Plasmonic Absorption of Gold and Silver Nanoparticles in Water

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ABSTRACT

Gold and silver nanoparticles were prepared as colloidal in water by pulsed laser ablation method. Nanoparticles are characterized by UV-Vis, FTIR and Atomic absorption spectroscopy. Absorbance spectrum has been measured as a function of time and laser energy. Both types of colloidal nanoparticles showed plasmonic absorption in the visible spectrum at 525 nm and 400 nm for Au and Ag nanoparticles, respectively.

الامتصاص البلازموني لجسيمات الذهب والفضة النانوية بالماء

الخلاصة:

حضرت الجسيمات النانويه للفضه والذهب في الماء باستخدام طريقه الاستئصال بالليزر. وقد تم قياس خصائص الجسيمات النانويه بواسطه مطياف الامتصاص , مطياف الاشعه تحت الحمراء ومطياف الامتصاص الذري. وتم قياس طيف الامتصاص كداله للزمن ولطاقه الليزر. طيف الامتصاص البلازموني للمواد النانويه عند 400 نانومتر للفضه و525 نانومتر للذهب.

INTRODUCTION

Plasmonic is a recent approach to enhance light trapping in Photovoltaic devices [1]. Pillai and Green [2] were the first to propose using plasmonic effects to improve the absorption in these devices. Since then a lot of methods has been proposed to deposit nanoparticles on the surface or even inside the active layers to increase the trapping of light and consequently enhance the absorption efficiency [3, 4]. For example Szczepanowics [4] and Jana *et al.* [1] used chemical reduction method to prepare silver nanoparticles. Lee *at el.* [5] used electrostatic assembly approach to prepare gold nanorods. However, because of its simplicity there was a growing interest in laser ablation method. Imam *et al.* [6] have studied the effect of experimental parameters on the fabrication of gold nanoparticles via laser ablation. They showed that when the laser energy increases, the size of the gold nanoparticles decreases until they reach their critical size below which the particle becomes insensitive to the laser energy. In his PhD thesis, A. K. Ali [7] extensively studied the

experimental parameters to prepare Au and Ag nanoparticles in water and ethanol. Hahn *et al.* [8] compared between non-polar and polar liquid as colloidal mediums. The agglomeration of gold nanoparticles is likely to happen in non-polar liquids like hexane and they show higher stability in water. Mafune *et al.* [9] observed that Ag nanoparticles shifts to smaller sizes associated with increase in the concentration of SDS solution. Imam *et al.* [10] prepared silver nanoparticles by laser ablation in distilled water at different ablation times. The produced average diameter was ranged from 30-50 nm. They found that the average size of the produced particles is increased as ablation time increased and as the laser power increases the size of nanoparticles decreases until they reached their critical size below which the fluence increases above this value and the nanoparticles begin to agglomerate again and the size increased. Machmudah *et al.* [11] prepared Au and Ag nanoparticles in pressurized CO_2. The structure of both Au and Ag nanoparticles were seriously affected by the changes in CO_2 pressure, temperature and ablation time.

In this paper we study the effect of laser energy and time on the plasmonic absorbance of gold and silver nanoparticles in deionized water.

Theoretical Part

Plasmonic (noble metal) NPs distinguish themselves from other nanoplatforms, like magnetic and polymeric nanoparticle by their unique surface plasmon resonance (SPR) [12]. The brilliant colors of the noble metal NPs are found to depend on the shape and size of the nanoparticle and dielectric constant of the surrounding medium [13]. Production of NPs under laser ablation of solids either in vacuum or in gas has been extensively explored during last decade [14]. PLA is a simple promising method for preparation of high-quality MNPs in liquid, especially in water [15]. Above the ablation threshold, the irradiation of solid targets with laser pulse of fluence leads to material removal forming NPs [16]. Light intensity which propagates through a medium containing small particles is reduced by scattering and absorption. The light beam extinction is given by [7]:

$$I(z) = I_0 \exp(-n_0 \sigma_{ext} z), \quad \ldots(1)$$

Where I(z) : Intensity of the incoming beam after a distance z

n_0 : Number of particles per unit volume

σ_{ext} :Extinction cross section of a single particle

$$\sigma_{ext} = \sigma_{abs} + \sigma_{sca}, \quad \ldots(2)$$

Where σ_{abs}: Absorption cross sections

σ_{sca}: Scattering cross sections

Theoptical properties of such particles, as a consequence of their reduced dimensions, are dominated by a coherent collective oscillation of their conduction band electrons. Such collective oscillation is known as surface plasmon resonance [7].

