



## **FABRICATION OF COPPER NANOPARTICLES BY PULSE LASER ABLATION**

**Mohsin T. Mohammed<sup>1</sup>, Abbas A. Diwan<sup>2</sup>, Salah M. Saleh<sup>3</sup>, and Bassam A. Salih<sup>4</sup>**

<sup>1</sup> Mechanical Engineering Department, Faculty of Engineering, University of Kufa, Iraq.  
Email: [mohsint.alyasiri@uokufa.edu.iq](mailto:mohsint.alyasiri@uokufa.edu.iq)

<sup>2</sup> Nanotechnology and Advanced Materials Research Unit, Faculty of Engineering, University of Kufa, Iraq. Email: [abbas.albosalih@uokufa.edu.iq](mailto:abbas.albosalih@uokufa.edu.iq)

<sup>3</sup> The general in Directorate of Education in Najaf, Ministry of Education, Najaf, Iraq.  
Email: [mm.salah47@gmail.com](mailto:mm.salah47@gmail.com)

<sup>4</sup> Electrical Engineering Department, Faculty of Engineering, University of Kufa, Iraq.  
Email: [bassama.albaidhani@uokufa.edu.iq](mailto:bassama.albaidhani@uokufa.edu.iq)

<http://dx.doi.org/10.30572/2018/kje/100101>

### **ABSTRACT**

Copper (Cu) nanoparticles have attracted considerable attention because of their applications in many different fields. In this paper, Cu particles have been produced by means of a pulse laser ablation (PLA) process to ablate Cu metallic target submerged in two different mediums, water, and ethanol. The laser ablation process was occurred at energy by 900 and 700 mJ with wavelengths of 532 and 1064 nm. The UV visible spectrum was also characterized to investigate the optical properties. The atomic force microscope (AFM) and scanning electron microscope (SEM) were used to detect the nanoparticles of Cu. The results showed that the Cu nanoparticles could be prepared successfully in ethanol media at both laser energies 900 and 700 mJ for 532 and 1064 nm wavelength. Peak at 575 nm appeared in the U.V visible spectrum which indicates the formation of Cu nanoparticles. Furthermore, there is a slight chance for preparation of Cu nanoparticles in water media owing to the incidence of Cu oxides instead of Cu nanoparticles.

**KEYWORDS:** Copper, nanoparticles, pulse laser ablation, U.V visible, laser energy.

## 1. INTRODUCTION

Synthesis of metallic nanoparticles is very important for different applications owing to their unique optical properties compared with bulk materials. Recently, great attention from researchers and scientists has been devoted to Cu nanoparticles to be used in various applications such as conductive films, lubrication, Nano fluids and catalysis (Zhu et al., 2005; Larsen and Noriega, 2004; Wang et al., 2004; Patel et al., 2005). As is well known, the nanoparticles have a high surface to volume ratio compared to bulk materials, which enables them for catalysis applications. Furthermore, nonlinear visual devices are the main applications of Cu nanoparticles embedded in a dielectric environment like polymeric matrix (Gotoh et al., 2000; Rostovshchikov et al., 2005; Quaranta et al., 2004).

The type of fabrication technique has a substantial effect on different structural features such as size, shape, and distribution of nanoparticles. Therefore, huge developments have been achieved for fabrication Cu nanoparticles using novel techniques such as micro emulsion, reverse micelles, pulsed laser ablation, etc. (Wang et al., 2004; Ponce and Klabunde, 2005). PLA is widely utilized for fabrication nanostructured materials with improved characteristics (Fumitaka et al., 2000; Tarasenko et al., 2005; Zhang et al., 2003; Tilaki et al., 2006; Fumitaka et al., 2002).

The process of laser ablation is used for the preparation of numerous metals and also semiconductor materials in various media such as vacuum, liquid, and reactive gas. Ablation in liquid, as an approach for particle formation, is flexible, spherical and expensive in spite of the intricate mechanism of laser matter interactions. Under laser exposure, different targets can be used for ablation in this process such as bulk target, splitting of microparticles or suspended powders (Fumitaka et al., 2002). Hence, many metals and materials such as gold, silver, palladium, titanium oxide and magnetic nanoparticles can be produced in a liquid carrier medium (Fumitaka et al., 2000; Tarasenko et al., 2005; Zhang et al., 2003; Tilaki et al., 2006; Fumitaka et al., 2002; Kaname et al., 2004; Simakin et al., 2004; Mafune et al., 2003; Tilaki et al., 2007).

