# Study the Effect of the Aqueous Media on the Properties of Produced Copper Nanoparticles Colloidal by Using Laser Ablation Technique

The 5<sup>th</sup> International Scientific Conference for Nanotechnology and Advanced Materials and Their Applications ICNAMA 2015 (3-4) Nov. 2015

# Wasan Mubdir Khilkhal

Laser Physics Department, Babylon University, College of science for women, Hilla Email: mubderz@yahoo.com

Dr. Ghaleb A. Al-Dahash

Laser Physics Department, Babylon University, College of science for women, Hilla **Dr. Sahib N. Abdul Wahid** 

Physics Department, Kufa University, College of Education for girl, Kufa.

# Abstract

This paper reports our recent studies on the generation of Cu NPs by ablation of metal targets using Q-switch Nd-YAG laser with Second Harmonic Generation(S.H.G) ( $\lambda$ =532nm) immersed in different aqueous media( Double Disteled Deionised Water (DDDW) and 1-Propanol). Higher productivity and Smallest size have been produced by using 1-propanol solution compared to DDDW, which indicated that the productivity and NPs size were affected by the solution type. Optical properties measurements showed indirect optical energy gap of the produced Cu nanoparticle (3.717 and 4.887) eV, when the solution type change from DDDW to 1-Propanol respectively. The Surface topography studied by Atomic Force Microscopy, and shape were measured by using Scanning Electron Microscope SEM shows spherical shape while the composing of the prepared nanoparticle were determined by X-ray diffraction ,UV-Visible spectroscopy has been employed for the optical properties measurements.

**Keywords:** Laser Ablation, Collide Nanoparticles, 1-propanol solution, DDDW, Cu NPs.

الخلاصة:

هذا البحث يمثل دراستنا الاخيرة حول توليد جسيمات النحاس النانوية باستخدام ليزر الاندياك ( 532نانومتر) في محاليل مائية مختلفة (1-بروبانول والماء عالي النقاوة). اعلى انتاجية واصغر حجم لجسيمات النحاس النانوية حصل عليها في محلول 1-البروبانول, والذي يدل على ان حجم وتركيز الجسيمات النانوية قد تأثر بنوع المحلول اظهرت قياسات الخواص البصرية ان فجوة الطاقة البصرية غير المباشرة (3.717في الماء عالي النقاوة وفي 1-بروبانول7808) الكترون فولت. تمت دراسة طبغرافية السطح لجسيمات النحاس النانوية باستخدام مجهر القوة الذرية وشكل الجسيمات النانوية باستخدام مجهر المسح الالكتروني وتركيب المادة باستخدام حجهر القوة الذرية وشكل الجسيمات النانوية الاشعة فوق البنفسجية –المرئية لدراسة الخواص البصرية.

830

https://doi.org/10.30684/etj.33.5B.8

2412-0758/University of Technology-Iraq, Baghdad, Iraq This is an open access article under the CC BY 4.0 license <u>http://creativecommons.org/licenses/by/4.0</u>

## **INTRODUCTION**

The term Nanotechnology is often used as an all-encompassing term for nanoscale science, engineering, and technology. Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers, the size-scale between individual atoms and bulk materials, where unique phenomena enable novel applications.<sup>[1]</sup> Particles in the nanometer size range have attracted increasing attention with the growing interest in nanoscience and nanotechnology<sup>[2]</sup>.

Laser ablation has shown itself as one of the most efficient physical methods for nanofabrication. The method consists in the ablation of a target (mostly solid) by an intense laser radiation, yielding to an ejection of its constituents and to the formation of nanoclusters and nanostructures<sup>[3]</sup>. The technique of pulse laser ablation in liquid PLAL has many distinct advantages. These include (i) a chemically 'simple and clean' synthesis, the final product is usually obtained without by-products and no need for further purification; (ii) low cost of experimental setup and easily controlled parameters; (iii) the extreme confined conditions and induced high temperature, high pressure region favour the formation of unusual metastable phases<sup>[4]</sup>, in addition to a series of chemical reactions between solvent and solid target, and among their ions. <sup>[5]</sup>.

