Journal of Theoretical and Applied Physics (JTAP), Vol.16, No. 3, 162231 (1-6), 2022
Received 8 March 2022 ; Accepted 21 July 2022 ; [http://dx.doi.org/10.30495/jtap.162231]

Study of the nonlinear optical properties of platinum and gold nanoparticles

Mina Eslamifar

Abstract
This work presents a study on the thermo-optical properties of colloidal gold nanoparticles (AuNPs) and platinum nanoparticles (PtNPs) under a low power laser irradiation at 532 nm. Samples of gold and platinum were synthesized by nanosecond pulsed laser ablation of pure gold and platinum plates in the distilled water. The formation of the AuNPs and PtNPs was evidenced by optical absorption spectra and transmission electron microscopy. The thermo-optical properties of AuNPs and PtNPs were studied using Z-scan technique. The nonlinear optical measurments exhibited a very large nonlinear refraction close to the surface plasmon resonance frequency of the nanoparticles. Our results revealed that the diffusion in the colloids is due to nonlocal thermal process. This work suggests that thermal nonlinear refraction will play an important role in development of photonic application involving metal nanoparticles colloids.

Keywords
Platinum nanoparticles, Gold nanoparticles, Thermo-optical properties, Nonlinear refraction.

Physics Department, Behbahan Khatam Alanbia University of Technology, Behbahan, Iran
***Corresponding author**: eslamifar@bkatu.ac.ir

1. Introduction

The increasing availability of nanostructures with highly controlled nonlinear optical properties has created widespread interest in different fields such as photonics devices [1–3], photo-thermal therapy [4] and cooling systems [5]. Temperature change within and around metal nanoparticles may lead to high third order nonlinear refractive index of the medium [6]. It has demonstrated that metallic nanoparticles improve nonlinear optical properties of colloids [7–9]. As a result, these materials can be a good candidate for many nonlinear optical devices such as optical limiting and optical switching [10, 11]. Recently, various nanoscale metals have been extensively studied for their application as an optical limiter toward nanosecond laser pulses at 532 nm due to the enhancement in nonlinear optical properties [11–18]. So far, metal nanoparticles have been successfully fabricated by a variety of methods, such as chemical reduction, ultraviolet photochemistry and laser ablation. It has been shown that pulsed laser ablation of metal targets in liquid environment is a simple technique to synthesize nanoparticles [19–21]. Laser ablation in liquids has received much attention as an effective technique for producing various nanoparticles such as metals [19–27], metal oxides [28, 29] and semiconductors [30–32].
While there have been many reports on the nonlinear optical properties of metal nanoparticle colloids, few have been investigated under continuous laser irradiation. The nonlinear refractive index of metal nanoparticles is very sensitive to the pulse length of the laser beam. The heat effect has been shown to be effective even for nanosecond pulses. In studying the effects of thermal nonlinear optical on materials, the coefficient of thermal nonlinear refractive index is an important physical quantity. Therefore, researching the thermal nonlinear optical properties of metal nanoparticles is valuable.
On the other hand, most reports on the thermal nonlinear optical properties in the CW regime are based on compounds of metal nanoparticles such as silver sulfide nanoparticles [33], cadmium sulfide nanocrystals [34] and phosphate nanoparticles [35]. The necessity of research and study on the thermal nonlinear optical behaviors of metal nanoparticles requires.
In this work, we report on the experimental investigation of thermo-optic nonlinear response of colloids containing gold and platinum nanoparticles. Using the Z-scan technique, the behavior of the thermal nonlinear refractive index of colloids is studied and compared. Asymmetrical configuration of the Z-scan data indicates that nonlinear refraction occurring in the samples is related to the thermo-optic process [36].The results are analyzed based on nonlocal thermo-optic models [37, 38]. It will be shown that the thin thermal lens model is in excellent agreement with the experimental results. Fits have allowed extracting the values of nonlinear refractive index coefficient of the samples.

2. Experimental procedure

Gold and platinum nanoparticle colloids were prepared by nanosecond pulsed laser ablation of pure gold and platinum plates in distilled water. The laser ablation of samples was carried out using a Q-switched Nd:YAG laser operating at fundamental wavelength. The laser generated 18 ns (full-

