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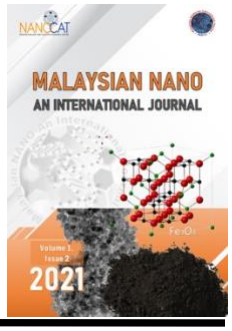

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Nonlinear Optical Properties of ZnO variants

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Abstract

Investigation on nonlinear optical properties of ZnO with Au-Ag NPs was done in this report using a femtosecond laser with a wavelength of 720 nm using Z-scan measurement. ZnO sample was prepared by a two-step process: seeding process via ultrasonic spray pyrolysis and growth process via hydrothermal methods, while ZnO with Au-Ag NPs was done by chemical reduction. ZnO shown saturable absorbance properties with nonlinear absorption coefficient, $\beta = 1.63\times10^{-6}$ cm/W, while ZnO deposited with Au-Ag NPs, shows reverse saturable absorption properties, for which ZnO Au NPs have the highest value of 5.60×10^{-6} cm/W, nonlinear refractive index response for pristine ZnO gave self-focusing effect with the value of a nonlinear refractive index, $\gamma = 2.29\times10^{-12}$ cm^2/W. In contrast, the rest of ZnO with Au-Ag NPs gave the self- defocusing effect, with the Au NPs having the lowest response with $\gamma = -5.79\times10^{-12}$ cm^2/W. This gives ZnO Au NPs have the highest third-order nonlinear susceptibility, $\chi^{(3)} = 14.62\times10^{-10}$ esu, which is an enhancement from pristine ZnO.

Keywords: ZnO; Au; Ag; Nanoparticles and nonlinear optical properties

1. Introduction

Two-dimensional material has been a long interest in material studies. The properties of various 2D materials have shown promising applications in the recent technological era. One of the 2D materials is zinc oxide which is a part of the metal oxide semiconductor family. The nonlinear optical property of a material is one of the aspects to verify the quality of an optical device. The nonlinear optical response occurs when a high-intensity light source is an incident on sample material, and the polarization of the material changed at a certain degree of susceptibility. From this point forth, we describe a response from low-intensity light as linear optical, and response from high-intensity light as nonlinear optics [1]. Fundamentally, the nonlinear optical response can be explained by relating to the polarization in a material due to the optical field strength. In principle, the polarization of a material depends on the applied optical strength. Thus, for linear polarization, let P(t) be polarization and E(t) be the optical field strength, and it can be described as [2],

$$P(t) = \varepsilon_0 \chi^{(1)} E(t) \quad (1)$$

From here, it can be seen that the dependant coefficient is the permittivity of free space, and the first degree of susceptibility of a material, also known as linear susceptibility. This expression will be then expended to a higher degree by Taylor series expansion and can be written as,

$$P(t) = \varepsilon_0 [\chi^{(1)} E(t) + \chi^{(2)} [E(t)]^2 + \chi^{(3)} [E(t)]^3 + \cdots] \quad (2)$$

Thus, from the expression above, it can be said that the material that was applied a high-intensity optical field strength can give response to many degrees of polarization even in a small quantity of susceptibility.

In this report, nonlinear optical properties of ZnO, ZnO-Au, ZnO-Au/Ag, and ZnO-Au3Ag1 are reported. The synthesis of the materials is done by the chemical reduction method. The investigation of nonlinear optical properties is by Z-scan measurement. The physical quantities that will be presented are the nonlinear absorption coefficient, β, nonlinear refractive index, γ, and third-order nonlinear susceptibility(χ(3))

2. Materials and Methods

For the preparation of the sample, ZnO was prepared by a two-step process: seeding process via ultrasonic spray pyrolysis and growth process via hydrothermal methods. The ZnO seed solution, 0.2 M $C_4H_6O_4Zn{\bullet}2H_2O$ in deionized water was put into a commercial ultrasonic nebulizer and sprayed onto a glass substrate for 15 min at temperature 450°C and continuously heated for 1 hour.

When the substrate was cooled down to room temperature, the samples were soaked in 10 mL mixture of $N_2O_6Zn{\bullet}4H_2O$ and $C_6H_{12}N_4$ with an equimolar concentration of 0.05 M and heated at 95°C for 6 hours. After that, the samples were removed, cleaned using DI water, and dried using hot air. As for Au-Ag nanoparticles, the method used was a chemical reduction. Firstly, the ZnO NRs samples was soaked in 0.1% poly-L-lysine solution for 10 min with the grown ZnO surface facing upward. The Au-Ag precursor solution contained 5 mM $HAuCl_4$ and $AgNO_3$ with different mole ratios 1:0, 3:1, and 1:1, that were mixed with 2 mL 0.5% trisodium citrate and 0.6 mL 0.1 M of ice cold $NaBH_4$. The ZnO NRs were then immersed in the precursor Au-Ag solution and heated in the oven at 100°C for 1 hour. The samples were then removed, dried, and annealed on a hotplate at 200°C for 1 hour and then at 400°C for 30 min in surrounding air. This process was referred to previous studies along with the characterization of thickness and morphological view [3].

