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Linear and nonlinear optical properties of ZnO-TiO_2-PMMA nanohybrids

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In this paper the linear and nonlinear optical (NL) properties of ZnO-TiO_2-PMMA nanohybrids films prepared via solution casting method were investigated. The effect of film thickness on the linear optical properties has been studied using UV-Vis spectrophotometer while the NL properties have been characterized using Z-Scan technique. The results show that the energy band gap (Eg) and nonlinearity are increased as the sample thickness increased. The nonlinear refractive index (NLR) (cm/W^2), nonlinear absorption coefficient (NLA) (cm/W) and third order susceptibility $\chi^{(3)}$ (esu) are of the order 10^{-7}, 10^{-6} and 10^{-5} respectively. The optical limiter threshold around (35-66) mW and depend on the sample thickness (optical limier increased as the sample thickness increased).

Keywords: ZnO-TiO_2-PMMA; Nanohybrids; Z-scan technique; Optical properties.

1. INTRODUCTION

NL materials have been explored greatly for their various applications in all-optical switches, photonic devices, optical modulation and optical sensor protection [1–6]. A high nonlinearity and ultra-fast response time of organic materials improves their importance for optical limiting, Also, among all organic materials, p-conjugated polymers have received significant interest as third-order nonlinear optical materials for photonic switching devices, optoelectronic materials for light emitting diodes and solar cells [2,7,8]. In the recent years, many researchers interested in the linear and NL properties of a matrix transparent films consisting of polymer, organic dyes, and TiO_2 or ZnO nanoparticles [9-17]. A matrix of Polymer-TiO_2 nanohybrids has been studied for their novel optical properties. They show a very fast recovery time of 1.5 picosecond and high optical nonlinearity up to 1.93×10^{-9} esu as observed by Z-scan technique using 250 femto-second laser pulses at 780 nm [10]. The dependence of the optical limiter and nonlinear optical properties on the dopant concentrations of TiO_2 in PMMA was studied in [18]. TiO_2-ZnO nanohybrids shows a great enhancement in the optical nonlinearity [19, 20]. In this paper the linear and nonlinear optical properties of PMMA-TiO_2-ZnO nanohybrids films of different thickness have been studied.

2. EXPERIMENTAL PART

PMMA-TiO_2-ZnO nanohybrids were prepared using solution casting method [7] where poly(methyl methacrylate) (PMMA, Veracril, Colombia) was first dissolved in chloroform ($CHCl_3$, 99% , BDH chemicals Ltd Poole England) in beaker 1 meanwhile 2 wt% of titanium peroxide nanoparticle (TiO_2, 99.8%, particle size = 50 nm, Hongwunanometer, China) and 0.2 wt% of zinc oxide (ZnO, 99.8%, particle size = 80 nm, Hongwunanometer , China) were dispersed in chloroform in beaker 2. Both beakers were stirred for 4 hours, then sonicated for 30 minutes, finally both solutions were mixed together and stirred for 10 hours, then sonicated for 20 min to obtain the homogenous mixture. The mixture of the solutions was poured into a Petri dish and left at room temperature for 24 hours to evaporate the solvent. The films coded as (TZ125, TZ195, TZ290 and TZ420) for thickness (125, 195, 290, and 420) μm respectively. The UV-visible spectrum of these samples was measured using (Metertech SP8001, Taiwan). The nonlinear optical properties of the nanohybrids were measured using Z-scan Technique. The excitation source of this system is CW Nd-YAG laser (MIL-111, Changhun new industry, china) with wavelength of 1064 nm. The output beam is focused onto the sample by using a bi-convex lens with a focal length of 15 cm, giving a spot size of ~ 60 μm. Open aperture form of the Z-scan setup is used to determine the two photon absorption coefficient by assuming the total nonlinear absorption effect as $= \alpha_o + \beta I$. For Gaussian laser beam, the normalized change in transmittance ΔT (z) for open aperture is described by [21]

$$\Delta T(z) \approx -\frac{q_o}{2\sqrt{2}} \frac{1}{[1+Z^2/Z_o^2]} \quad (1)$$

Where $q_o = \beta I_o L_{eff}$, z_o is the diffraction length of laser beam, β is the two photon absorption coefficient, I_o is the intensity of the laser beam, L_{eff} is the effective thickness. The closed aperture form of the Z- Scan is used to obtain the nonlinear refractive index (n_2) by using [22].