In comparison with other traditional methods, the PLA process can effectively prepare nanoparticles in arbitrary liquids such as water, ethanol, acetone, and others. This process is a crucial approach for preparing Nano composite using nanoparticles in an organic liquid or polymeric matrix.

The final properties of the products depend primarily upon the physical characteristics of the ablation solution. It is necessary to mention here that the type of liquids used as ablation media,

like reactive materials, supports the oxides or restricts the formation of nanostructured materials. As well known that the oxide nanostructure and /or metal core oxide shell materials can be produced by simple oxidation method of the nanoparticles (Craig and Donald, 1998; Zhu et al., 2004; Hui et al., 2002).

This research aims to prepare and characterize the colloidal Cu nanoparticles in liquid using PLA technique of a bulk Cu. The composition, size, shape, and stability of the colloidal Cu nanoparticles are the main results required. For ablation medium, both ethanol and water, as organic and inorganic liquids respectively, were utilized. The use of water is based on the scientific experiments that proved water as a base environment for many chemical reactions. On the other hands, producing of nanoparticles in ethanol can be used as a raw material for fabricating Nano composite materials using other organic polymer solvents. Furthermore, the optical transmission was carried out with the intention of investigating the stability of the colloidal Cu and oxidized Cu nanoparticles.

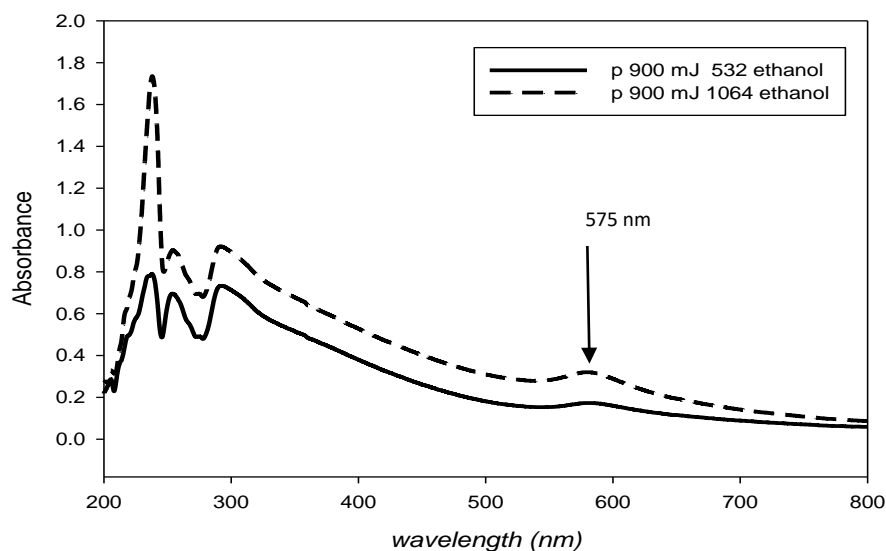
## **2. MATERIALS AND METHODS**

PLA of a bulk Cu was used to prepare colloidal Cu nanoparticles. An ultrasonic cleaner by deionized water was employed in several times to clean the Cu target (98.3% purity) after rinsing it with ethanol. The cleaned target was immersed in 10mL of liquid placed in a glass vessel. The distance between the cleaned target and liquid surface was kept at 10mm. In this work, the liquid media for laser ablation process was pure ethanol and deionized water. It is important to mention here that the target was shifted in various directions throughout the process in order to obtain homogenous ablation without texturing effect. The following is the main parameters for the target ablation using pulsed ND-YAG laser: 1064 nm and 532 nm wavelengths, 700 and 900 mJ energies and 10 ns pulse length. The laser was operated at a frequency of 6 Hz with 200 pulses laser. After ablation process, a UV–visible spectrometer (model T 90+, PG instrument Ltd., U.K), atomic force microscope AFM (model- AA3000) and SEM tests was directly determined for the colloidal Cu liquid.

