Effect of Laser Ablation Parameters on Nonlinear Optical Properties of ZnO/Au Nanoparticles

Yasemin GÜNDOĞDU, Serap YİĞİT GEZGİN and Hamdi Şükür KILIÇ

Abstract**—**In this study, ZnO as the group II-VI materials and Au noble metal synthesized by pulsed laser ablation (PLA) method in ethanol medium based on laser parameters. Laser ablation method applied on ZnO, Au and ZnO/Au high purity bulk materials to produce nanoparticles which have been carried out using Ti:Sapphire femtosecond (fs) laser system. Linear absorption spectra were recorded using Uv-Vis spectrometer and surface plasmon resonance have been observed between 520 nm and 540 nm wavelengths. The nonlinear optical properties for ZnO, Au and ZnO/Au nanoparticles have been determined by using a z-scan experimental system using an open&closed aperture results and third order susceptibilities have been calculated. The calculated results for nanoparticles produced in ethanol medium, the nonlinear absorption coefficient, β, (~10^{-11} cm/W), the nonlinear refraction coefficient, n_2 (~ 10^{-16} cm^2/W) and third order susceptibilities, $\chi^{(3)}$, (~ 10^{-14} esu) for each of ZnO, Au and ZnO/Au nanoparticles have been presented in this work and it has been concluded that the results obtained are all in agreement with data reported in literature.

Keywords**—**Pulsed laser ablation, nanoparticle, ZnO, Au, nonlinear optic.

I. INTRODUCTION

In recent years, semiconductor technology rising rapidly to give demanding some novel materials. Semiconducting nanostructures-based materials have characteristically effective compared to bulk materials due to their optical, chemical, electronic and morphologic properties which give excellent and unique results. Nanostructure based metal oxide ZnO material have attracted more attention due to optical high band gap value (3.37 eV) at room temperature and broad exciton binding energy (60 MeV) [1].

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ZnO has valuable properties as a semiconductor which they are high infrared reflectivity and high transparency in the visible region as well as electronic and optic properties. The nonlinear optical properties attracting researchers as well as investors to produce a major variety of optical devices such as lasing [2], waveguides [3], all optical switches [4], gates [5], detectors [6], sensors, spectrometers [7], microscopes [8] and optical storage devices [9] due to their nonlinear responses and energy gaps. Synthesis of nanostructure-based materials have been studied worldwide with lots of efforts performed by researchers due to wide range of applications. Employing PLA technique in different solvents is one of the most popular production methods of nanoparticles which gives some great opportunities such as controlling particle size and different structure types [10].

ZnO-metal composite nanostructured materials exhibit a wide and direct photon energy band-gap range which is very important for the photonics applications [11]. ZnO in pure structure shows low absorption in the visible region which very poor performance for photoenergy conversion efficiency. Au is a noble metal and its nanoparticles gives opportunity to facilitate charge carrier separation and surface plasmon resonance effect. These materials and PLA in different solvents are environment remedial and cost-effective method to produce nanoparticles [12].

In this study, it was investigated nonlinear optical properties for ZnO, Au and ZnO/Au nanoparticles which have been prepared using femtosecond laser ablation in liquid method. The optical nonlinearities of these nanomaterials were studied in ethanol medium with z-scan method. Obtained results are given in details.

II. MATERIALS AND METHOD

A. Femtosecond Laser Ablation System for Nanoparticle Production

Femtosecond laser system have been used both ablation for nanoparticle production and z-scan experimental procedure for Au, ZnO, ZnO/Au nanoparticles in ethanol medium. Ti:Sapphire femtosecond (fs) laser system has 90 fs pulse duration, 1 kHz repetition rate with the wavelength of 800 nm (Quantronix, NY, USA). Laser ablation for nanoparticle production experimental system design is given in figure 1 [13-16].

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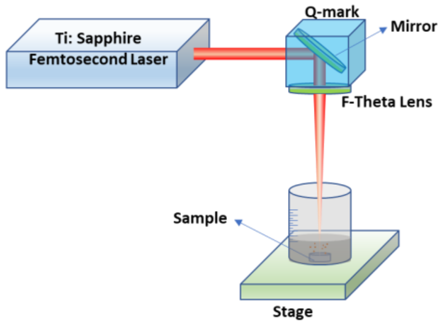


Fig. 1. Femtosecond laser ablation system design to produce nanoparticle forms.

