannot be considered as an stabilize agent for silver nano particles although the presence of graphitic carbon onto crystalline silver nanoparticles, which could have blocked their growth [30].

3. CONCLUSION

We have successfully obtained silver nanoparticles in three organic liquids without stabilizing agent (acetone, toluene and cyclohexane) using the same laser ablation conditions. We observed that the size distributions predominant were 23, 33, 18 nm of nanoparticles obtained in acetone, toluene and cyclohexane respectively. SPR of the silver colloidal NPs is influenced by the surfactant molecules attached to the particle surface, Silver Nanoparticles in toluene did not have surface Plasm one resonance in their optical absorption spectrum unlike Nanoparticles in acetone and cyclohexane because of the existence of the non-crystalline carbon which it is covering them and inhibiting the Plasmon band of Ag NPs. Silver nanoparticles in acetone are highly stable in suspension due to the high relative polarity of liquid compared to silver Nps in non-polar toluene and cyclohexane.

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