Experimental part

The generation of nanoparticles carried out using a commercial Nd:YAG laser system (HUAFEI), delivering energy in the range (100-400 mJ) at wavelength 1064 nm and pulse frequency of 1 Hz. The procedure of laser ablation in liquid is presented in details elsewhere [6, 7]. Deionized water was used as a solvent during the whole preparation. The absorbance spectra were measured by UV-Vis single beam spectrophotometer. All absorbance spectra were measured at room temperature in

quartz cuvettes with 1 cm path length. The fresh NPs solution without any further treatment was used as the samples for UV-Vis measurement using deionized water as a standard for background correction.The concentration of nanoparticles was measured by Atomic Absorption Spectroscopy AAS, phonex 986AA. Standard solutions of $AuNO_3$, $AgNO_3$ were used to establish the relation between the measured absorbance and the analytic concentration.The surface morphology and size distribution of the Ag, Au nanoparticles were examined by Atomic Force Microcopy AFM.

Result and discussion

Figure (1). shows two photographic images of the Ag NPs and Au NPs prepared by laser ablation in distilled water for different laser energies (100-400mJ). The solutions are different in colors because there are different particle sizes in each cuvette associated with each laser energy used to prepare the solution. It is found that the opacity of nanoparticle solutions increase with increasing of laser energy. The color of solution changes from light pink to dark pink for Au NPs and from light yellow to dark yellow for Ag NPs.

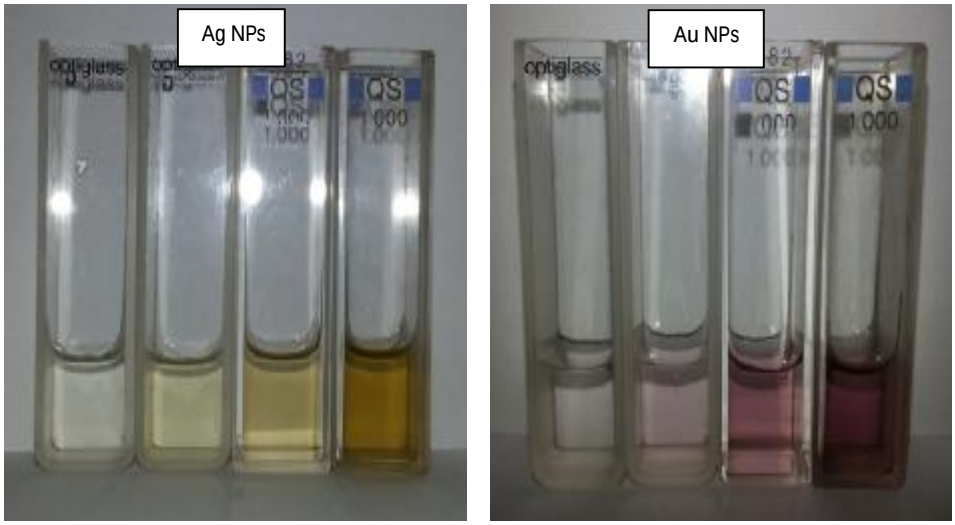


Figure. (1). Distinctive colors prepared by different laser energy.

Figure (2) shows the typical absorption spectra of Au and Ag colloidal solutions at various laser energy. These spectra exhibit characteristic absorption bands with peak located at around 400 nm for Ag NPs and at around 525 nm for Au NPs, which is corresponds to the surface plasmon resonance (SPR) for gold and silver NPs [17, 18]. The presence of single surface plasmon peak is consistent with that the NPs present in the solution are predominantly spherical in shape [9].

