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Study the Effect of the Particle Size of the Scattering Centers in Each of Linear and Non-Linear Optical Properties for the Laser Random Media

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Abstract: Four different mixtures of 10^{-3} mol/L styryl 9M laser dye, 0.1 g PMMA and one of TiO_2 microparticles, Ag and ZnO nanoparticles weights 0.02, 0.04, 0.06 and 0.08 g had been prepared using chloroform solvent. The 4 different thin films had been made from these mixtures for each particles type using drop casting method. The absorption spectrums of these thin films had been taken. The absorption spectral properties as (peak wavelength, peak absorbance and frequency difference at half absorbance maximum) had been measured depending on the absorption spectrums for thin films. The non-linear optical properties as (transmittance difference $\Delta T_{p\text{-}v}$), non-linear phase shift $\Delta\Phi_0$, non-linear refractive index n_2, minimum normalized transmittance T(Z) and non-linear absorption coefficient β) were calculated according to normalized transmittance data obtained from Z-scan setup with closed and open aperture. The effect of the particle size of the scattering centers in the linear and nonlinear optical properties of the styryl 9M laser doped in PMMA thin films had been studied. The main conclusion is that the Ag nanoparticles causes a shift of the absorption wavelengths to longer wavelengths (red shift), so, this helps in choosing the medium and nanoparticles with appropriate excitation wavelengths.

Key words: Styryl 9M laser dye, TiO_2 microparticles, Ag and ZnO nano particles, linear, non-linear, properties

INTRODUCTION

Titanium dioxide which is also named as titania is the obviously resulted fromthe titanium oxidation and has the molecular formula of TiO_2 (Latroche *et al*., 1989). The important physical properties of TiO_2 which is illustrated in Table 1, makes it is used in different fields as: it used as a white pigment to coloring the food, the sunscreen, the study, the plastics, the printing liquid inks and the children candy. There are other applications for TiO_2 such as in the making of glass or glass ceramics and the conductors. It can be used to cut the harmful proteinand it is used to improve the energy conversion of the solar cell. It can be used as a dielectric mirrors in Bragg pattern due to it has higher value of refractive index (Jones *et al*., 2007; Sato *et al*., 1991).

Silver nanoparticlesarethose silver particles of size range (1-100 nm) and they exist on spherical, thin sheets shapes (Graf *et al*., 2003).

Ag nanoparticles have large ratio of surface area to volume which allowed to they utilized in more improvement applications. Where it can be used in human treatments, animal medical studies in laboratories, the manufacturing of sensors, it can be used as a pigments which Ag nanoparticles have a color is the size and the shape dependent. It may be utilized biosensors manufacturing, so, the Ag nanoparticles act as biological analyzing tags. It used in wound dressings, cosmetics materials, plastic manufacturing, inks production with suitable electrical and thermal properties (Brennan *et al*., 2015; Dong *et al*., 2010; Shan *et al*., 2008).

Table 1: The chemical, physical properties of TiO_2 microparticles, Ag and zinc oxide nanoparticles (Pietrobon *et al*., 2008; Zhang *et al*., 2010; Swati and Mahendra, 2015; Wang *et al*., 2014; Hanley *et al*., 2009; Kurtoglu *et al*., 2011; Fujishima and Honda, 1972)

	Values		
Properties	TiO_2	Ag	ZnO
Chemical formula	TiO_2	Ag	ZnO
Molar mass	79.866 g/mol	107.8682	81.40 g/mol
Appearance	White solid	Black powder	White powder
Density	4.23 g/cm^3	10.49g/cm^3	5600 kg/m^3
Melting point	1,84348°C	961.78°C	1975°C
Boiling point	2,972°C	2162°C	2360°C
Solubility in water	Insoluble	Insoluble	Insoluble
Magnetic susceptibility (χ)	+5.9.10^{-6}cm^3/mol	-19.5.10^{-6} cm^3/mol	-
Refractive index (n_D)	2.488	-	2.013
Dielectric constant	-	Over 81	8.5
Thermal conductivity	-	429 W/(m.k)	60 W/m.k

The Ag nanoparticles have more conduction electrons, the strong interaction between the particles and the light photons had been occurred which leads to a

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collective resonance oscillation. This behavior can be attributed to the higher cross sections for both of scattering and absorption. Depending on the size of the particle and the refractive index of the metal surface, the peak resonance wavelength may be varied at the range of 400-530 nm. While The shift of the peak resonance wavelengths to a longer wavelengths had been resulted with the increasing of particle diameter. And with using a rod or plate silver nanoparticles (Wiley *et al*., 2007; Pietrobon *et al*., 2008; Zhang *et al*., 2010).

Zinc Oxide (ZnO) nanopowders had several other names as zinci oxicum or ketozinc and oxozinc. ZnO nanoparticles powder is a white powder and has antibacterial charcteristics (Heim *et al*., 2015).