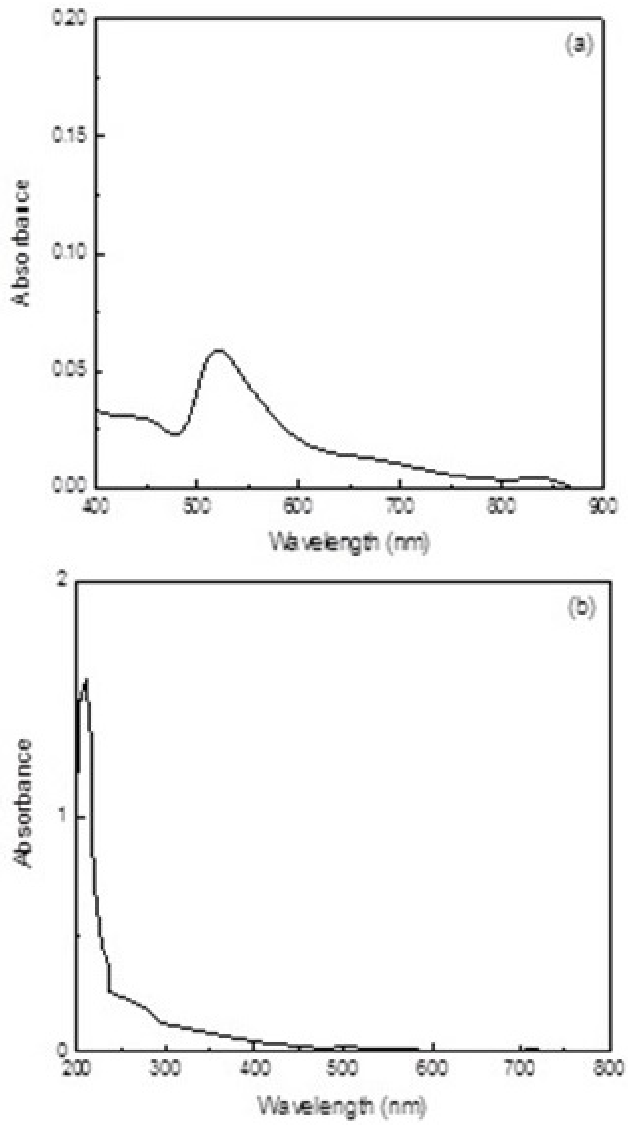

Figure 1. (a) Absorption spectrum of gold nanoparticles, (b) Absorption spectrum of platinum nanoparticles in the water.

width at half maximum, FWHM) pulses at 1064 nm with a repetition rate of 1 Hz. The laser beam was focused by a 50 cm focal length lens on the surface of gold and platinum plates placed inside a 10 mm cell. The samples were irradiated with the laser fluence level of about 200 mJ/cm^2 for one hour. The volume fraction of the platinum and gold nanoparticles was 0.02×10^{-3} and 0.45×10^{-3}, respectively. The volume fraction, φ_V, of the nanoparticles is defined by

$$\varphi_V = \frac{V_S}{V_S + V_L} \tag{1}$$

where V_S is the volume of the particles and V_L is the volume of the liquid. The volume of the nanoparticles is $V_S = m/\rho$, ρ is the mass density and m is the mass of the particles dispersed in the liquid. Transmission electron microscopy (JEOL JEM-2000EXII) was carried out to determine the size distribution and shape of nanoparticles. The prepared platinum and gold nanoparticles were studied using an UV-Vis optical absorption spectrophotometer, (Shimadzu UV-1200 spectrometer). A continuous wave low power (100 mW) diode-pumped Nd:YVO_4 laser operating at wavelength of 532 nm was used to measure the nonlinear absorption coefficient of the colloids. The nonlinear optical properties of AuNP and PtNP colloids were also studied by transmittance and the Z-scan measurements using this laser. For the open Z-scan measurements, the optical geometry used in this work is shown in [39]. An attenuator and a beam splitter were used to control the power of the laser beam. The beam was focused onto the sample (5 mm cell) by using a lens with 50 cm focal length. The nanoparticle-containing cell 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 gradually decrease in either direction from the focus.

3. Results and discussion

Figures 1 show UV-vis absorption spectrum of the colloids of gold and platinum nanoparticles prepared by laser ablation of gold and platinum plates immersed in the water. The AuNP and PtNP samples show typical surface plasmon absorption (SPA) peak about 540 nm and 210 nm respectively.

The shape and size distribution of the nanoparticles are studied by TEM and the measurements conducted just after laser ablation. Figure 2 presents the TEM image and size distribution of gold and platinum nanoparticles in the water. Average gold and platinum nanoparticles radius is found to be about 7 nm and 9 nm with a standard deviation of 3 nm. The nanoparticles are spherical in shape.

Figure 3 shows transmission measurements of the PtNP colloids (●), water (■) and AuNP colloids (▲), under exposure to low power laser at 532 nm. Up to the applied laser power of 90 mW, we have not measured any nonlinear absorption in the tested samples. The solid curves are fitted based on linear absorption theory and the absorption coefficients of the water and the AuNPs and PtNPs dispersed in the water are found to be 0.11, 0.23 and 0.16 cm^{-1}, respectively. We have also experimentally investigated nonlinear absorption of the water and the colloids using the open Z-scan measurements by low power laser at 532 nm. The measurements do not show any nonlinear absorption in the all tested colloids.

The closed aperture Z-scan technique allowed us to determine the value of the thermal nonlinear refractive index of the AuNPs and PtNPs colloids. The setup used for determination of the nonlinear refractive index is sketched on figure 4 [40]. The experimental data were recorded by gradually moving the sample along the axis of propagation (z-axis) of a focused Gaussian beam through its focal plane and measuring the transmission of the sample for each z-position.