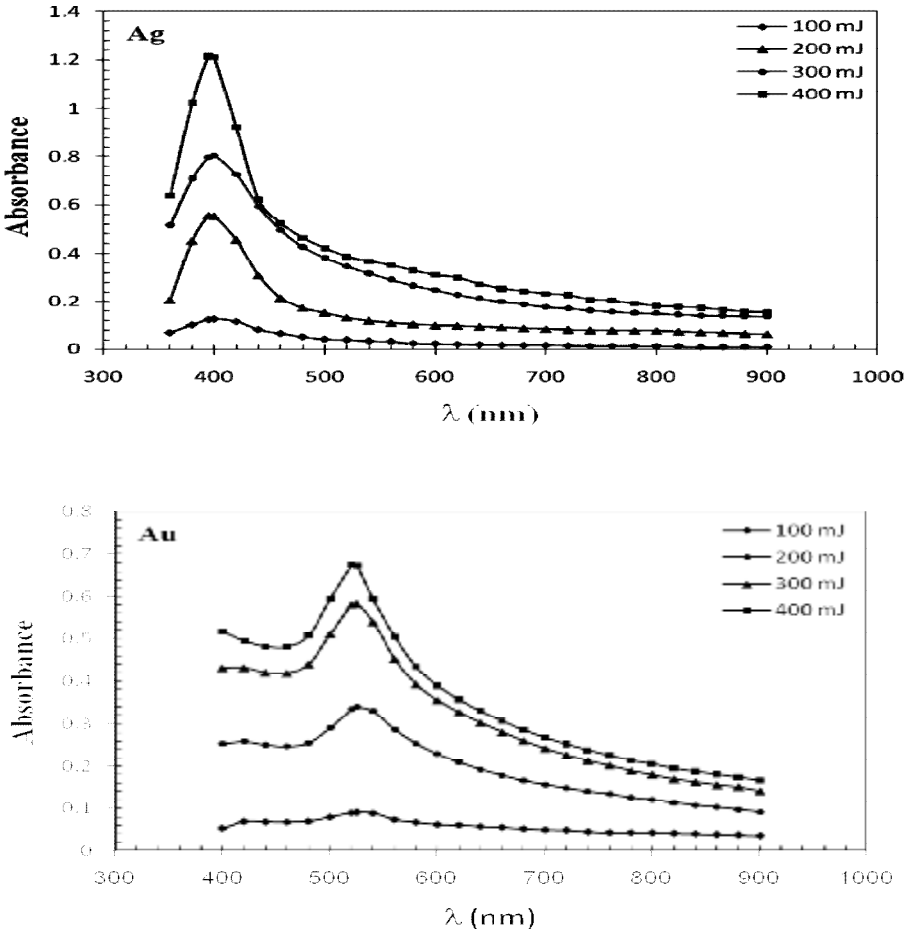


Figure. (2) Absorbance of Ag and Au nanoparticles as a function of wavelength.

The density of the ablated species can be changed by adjusting the laser fluence. As can be seen from Fig. (2), the value of the plasmon peak increases with increasing laser energy. Therefore, the obtained spectra of gold and silver colloids suggest increasing both the total abundance of gold and silver atoms in the solution and the concentration of nanoparticles having diameters in the nanometer range as the laser fluence increases.

To study the stability of the silver and gold colloids, absorption of the colloid prepared at 200 mJ was measured at different periods of time as shown in Fig. (3), there is no obvious change in peak position but the intensity of SPR band initially increases with time. The stable position of absorbance peak indicates that new particles do not aggregate. The stability of suspension depends not only on size, shape but also on liquid medium. The liquid in which nanoparticles suspend can affect on the surface charge of nanoparticles. Surface charge leads to repulsive forces between nanoparticles and keeps them far from each other, which results in a high stability of suspension [19].