ZnO is a semiconductor material of a wide band gap has more optical density and luminescence in a spectrum range of (visible to near ultraviolet). It has more binding energy of 60 meV. This leads to the ability of transition occurring in room temperature. Additionally, ZnO is considered as a environmental friend and ease to produce (Mitchnick *et al*., 1999; Kim *et al*., 2015; Wang *et al*., 2014; Hanagata and Morita, 2015) .

A more of researchers prefer the ZnO nanoparticles powder because of it has the properties mentioned above. So, it can be used in different fields as: it used as a gas, chemical and biological sensors, it may be utilized as superconductors materials, photo reagent, optoelectronic parts, it is useful to light emitting diodes manufacture and solar cells to produce the rubber and cigarettes which it is utilized as a filter. It may be used in cosmetics materials as calamine lotion manufacturing or the host for several creams and ointments which are utilized in skin treatment. ZnO is a material enter the industrial field, since, it helps to concrete construct, ceramic manufacture, paints create, UV filters production. Zno is used in foodstuff as breakfast cereals (Swati and Mahendra, 2015; Wang *et al*., 2014; Hanley *et al*., 2009).

The styryl 9M dye had been used as an active medium for the dye laser and the pulsed operation of the styryl 9M dye laser had been employed using flashlamp pumping (Lin and Marshall, 1984). The picosecond pulses had been obtained from the continuous operation of the Styryl 9 dye laser by a hybrid technique for mode locking (Smith *et al*., 1984).

Styryl 9M is a 2-(6-(4-Dimethylaminophenyl)-2, 4-neopentylene-1, 3, 5-hexatrienyl)-3-methyl-benzothiazolium Perchlorat and the molecular structure $C_{27}H_{31}N_2O_4SCl$. Styryl 9M had the green, crystalline solid appearance and the absorption maximum in ethanol is 585 nm and the molar absorptivity is 5.05×10^4 L mol/cm.

In this research we will present a study of the particle size effect in the linear and non-linear optical properties for the thin films samples prepared from styryl 9M laser dye, hosted by PMMA polymer and doped with three different particles at four different concentrations.

MATERIALS AND METHODS

Theory

Absorption spectral properties: Absorption process can be happened when an incident photon crash the dye molecule in its lower energy state, the dye will be excited due to that the photon is absorbed and its energy is utilized in the dye excitation. This process can be occurred only if the incident photon energy equals to the energy difference between the two states the absorption take place at them.

Absorbance a can be defined as the logarithmic relative decrease of intensity. So, the wavelength at the maximum absorbance may be called as peak wavelength (nm) while the maximum absorbance can be named as peak absorbance (arb.unit) and the width of absorption (curve at the half value of maximum absorbance is termed as $(\Delta\nu)1/2$ ($\sec^{-1}$) which is calculated from the absorption spectrum (Elmer, 2000).

Linear optical properties: The linear optical properties related with linear optical response had been formulated as below: The Absorbance (A) describes the amount of absorbed photons by molecules can be written as (Nicholas, 2007):

$$A = 1\text{-}\log\left(\frac{1}{T}\right) \quad (1)$$

where, T is the transmittance of medium which is related with refractive index n as (Nicholas, 2007):

$$T = \frac{2n}{n^2+1} \quad (2)$$

The absorption coefficient α of an optical medium can be related to the A absorbance according to Eq. 3 (Ara *et al*., 2010):

$$\alpha = \frac{1}{2.302\ A} \quad (3)$$

The effective length of an optical medium can be calculated by Eq. 4 (Ara *et al*., 2010):

$$L_{eff} = \frac{\left(1\text{-}\exp^{-\alpha L}\right)}{\alpha} \quad (4)$$

Where:

L = The Length of a sample

α = The absorption coefficient

Non-linear optical properties: Some of materials severe from the nonlinear effects as Kerr nonlinearity which is a change in the refractive index of a material in response to an applied electric field.

The Z-scan techniqueis used to measure the non-linear refractive index and the non-linear absorption coefficient using the closed and open aperture, respectively. The closed aperture form helps in determining the small distortions in the incident beam on the non-linear medium which behaves as a small non-linear lens and in measuring the non-linear refractive index as shown in Fig. 1a where illustrates the construction of a closed aperture and the diagram of the possible measured data of the normalized transmittance using it.

The open aperture Z-scan is used for measuring the non-linear absorption coefficient as the whole laser beam may be allowed to incident on the detector and the small distortions can be neglect. Figure 1b illustrates the construction of a Z-scan with open aperture and the diagram of the possible measured data of the normalized transmittance using it.

