

The Study of the Nonlinear Optical Properties of Copper Nanoparticle Prepared By Pulse Laser Ablation PLA.

Dr. Raad M. S. Al-Haddad*, Dr. Issam M. Ibrahim*, Abeer H. Khalid**

*Department of Physics, Science College, University of Baghdad,**Ministry of science and Technology ,Laser and optoelectronic center ,Iraq-Bagdad

Abstract

In this work the nonlinear optical properties and optical limiting performance of copper nanoparticles (Cu NPs) synthesized by pulse laser ablation (PLA) in different solution (distill water DW, deionized water DI, (Ethylene glycol (EG) mixed with (DI)) are presented.

The nonlinear absorption coefficient of the nanoparticle suspension are measured by the Z-Scan technique by using a second harmonic of Nd:YAG laser (532 nm) . The nonlinear refractive index occurs at high beam Intensity due to induced refractive mismatch between the copper nanoparticles and water. The synthesized nanoparticle is conform with the UV-Visible absorption and Scanning – Electron Microscopy (SEM) spectrum in different solutions .

Keywords: copper nanoparticle, Nonlinear refractive index, nonlinear absorption, optical characterization, laser ablation in aqueous medium

I. Introduction

In current years, the efforts of researcher has been devoted and development of new composites based on Large-bandgap semiconductors and insulators including metal nanoparticles, that composites consider promising material for optoelectronics and nonlinear optics. The phenomenon of combine excitation of conduction electrons in such nanoparticles expose to the electromagnetic (light) waves, called the surface plasmon resonance (SPR), accounts for a selective optical absorption and gives rise to nonlinear optical effects in the same spectral range, [1, 2] .When the excitation of light inter action with the noble metal ,the oscillation of free electrons in the conduction band occupying energy states near the Fermi level give a birth to the (SPR) .The surface plasmon resonance band (SPRB) of noble metal (Au, Ag, and Cu) NPs located in the UV-visible rang ,leading to boost the nonlinearity when they exposed to the lasers, [3-5]. So the noble metal NPs have attract comprehensive concerns in photonics researches . Optical limiters are devices required to protect the sensors and eyes from laser sources by keeping the transmitted energies below the damage threshold.[6] This is suppose with the support of one or more nonlinear optical (NLO) phenomena.[7] Silver,[8] copper,[9] in semicontinuous thin films, in colloids, and in different glass matrices are extensively studied for the NLO and OL applications.[10–12]

The Z-scan method provides a sensitive and straightforward method for the determination of the nonlinear refractive index and the nonlinear absorption coefficient.

The simplicity of both the experimental set-up and the data analysis has allowed the technique to become widely used by many research groups [13]. The electronic nonlinearity is induced by either population redistribution or distortion of electronic clouds. A molecule undergoes a transition from its ground state to its excitation state after absorbing a photon. The dipole moment of the molecule changes during such a transition. The change in the dipole moment will give birth to electronic nonlinearity, [14–16]. It has been well known that the nonlinear optical behavior of materials can vary greatly by changing different laser duration or different laser wavelengths. Z-scan technique is a simple and effective tool to determine the nonlinear properties [17]. It has been widely used in material characterization because it provides not only the magnitudes of the real part and imaginary part of the nonlinear susceptibility, but also the sign of the real part.

Both nonlinear refraction and nonlinear absorption in solid and liquid samples can be measured easily by Z-scan technique, which use the change of transmittance of nonlinear materials [16]. copper-based nanomaterials are of great interest because of their optical, catalytical, mechanical and electrical properties, resulting in a wide range of applications in the field of metallurgy, catalysis, nano and optoelectronics [18-20]. Cu₂O (cuprous oxide) and CuO (cupric oxide) are two important oxide compounds of copper and mostly be have like p-type semiconductor. Cuprous oxide is a II–VI semiconductor having direct bandgap of ~ 2 eV, while that of cupric oxide has a monoclinic crystal

structure with a bandgap of 1.21–1.51 eV [21]. Copper oxide nanomaterials have lower surface potential barrier than metals, which affects their electron field emission properties, and therefore are highly applicable as electron sources in cathode ray tube and flat panel display [22].

Laser ablation in liquid media is a ‘top down’ approach for the synthesis of nanomaterials having desired shape, size and chemical composition and surfaces free from chemical contamination, which are essential for further functionalization of nano materials for biological and sensing applications This technique is adopted by several workers [23-27] for the synthesis of colloidal solution of nanoparticles of different metals and semiconducting materials.