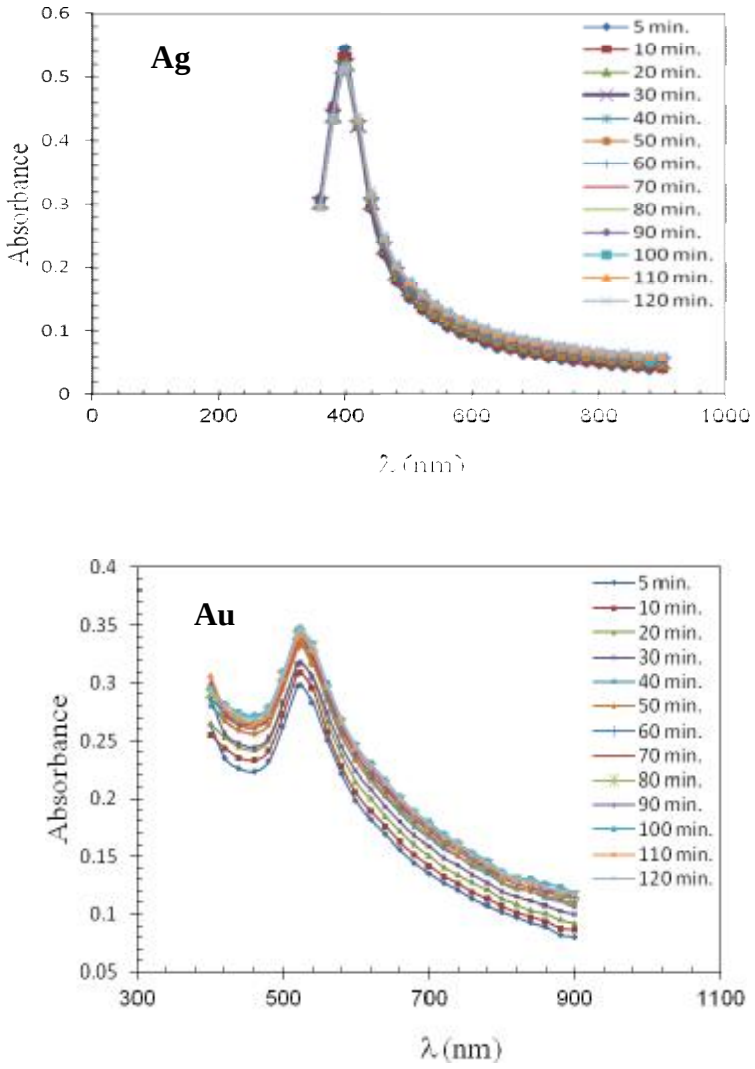


Figure. (3) Stability of Au and Ag nanoparticles with time.

Figure (4) shows the amount of the ablated silver and gold nanoparticles as a function of laser energy. It is observed that the concentration of nanoparticles increases with increasing laser energy. This has a good agreement with Fig. (2). Increasing the intensity of Plasmon Resonance peak can be assigned to the increase of the particle concentration in the solution.

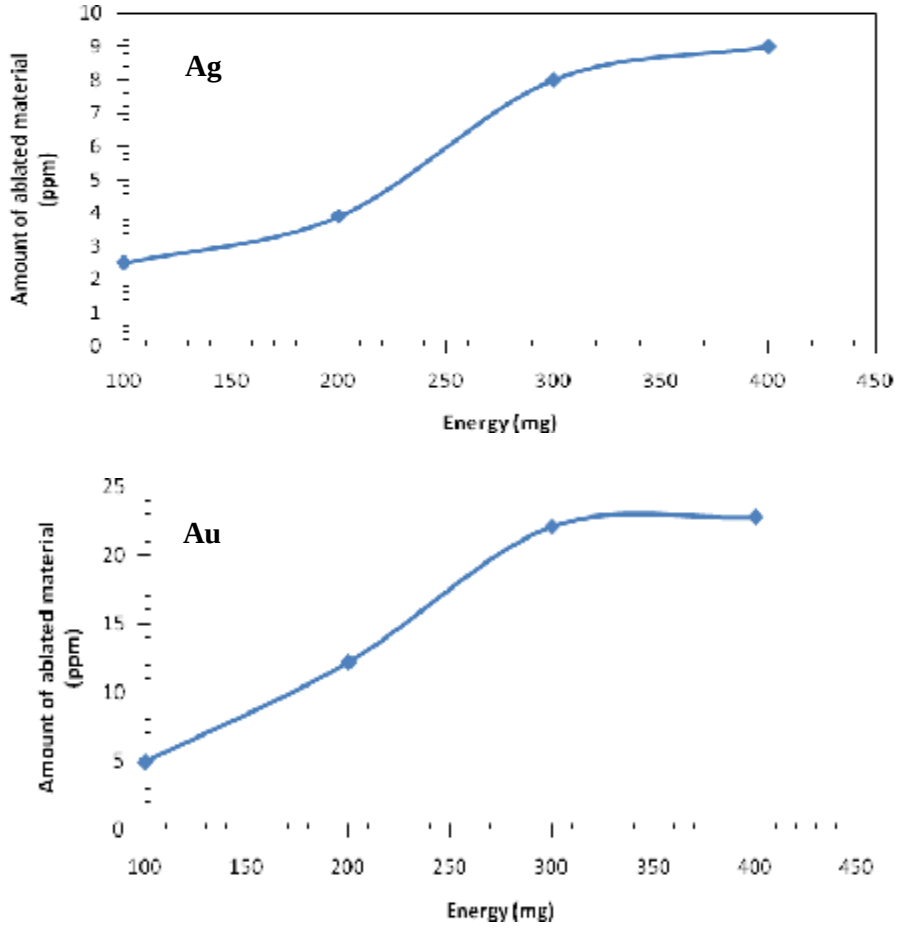


Figure. (4) Atomic absorption spectroscopy for Ag and Au nanoparticles.