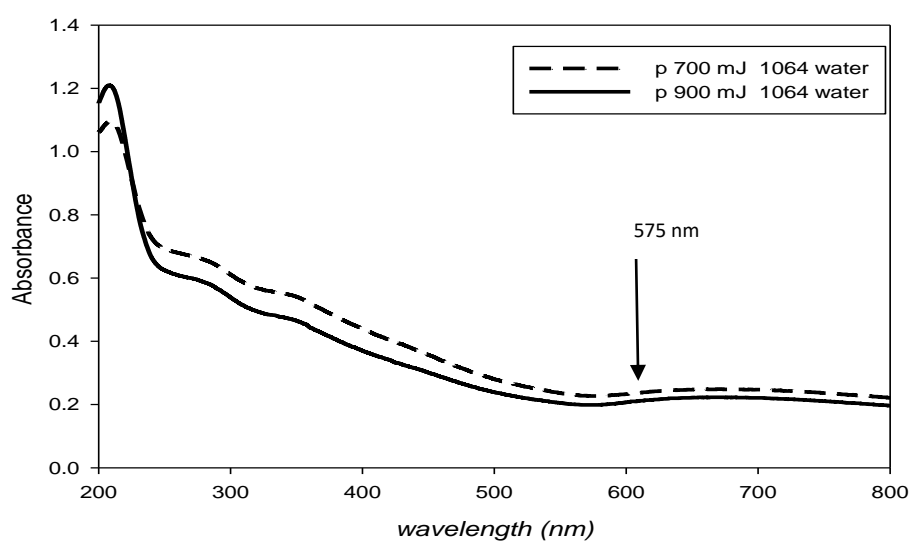
## **3. RESULTS AND DISCUSSION**

The characteristics of Cu nanoparticles produced using the PLA process were investigated by obtaining their absorption spectra as a function of fabrication settings. Fig. 1 and Fig. 2 show the comparative results of the spectral pattern related to the absorption of colloidal Cu nanoparticles produced in water at 700 and 900 mJ for the wavelength of 532 and 1064 nm, respectively. In both 532 and 1064 nm wavelengths, the results indicate that the colloidal

prepared at 900 mJ provides a higher absorption compared to 700 mJ. The further consequence is the oxidation of colloidal Cu because of the strong reaction with dissolved oxygen in water. This result is in high agreement with (Hee-Jung, 2016; Tilaki et al., 2007). The oxidation also causes the blue shift in both 700 and 900 mJ because the absorption bands peak of the Cu oxide increases at the short wavelengths, as is shown from the figures.



**Fig. 1.** Absorbance spectrum of colloidal Cu nanoparticles prepared in water at 532 nm for 700 and 900 mJ laser beam energy.

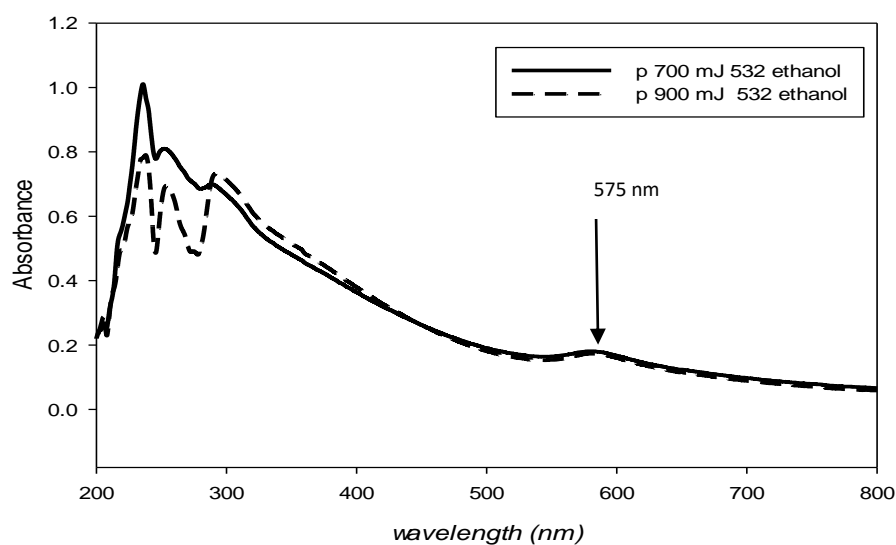


**Fig. 2.** Absorbance spectrum of colloidal Cu nanoparticles prepared in water at 1064 nm for 700 and 900 mJ, laser beam energy.