II. Z scan Technique

As the sample is translated through the focal region of the beam as shown in Fig.(1), the detector measures the fraction of intensity passing through the aperture which is transmitted through the sample . If the beam experiences any nonlinear phase shift due to the sample as it is translated through the focal region , then the fraction of light falling on the detector will vary due to the Kerr lens generated in the material by the intense laser beam [28] . When the sample interaction with the light ,The excitation may be possible due to abundance of incoming photons; this give rise to the nonlinear absorption, consequently increases and decreases in the maximum intensity incident of the sample produces wave front distortions created by nonlinear optical effect in the sample being observed. [29,30]

From the Maxwell's equations one obtains the refractive index n and the optical absorption α as functions of the intensity I of the incident laser beam:

$$\alpha = \alpha_0 + \beta I \quad \dots\dots(1)$$

where, β : the nonlinear absorption coefficient related to the intensity,

α_0 : linear absorption coefficient.

There is also a change in the refractive index when a material is placed in a strong electric field. In fact, the index of refraction becomes dependant on the intensity of the electric field. At high intensity, the refractive index is given by [29,30]

$$n = n_0 + n_2 I \quad \dots (2)$$

where, n_2 : the nonlinear refractive coefficient related to the fluence, n_0 : linear refractive index. The coefficients n , α are related to the intensity of the laser. The nonlinear refractive index is calculate from the peak to valley difference of the normalized transmittance by the following formula [30]

$$\Delta\phi_0 = kn_2 I_0 L_{eff} \quad (3)$$

Where $\Delta\phi_0$:- nonlinear phase shift, $k=2\pi/\lambda$ wave number, λ :- is the wave length of the beam. L_{eff} :- is the effective length of the sample.

$$n_2 = (\lambda / 2\pi) \Delta\phi_0 / I_0 L_{eff} \quad (4)$$

To found the nonlinear absorption coefficient β , the negative values for z indicate that the sample is positioned between the focusing lens and the beam waist at focus, and positive values of z indicate that the sample is between the beam waist at focus and the detector. As the sample is translated through the focal region of the beam , detector measures the total transmitted intensity as shown in Fig.(1) but without the part A (aperture) , because only the fluence at the sample is changing as the sample is translated , any deviation in the total transmitted intensity must be due to multi-photon absorption , the normalized change in transmitted intensity can be approximated by the following equation[30] .

$$T(z) = \sum_{m=0}^{\infty} \left[\frac{\beta I_0 L_{eff}}{1 + (Z / Z_0)^2} \right]^m \quad \dots\dots (5)$$

Z :- is the sample position at the minimum transmittance, Z_0 the diffraction length , m :- integer.

$T(z)$:- the minimum transmittance. The two terms in the summation are generally sufficient to determine the nonlinear absorption coefficient β .

III. Experimental Work

Cu NPs have been prepared by nanosecond pulsed laser ablation of highly pure copper target in DW, DI water and (2 ml EG mixed with 3 ml DI water). The laser ablation of copper was carried out using (Nd:YAG-Diamond-288 pattern EPLS) pulse laser at power 200mJ. The laser generated (10 ns) (FWHM) pulses at (1064 nm) with a repetition rate of (6 Hz). The distance between laser source and the target is 16.5 cm ,the copper plate placed at the bottom of glass vessel containing 5 ml of the liquid . The spatial profile of the laser pulse was Gaussian,. The copper sample was irradiated with the laser fluence level of about 1.591 J/cm².

The concentration of the Cu NPs is about 3.41 ppm for distillwater ,deionize water 3.71 ppm and 3.83 ppm (EG: DI water). Cu NPs suspension was studied using an ultraviolet-visible (UV-Vis) (SP-8001-MeterTech) spectrophotometer measure the linear absorption coefficient of the Cu NPs suspension.

The nonlinear optical properties of the prepared Cu NPs were studied by nonlinear absorption and nonlinear refraction of the Z-scan measurements using 30 ns Full width at half maximum (FWHM) laser pulse ND:YAG at 532 nm ,10.3 mJ the energy was used to perform the Z-scan experiments as in Fig.(1).The nonlinear absorption can be revealed by the study of the transmittance of open aperture for Z-scan experiment as in Fig.(1) but with out part A, and the nonlinear refraction can be revealed by dividing transmittance of the closed

aperture Z-scan by that of open aperture as in Fig.(1). The open and closed aperture of the Z-scan experiments, and the laser beam was focused by a lens with focal length of 10 cm. The nanoparticle-containing cell with thickness 1mm was moved using a translation system along the

propagation direction (Z-axis) through the focusing area. At the focal point, the sample experiences maximum laser irradiance, which will gradually decrease in either direction from the focus.