Figure (5) shows the AFM images of gold nanoparticles. The size of gold nanoparticles prepared in de-ionized water decreases as the laser energy increase. The decrease in the average size of gold nanoparticles can be attributed to large energy which excited the gold nanoparticles in a solution, the photon energy is readily converted to the internal modes of the nanoparticles as during a single laser pulse, one gold nanoparticle is considered to absorb consecutively more than one thousand photon and it's temperature rises significantly so that the nanoparticle starts to fragment. After the single laser pulse the diffused into the solution and the temperature of nanoparticles return to room temperature before the next one arrive. The heating and cooling of nanoparticles occur in every laser pulse [20]. It is observed that the average particle size gets smaller with increasing ablating laser pulse power. An explanation can be given by assuming that an increased laser energy obviously increases the temperature of the ablated material and a faster quenching rate may be involved which causes the reduction of the sizes of the nanoparticles [21]. Higher pulse energies might enhance the temperature gradient in the material. A higher temperature gradient results in a higher cooling rate. Former studies found out

that higher cooling rates cause smaller particles [22]. The size of silver nanoparticles decreases until they reached their critical size, where the particle size increases with increasing with laser energy. It is seen that the higher laser energy seemed to promote more collisions between the vapour atoms/ions, to coalesce within the ablated plume and eventually to form larger particles [23]. This can be explained as when the GNPs reach their critical size, small fragments such as gold atoms and small aggregates resulting from photo fragmentation are dispersed in solution, therefore the nanoparticles present in the solution grow by attracting these small fragments. The fragmentation rate must increase with increasing the laser energy because the internal energy of irradiated nanoparticles increases [20].