For the measurement of nonlinear properties, the Z-scan method was used to evaluate the nonlinear absorption, refractive index, and third-order susceptibility. For the laser source, femtosecond laser (Spectra-Physics-Tsunami) with a plane-polarized Gaussian beam profile and initial beam diameter of 3.5 mm was used, containing pulse width, τp of 100 fs, repetition rate of 82 MHz and wavelength, λ of 720 nm. The beam is propagated at Z-direction through the biconvex lens of focal length 25 mm; obtaining beam waist diameter at the focal point, $\omega 0$ of 3.2 μm, through the sample position, and detected by a power meter. The pulse energy of the laser, *Ep* is ~0.15 nJ, producing laser intensity at the focal point, *I0* of about 4.5 GW/cm^2 by using,

$$I_0 = \frac{E_p}{\tau_p \pi {\omega_0}^2} \quad (3)$$

The nonlinear absorption coefficient, β can be obtained by open aperture Z-scan, where the power meter received all the laser light, while the nonlinear refractive index, γ can be obtained by close aperture Z-scan, where an aperture was placed before power meter so that the laser signal entered a certain amount, thus could observe the change of refractive index of the material [4, 5].

The parameter that determines the signal enters is called S-parameter which can be written as, $S = 1 - \exp(-2r2/\omega 2)$, where the aperture radius is 0.5 mm, and beam radius at the aperture, ωa is aa 2.5 mm. For an open aperture, the S-parameter is S = 1, while for close aperture should be S < 1, for which S-parameter obtained for this experiment is S≈0.2. The nonlinear optical effects started to occur when the sample enters a region called Rayleigh length, z0 which can be written as $z0 = \pi\omega 2/\lambda$. This means that the nonlinear effect will only respond when it enters the region where 0 the laser started to converge, into the focal point, and diverge back.

Next, after running the experiment, the data will be analyzed by fitting with equations. For open aperture, the transmittance of the signal across the z-direction can be described as the following equation [6],

$$T_{OA}(x) = 1 \pm \frac{1}{2\sqrt{2}} \frac{\beta L_{eff} I_0}{\left[1+\left(\frac{z}{z_0}\right)^2\right]} \quad (4)$$

where β is nonlinear absorption coefficient, I0 is the intensity at the focal point, z_0 is the Rayleigh length, and $Leff = (1 - \exp(-\alpha L))/\alpha$, is the effective thickness of the sample for which α is the linear absorption coefficient, and L is the thickness of the sample. The linear absorption is obtained by evaluating the power transmitted through the sample with the substrate, p, and power transmitted only through the substrate, p^0 related through the equation,

$$\propto = -\frac{1}{L} ln\left(\frac{p}{p_0}\right) \quad (5)$$

where L is the sample thickness measured by the surface profiler. After that, for closed aperture measurement, the transmittance of the samples across z-direction can be described by the following equation [7],

$$T_{CA}(z) = 1 \pm \frac{4\Delta\emptyset_0\left(\frac{z}{z_0}\right)}{\left[9+\left(\frac{z}{z_0}\right)^2\right]\left[1+\left(\frac{z}{z_0}\right)^2\right]} \quad (6)$$

From here, Rayleigh length still plays its role, and $\Delta\phi 0$ is the nonlinear phase distortion defined as,

$$\Delta\emptyset_0 = \frac{2\pi}{\lambda}\gamma I_0 L_{eff} \quad (7)$$

where here, the nonlinear refractive index, γ is the main quantity that gave the phase distortion effect on the laser emitted. Finally, the third-order nonlinear susceptibility can be described in complex function as [8],

$$X^{(3)} = Re\{X^{(3)}\} + i\ lm\{X^{(3)}\} \quad (8)$$

$$X^{(3)} = \sqrt{(\{X^{(3)}\})^2 + (lm\{X^{(3)}\})^2} \quad (9)$$

where the real and imaginary part can be evaluated by [9, 10],

$$Re\{X^{(3)}\} = \frac{\varepsilon_0 {n_0}^2 c^2}{\pi}\gamma \times 10^{-4}(cm^2/W) \quad (10)$$

$$lm\{X^{(3)}\} = \frac{\varepsilon_0 {n_0}^2 c^2 \gamma}{4\pi^2}\beta \times 10^{-2}(cm/W) \quad (11)$$

where ε_0 is the permittivity is free space, c is the speed of light, n_0 is the linear refractive index, for which the value is analogous to that of the refractive index of water since the precursor solution is in a liquid state.