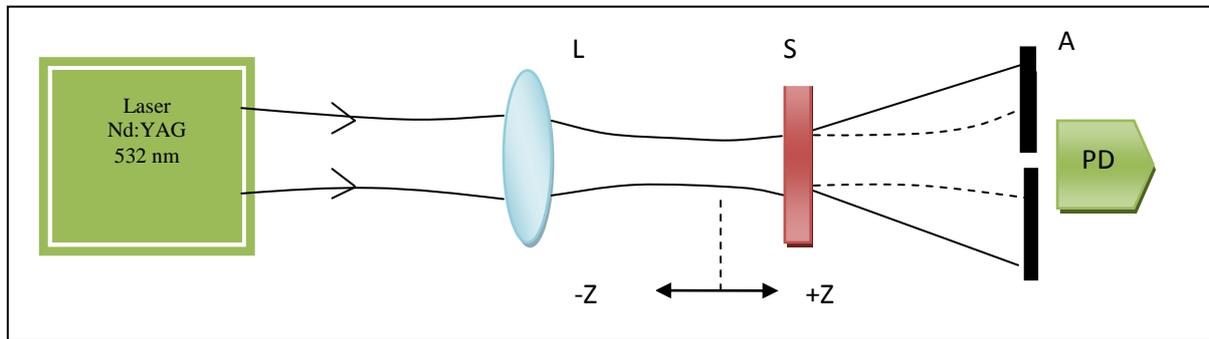


Figure (1) Closed-aperture z-scan

IV. Results and Discussion

A. Characterization of the sample

Fig.(2) shows the UV-Vis absorption spectrum for the solution of colloidal nanoparticle prepared by laser ablation of a copper plate immersed in (DW ,DI water and (EG:DI water)) at 200mJ (100-600)pulses. That we can see the Cu NPs show a surface plasmon absorption band about 624 nm for DW and 676 nm for DI water and 590 nm for (EG mixed with DI water) with the preparation condition 200mJ,400pulses in the UV-Vis spectrophotometer at a region about 200-900 nm. It exhibits an intense peak at between (590-676) nm, this peak is due to interband transition of copper electron from upper level of valence band ,which is also known as surface Plasmon resonance (SPR) peak. The SPR of colloidal copper nanoparticles reported previously [31] with a peak at 590-640 nm is in compatible with the present result, and we can see that when the pulsed laser increase the intensity of SPR increase .

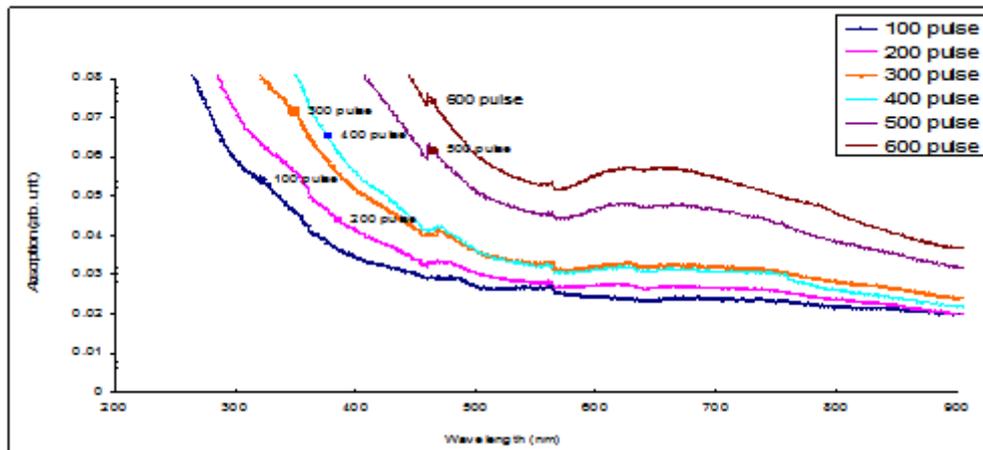
Fig.3 (a , c) shows ,the Scanning – Electron Microscopy- S-4160- HITACHI (SEM) mesurment for DW ,DI water (EG mixed with DI water that used

to obtain the diameter for Cu NPs ,this is conform the UV-Vis spectrum as shown in the table 1.