Laser ablation based nanoparticle production technique is well known with low cost, controllable parameters and minimum level required for amount of chemicals [17, 18].

B. Nonlinear Optical-Z-scan System

In z-scan method, nonlinear optical properties of materials can be determined in two phenomenon self-focusing and self-defocusing processes. The nonlinear refractive index (n_2) may have positive or negative values. Negative value of that represents self-defocusing which means the incident beam is higher in the center than edges. In this case, the same condition will occur for propagation via negative focal length lens and beam defocuses. In the case of positive value of n_2 results in the physical phenomena which is that of negative case and, therefore, self-focusing occurs.

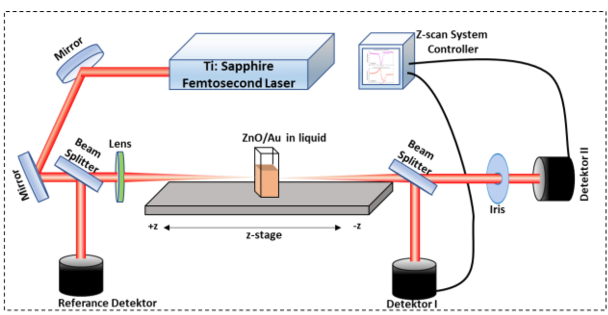


Fig. 2. Schematic representation of experimental set-up used in open&closed aperture z-scan methods

Ti:Sapphire femtosecond (fs) laser system can be adopted different laser applications. Z-scan set-up diagram in our laboratory shown in figure 2 which generally consists of two detector systems, open and closed aperture experiments. Reference detector is used to measure incident laser power before z-scan process started. NPs in liquid medium is injected in a quartz cuvette. The z-scan measurement technique, z-stage is used to measure by moving the materials between positive and negative end of the optical axes in stage along the optical axis to passing through the focal point of the Gaussian beam. The beam distribution on sample results in changing in the absorption correlation as well as refractive index in the sample

III. Results and Discussion

A. Linear Optical Results

Band gap values of nanoparticles (NPs) to be accessed by the photon energy are calculated using Tauc Plot formula in equation 1,

$$(\alpha h\nu)^2 = A(h\nu - E_g)^{1/2} \qquad (1)$$

where E_g is energy band gap of NPs, A and hv are area and photon energy which are constant during the experimenting, Eg is determined by straight line of $(\alpha h\nu)^2$ versus (hv) in Tauc plot in figure 3b. Band gap values for Au, ZnO, ZnO/Au Nps have been determined to be 2.80 eV, 1.85 eV and 2.45 eV, respectively.

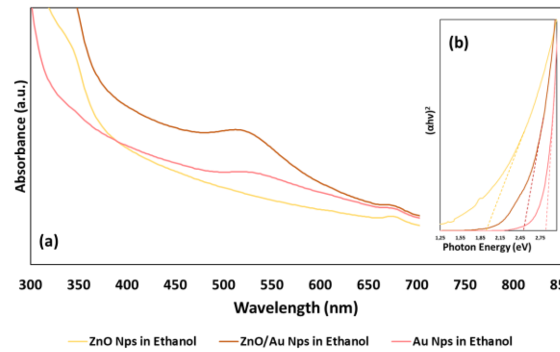


Fig. 3. a) Linear optical absorption spectra and b) Photon energy band gap diagrams for ZnO, Au and ZnO/Au nanoparticles

Surface plasmon resonance (SPR) phenomenon represents at the surface by the conduction electrons which they are oscillate collectively with the incident light. The surface plasmon resonance (SPR) peaks shown in clearly between 520 nm and 580 nm in visible region spectrum [19]. In this study, obtained Uv-Vis spectra shown in figure 3 for Au, ZnO, ZnO/Au NPs in ethanol medium. Particularly, absorption peaks for Au NPs and ZnO/Au NPs in visible region exhibit SPR effects in 540 nm and 520 nm wavelengths, respectively. Pure ZnO nanoparticles in ethanol medium does not show any peaks in visible region. However, Au and ZnO/Au NPs in ethanol have demonstrated peaks in visible region. Size distribution of metallic NPs can be investigated and determined considering Uv-Vis spectra in which Au and ZnO/Au NPs size (dimension) distribution are about ~36 nm and ~68 nm and are in consisted with literature [19].