Thus the final properties of NPs depend on such parameters as laser pulse duration, laser wavelength, laser fluency on the target, nature of surrounding liquid, number of laser shots, etc. <sup>[6,7]</sup>. Generating of NPs through Pulse laser ablation technique passes through three fundamental steps. Firstly plasma generates, Secondly the ultrasonic adiabatic plasma expands leads to quick cooling of the plume. Finally after plasma extinguishing the formed nanoparticles clusters encounter and interact with the solvent and surfactant molecules in the surrounding solution .those processes involve the nucleation and phase transition of nanocrystals<sup>[8,9]</sup>.

The aim of the work is to study the effects of the aqueous solution on the properties of prepared NPs since aqueous solution represents the base medium for many chemical reactions occur during nanoparticles formation, and also the effects of laser energy on the concentration of the synthesis NPs.

#### **Experimental methods**

Fig.(1) shows the schematic diagram of PLAL experimental setup for synthesis colloidal solution of Copper NPs. The beam from Nd-YAG laser (type HUAFEI) was focused by lens(F=15.3mm) on the surface of Copper plate. Copper target (purity 99.99%) was placed at the bottom of the quarts cell and immersed at 8mm depth in the solution of DDDW and 1-Propanol . The used Nd-YAG laser where operate at wavelength (S.H.G) 532 nm, pulses number 50, pulsed repetition rate 6Hz, laser energy (20 to 260) mJ and pulse duration was about 10ns,the laser beam is focused on the target surface with diameter of 1mm .

The absorption spectra of the colloidal solutions was immediately measured using UV-Visible (CECIL CE 7200(ENGLAND), NPs size and surface morphology where examine using AFM (CSPM model AA3000), while the shape of NPs examined by SEM (INSPECT-S50, FEI company, Netherlands).

Eng. &Tech.Journal, Vol.33, Part (B), No.5, 2015

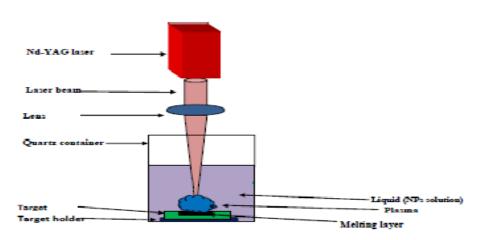
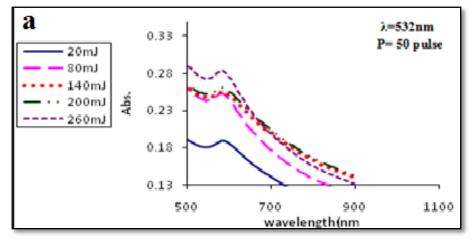


Figure (1) Experimental arrangement

## **Results and Discussion**

Fig.(2) show the absorption spectra of copper nanoparticle (Cu NPs) produced in 1-propnol and DDDW medium. From Fig.2 as the laser ablation energy increase the absorption intensity increase, which indicating the increase of Cu NPs concentration <sup>[10,11]</sup>. UV-Visible absorption spectrum of the synthesized colloidal solution of Cu NPs shows red shift in the absorption peak position by change the solution type from 1-propanol to DDDW which indicated the increase of Cu NPs size<sup>[12]</sup>, as appeared in Table (1), absorbance spectra peak around 586nm in 1-propanol ; which indicating the formation of Cu NPs<sup>[13,14]</sup>



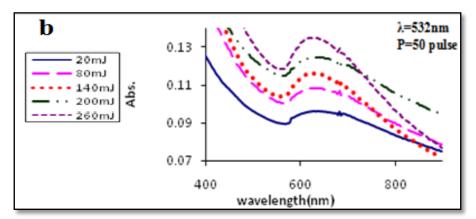


Figure (2) absorption spectrum of Cu NPs in, (a)1-propanol and (b)DDDW.

| Table (1) The peak position and NPs properties as a function of solution ty |
|---|
|---|

| Solution type | Average Peak<br>Position(nm) | Average NPs<br>size(nm) |
|---------------|------------------------------|-------------------------|
| 1-Propanol    | 586                          | 45                      |
| DDDW          | 600                          | 183                     |

The energy Band gap( $E_g$ ) was determined from the absorbance spectra as shown in Fig.(3).  $E_g$  is obtained using the following equation for a semiconductor<sup>[15]</sup>

$$(\alpha hv)^n = B(E - E_g)$$

..... (1)

Where B is constant,  $E_g$  the band gap energy ,E=hv the photon energy ,and n=1/2or 2 depending on whether the transition is indirect or direct respectively. It was reported that the band gap of semiconductor material will increase with the decrease in particle size<sup>[16]</sup>. The average energy band gap was calculated for Cu NPs to be around 4.887eV in 1-Propanol and 3.717eV in DDDW aqueous media.