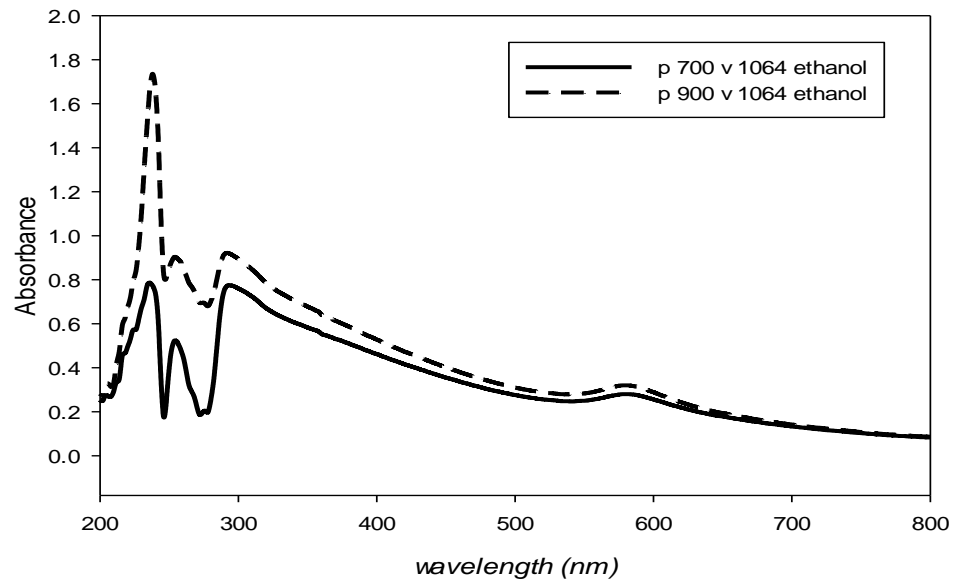
Fig. 3 and Fig. 4 illustrate the results related to the spectral pattern of the absorption of colloidal Cu nanoparticles prepared in ethanol at 700 and 900 mJ for the wavelength of 532 and 1064 nm, respectively. It was observed that the ethanol in the cell is polluted with the ablated Cu particles through the PLA process. In both 532 and 1064 nm wavelengths, the results indicate that the colloidal prepared using 900 mJ provides a higher absorption compared to 700 mJ. Moreover, for Cu nanoparticles, the colloidal has best absorption bands with peaks located at approximately 575 nm for both 700 and 900 mJ. However, the partial oxidation also occurs at the short wavelengths in both 700 and 900 mJ for 532 and 1064 nm wavelengths.

Fig. 5 and Fig. 6 show the results of the spectral absorption pattern of both ethanol and water mediums in 700 mJ and 900 mJ at a wavelength of 532 nm and 1064 nm respectively. For the sample prepared in ethanol medium, it can be clearly seen that the Nano Cu particles appeared at approximately 575 nm, while there is no clear peak for nano Cu particles in a water medium. Moreover, the colloidal prepared in 900 mJ at wavelength 1064 nm has the best absorption.

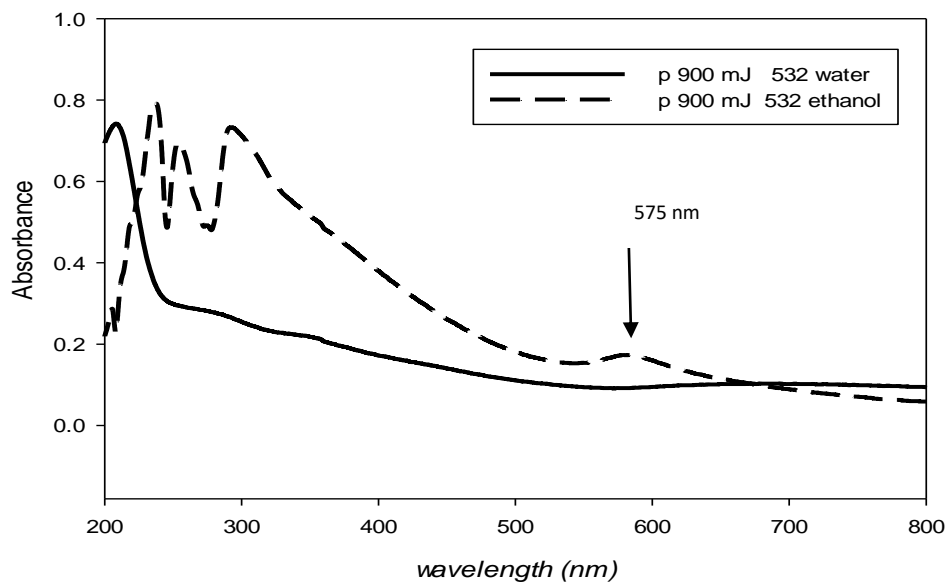
Fig. 7 and Fig. 8 show the results of the spectral absorption pattern of both ethanol and water mediums in 900 mJ at a wavelength of 532 nm and 1064 nm respectively. The results showed that the ethanol medium awards nano Cu particles at peak 600 nm, while there is no clear peak in water medium when the colloidal prepared in same laser power 900 mJ and at both wavelengths 1064 nm and 532 nm. Furthermore, the colloidal prepared in 900 mJ at 1064 nm has the best absorption in both ethanol and water mediums.