There are some of the changes must be taken into account in the study of the non-linear coefficients as: the non-linear response of the medium due to the laser beam in limited region laser spot area on the medium may be affected by the laser beam intensity in the surrounding regions. This effect can be named asnon local response. The other effect appears in the liquid samples of the colloid non-linear medium in the dielectric solution, the photonic incident field in the non-local points of a medium induces many changes as reorientation of the molecular dipoles due to the changes in the electric fields in different parts of a non-linear medium (Ali and Mahdi, 2012). The non-linear refractive index can be calculated using Eq. 5:

$$n_2 = \frac{\Delta\Phi_o}{I_o L_{eff}\ k} \quad (5)$$

Where:

- I_o = The incident laser intensity
- K = The wavenumber of the incident laser beam, equals to $K = 2\pi/\lambda$
- λ = The wavelength of the incident laser beam
- $\Delta\phi_o$ = The non-linear phase shift and equals to (Ara *et al.*, 2010; Ali and Mahdi, 2012; Ao *et al.*, 2015):

$$\Delta T_{p\text{-}v} = 0.406\left|\Delta\Phi_o\right| \quad (6)$$

where, $\Delta T_{p\text{-}v}$ is the normalized transmittance difference between the top and the valley transmittance values which can be calculated using closed aperture Z-scan setup. The nonlinear absorption coefficient β may be calculated using Eq. 7 (Ara *et al.*, 2010; Ali and Mahdi, 2012; Ao *et al.*, 2015):

(a)

(b)

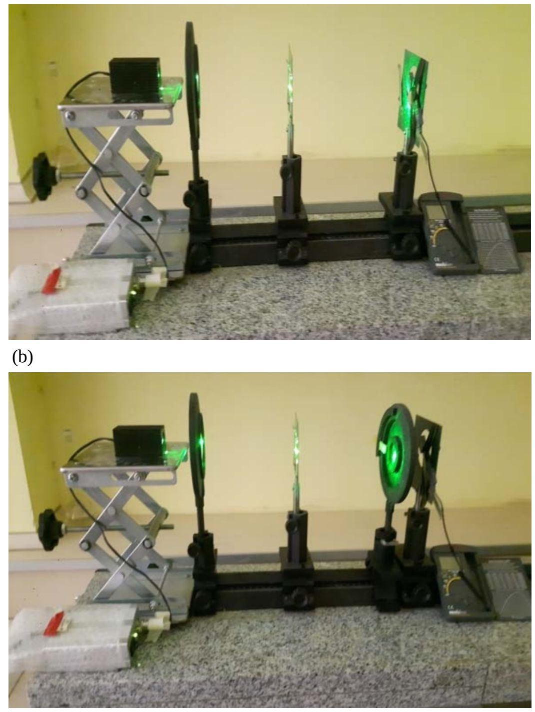

Fig. 1: The construction of a Z-scan with two different designs and the diagram of the possible measured data of the normalized transmittance using them used in this research: a) Closed aperture and b) Open aperture

$$\beta = \frac{2\sqrt{2}T(Z)}{I_o L_{eff}} \quad (7)$$

Since, T(Z) means the minimum normalized transmittance obtained using open aperture Z-scan setup.

Experimental setup: A four different concentrations of styryl 9M laser dye MW = 515.06 g/mol, product of USA, Sigma-Aldrich had been prepared by weighting 0.001 g using digital balance model-HR-200, made in Japan from laser dye. This weight had been dissolved in 10 mL of chloroform solvent D-30926 seelze, Sigma-Aldrich Laborchemikalien GmbH, Germany and diluted to obtain 10^{-4}-10^{-6}) mol/L concentrations. To perform a homogeneous solution, A magnetic stirrer model-HP-3000, lab. companion had been used.

A 10^{-3} mol/L molar concentration of styryl 9M laser dye R 6626-25G, product of USA, Sigma-Aldrich had been prepared by weighting 0.001 g using digital balance Model-HR-200, made in Japan from laser dye. This weight had been dissolved in 10 mL of chloroform solvent D- 30926 seelze, Sigma-Aldrich Laborchemikalien GmbH, Germany. A 0.1 g of PMMA polymer Sc-255435, Santa

Cruz Biotechnology, Dallas had been added to the dye solution. A 4 different weights of Ag nano particles MW = 107.87 g/mol, mp = 960 C, product of USA, Sigma-Aldrich, CAS = 7440-22-4 and ZnO nano particles of particle size of 10-30 nm, Sky Spring Nanomaterials, Inc., SSNANO, made in USA at 0.02, 0.04, 0.06 and 0.08 g had been weighted using the same balance and added to the dye mixtures. So, a four different mixtures were obtained, contain 10^{-3} mol/L styrB, styryl 9M laser dye, 0.1 g PMMA and TiO_2 microparticles, Ag and ZnO nanoparticles. To perform a homogeneous solution, A magnetic stirrer Model-HP-3000, Lab and companion had been used.

These mixtures had been prepared as a thin films using drop casting method. Figure 2-4 show the pictures for the prepared thin films.