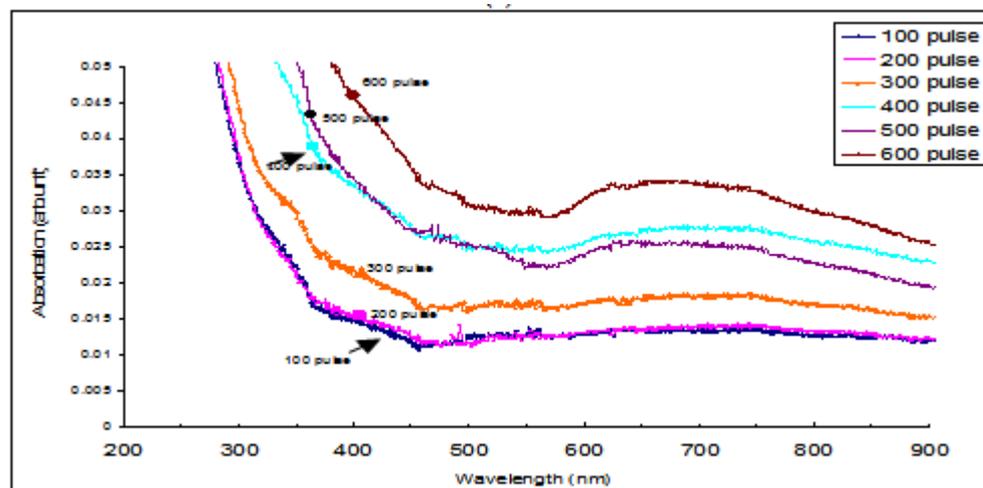
The optical band gap of the colloidal nanoparticle calculated using the Tauc relation [32] $\alpha hv = (hv - E_g)^n$, where hv is the incident photon energy and n is the exponent that determines the type of electronic transition causing the absorption. The best linear relationship is obtained by plotting $(\alpha hv)^{1/2}$ against hv , indicating that the optical bandgap of these nanoparticles is due to a direct allowed transition. Tauc plot for as synthesized colloidal nanoparticles are shown in figure (4) for DW. The bandgap of as synthesized colloidal nanoparticles is determined from the intercept of the straight line at $\alpha = 0$, as shown in table .1, the result agreement with [21] ,the lower energy gap in solution (EG mixed with DI water) that is refer to the optimum shift blue for SPR peak position and have the optimum nanoparticales diameter comparable with the other solution , it is clear that the Ethylene glycol mixed with deionized water represent as a good capping agent .

Table .1 The energy gap ,SPR peak, diameter size and Cu NPs concentration in different solutions

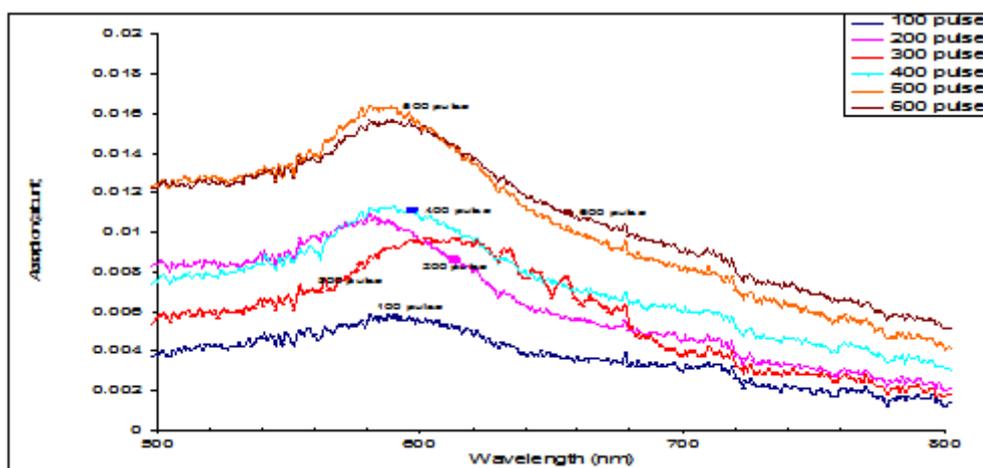
Solutions of Cu NPs	Dimeter of the Cu NPs (nm)	Concentration (ppm)	SPR peak (nm)	Eg (ev)
Distill water	19.84	3.41	624	2.5
Deionized water	21.25	3.71	676	2.4
(EG:deionized water)	13.16	3.83	590	2.8



(a)



(b)



(c)

Fig. (2) Uv-Visible absorption spectrum of as synthesized colloidal solution of Cu NPs by laser ablation at 200 mJ in (a) distillwater ,(b) for deionized water, (c) for (2ml EG mixed with 3ml deionized)