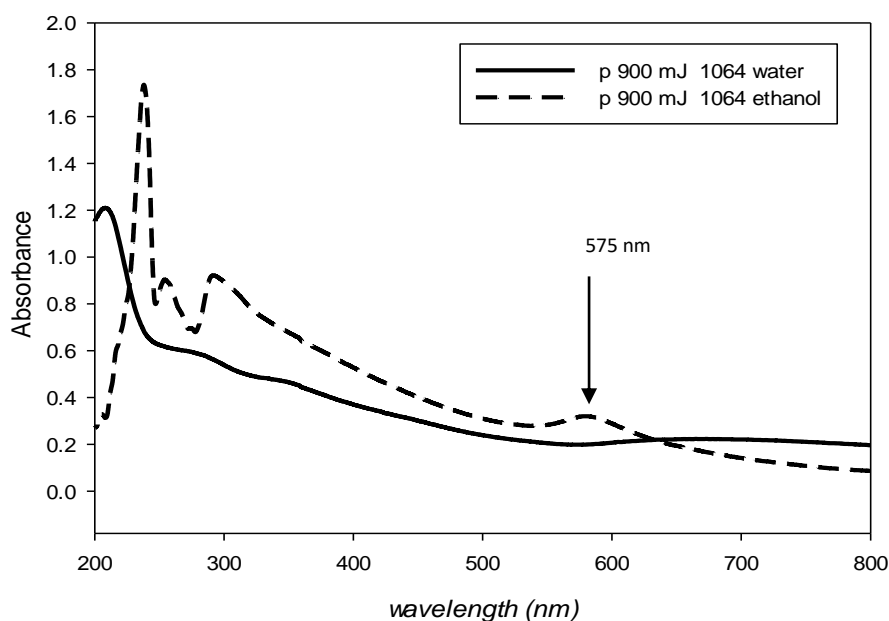
**Fig. 3. Absorbance spectrum of Cu for different values of the energy of the laser beam in ethanol for wave length 532nm.**



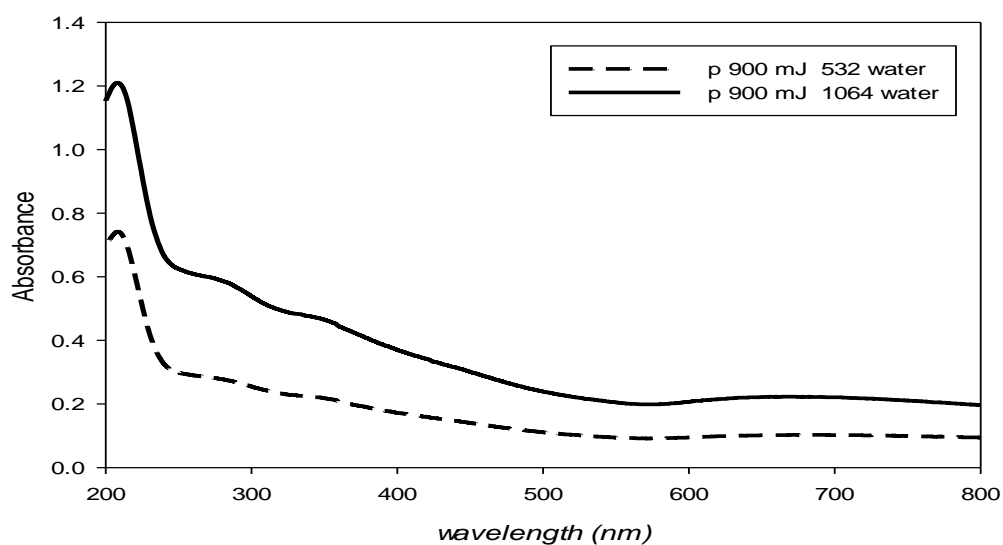
**Fig. 4.** Absorbance spectrum of Cu for different values of the energy of the laser beam in ethanol for wave length 1064nm.