$$\Delta T_{pv} = 0.406(1-S)^{0.27}|\Delta\Phi_o| \quad (2)$$

Where $\Delta\Phi_o = \frac{2\pi}{\lambda} n_2 I_o L_{eff}$, ΔT_{pv} is the normalized difference of the maximum (peak) and minimum (valley) transmission in the closed aperture scheme, $\Delta\Phi_o$ is the induced phase shift in focus due to nonlinear refraction, S is the aperture transmission.
The imaginary and real parts of the third order nonlinear optical susceptibility of nonlinear optical material is calculated by the relations [23]

$$\mathrm{Im}(\chi^{(3)}) = (n_o^2 \varepsilon_o c\lambda/2\pi)\beta \quad (3)$$

$$\mathrm{Re}(\chi^{(3)})(esu) = \frac{n_o^2}{0.0395} n_2 (cm^2 W^{-1}) \quad (4)$$

Where $n_o = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - K^2}$ is the linear refractive index, ε_o is the vacuum permittivity and c is the light velocity
The value of the third order nonlinear optical susceptibility of these films was calculated using [7]

Exp. Theo. NANOTECHNOLOGY 3 (2019) 1-8

$$\chi^{(3)} = \left[\left(\mathrm{Re}\chi^{(3)}\right)^2 + \left(\mathrm{Im}\chi^{(3)}\right)^2\right]^{1/2} \quad (5)$$

3. RESULTS AND DISCUSSION

3.1 Characterization, formation of TiO_2 phase

Chemical composition, properties of ZnO-TiO_2-PMMA nanohybrids are shown in figure 1. This Figure shows a broad band around 3600-3805 cm-1 which is due to OH stretching (39) on the surface of titania particles, and the band around 2839-2964 cm-1 indicates the O –CH3 stretching of the PMMA. The peaks around 1728, 1458, and 1150 cm-1 assigned to C=O stretch, C-H bending, and C-O stretch of the PMMA respectively [13.14]. The peak at 744 cm-1 is the stretching vibration of Ti-O band [19]. The figure shows a peak at 478 cm-1 indicate the ZnO stretching vibration.

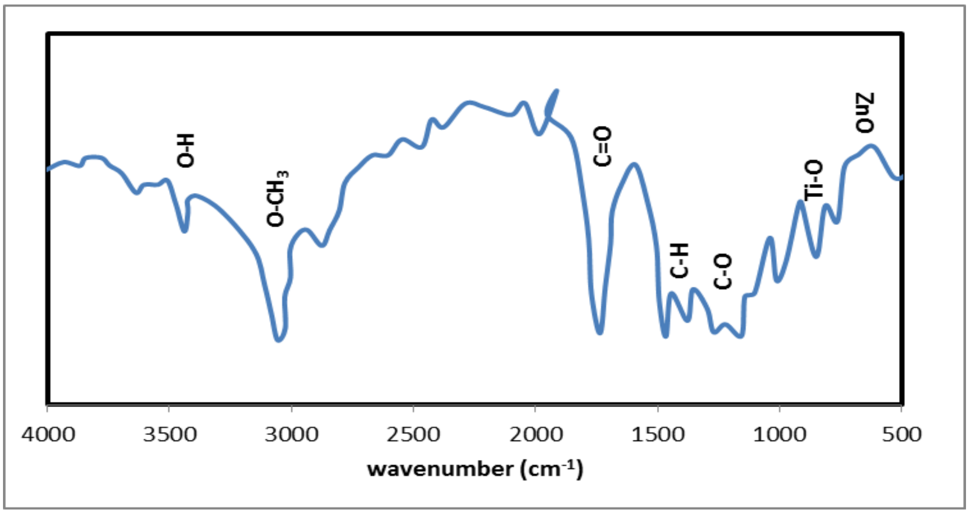

Figure .1, FTIR spectrum for ZnO (0.2w %) film.

3.2 Linear optical properties

The linear optical transmittance, absorbance and the band gap values of the Nano-composites for different sample thickness (200-1100) nm has been shown in Figures 1, 2 and 3 respectively.

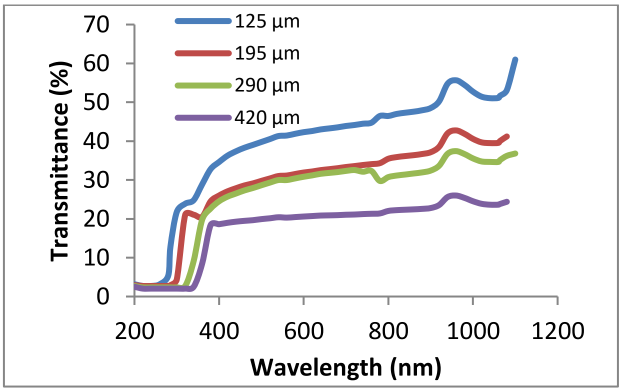

Figure 1. Transmittance spectra of PMMA-TiO_2-ZnO nanocomposite thin films (zno=0.2) with different thickness TZ125, TZ195, TZ290 and TZ420 respectively.