B. Nonlinear optical Z-scan results

The sample position dependence of laser intensity gives different beam signals to the detectors as open and closed aperture experimental results to determine nonlinear optical parameters calculating theoretically in z-scan curves. Open aperture and closed aperture data were fitted to equation (2) and equation (3), respectively.

$$T_{open}(x) = (\beta I_0 L_{eff} / 2.83)(1/x^2) \qquad (2)$$

$$T_{closed}(x) = 1 + (4\Delta\Phi_0 x / (x^2+9)(x^2+1)) \qquad (3)$$

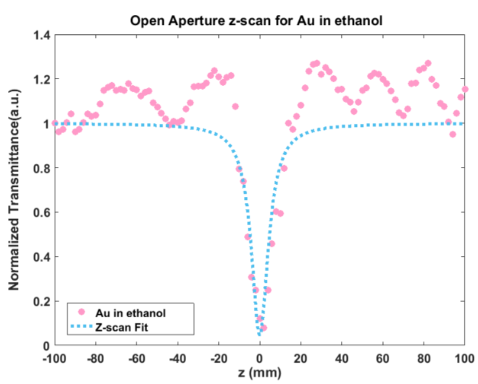
Effective optical path length L_{eff} is equal to $(1- e^{-\alpha L}) / \alpha$ [20] and closed aperture z-scan data was fitted to equation(3) where $x=z / z_0$ in which z is the position of sample and z_0 is equal to $\pi\omega_0^2/\lambda$ and identified as Rayleigh range. $\Delta\Phi_0$ was also calculated by using equation

$$\Delta\Phi_0=2\pi / \lambda(n_2 I_0 L_{eff}) \quad (4)$$

In equations, ω_0 is investigated as the beam waist at the focal point, λ is always represented as the wavelength, intensity of incident laser beam is I_0, and α known as the absorption coefficient [20]. Open aperture z-scan data for ZnO, Au and ZnO/Au Nps have been fitted using experimental data exhibits in figure 4.

TABLE I. LIST OF CALCULATED B AND N2 PARAMETERS USING FS LASER Z-SCAN METHOD AT A POWER INTENSITY OF 2.37 X1011 (W/CM2).

Nanoparticle Sample	β (cm/W)	n_2(cm²/W)
Au Nps in ethanol	-9.946×10^{-11}	1.331×10^{-16}
ZnO Nps in ethanol	-6.227×10^{-11}	7.448×10^{-16}
ZnO/Au Nps in ethanol	7.166×10^{-11}	7.328×10^{-16}



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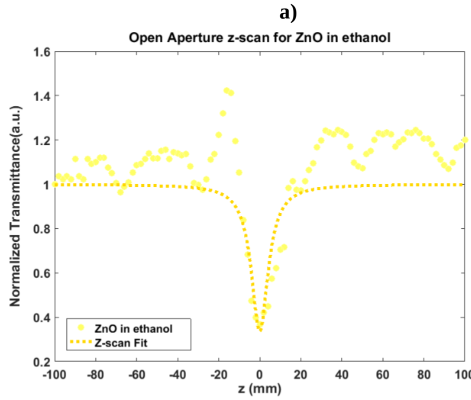

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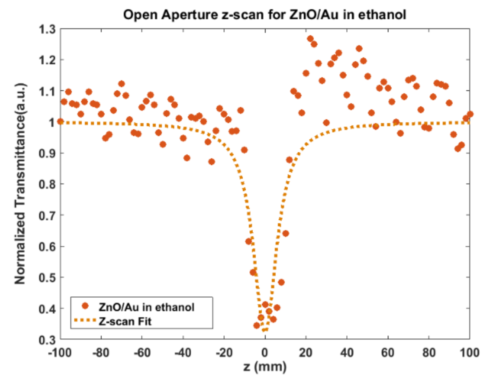

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Fig. 4. Open aperture z-scan data for ZnO, Au and ZnO/Au Nps have been fitted using experimental data.