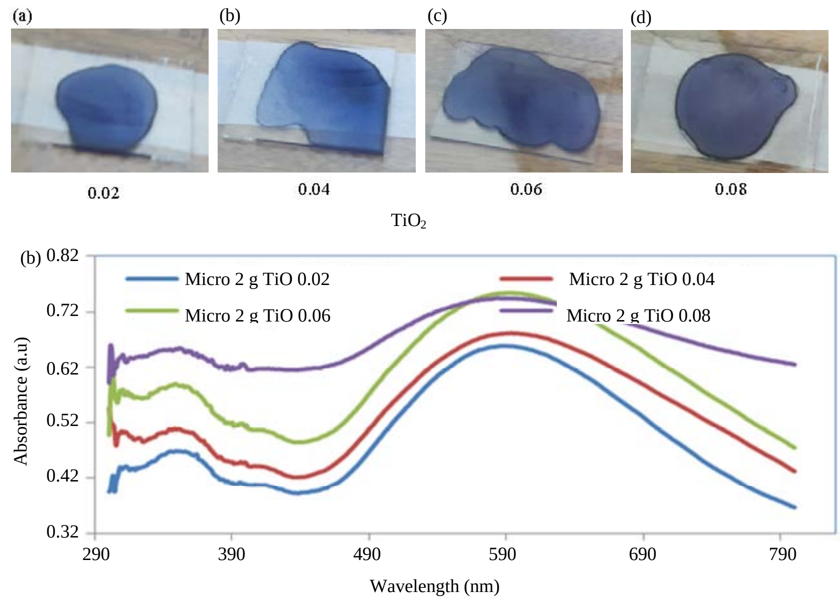

Fig. 2: a-d) The pictures for the prepared thin films of 10^{-3} mol/L styryl 9M, 0.1 g PMMA and TiO_2 microparticles and e) The absorbance spectrum for them

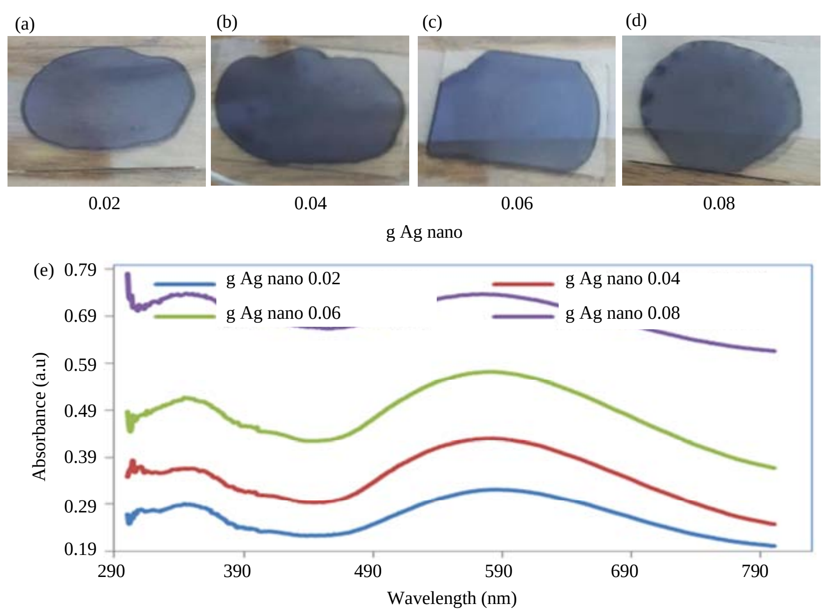

Fig. 3: a-d) The pictures for the prepared thin films of 10^{-3} mol/L styryl 9M, 0.1 g PMMA and Ag nanoparticles and e) The absorbance spectrum for them

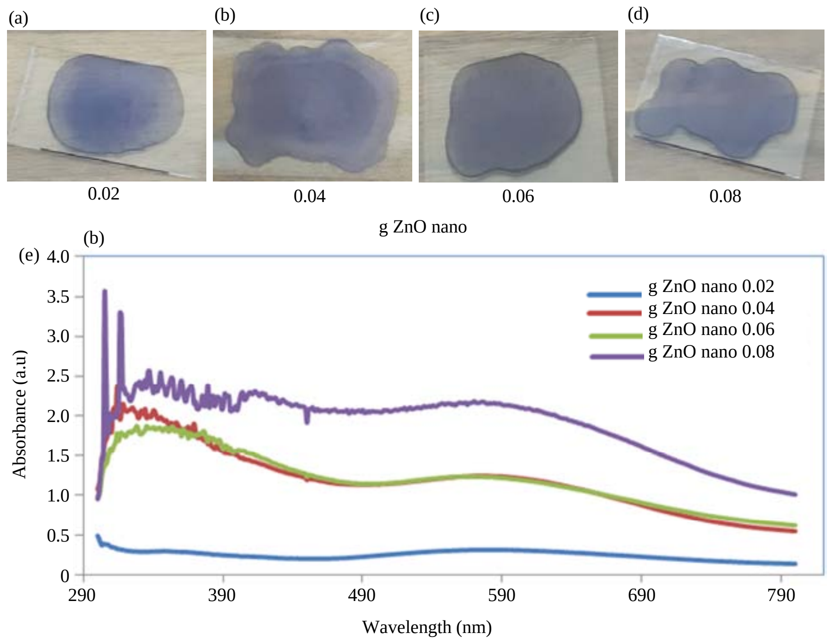

Fig. 4: a-d) The pictures for the prepared thin films of 10^{-3} mol/L styryl 9M, 0.1 g PMMA and ZnO nanoparticles and e) The absorbance spectrum for them