Eng. &Tech.Journal, Vol.33, Part (B), No.5, 2015

Study the Effect of the Aqueous Media on the Properties of Produced Copper Nanoparticles Colloidal by Using Laser Ablation Technique

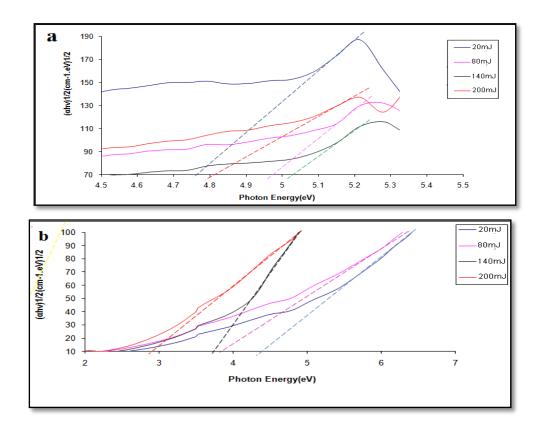


Figure (3) Indirect band gap estimation of Cu nanoparticles prepared by using ND-YAG laser (532nm)in ,(a)1-propanol and (b) DDDW.

Also the absorbance shows an increase in the Plasmon peak by using 1-propanol solution as compared to DDDW which indicating the increase in the NPs concentration,<sup>[10,11]</sup> also the color of produced colloidal have been changed by changing the solution type as shown in Fig.(4).So the Surface Plasmon Resonance (SPR) affected by both the NPs size and by the solution type in this research.

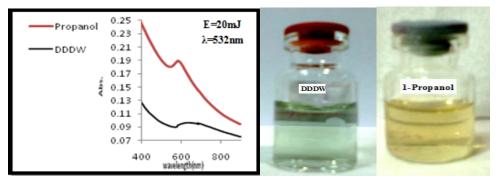


Figure (4) Absorption spectrum and photo image of Cu NPs colloidal in DDDW and 1-Propanol respectively.

Fig.(5) (A,B) shows AFM image of the Cu NPs obtained in DDDW and 1-propanol aqueous solution, The average particles size were (45 nm) at 1-propanol and(183nm) at DDDW, SEM measurements appeared that the formed particle is spherical in their shape Fig.(5) (C,D).

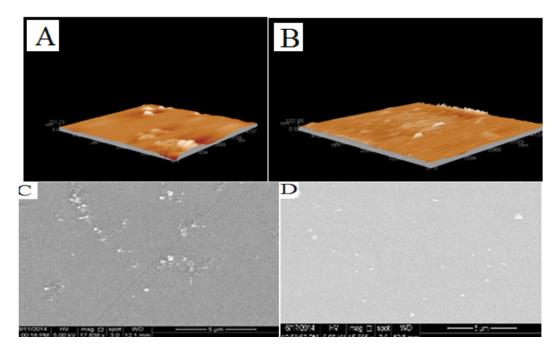


Figure (5) AFM of Cu nanoparticle in (A)DDDW, (B)1-Propanol, and SEM image in(C)DDDW and (D)1-propanol.

According to X-ray measurement the particle formed was Cu as revealing in Fig.(6). The diffraction patterns consist of two peaks at  $2\theta=43^{\circ}$  and  $2\theta=50.4$ .

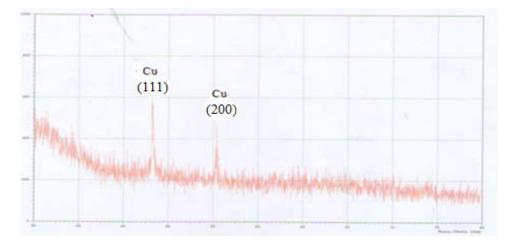


Figure (6) X-ray of prepared Cu NPs colloidal in DDDW

#### Conclusion

In summary, this research work has successfully produced spherical Cu NPs colloidal by using a simple method of nanosecond pulsed laser ablation in DDDW and 1-Propanol. Optical measurements of colloidal Cu NPs exhibit single maximum optical extinction. The productivity and the NPs size as well as the energy band gap were highly affected by the solution type, thus by changing the aqueous medium the nanoparticle size and the energy band gap can be controlled . Also the result showed that the color of the produced colloidal has been changed due to the effect of the aqueous solution type and also due to the NPs size. The higher productivity and smallest size has been produced in 1-Propanol medium as compared with DDDW, which indicated that the agglomeration process more active in DDDW than in 1-propanol. Finally in pulse laser ablation in solution the concentrations and the size of NPs can be controlled by controlling the laser parameters and the aqueous medium type, thereby different concentrations and size of NPs can be produced in easy ,fast and one –step method called pulsed laser ablation in solution.