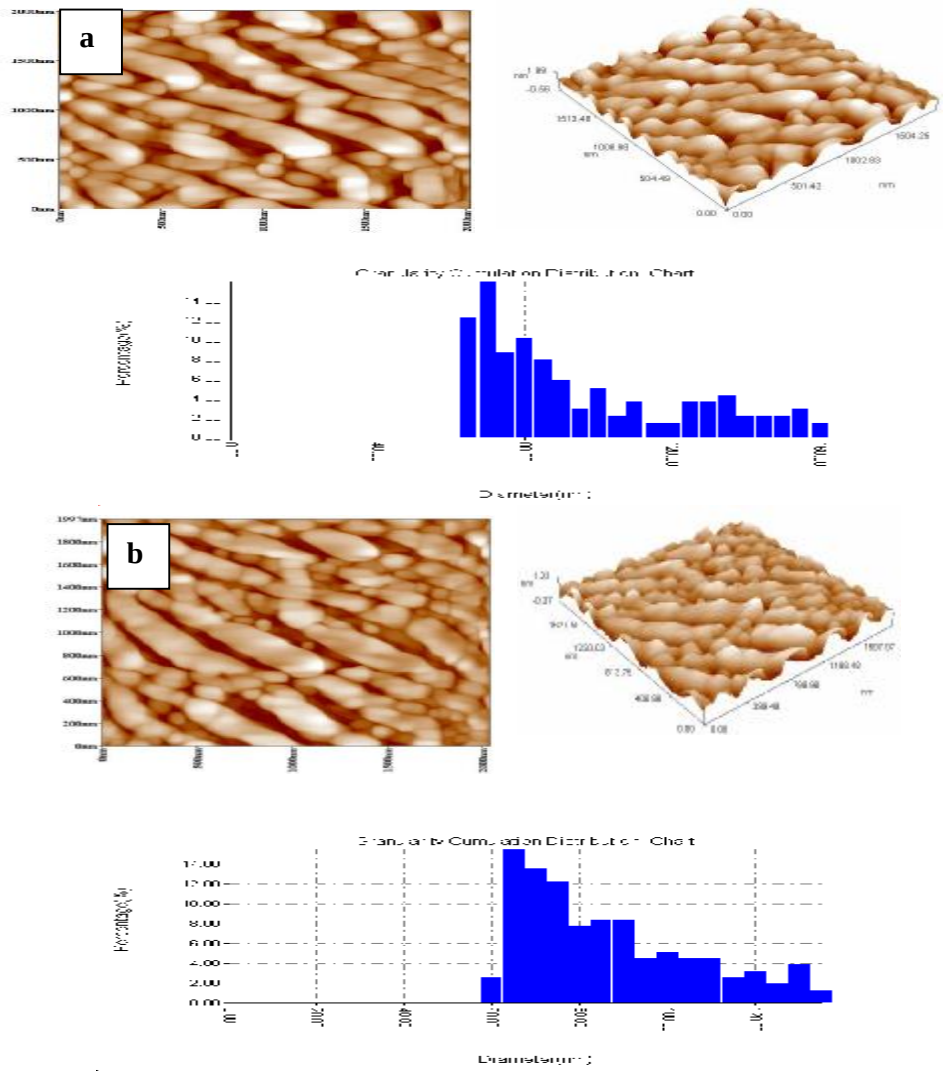


Figure. (5) AFM image for Ag NPs at (a)100 mJ and (b) 200 mJ.

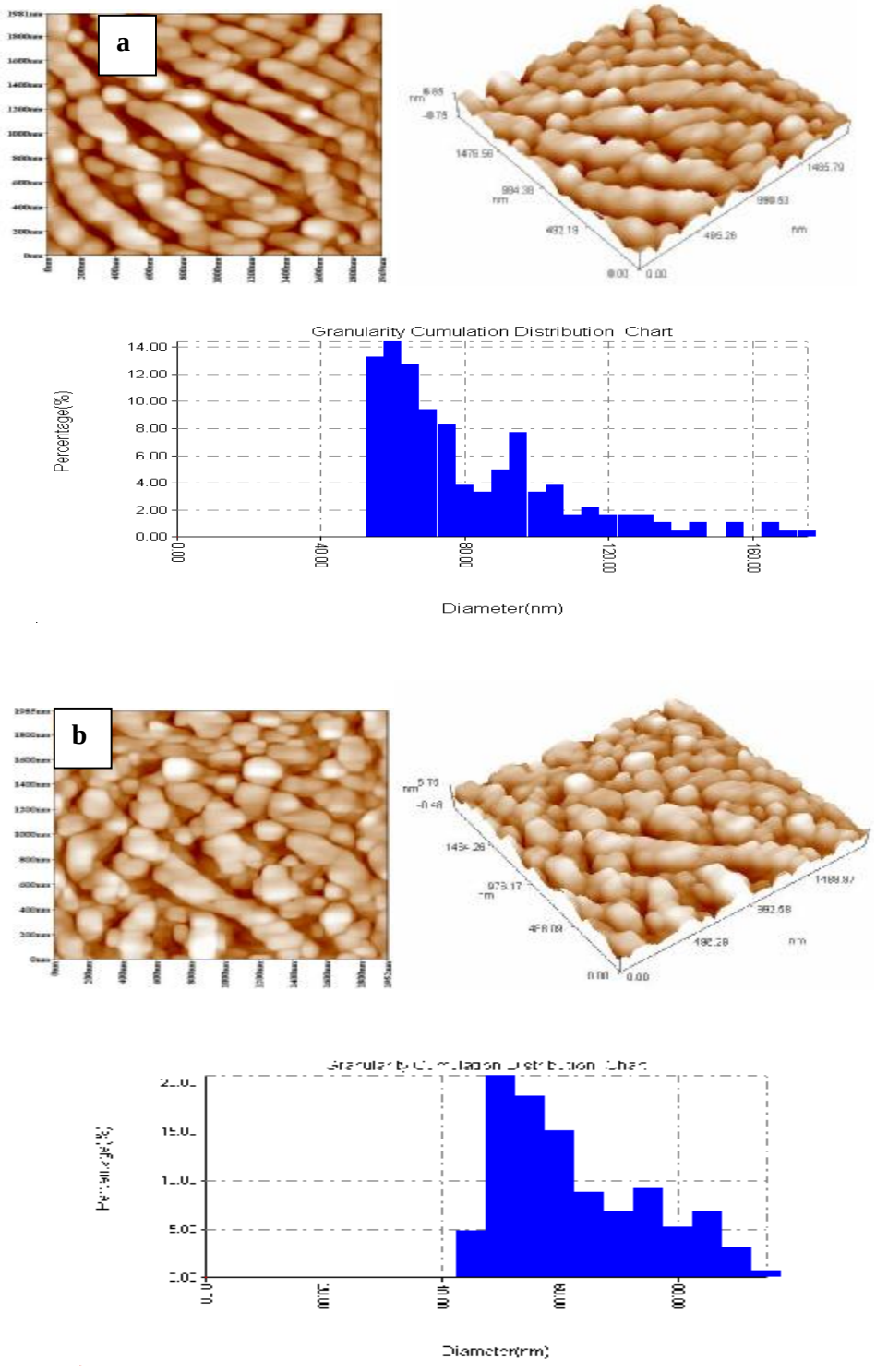
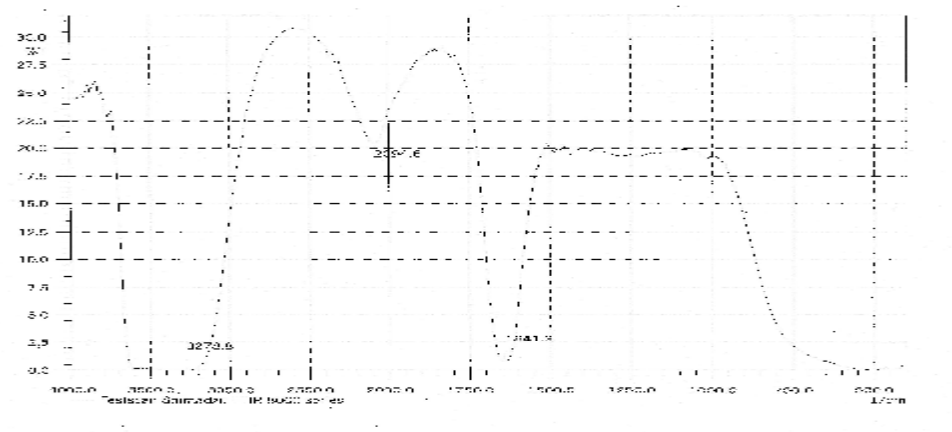