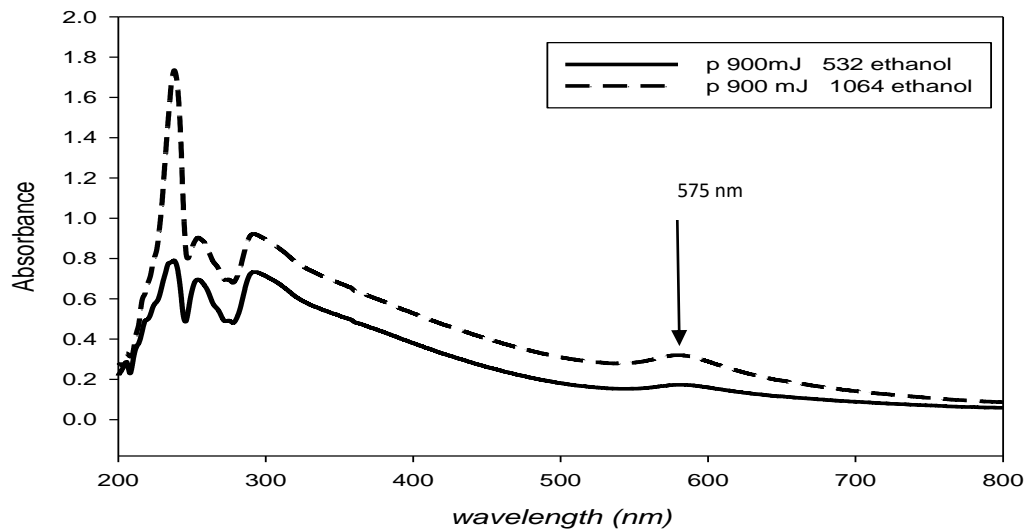
**Fig. 5.** Absorbance spectrum of Cu for different values of the energy of the laser beam in water and ethanol for wave length 532nm.



**Fig. 6.** Absorbance spectrum of Cu for different values of the energy of the laser beam in water and ethanol for wave length 1064nm.

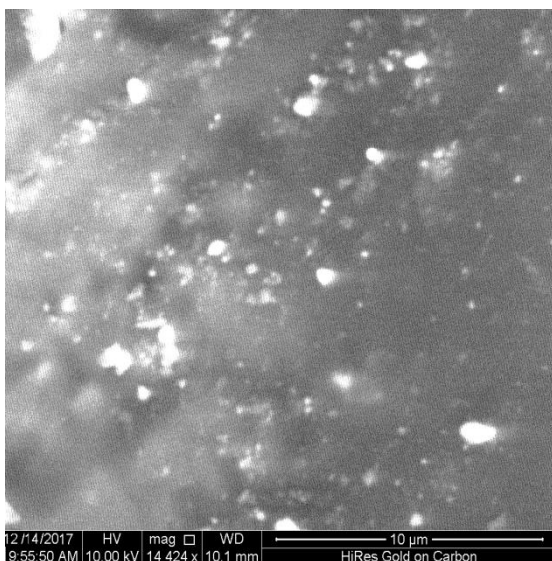


**Fig. 7.** Absorbance spectrum of Cu for different values of the energy of the laser beam in water for wave length 532nm and 1064nm.