Exp. Theo. NANOTECHNOLOGY 3 (2019) 1-8

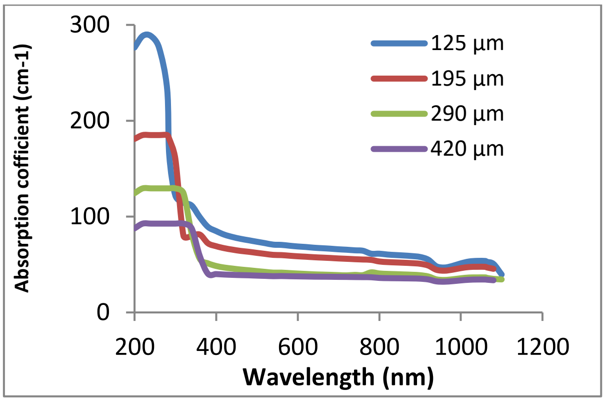

Figure 2. Absorption coefficient of PMMA-TiO_2-ZnO nanohybrids thin films with different thickness TZ125, TZ195, TZ290 and TZ420 respectively.

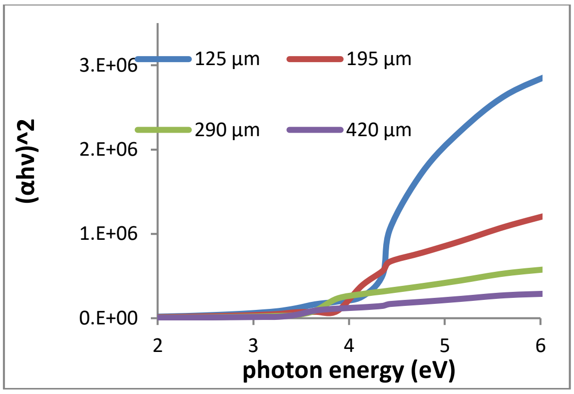

Figure 3. Optical band gap energy of PMMA-TiO_2-ZnO nanohybrids film with different thickness TZ125, TZ195, TZ290 and TZ420 respectively.

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Figure 1 indicates that the transparency of the films decreasing with the increasing in film thickness due to the electrostatic interaction between particles becomes larger leading to increase the probability of particles to be gathered forming agglomerated particles which causes light to be scattered [8]. The linear absorption spectra shown in Figure 2, demonstrate that all four nanohybrids thin films are highly transparent in the visible region. It can also be seen that the higher sample's thickness TZ420 exhibit a higher absorbance than other samples (TZ125, TZ195, and TZ290).

The direct optical energy band gap energy (E_g) was obtained from Tauc'splot of $(\alpha h\nu)^2$ versus photon energy for all thin film thickness were presented in figure (3). The band gap Eg were calculated to be (4.33, 3.62, 3.54 and 3.10) eV for TZ125, TZ195, TZ290 and TZ420 respectively. |It was shown that as the thin film thickness increased, the band gap energy of TiO_2 decreased, which improve minimum energy required for electron excitation from valence band to conduction band [16].

The linear refractive index (n_o) of the nanohybrids measured at 1064 nm is 2.592, 2.630, 2.577 and 2.187 for TZ125, TZ195, TZ290 and TZ420 thickness respectively.

Exp. Theo. NANOTECHNOLOGY 3 (2019) 1-8

Table 1 Linear properties of TiO2-PMMA with different film (zno=.2) thickness TZ125, TZ195, TZ290 and TZ420.

Sample Code	Film thickness µm	α_o (cm-1)	Eg (eV)	n_o
Tk125	125	52.83	4.33	2.592
TK195	195	47.58	3.62	2.630
TK290	290	36.08	3.54	2.577
TK420	420	34.15	3.10	2.187

3.3 Nonlinear optical properties

The NL properties of PMMA-TiO_2-ZnO nanohybrids films as a function of film thickness were characterized using Z-Scan technique. Figure 4 shows the open and closed aperture Z scan for all transparent films.