Based on the real and imaginary parts above, it can be said that the real part of nonlinear susceptibility depends on the nonlinear refractive index and the imaginary part depends on the nonlinear absorption coefficient. Thus, a set of quantitative results can be tabulated.

3. Results and discussion

For the thickness of the sample, a surface profiler was used, and this result has supported the thickness of ZnO embedded on the substrate based on the FESEM obtained. Then, the effective thickness (L_{eff}) and the linear absorption, α is calculated using the initial power and the after-entry power. The thickness (L) effective thickness(L_{eff}) of each sample studied are tabulated in Table 1.

Table 1: Thickness of sample using Surface Profiler, along with the linear absorption, α and effective thickness, L_{eff} of each sample.

Material	L ($\times 10^{-5}$ cm)	α ($\times 10^{3}$ cm^{-1})	L_{eff} ($\times 10^{-7}$ cm)
ZnO NRs	14.0	6.06	9.44
ZnO Au NPs	6.00	0.12	5.98
ZnO AuAg NPs	9.00	11.3	5.66
ZnO Au_3Ag_1 NPs	8.00	7.66	5.98

As for the Z-scan measurement, the results of open and close aperture are as depicted in Figure 2. As shown in Figure 2(a), the ZnO NRs, have shown saturable absorption (SA) properties while other NPs variants have changed their properties into reverse saturable absorption (RSA). Nevertheless, the NPs variants gave different intensities between each other, thus it can also be said that each NPs absorbed light at different capabilities. Au NPs, can absorb light at a higher rate, thus giving the lowest transmittance in the graph.

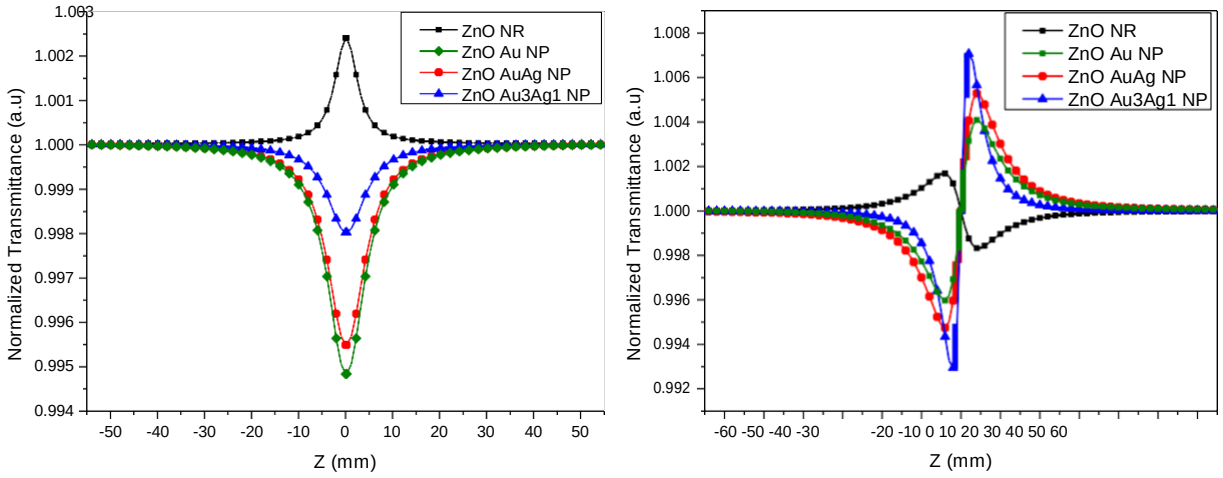

Figure 1: Z-scan measurement (a) Open aperture, (b) Closed aperture.

For close aperture, only pristine ZnO gave a peak-to-valley response, while other variants exhibited a valley-to-peak response. Those responses referred to the Kerr optical response, for which the peak-to-valley respond to nonlinear self-focusing refractive index, and valley-to-peak responded to nonlinear self-defocusing refractive index. Thus, from the graph, ZnO exhibits a self-focusing process, while ZnO variants exhibit a self-defocusing process. It can be shown that the nonlinear refractive index properties of material change when the composition of the material changes. From here, the sample of ZnO is different than that mixed with Au-Ag NPs, despite the different ratio composition of the NPs themselves. This can also be said for the nonlinear absorption properties. For closed aperture, the graphical response is due to the minor change of refractive index towards high-intensity laser thus showing whether they are focusing of defocusing from its original intensity. The minor change of refractive index gives arise to the nonlinear susceptibilities, in this case, third-order nonlinearity. Table 2 shows the qualitative results from this experiment.

Table 2: Nonlinear optical parameters of each sample investigated.