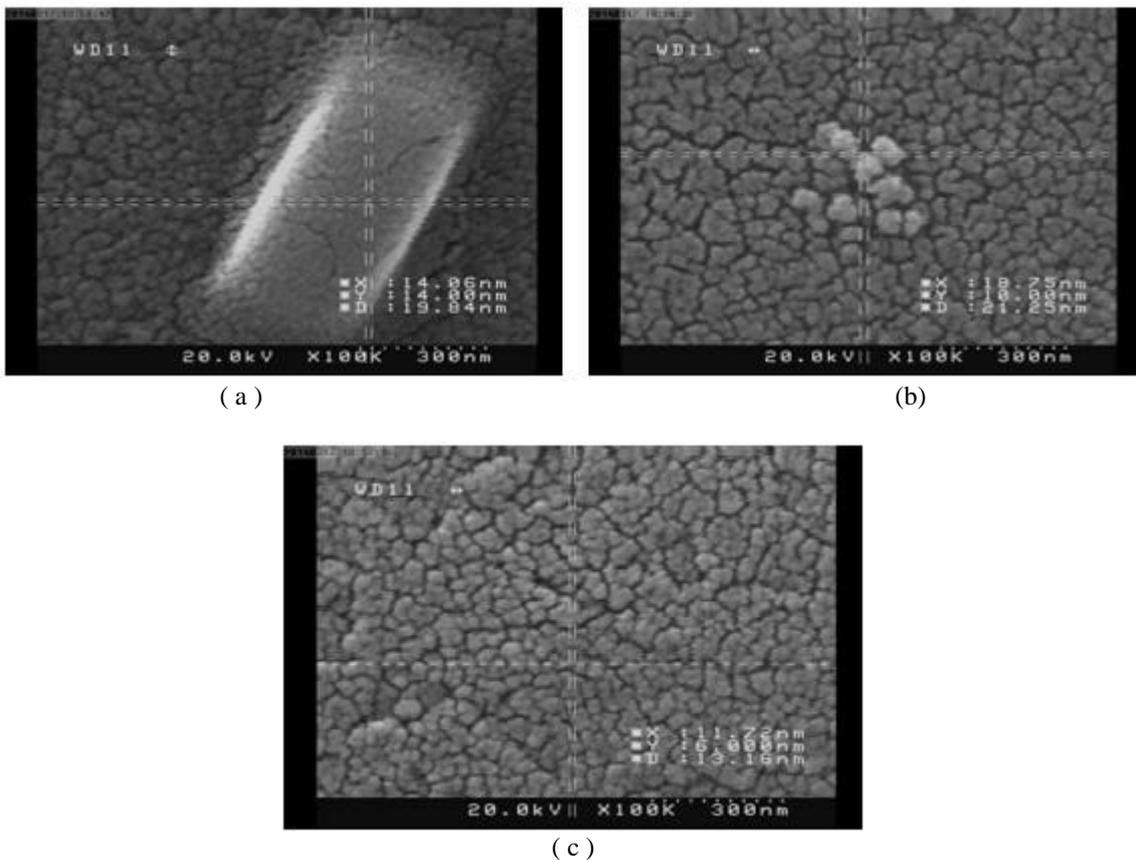


Fig. 3- SEM photography of as synthesized colloidal nanoparticle In (a) distill water, (b) deionized water, (c) (EG mixed with deionized water)

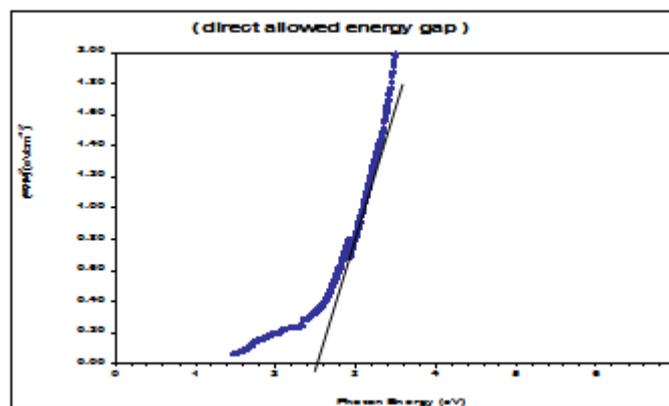


Fig. 4- Tauc plot of UV-Visible absorption of as synthesized colloidal nanoparticle for the calculation of band gap energy in distill water

B-Nonlinear optical properties of Cu nonparticales solution

The Cu NPs are formed in distill water ,deionize water and (EG mixed with deionized water with concentration 3.41 ppm for distill water ,deionize water 3.71 ppm and 3.83 ppm (EG:deionzewater) when the laser exposure of as prepared Cu NPs solutions filled in a cell with optical path 1mm, localized absorption of a tightly focused beam propagating through as absorbing solution produces a spatial distribution of temperature in the

solution and consequently , a spatial variation of the refractive index , that acts as athermal lens resulting in severe phase distortion of the propagating beam. Generally the measurement of the normalized transmittance versus sample position , allow the determination of the nonlinear refractive index n_2 and nonlinear absorption coefficient β [33,34] as in Fig (5-7) respectively,

Fig 5 (a) for DW shows the result obtained at intensity $I_0 = 2.799150743 \text{ GW/cm}^2$ which is the on-axis peak radiation intensity at focus point. When

the sample is far from the focal point of the lens ,the laser radiation intensity is low and the normalized transmission is less than unity, when the sample moves closer to the focal point the transmission decreases monotonically, a curve with symmetrical valley and two humps are presented, the hump – valley –hump structure indicated the nonlinear absorption of the sample is reverse saturable absorption RSA which is equal $B=12.68653 \text{ cm/GW}$ while the linear absorption coefficient is 0.248953 cm^{-1} .