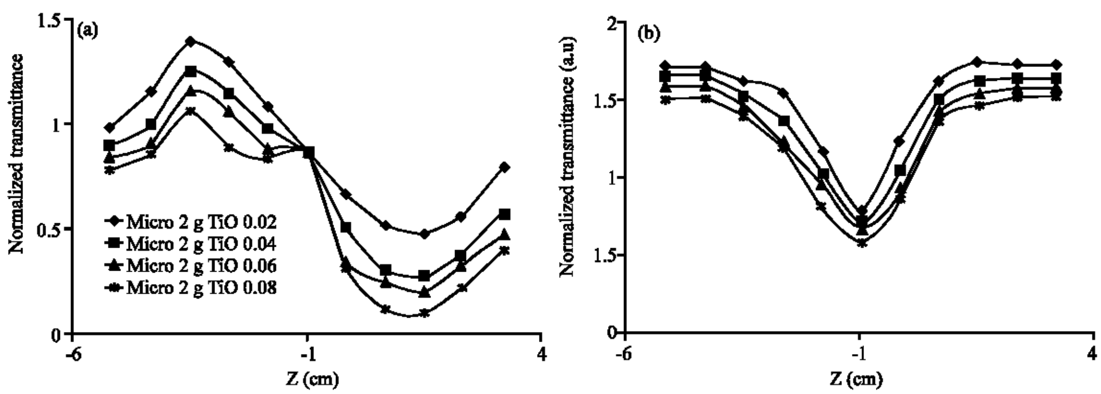

Fig. 5: The normalized transmittance for thin film samples of 10^{-3} styryl 9M, 0.1 g PMMA and different weights of TiO_2 micro particles using Z-scan setup of: a) Closed aperture and b) Open aperture

Figure 3 and 4, the absorption spectrum for thin films samples had been recorded using UV-Vis spectrophotometer Scinco, Mega -2100, made in Korea and Fig. 5 shows the absorption spectrum for these samples.

The used Z-scan set up as described in above paragraph, contained from SHG-Nd: YAG laser at 532 nm (green light) as a laser source had been focused to a sample using a lens of 15 cm focal length where the radius of laser spot was 0.05 cm and the incident laser intensity on the sample of 778 W/m^2. The normalized transmittance can be measured using a laser power meter LP1-mobiken.

The normalized transmittance data for the prepared thin film samples of 4 cm length and 1 mm thickness, contained from 10^{-3} styryl 9M laser dye, 0.1 g PMMA and different weights of Ag nano particles had been measured using Z-scan setup of closed aperture and open aperture with aid of Laser Power meter (LP1- mobiken) and had been plotted in Fig. 1, closed aperture and open aperture.

The normalized transmittance data for the prepared thin film samples of (10^{-3} styryl 9M, 0.1 g PMMA and different weights of TiO_2 micro particles) are measured using Z-scan setup had been plotted in Fig. 5 closed aperture and open aperture. The normalized transmittance

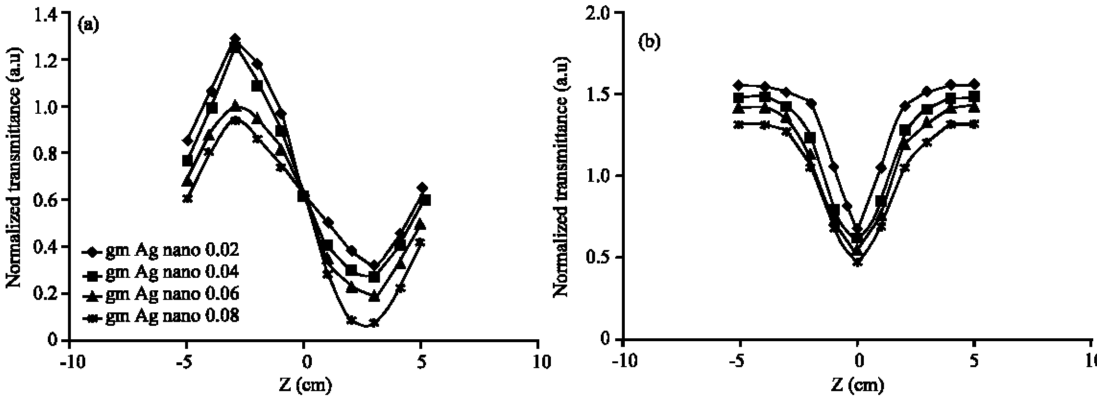

Fig. 6: The normalized transmittance for thin film samples of 10-3 styryl 9M, 0.1 g PMMA and different weights of Ag nano particles using Z-scan setup of: a) Closed aperture and b) Open aperture