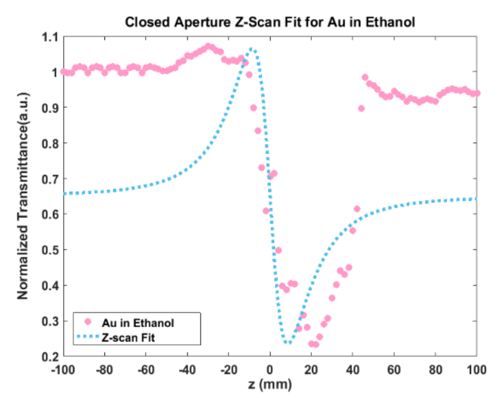
In this study, the first measurements were done for ZnO, Au and ZnO/Au. Z-scan data have been fitted using MATLAB program. Z-scan experiemtal results give us us to determine real and imaginary parts of third order susceptibilities for ZnO, Au and ZnO/Au using equation (5) and equation (6).

$$ReX^{(3)}(esu) = 10^{-4}\frac{\varepsilon_0 c^2 n_0^2}{\pi} n_2 \quad (5)$$

$$ImX^{(3)}(esu) = 10^{-2}\frac{\varepsilon_0 c^2 n_0^2 \lambda}{4\pi^2} \beta \quad (6)$$

$$|X^{(3)}| = \left[\left(Re(X^{(3)})\right)^2 + \left(Im(X^{(3)})\right)^2\right]^{1/2} \quad (7)$$

where ε_0, c are represented as the vacuum permittivity and the velocity of laser light, respectively. Third order susceptibilities of Au, ZnO, ZnO/Au NPs have been used to determine using equation (7). Therefore, nonlinear optical parameters of Au, ZnO, ZnO/Au NPs obtained in this study are reliable. $X^{(3)}$ values for Au, ZnO, ZnO/Au NPs are given in table 2.



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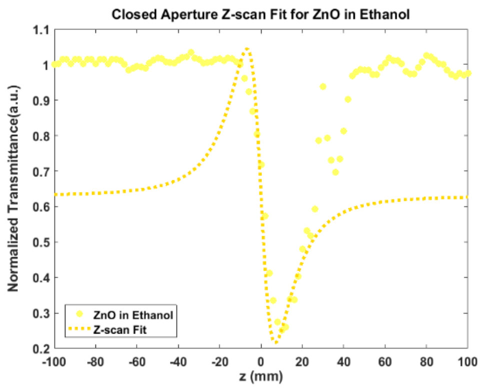

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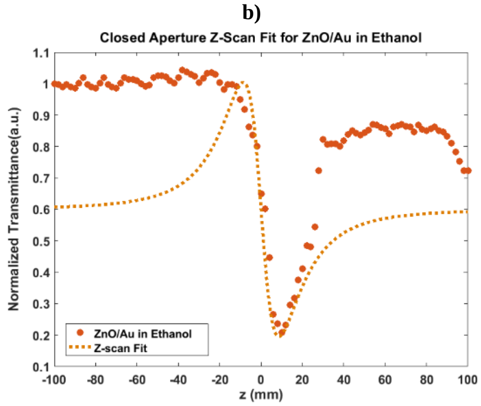

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Fig. 5. Closed aperture z-scan data for ZnO, Au and ZnO/Au Nps have been fitted using experimental data.

TABLE II. AU, ZNO, ZNO/AU NPS REAL, IMAGINARY AND THIRD ORDER NONLINEAR SUSCEPTIBILITY

Sample Name	$Re(X^{(3)})esu$	$Im(X^{(3)})esu$	$X^{(3)}$
Au Nps in ethanol	-1.891 x 10^{-16}	-8.994 x 10^{-14}	8.994 x 10^{-14}
ZnO Nps in ethanol	-0.103 x 10^{-16}	-5.485 x 10^{-14}	5.486 x 10^{-14}
ZnO/Au Nps in ethanol	-0.118 x 10^{-16}	-7.354 x 10^{-14}	7.355 x 10^{-14}

IV. CONCLUSION

As a summary, we have synthesized and characterized Au, ZnO, ZnO/Au NPs with average size ranging from 36 nm nm to 68 nm obtained using UV-Vis spectra. Then we have evaluated nonlinear optical properties of these samples using femtosecond z-scan method wherein 2.37 x 10^{11} W/cm^2 laser intensity at 800 nm was used. It was found that these results show strong nonlinear properties at near infrared region. Closed aperture z-scan data for ZnO, Au and ZnO/Au Nps have been fitted using experimental data shown in figure 5. For these structures, nonlinear absorption coefficient values were observed to be between -6.227 x 10^{-11} cm/W and -9.946 x 10^{-11} cm/W, while nonlinear refraction indexes were measured to be varying from 1.331 x 10^{-16} cm^2/W to 7.328 x 10^{-16} cm^2/W. In addition, third order nonlinear optical susceptibility for these NPs were calculated to be between 5.486 x 10^{-14} (esu) and 8.994 x 10^{-14} (esu).

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