Fig 6 (a) for DI water shows the result at intensity $I_0=2.799150743 \text{ GW/cm}^2$ which is the on-axis peak radiation intensity at focus point. When the sample is far from the focal point of the lens ,the laser radiation intensity is low and the normalized transmission is less than unity, when the sample moves closer to the focal point the transmission increases monotonically ,the symmetrical peak in the curve indicates saturable absorption SA dominates the nonlinear absorption is $B=13.50615 \text{ cm/GW}$ while the linear absorption coefficient is 0.321953 cm^{-1} .

Fig 7 (a) for (2ml EG mixed with 3ml DI water) at intensity $I_0= 2.799150743 \text{ GW/cm}^2$,When the sample is far from the focal point of the lens ,the laser radiation intensity is low and the normalized transmission is less than unity, when the sample moves closer to the focal point the transmission decreases monotonically,symmetrical peak in the curve indicates two photon absorption TPA . dominates the nonlinear absorption, $B= 7.72426 \text{ cm/GW}$ while the linear absorption coefficient is 0.141181 cm^{-1} .

The nonlinear refraction index in Fig.5 (b), 6(b) ,7(b) shows self focusing as the intensity equal $I_0=2.799150743 \text{ GW/cm}^2, n_2=1.27757 \times 10^{-5} \text{ cm}^2/\text{GW}$ for DW, $n_2=2.36918 \times 10^{-5} \text{ cm}^2/\text{GW}$ for DI water, $n_2=1.26501 \times 10^{-5} \text{ cm}^2/\text{GW}$ for (EG:DI water). The Z scan experiment was also performed with DW , DI water and (2ml EG mixed with 3ml DI water) with out Cu NPs , no significant absorption and refraction can be observed .This indicated that the nonlinear absorption and refraction of the solution arise mainly from Cu NPs.As for metal NPs, only the electrons in the energy bands adjacent to the Fermi level can absorb the photons of visible and near infrared light.That is the optical properties of Cu NPs around the visible wave length region are influenced by the localized outmost electrons in d band and the quasifree – electrons in s-p conduction band .

For both interband and intraband transition, the electron in the ground state band absorbs one photon ,it can be excited to the higher excited band , this process corresponds to two- level transition saturation and lead to SA. However, when the electron in the d band absorb two photon simultaneously and is excited to the s-p conduction band ,or the electron in the ground state band absorbs two photons simultaneously and is excited to the higher band , these processes are called TPA which are not saturable with the irradiation intensity increases . when these free carriers on excited states absorb photons ,excited state absorption can be introduced . If the excited state absorption of free carriers which are only generated by the SA decreases the transmittance of the sample , the overall effect is opposite to that of SA, and it can be referred to as RSA.

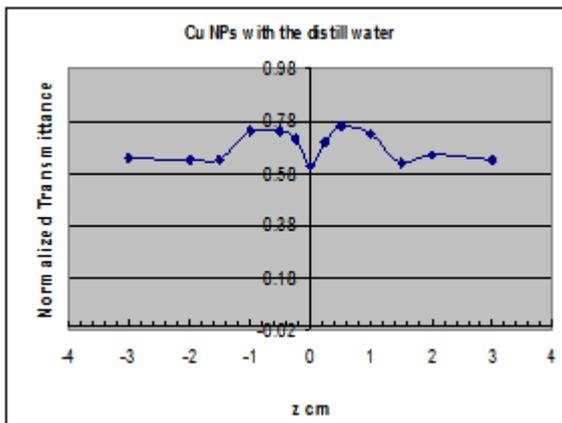


Fig 5 (a)

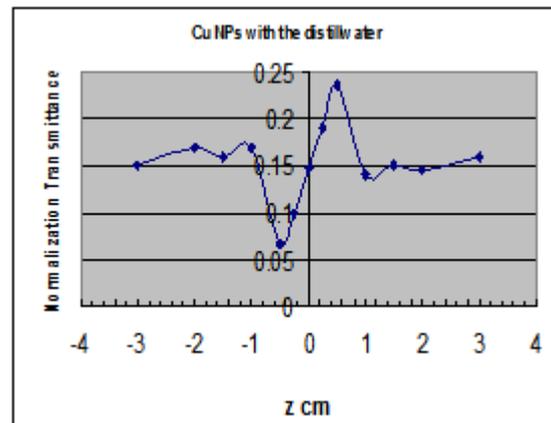


Fig 5(b)