Figure. (6) AFM image for Au NPs at (a)100 mJ and (b) 200 mJ.

Figure (6) shows the FTIR spectrum for silver nanoparticles prepared at 800 mJ. The spectrum was recorded in the range (450-4000 cm^{-1}). The peak at 3278.8 cm^{-1} is due to O-H stretching, the peak at 1641 cm^{-1} is due to H-O-H bending [24, 25].



Figure(7): FTIR spectra of Ag NPs at 400 mJ.

Conclusions

Gold and silver nanoparticles were successfully prepared by laser ablation in distilled water at various laser energy. The resonance of Ag and Au NPs falls into the visible region of electromagnetic spectrum. The optical spectrum shows a maximum at 400 nm for Ag NPs and 525 nm for Au NPs. The high stability of metal nanoparticles synthesized by laser ablation in deionized water is reported. The peak location of plasmon absorption is constant with time. As the ablation energy increases, the size of nanoparticles decreases and the concentration increase. The FTIR spectrum was showed that the peak of Ag-O is not formed in this spectrum.

References

[1] S. K. Jana, A. L. Donne and S. Binetti, "Enhancement of silicon solar cell performances due to light trapping by colloidal metal nanoparticles", Journal of Physics and Chemistry of Solids **73** (2012) 143–147.

[2] S. Pillai, K. R. Catchpole, T. Trupke, and M. A. Green, "Surface plasmon enhanced silicon solar cells", Journal of Applied Physics **101**(2007) 093105.

[3] N. Adamovic and U. Schmid, "Potential of plasmonics in photovoltaic solar cells", Elektrotechnik & Informationstechnik **128/10** (2011) 342-347.

[4] K. Szczepanowics, J. Stefanski, R. P Socha, and P. Warszynski
Preparation of silver nanoparticles via chemical reduction method and their antimicrobial activity, Physicochem Probl Minor Process **45** (2010) 85-98

[5] J. H. Lee, J. H. Park, J. S. Kim, D. Y. Lee, and K. Cho, High efficiency polymer solar cell with wet deposited plasmonic gold nanodots, Organic Electronics **10** (2009) 416-420.