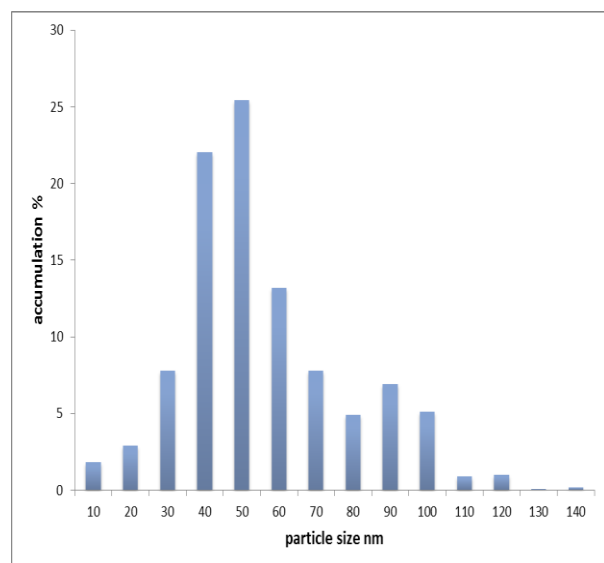


**Fig. 8. Absorbance spectrum of Cu for different values of the energy of the laser beam in ethanol for wave length 532nm and 1064nm.**

As Cu-based nanoparticles fabricated in ethanol at 900 mJ and 1064 nm provided the optimal result in this study, SEM and AFM analyses for these nanoparticles have been made. As can be seen from Fig. 9, the presence of Cu nanoparticles in these conditions was clarified. The figure indicated that the produced Cu nanoparticles are in different grain size and with quasi-spherical structure. The normal distribution of Cu nanoparticles has been obtained from AFM test as shown in Fig. 10. The AFM results showed that the average diameter of produced Cu nanoparticles is almost 51nm.



**Fig. 9. SEM image for copper nanoparticles prepared in ethanol at wavelength 1064 nm in 900 mJ.**



**Fig. 10. Normal distribution of particle size.**



#### 4. CONCLUSION

This work presents the evaluated results related to producing Cu nanoparticles colloidal using PLA process of Cu in two ablation mediums, ethanol, and water. The following conclusions can be drawn from the obtained results:

- There is a weak opportunity to prepare Cu nanoparticles by laser ablation process in a water medium. Instead, Cu oxide becomes visible.
- Cu nanoparticles appear obviously in ethanol medium with a higher spectral pattern of absorption compared to water medium.
- The best absorption results of Cu nanoparticles appears at 900 mJ as the energy of laser used compared to an energy power of 700 mJ.
- The laser wavelength used at 1064 provides a higher spectral pattern of absorption in comparison to a wavelength of 532 nm.
- SEM and AFM test indicated that average particle size of nano Cu particle was 51 nm prepared in ethanol media by 900 mJ.

#### 5. REFERENCES

- Aldo A. Ponce. Kenneth J. Klabunde, (2005), "Chemical and catalytic activity of Cu nanoparticles prepared via metal vapor synthesis" *Journal of Molecular Catalysis A: Chemical*, Volume 225, Issue 1, pp.1-6.
- Craig F. Bohren and Donald R. Huffman, "Absorption and Scattering of Light by Small Particles", Wiley, New York, 1998.
- Fumitaka Mafuné, Junya Kohno, Yoshihiro Takeda, and Tamotsu Kondow, (2000), "Formation and Size Control of Silver Nanoparticles by Laser Ablation in Aqueous Solution", *Journal of Physics and Chemistry*, 104, pp. 9111-9117.
- Fumitaka Mafuné, Jun-ya Kohno, Yoshihiro Takeda and Tamotsu Kondow, (2002), "Full Physical Preparation of Size-Selected Gold Nanoparticles in Solution: Laser Ablation and Laser-Induced Size Control", *Journal of Physics and Chemistry B*, 106 (31), pp. 7575–7577.
- Gotoh, Y., Igarashi, R., Ohkoshi, Y., Nagura, M., Akamatsu, K., and Deki, S., (2000), "Preparation and structure of Cu nanoparticle/poly (acrylicacid) composite films" *J. Mater. Chem.* 10, pp. 2548–2552.