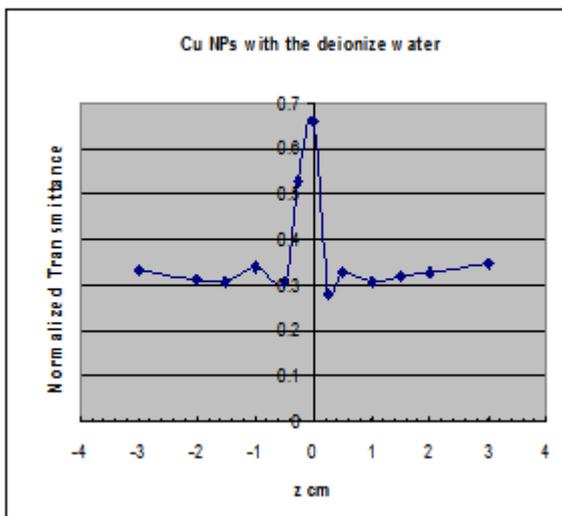


Fig 6 (a)

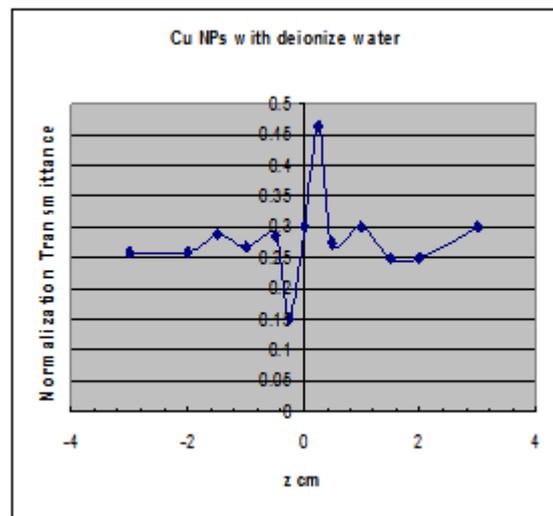


Fig 6 (b)

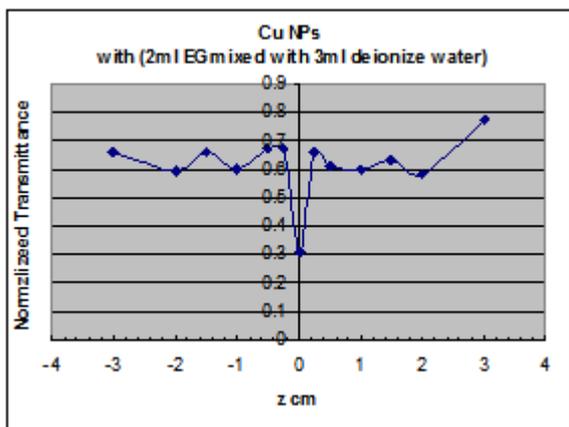


Fig 7 (a)

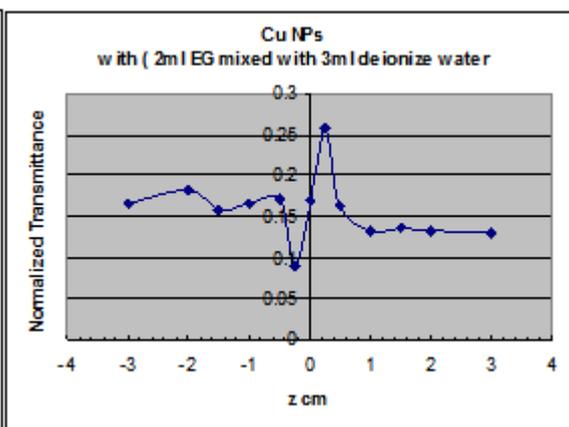


Fig 7 (b)

V. Conclusions

The Cu NPs prepared successfully via a physical method PLA laser ablation with range (13-22 nm), The energy gap range of the Cu NPs for the linear optical properties (2.4-2.8) eV and the nonlinear optical properties of the Cu NPs were investigated. The intensity related nonlinearity absorption and refraction were found with Z-scan technique, the nonlinear absorption was RSA, SA, TPA, according to the types of solution and the nonlinear refraction index self-focusing.