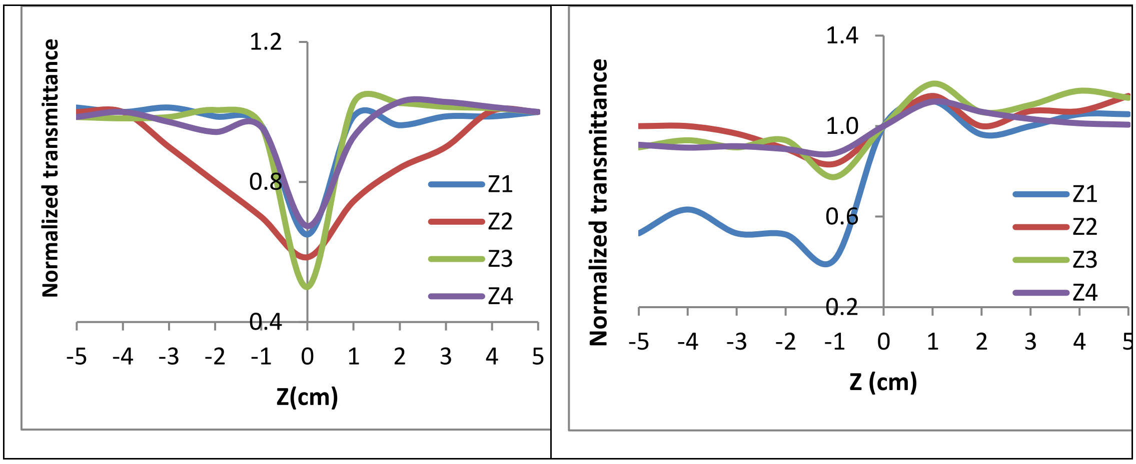

Figure 4. Open aperture and (b) Closed aperture Z-scan measurement results for TZ125, TZ195, TZ290 and TZ420 films respectively performed with 1064nm. The input irradiance was 2.12×10^{-3} MW/cm^2 and beam waist 60 µm.

From Figure (4.a) the curves show symmetrical and minimum values at z=0 which correspond to β >0 and the two-photon absorption behavior of the nanohybrids. Figure (4.b) show that all the films exhibit self-focusing behavior (n_2>0), normalized transmission exhibit minimum “valley” followed by maximum "peaks", the values of β , n_2 , and the third order nonlinear optical susceptibility of these films $\chi^{(3)}$ are shown in table(2).

3.4 Optical limiter

From figure 5, It is shown that adding ZnO 0.2wt % nanoparticles into the nanohybrids TiO2+PMMA enhance the optical limiting behavior of the hybrid samples compared with pure TiO2+PMMA films, also as the film thickness TZ125 increased the limiting threshold increased (see table.2).

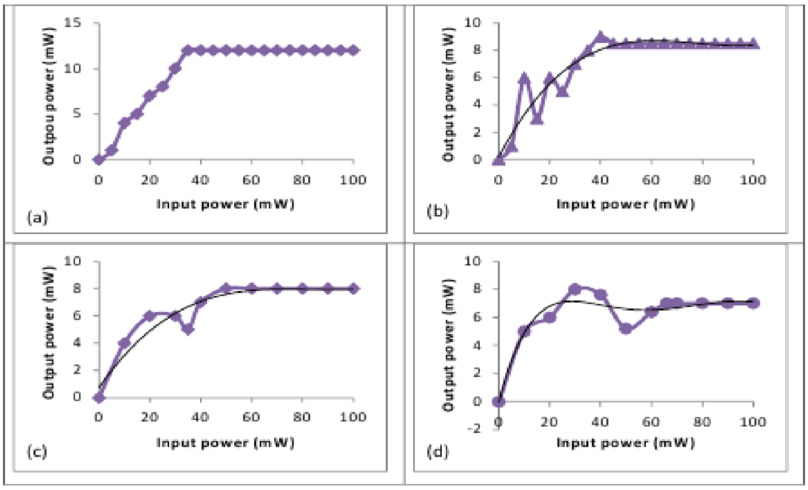

Figure 5. (a-d) optical limiting behavior of 0.2wt% ZnO in TiO_2+PMMA for different film thickness TZ125, TZ195, TZ290 and TZ420 respectively.

Table 1 Nonlinear optical properties of TZ125, TZ195, TZ290 and TZ420 films.

Sample thickness Code	n_2 (cm^2/W) x10-7	β (cm/W) ×10-6	$\chi^{(3)}$ (esu) x10^{-5}	Optical limiting threshold (mW)
TZ125	15.5	8.83	26.4	35
TZ195	4.79	7.54	8.39	45
TZ290	4.66	6.42	7.83	50
TZ420	3.17	3.37	3.84	66

4. CONCLUSIONS

The optical response of ZnO doped TiO_2 – PMMA nanohybrids prepared via solution casting method are investigated using UV-Vis spectrometer and it found that film transparency and band gap energy is decreased as the film thickness increased. The nonlinear optical response was characterized using Z scan technique and it found that the nanohybrids exhibit decreasing in optical nonlinearity as the film thickness increased. The observed NLA is explained by two photon absorption and the NLRis explained by self-focusing.