### References

[1] John F., Sargent Jr., "The National Nanotechnology Initiative: Overview, Reauthorization, and Appropriations Issues", 2013.

[2] Elena Messina, "Metal Nanoparticles Produced by Pulsed Laser Ablation in Liquid Environment", 2010.

[3] Perrier J., Millon E., Fogarassy E., Recent Advances In Laser Processing Of Materials, 2006.

[4] Ogale, S.B.; Patil, P.P.; Phase, D.M.; Brandarkar Y.V.; Kulkarni S.K.; Kulkarni, S.; Ghaisas, S.V.; Kanetkar, S.M.; Bhide, V.G. and Ghua, S., Phys. Rev. B, 1987, **36**, 8237.

[5] Scalisi, A.; Compagnini, G. and Puglisi O., J. Appl. Phys., 94, 7874, 2003.

[6]G.A. Shafeev, "Laser-based formation of nanoparticles, Chemistry, Volume 2: Influencing matter. Edited by M. Lackner, Wiley VCH, Wienheim,, 713–741, 2008. [7]G.W. Yang, "Progress In Material Science", 52, 648–698, 2007.

[8]R.K. Swankar, S.C.Singh and R. Gopal, "optical Characterizations of Copper Oxide Nanomaterial", International Conference on Optics and Photonics, Chandigarh, India, 30 Oct. -1 Nov, 2009.

[9]F.Mafune, J.Kohno ,Y. Takeda, T. Kondow ,"Full Physical Preparation of Size-Sellected Gold Nanoparticles inSolution :Laser Ablation and laser-Induced Size Control", Journal Physics Chimistry B,106,7575-7577, 2002.

[10] Hisham Imam, Khaled Elsayed, Mohamed A. Ahmed, Rania Ramdan, "Effect of Experimental Parameters on the Fabrication of Gold Nanoparticles via Laser Ablation", Optics and Photonics Journal, 2, 73-84, 2012.

[11] Wasan Mubdir Khilkala, Ghaleb A. Al-Dahash and Sahib N. Abdul Wahid, "

Preparation and Characterization of Cu nanoparticles by Laser Ablation in NaOH Aqueous Solution", International Journal of Current Engineering and Technology, Vol.4, No.4, 2014.

[12] Wasan Mubdir Khilkal, Ghaleb A. Al-Dahash, and Sahib Ne'ma, "Preparation of Gold NPs Colloidal by Laser Ablation Under the Effects of Magnetic Field", Australian Journal of Basic and Applied Sciences, pp.: 159-162,2014

[13] J. Lee, D.K. Kim, and W. Kang ,"Preparation of Cu Nanoparticles from Cu Powder Dispersed in 2-Propanol by Laser Ablation", Bull. Korean Chem. Soc., Vol. 27, No. 11, pp.1869-1872 ,2006.

[14] A.N.Pestryakov, V.P Petranovskii, A.Kryazhov, O. Ozhereliev, N.Pfänder, A.Knop-Gericke, "Study of Copper Nanoparticles Formation on Supports of Different Nature by UV-visible diffuse reflectance spectroscopy ", Chemical Physics Letters, 385, 3-4, 173-176,2004.

[15] P. Smejkal, J. Pfleger, B. Vlckova and O. Dammer, "Laser Ablation of Silver in Aqueous Ambient: Effect of Laser Pulse Wavelength and Energy on Efficiency of the Process," Journal of Physics: Conferences Series, Vol. 59, p. 185,2007.

[16] S. C. SINGH\*, R. K. SWARNKAR and R. GOPAL," Zn/ZnO core/shell nanoparticles synthesized by laser ablation in aqueous environment: Optical and structural characterizations", Bull. Mater. Sci., Vol. 33, No. 1, pp. 21–26, 2010.