REFERENCES

- [1] U. Kreibig and M. Vollmer, Optical Properties of Metal Clusters, Springer-Verlag, Berlin, 1995.
- [2] A. L. Stepanov and D. E. Hole, in Recent Research & Development in Applied Physics, Ed. by A. Pandalai, Transworld Res. Network, Kuala, Vol. 5, pp. 1-26, 2002.
- [3] S. Qu, Y. Zhang, H. Li, J. Qiu, and C. Zhu, Opt. Mater. 28, 259, 2006.
- [4] U. Gurudas, E. Brooks, D. M. Bubb, S. Heiroth, T. Lippert, and A. Wokaun, J. Appl. Phys. 104, 073107, 2008.
- [5] R. F. Haglund, L. Yang, R. H. Magruder, J. E. Wittig, and R. A. Zuhr, Opt. Lett. 18, 373, 1993.
- [6] Bozio and F. Kajzar, Optical Power Limiting, Proceedings of the Second International Symposium [ISOPL 2000], Venice, Italy, 2-5 July, 2000.
- [7] L. W. Tutt and T. F. Boggess, Prog. Quantum Electron. 17, 299, 1993.
- [8] Q. F. Zhang, W. M. Li, Z. Q. Xue, J. L. Wu, S. Wang, D. L. Wang, and Q.
- [9] J. Olivares, et al., J. Appl. Phys. 90, 1064, 2001.
- [10] S. Qu, et al., Opt. Commun. 203, 283, 2002.
- [11] M. R. V. Sahyun, S. E. Hill, N. Serpone, R. Danesh, and D. K. Sharma, J. Appl. Phys. 79, 8030, 1996.
- [12] K. Uchida, et al., J. Opt. Soc. Am. B 11, 1236, 1994.

- [13] Nalda R., Del Coso R., Requejo-Isidro J., Olivares J., Suarez-Garcia, Solis and Afonso, Nalda," Limits to the determination of the nonlinear refractive index by the Z-scan method",19, (2) ;1-9, 2002 .
- [14] Rangel-Rojo R., Yamada S., Matsuda H., Yankelevich D., Large near-resonance third-order nonlinearity in an azobenzene-functionalized polymer film, *Appl. Phys. Lett.* 72, 1021-1023, 1998.
- [15] G ayathri C., Ramalingam A., *Spectrochim. Acta Part A* 69, 96, 2007.
- [16] He T., Wang C., Study on the nonlinear optical properties of three azo dyes by Z-scan measurements. *J. Mod. Opt.* 55, 3013-3020, 2008 .
- [17] Ting jian J., Zhiguo S. ,Yong guang C. , The nonlinear optical response of a fluorine Containing azoic dye, *Optics Communi.*, 283(6), 1110-1113, 2009 .
- [18] Rakshani A E , *Solid State Electron.* 7 29, 1986 .
- [19] Cao H S, Bonnet R, Hunsinger J J and Elkedim O , *ScriptaMater.* 48 ,531, 2003 .
- [20] Ji C and Park H S , *Nanotechnology* 18, 305704, 2007 .
- [21] Serin N, Serin T, Horzum S and Celik Y , *Semicond. Sci.Tech.* 20 ,398, 2005 .
- [22] Hsieh C T, Chen J M, Lin H H and Shih H C , *Appl. Phys.Lett.* 83, 3383, 2003 .
- [23] Link S, Burda C, Nikoobakht B and El-Sayed M A, *J. Phys. Chem. B*104, 6152, 2000.
- [24] Liang C H, Shimizu Y, Sasaki T and Koshizaki N, *Appl.Phys.* A80 819
- [25] Sylvestre J P, Kabashin A V, Sacher E and Meunier M 2005 *Appl. Phys.* A80, 753, 2005 .
- [26] Singh S C and Gopal R , *J. Phys. Chem. C*112, 2812, 2008 .
- [27] Singh S C, Swarnkar R K and Gopal R, *J. Nanopart. Res.* 11, 1831, 2009a.
- [28] M. Sheik-Bahae, A. A. Said, D. J. Hagan, M. J. Soileau, and S. E. W. Van Stryland, *Technology and Applications Center New port Corporation* , 2007 .
- [29] DawoodAltaify, M.Sc thesis, Institute of Laser for Postgraduate Studies, University of Baghdad, 2007.
- [30] Sheik-Bahae M., Said A., Wel, Hagan D. J. and Van E. W., "Sensitive Measurement of Optical, 1990.
- [31] Curtis A C, Duff D G, Edwards P P, Jefferson D A, Johnson B F G, Kirkland A I and Wallace A S , *J. Phys. Chem.* 92, 2211, 1988.
- [32] Singh S C, Swarnkar R K and Gopal R , *J. Nanosci.Nanotech.* 9, 5367, 2009b.
- [33] Mathews S.J., Chaitanya Kumar S., Giribabu L. and VenugopalRao S. Nonlinear optical and optical limiting properties of phthalocyanines in solution and thin films of PMMA at 633 nm studied using a cw laser. *Mater. Lett.*, 61, 4426-4431, 2007 .
- [34] Hussain A. Badran, Alaa Y. Al-Ahmad and Mohammad FadhilMudhaffer. Study of the linear and nonlinear optical properties of Neutral Red doped Polyvinylpyrrolidone film. *J. Bas. Res. Sciences Mat.* 32, 12–17, 2009. 37, 57-63, 2011 .