References

[1] K.J. Ghaleh, S. Salmani, M.H. Majles Ara, Optics Communications 271 (2007) 551
[2] Y. Al-Douri, A. J. Haider, A.H. eshak, A. ouhemadou, M. Ameri, Optik-International journal for light and Electronics Optics 127 (2016) 10102
[3] M.D. Zidan, A.W. Allaf, Z. Ajji, A. Allahham, Optics and Laser Technology 43 (2010) 531
[4] S.J. Mathews, S. Chaitanya Kumar, L. Giribabu, S. VenugopalRao, Optics Communications 280 (2007) 206
[5] Fryad Z. Henari, Seamus Cassidy, Optik 123 (2011) 711
[6] Rida Ahmed Ammar, Exp. Theo. NANOTECHNOLOGY 2 (2018) 1

[7] H. Antoniadisa, B.R. Hsieha, M.A. Abkowitza, S.A. Jenekhea, M. Stolkaa,Synthetic Metals 62 (1994) 265
[8] S.R. Marder, J.E. Sohn, G.D. Stucky (Eds.), Materials for Nonlinear Optics: Chemical Perspectives, American Chemical Society, Washington, DC, 1991
[9] Srilatha Koteswara, Ishwarya Punati, Avireni Srinivasulu, Exp. Theo. NANOTECHNOLOGY 2 (2018) 11
[10] Ali H AL-Hamdani, Alaa H Ali,Mariam H Mohamed," Ecipsing Z-scan measurement for mixture of dyes (R6G, RB, AND RC) in liquid and solid media", ARPN, Journal of Engineering and applied Sciences 10 (2015) 1
[11] A. H. Reshak, Journal of Applied Physics 119 (2016) 095709.
[12] A. H. Reshak, Journal of Applied Physics 119 (2016) 105706
[13] A.H.Yuwono, J.Xue ,J.Wang, H.I.Elim,W.Ji, Y.Li, and T.J. White, "Transparent nanohybrids of nanocrystalline TiO2 in PMMA with unique nonlinear optical behavior", J. mater. Chem. 13 (2003) 1475
[14] J. L. H. Chaua, Y. M. Lina, A. K. Lia, W. F. Sub, K. S. Changb, S. L. C. Hsuc, T. L. Li, "Transparent high refractive index nanocomposite thin films", Materials Letters 61 (2007) 2908
[15] H.I.Elim, W.Ji, A.H. Yuwono, J.M.Xue and J.Wang, "Ultrafast optical nonlinearity in poly(methylmethacrylate)-TiO_2 nanocomposites", Applied physics letter 82 (2003) 2691
[16] A.H. Yuwono, J. Xue, J. Wang, H. I. Elim, W. Ji, " Titania-PMMA nanohybrids of enhanced nanocrytallinity", J. Electrocream 16 (2006) 431
[17] A.H.Yuwono,J.Xue and J.Wang," Transparent TiO2-PMMA nanohybrids of High nanocrystallinity and enhanced nonlinear optical properties",journal of applied physics and materials 14 (2005) 281
[18] Aya H. Makki, Ali H. AL-Hamadani, Mohammed Abdulridha Husien, "Dopant effect on the nonlinear optical properties of TiO2-PMMA nanocomposites for optical limiter applications", Eng. &Tech. Journal 34 (2016) 1012
[19] Litty Irimpan, V. P. N. Nampoori , and P. Radhakrishnan , "Optical Limiting in ZnO Nanocomposites", science of advanced materials 2 (2010) 578
[20] E.W.Van Stryland, and M.S.Bahae,"Z-scan measurements of optical nonlinearities", Characterization technique and tabulations for organic nonlinear materials 65 (1998) 655
[21] C. M. Firdausa , M. S. B. Shah Rizamb , M. Rusopa , S. R. Hidayahc, "Characterization of ZnO and ZnO: TiO2 Thin Films Prepared by Sol-Gel Spray-Spin Coating Technique", Procedia Engineering 41 (2012) 1367
[22] C. Kittel, "Introduction to solid state Physics",7th edition, Wiley,2011.
[23] Rashid A. Ganeeev,"Nonlinear Optical Properties of Materials", Springer,2013.

Exp. Theo. NANOTECHNOLOGY 3 (2019) 1-8

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