[6] H. Imam, K. Elsayed, M. A. Ahmed, and R. Ramdan, Effect of experimental parameters on the fabrication of gold nanoparticles via laser ablation, Optics and Photonics J. **2** (2012) 73-84

[7] Abdulrahman K. Ali, PhD thesis (2010), University of Technology, Baghdad, Iraq.
[8] A. Hahn, S. Barcikowski and B. Chickkov, Influence on nanoparticle production during pulsed laser ablation, JLMN-Journal of Laser Micro/Nanoengineering, **3**, 2 (2008) 73.
[9] F. Mafune, J. Kohno, Y. Takeda, T. Kondow and H. Sawabe, Formation and size control of silver nanoparticles by laser ablation in aqueous solution, J. Phys. Chem. **B 104**(2000) 9111-9117.
[10] H. Imam, K. A. Elsayed, L. Z. Ismail, M. Afify and M. A. Khedr, "Fabrication of Silver Nanoparticles by Laser Ablation in Liquid Solution," Life Science Journal **10** (2013) 401-404.
[11] S. Machmudah, Wahyudiono, N. Takada, H. Kanda, K. Sasaki and M. Goto, "Fabrication of gold and silver nanoparticles with pulsed laser ablation under pressurized CO_2," Adv. Nat. Sci.: Nanosci. Nanotechnol. **4** 045011 (2013)1-7.
[12] X. Huang and M. A. El-Sayed, "Gold Nanoparticles: optical properties and implementations in cancer diagnosis and photothermal therapy" Journal of Advanced Research **1** (2010) 13–28.
[13] S. Eustis and M. A. El-Sayed, "Why gold nanoparticles are more precious than pretty gold: Noble metal surface plasmon resonance and its enhancement of the radiative and nonradiative properties of nanocrystals of different shapes", The Royal Society of Chemistry Journal **35** (2006) 209–217.
[14] S.I. Dolgaev, A. V. Simakin, V. V Voronov, G. A. Shafeev and F. Bozon-Verduraz, "Nanoparticles produced by laser ablation of solids in liquid environments", Applied Surface Science **186** (2002) 546–515.
[15] M. Kawasaki and Kazuhisa Masuda, "Laser fragmentation of water suspended gold flakes via spherical submicroparticles to fine nanoparticles", Journal of Physical Chemistry B **109** (2005) 9379–9388.
[16] A. Menendez-Manjon, J. Jakobi, K. Schwabe, J. K. Krauss and S. Barcikowski, "Mobility of nanoparticles generated by femtosecond laser ablation in liquids and Its application to surface patterning", Journal of Laser Micro/Nanoengineering **4** (2009) 95–99.
[17] H. Muto, K. Miyajima, and F. Mafune´, "Mechanism of Laser-Induced Size Reduction of Gold Nanoparticles As Studied by Single and Double Laser Pulse Excitation," *J. Phys. Chem. C* **112** *(*2008) 5810-5815.
[18] G.A. Shafeev, E. Freysz and F. Bozon-Verduraz , "Self-influence of a femtosecond laser beam upon ablation of Ag in liquids," Applied Physics A **78** (2004) 307–309.
[19] F. Mafune, J-y Kohno, Y. Takeda, and T. Kondow, "Formation of Stable Platinum Nanoparticles by Laser Ablation in Water" Journal of Physical Chemistry **107** (2003) 4218–4223.
[20] H. Imam, K. Elsayed, M. A. Ahmed and R. Ramdan, "Effect of Experimental Parameters on the Fabrication of Gold Nanoparticles via Laser Ablation," Optics and Photonics Journal **2** (2012) 73-84.
[21] A.I. Talukder, P. Sultana, A.F.M.Y. Haider, M. Wahadoszamen, K.M. Abedin, and S.F.U. Farhad, "Power dependence of size of laser ablated colloidal silver nanoparticles," The European Physical Journal D 2010.
[22] A. Hahn, S. Barcikowski and B. N. Chichkov, "Influences on Nanoparticle Production during Pulsed Laser Ablation," Journal of Laser Micro/Nanoengineering **3** (2008) 73-76.

[23] V. Piriyawong, V. Thongpool, P. Asanithi, and P. Limsuwan, "Preparation and Characterization of Alumina Nanoparticles in Deionized Water using Laser Ablation Technique," Journal of Nanomaterials 2012 1-6.
[24] K. Mallikarjuna, G. Narasimha, G. R. Dillip, B. Praveen, B. Shreedhar, C. S. Lakshmi, B. V. S. Reddy and B. D. P. Raju, "Green Synthesis of Silver Nanoparticles using Ocimum Leaf Extract and Their Characterization," Digest Journal of Nanomaterials and Biostructures **6** (2010) 181-186.
[25] Y. B. Wankhede, S. B. Kondawar, S. R. Thakare and P. S. More, "Synthesis and characterization of silver nanoparticles embedded in polyaniline nanocomposite," Advanced Materials Letters 4 (2013) 89-93.