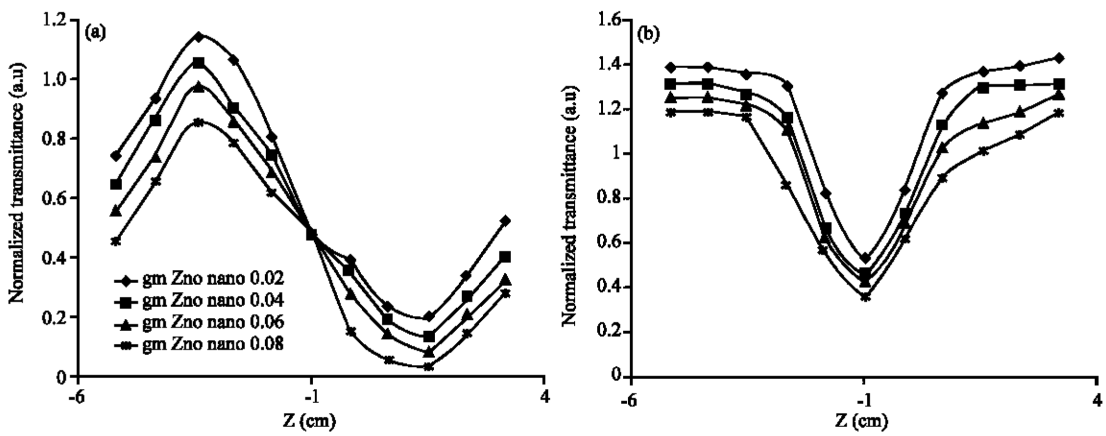

Fig. 7: The normalized transmittance for thin film samples of 10-3 styryl 9M, 0.1 g PMMA and different weights of ZnO nano particles using Z-scan setup of: a) Closed aperture and b) Open aperture

data for the prepared thin film samples of 10^{-3} styryl 9M, 0.1 g PMMA and different weights of Ag nano particles are measured using Z-scan setup had been plotted in Fig. 6 and 7 closed aperture and open aperture. The normalized transmittance data for the prepared thin film samples of 10^{-3} styryl 9M, 0.1 g PMMA and different weights of ZnO nano particles are measured using Z-scan setup had been plotted in Fig. 7: closed aperture and open aperture.

RESULTS AND DISCUSSION

According to the absorption spectrums shown in Fig. 4, the absorption spectrum characteristics for thin films of 10^{-3} styryl 9M laser dye, 0.1 g PMMA and different types of nanoparticles, like peak wavelength nm, peak absorbance arb.unit and sec^{-1} had been listed in Table 2.

The linear optical parameters for thin film samples of 10^{-3} Styryl 9M, 0.1 g PMMA and different weights micro and nano particles are dependent in non-linear optical properties had been shown in Table 3.

The non-linear optical parameters such as (Transmittance difference ($\Delta T_{p\text{-}v}$), non-linear phase shift ($\Delta\Phi_o$), non-linear refractive index (n_2), minimum normalized transmittance T(Z) and non-linear absorption coefficient (β)) for thin film samples of (10^{-3} styryl 9 M, 0.1 g PMMA and different types of nano particles) had been calculated according to the measured data of normalized transmittance using Z-Scan setup of both closed aperture and open aperture and the equations of non-linear optical properties. These non-linear optical coefficients had been listed in Table 4.

The normalized transmittance data for thin film samples of 10^{-3} styryl 9M, 0.1 g PMMA and Ag nano particles with a good agreement with the published data by Ara *et al*. (2010).

The normalized transmittance data for thin film samples of 10^{-3} styryl 9M, 0.1 g PMMA and ZnO nano

Table 2: Absorption spectrum characteristics for thin films of 10^{-3} styryl 9M laser dye, 0.1 g PMMA and three different types of particles

	Peak wavelength (nm)			Peak absorbance (arb.unit)			$(\Delta\nu)1/2\ sec^{-1}\times10^{+15}$		
Weights of Ag nano particles (g)	TiO_2	Ag	ZnO	TiO_2	Ag	ZnO	TiO_2	Ag	ZnO
0.02 g	590	590	570	0.165	0.107	0.077	1.33	1.66	1.5
0.04 g	600	592	580	0.17	0.123	0.315	1.46	1.69	2.8
0.06 g	602	594	585	0.185	0.145	0.325	1.5	1.74	3.01
0.08 g	604	596	590	0.187	0.185	0.537	1.57	1.87	3.33

Table 3: The linear optical parameters for thin film samples of (10^{-3} styryl 9M, 0.1 g PMMA and different weights micro and nano particles) are dependent in non-linear optical properties

Particles	Weights of particles (g)	Absorbance (A)	Transmittance (T)	Absorption coefficient (α)	Refractive index (n)	Effective length L_{eff} (m)
TiO_2 micro particle	0.02	0.165	0.683	2.632	2.533	0.0395
	0.04	0.170	0.676	2.555	2.569	0.0396
	0.06	0.185	0.653	2.348	2.691	0.0396
	0.08	0.187	0.650	2.323	2.707	0.0396
Ag nano particles	0.02	0.107	0.781	4.059	2.080	0.0396
	0.04	0.123	0.753	3.531	2.201	0.0395
	0.06	0.145	0.716	2.995	2.371	0.0395
	0.08	0.185	0.653	2.348	2.691	0.0395
ZnO nano particles	0.02	0.077	0.837	5.641	1.848	0.0394
	0.04	0.315	0.484	1.379	5.230	0.0396
	0.06	0.325	0.473	1.336	5.396	0.0396
	0.08	0.537	0.290	0.808	6.739	0.0396