- Hee-Jung Im Euo Chang Jung, (2016), “ Colloidal nanoparticles produced from Cu metal in water by laser ablation and their agglomeration”, *Radiation Physics and Chemistry* 118, pp. 6-10.
- Hui Wang, Jin-Zhong Xu, Jun-Jie Zhu, Hong-Yuan Chen, (2002), “Preparation of CuO nanoparticles by microwave irradiation” *Journal of Crystal Growth* 244, pp.88–94.
- Jin Zhang, Jessica Worley, Stephane Dénoimée, Christopher Kingston, Zygmunt J. Jakubek, Yves Deslandes, Michael Post, and Benoit Simard , (2003), “Synthesis of Metal Alloy Nanoparticles in Solution by Laser Irradiation of a Metal Powder Suspension”, *Journal of Physics and Chemistry*, 107 (29), pp.6920–6923.
- Kaname Sakiyama, Kenji Koga, Takafumi Seto, Makoto Hirasawa, and Takaaki Orii ( 2004), “Formation of Size-Selected Ni/NiO Core–Shell Particles by Pulsed Laser Ablation” , *Journal of Physics and Chemistry B*, 108 (2), pp. 523–529,
- Larsen, G., and Noriega, S., (2004), “Dendrimer-mediated formation of Cu- CuOx nanoparticles on silica and their physical and catalytic characterization” *Appl. Catal. A-Gen.* 278, pp.73-81.
- Mafune, F., Kohno, J., Takeda, Y., Kondow, T., (2003), “Formation of Stable Platinum Nanoparticles by Laser Ablation in Water”, *Journal of Physics and Chemistry B*, 107 (18), pp. 4218–4223.
- Quaranta, R. Ceccato, C. Menato, L. Pederiva, N. Capra, and R. Dal Maschio, (2004), “ Formation of Cu nanocrystals in alkali-lime silica glass by means of different reducing agents,” *J. Non-Cryst. Solids* 345–346, pp.671–675.
- Patel, M. K., Nagare, B. J., Bayul, D. M., Haram, S. K., and Kothari, D. C., (2005), “Controlled synthesis of Cu nanoparticles in fused silica and BK7 glasses using ion beam induced defects”, *Surf. Coat. Technol.* 196, pp. 96–99
- Rostovshchikov, T. N., Smirnov, V. V., Kozhevin, V. M., Yavsin, D. A., Zabelin, M. A., Yassievich, I. N., and Gurevich, S. A., (2005), “ New size effect in the catalysis by interacting Cu nanoparticles,” *Appl. Catal., A* 296, pp.70–79.
- Simakin, A. V., Voronov, V. V., Kirichenko, N. A., Shafeev, G. A., (2004), “Nanoparticles produced by laser ablation of solids in liquid environment”, *Appl. Phys. A* 79, pp.1127-1132,

- Tarasenko, N. V., Butsen, A.V., Nevar, E. A., (2005), "Laser-induced modification of metal nanoparticles formed by laser ablation technique in liquids", *Applied Surface Science* 247, pp. 418–422.
- Tilaki, R. M., Irajizad, A., Mahdavi, S. M., (2006), "Stability, size and optical properties of silver nanoparticles prepared by laser ablation in different carrier media", *Applied Physics A* 84, pp.215-219.
- Tilaki, R. M., Irajizad, A., Mahdavi, S. M., *Nanopart. J. Res.*, (2007), "The effect of liquid environment on size and aggregation of gold nanoparticles prepared by pulsed laser ablation", *Journal of Nanoparticle Research*, Volume 9, Issue 5, pp. 853–860.
- Tilaki, R. M., Irajizad, A., Mahdavi, S. M. (2007), "Size, composition and optical properties of Cu nanoparticles prepared by laser ablation in liquids", *Appl. Phys. A* 88, pp. 415-419.
- Wang, H., Huang, Y., Tan, Z., and Hu, X., (2004), "Fabrication and characterization of Cu nanoparticle thin-films and the electrocatalytic behavior" *Anal. Chim. Acta* 526, pp.13–17.
- Zhu, J., Li, D., Chen, H., Yang, X, Lu, L, Wang, X, (2004), "Highly dispersed CuO nanoparticles prepared by a Novel quick-precipitation method" *Mater Lett.*, 58, pp. 3324–3327.
- Zhu, H., Zhang, C., and Yin, Y., (2005), "Novel synthesis of Cu nanoparticles: influence of the synthesis conditions on the particle size" *Nanotechnology*, vol. 16, no. 12, pp. 3079–3083.