Material	β **(×10^{-6} cm/W)**	γ **(×10^{-12} cm^2/W)**	**Re[$\chi^{(3)}$] (×10^{-10} esu)**	**Im[$\chi^{(3)}$] (×10^{-10} esu)**	$\chi^{(3)}$ **(×10^{-10} esu)**
ZnO NRs	−1.63	2.29	1.02	−4.18	4.30
ZnO Au NPs	5.60	−5.79	−2.60	14.39	14.62
ZnO AuAg NPs	5.17	−11.97	−5.36	13.27	14.31
ZnO Au$_3$Ag$_1$ NPs	2.16	−15.28	−6.85	5.53	8.80

From the coefficient obtained in Table 2, it has been proven that ZnO Au NPs have the highest nonlinear susceptibility compared to the other variants. This shows that the Au NPs allow a higher nonlinear response towards the high-intensity laser. This also has shown that, due to the high absorption of light, a change of nonlinear refractive index along Z-direction will occur minimally. Other than that, since pristine ZnO acts as the baseline of this investigation, the addition and/or mixing with nanoparticles is an enhancement towards the nonlinear optical measurement, regardless of Au, Ag, or Au-Ag compound. When compared between Au/Ag and Au3Ag1, it can be seen that the 1:1 ratio gave higher susceptibilities towards high-intensity laser compared to the 3:1 ratio. This shows that reducing the content of Ag-to-Au will lower its nonlinearity response in the materials.

4. Conclusion

In conclusion, the Z-scan measurement was a success since it gave a promising result. ZnO deposited with Au-Ag NPs shows enhancement towards the value of the nonlinear optical response. ZnO shown saturable absorbance properties with nonlinear absorption coefficient, β = 1.63×10^{-6} cm/W, while ZnO deposited with Au-Ag NPs, shows reverse saturable absorption properties, for which ZnO Au NPs have the highest value of 5.60×10^{-6} cm/W, followed by Au-Ag 1:1 ratio, and Au-Ag 3:1 ratio with the lowest RSA properties. Simultaneously, the nonlinear refractive index also differs between pristine ZnO and ZnO with Au-Ag NPs. The response for pristine ZnO gave self-focusing effect with the value of the nonlinear refractive index, γ = 2.29×10^{-12} cm^2/W, while the rest ZnO with Au-Ag NPs gave self-defocusing effect with the Au NPs have the lowest response with $\gamma = -5.79\times10^{-12}$ cm^2/W, followed by Au-Ag 1:1 ratio, and Au-Ag 3:1 ratio with the highest nonlinear refractive index. As a result, ZnO Au NPs have the highest third-order nonlinear susceptibility, $\chi^{(3)} = 14.62\times10-10$ esu which is an enhancement from pristine ZnO.

Competing interest

The authors declare no conflict of interest.

References

[1] N.C Panoiu., et al. Nonlinear optics in plasmonic nanostructures. *Journal of Optics*. 2018: 20;8.

[2] X. Wen, Z. Gong and D. Li. Nonlinear optics of two-dimensional transition meta dichalcogenides. *InfoMat*. 2019: 1;3; 317-337.

[3] V. Fauzia., et al. The impact of the Au/Ag ratio on the photocatalytic activity of bimetallic alloy AuAg nanoparticle-decorated ZnO nanorods under UV irradiation. *Journal of Physics and Chemistry of Solids*. 2021:154.

[4] X. Zheng., et al. Z-scan measurement of the nonlinear refractive index of monolayer WS(2). *Opt Express*. 2015: 23;12; 15616-23.

[5] S. Bikorimana., et al. Nonlinear optical responses in two-dimensional transition metal dichalcogenide multilayer: WS2, WSe2, MoS2 and Mo0.5W0.5S2. *Opt Express*. 2016: 24;18; 20685-95.

[6] R.S.S. Kumar., et al., Femtosecond and nanosecond nonlinear optical properties of alkyl phthalocyanines studied using Z-scan technique. *Chemical Physics Letters*. 2007: 447;4-6; 274-278.

[7] L.F. Wu., et al., Enhanced nonlinear optical behavior of graphene-CuO nanocomposites investigated by Z-scan technique. *Journal of Alloys and Compounds*. 2019: 777; 759- 766.

[8] S.P. Ramteke., et al. Novel report on SHG efficiency, Z-scan, laser damage threshold, photoluminescence, dielectric and surface microscopic studies of hybrid inorganic ammonium zinc sulphate hydrate single crystal. *Optics & Laser Technology*. 2018:104; 83-89.

[9] E. Mathew., et al. Third-order nonlinear optical studies of two novel chalcone derivatives using Z-scan technique and DFT method. *Optics & Laser Technology*. 2019: 120.

[10] Y.I. Jhon., Y.M. Jhon, and J.H. Lee. Nonlinear optics of MXene in laser technologies. *Journal of Physics: Materials*. 2020: 3;3.