Table 4: The non-linear optical parameters for thin film samples of (10^{-3} styryl 9M, 0.1 g PMMA and different types of micro and nano particles) using Z-scan setup of both closed aperture and open aperture

Nano particle	Weights of particles (g)	Transmittance difference (Δt_{p-v})	Non-linear phase shift ($\Delta\Phi_0$)	Non-linear refractive index n_2 ($\times10^{-9}$)	Minimum normalized transmittance T(Z)	Non-linear absorption coefficient (β)
TiO_2 micro particle	0.02	0.90	2.216	6.113	0.78	0.071
	0.04	0.97	2.389	6.572	0.7	0.064
	0.06	0.95	2.339	6.437	0.67	0.061
	0.08	0.96	2.364	6.504	0.58	0.053
Ag nano particles	0.02	0.94	2.315	6.369	0.7	0.064
	0.04	0.95	2.339	6.453	0.62	0.057
	0.06	0.81	1.995	5.501	0.57	0.052
	0.08	0.86	2.118	5.841	0.5	0.046
ZnO nano particles	0.02	0.89	2.192	6.062	0.57	0.052
	0.04	0.87	2.142	5.894	0.5	0.045
	0.06	0.84	2.068	5.691	0.47	0.043
	0.08	0.78	1.921	5.287	0.39	0.035

particles with a good agreement with the published data by Ning *et al.* (2008) and Al-Sultani (2017).

The results in Table 4 illustrate that the increasing in the nanoparticles weights increases both of absorbance and refractive index while it decreases both of transmittance and absorption coefficient. This behavior is attributed to that the highest number of scattering particles consolidates the absorption process with scattering process and makes this medium has more optical density which causes highest refraction.

It is shown from Table 4 that, the Transmittance difference (ΔT_{p-v}), non-linear phase shift ($\Delta\Phi_o$), non-linear refractive index (n_2) are increased with the increasing of nanoparticles weights while both of minimum normalized Transmittance T(Z) and non-linear absorption coefficient (β) are decreased non-linear optical properties are decreased with increasing of nanoparticles weights because of highly multiple scattering for high scatters medium.

It had been clear noticed that the TiO_2 micro particles give highest non-linear optical properties than Ag nanoparticles and the ZnO nanoparticles have the lowest values of nonlinear optical properties compared with TiO_2 micro particles and Ag nanoparticles. While ZnO nanoparticles give more linear optical properties than Ag nanoparticles and the TiO_2 have less values of linear optical properties than Ag and ZnO nanoparticles. This can be attributed to the particle size which explains that the smallest particle causes a highly increasing in nonlinear absorption coefficient and nonlinear refractive index in vice inverse with the largest particles have highly linear absorption coefficient and linear refractive index.

It had been shown from the linear and nonlinear optical properties data and the properties of micro and nanoparticles in Table 1, that ZnO nanoparticles have the highest values for both of density, melting point and it have less values for both of dielectric constant and thermal conductivity. That is the main reason to Zno nanoparticles have the highest nonlinear optical properties as well as the smallest particle size. The TiO_2 micro particles have the highest values of boiling point, so, this is the reason to the thin films samples are contained them give more linear optical properties than ZnO and Ag nanoparticles as well as the largest particles size.

CONCLUSION

It can be concluded that the nanoparticles are the main reason to more nonlinear response to laser fields. The two photon or reverse saturation absorption or the saturation absorption are main nonlinear effects controlled the less values of nonlinear absorption coefficient. The main conclusion is that the ZnO nanoparticles causes highest nonlinear optical response due to the smallest values for each of particle size, dielectric constant and thermal conductivity. TiO_2 micro particles have more linear optical properties due to that they possessing larger particle size and lowest density.

REFERENCES

Al-Sultani, M.M.M., 2017. The study of a linear and non-linear optical property for PMMA thin films doped with the rhodamine B laser dye and Ag nano particles are used in medicine. J. Global Pharma Technol., 9: 207-213.

Ali, A.A. and Z.F. Mahdi, 2012. Investigation of nonlinear optical properties for laser dyes-doped polymer thin film. Iraqi J. Phys., 10: 54-69.

Ao, G., Z. Xiao, X. Qian, Z. Li and Y. Wang *et al*., 2015. Nonlinear optical properties tuning in meso-tetraphenylporphyrin derivatives substituted with donor/acceptor groups in picosecond and nanosecond regimes. Mol., 20: 5554-5565.

Ara, M.M., Z. Dehghani, R. Sahraei and G. Nabiyouni, 2010. Non-linear optical properties of silver nanoparticles prepared by hydrogen reduction method. Opt. Commun., 283: 1650-1653.

Brennan, S.A., C.N. Fhoghlu, B.M. Devitt, F.J. O'Mahony and D. Brabazon *et al*., 2015. Silver nanoparticles and their orthopaedic applications. Bone Joint J., 97: 582-589.

Dong, X., X. Ji, J. Jing, M. Li and J. Li *et al*., 2010. Synthesis of triangular silver nanoprisms by stepwise reduction of sodium borohydride and trisodium citrate. J. Phys. Chem. C., 114: 2070-2074.

Elmer, P., 2000. An Introduction to Fluorescence Spectroscopy. PerkinElmer Inc., Waltham, Massachusetts, USA.

Fujishima, A. and K. Honda, 1972. Electrochemical photolysis of water at a semiconductor electrode. Nature, 238: 37-38.

Graf, C., D.L. Vossen, A. Imhof and A.V. Blaaderen, 2003. A general method to coat colloidal particles with silica. Langmuir, 19: 6693-6700.

Hanagata, N. and H. Morita, 2015. Calcium ions rescue human lung epithelial cells from the toxicity of Zinc Oxide nanoparticles. J. toxicol. Sci., 40: 625-635.

Hanley, C., A. Thurber, C. Hanna, A. Punnoose and J. Zhang *et al*., 2009. The influences of cell type and ZnO nanoparticle size on immune cell cytotoxicity and cytokine induction. Nanoscale Res. Lett., 4: 1409-1420.

Heim, J., E. Felder, M.N. Tahir, A. Kaltbeitzel and U.R. Heinrich *et al*., 2015. Genotoxic effects of zinc oxide nanoparticles. Nanoscale, 7: 8931-8938.

Jones, B.J., M.J. Vergne, D.M. Bunk, L.E. Locascio and M.A. Hayes, 2007. Cleavage of peptides and proteins using light-generated radicals from titanium dioxide. Anal. Chem., 79: 1327-1332.

Kim, Y.H., K.A. Kwak, T.S. Kim, J.H. Seok and H.S. Roh *et al*., 2015. Retinopathy induced by zinc oxide nanoparticles in rats assessed by micro-computed tomography and histopathology. Toxicol. Res., 31: 157-163.

Kurtoglu, M.E., T. Longenbach and Y. Gogotsi, 2011. Preventing sodium poisoning of photocatalytic TiO_2 films on glass by metal doping. Intl. J. Appl. Glass Sci., 2: 108-116.

Latroche, M., L. Brohan, R. Marchand and M. Tournoux, 1989. New hollandite oxides: TiO_2(H) and $K_{0.06}TiO_2$. J. Solid State Chemi., 81: 78-82.

Lin, C.H. and B. Marshall, 1984. Flashlamp-pumped styryl 9 dye laser. Appl. Opt., 23: 2228-2228.

Mitchnick, M.A., D. Fairhurst and S.R. Pinnell, 1999. Microfine zinc oxide (Z-cote) as a photostable UVA/UVB sunblock agent. J. Am. Acad. Dermatol., 40: 85-90.

Nicholas, M., 2007. Electromagnetic spectrum: Transmittance, absorbance and reflectance. RST Instruments Ltd., Maple Ridge, British Columbia.

Ning, T., Y. Zhou, H. Shen, H. Lu and Z. Sun *et al*., 2008. Nonlinear optical properties of Au/ZnO nanoparticle arrays. Appl. Surf. Sci., 254: 1900-1903.

Pietrobon, B., M. McEachran and V. Kitaev, 2008. Synthesis of size-controlled faceted pentagonal silver nanorods with tunable plasmonic properties and self-assembly of these nanorods. ACS. Nano, 3: 21-26.

Sato, H., S. Endo, M. Sugiyama, T. Kikegawa and O. Shimomura *et al*., 1991. Baddeleyite-type high-pressure phase of TiO_2. Sci., 251: 786-788.

Shan, Z., J. Wu, F. Xu, F.Q. Huang and H. Ding, 2008. Highly effective silver/semiconductor photocatalytic composites prepared by a silver mirror reaction. J. Phys. Chem. C., 112: 15423-15428.

Smith, K., W. Sibbett and J.R. Taylor, 1984. Subpicosecond generation via hybrid mode-locking of Styryl 9 in the near infra-red. Opt. Commun., 49: 359-361.

Swati, S.K. and D.S. Mahendra, 2015. Optical and structural properties of Zinc Oxide nanoparticles. Intl. J. Adv. Res. Phys. Sci., 2: 14-18.

Wang, B., Y. Zhang, Z. Mao, D. Yu and C. Gao, 2014. Toxicity of ZnO nanoparticles to macrophages due to cell uptake and intracellular release of zinc ions. J. Nanosci. Nanotechnol., 14: 5688-5696.

Wiley, B., Y. Sun and Y. Xia, 2007. Synthesis of silver nanostructures with controlled shapes and properties. Acc. Chem. Res., 40: 1067-1076.

Zhang, Q., W. Li, C. Moran, J. Zeng and J. Chen *et al*., 2010. Seed-mediated synthesis of Ag nanocubes with controllable edge lengths in the range of 30-200 nm and comparison of their optical properties. J. Am. Chem. Soc., 132: 11372-11378.