As the sample experiences different intensities at different positions, the recording of transmission as a function of z

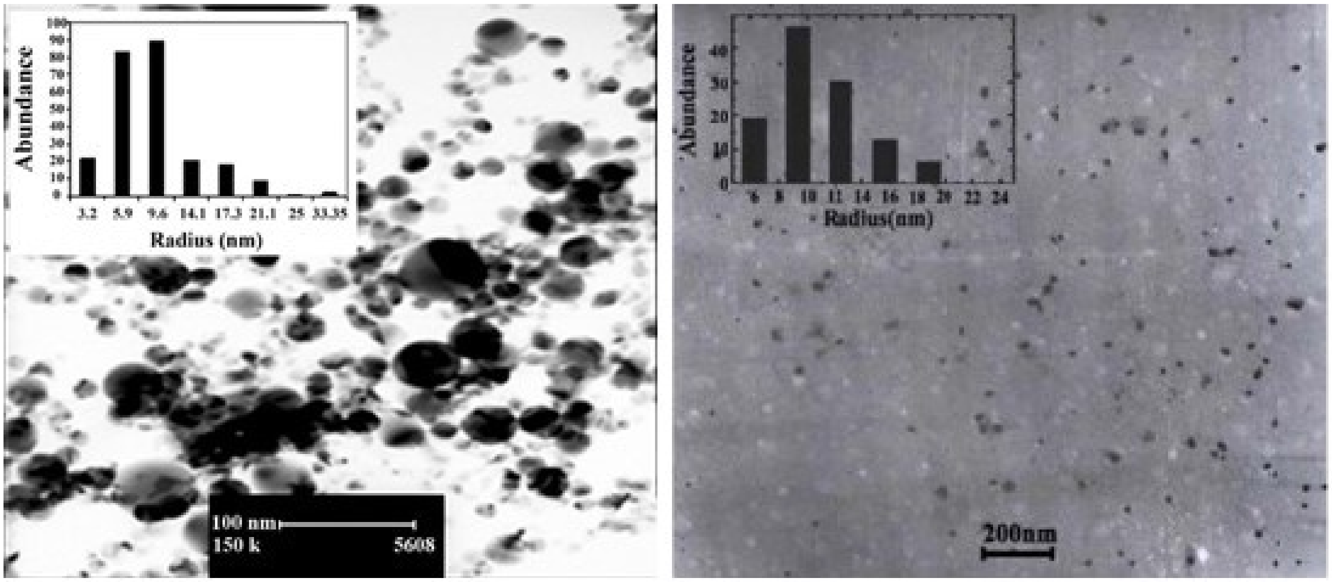

Figure 2. TEM images and size distribution of the (a) platinum and (b) gold nanoparticles in the water.

coordinate provides accurate information about the presence nonlinear refraction effect. Figures 5(a) and 5(b) show the normalized transmittance of Z-scan measurements as a function of distance from the focus of the Gaussian beam at applied incident laser power of 40 mW for the colloids. The Z-scan results of the samples exhibit an asymmetric peak followed by valley, typical of negative nonlinearity for refractive index. Generally speaking, such a behavior is observed when nonlinear materials are submitted to ultrashort laser pulses [41]. The observed asymmetric nature of the Z-scan measurements along with the fact that the laser light is CW suggests that the origin of the nonlinear refractive index is thermo-optic [42]. The pure liquid of the water does not show any closed Z-scan signal for the applied laser power up to about 40 mW.

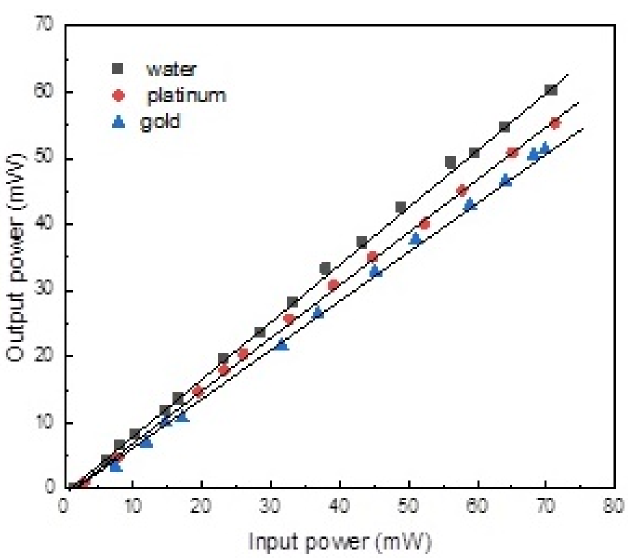

Figure 3. Transmittance measurement of the water, platinum nanoparticles and gold nanoparticles in the water.

Our experimental results for the closed Z-scan measurement of PtNP and AuNP colloids [figures 6(a) and 6(b)] cannot be explained with the Sheik-Bahae formalism [43]. An essential feature of this formalism in analyzing the transmittance is assumption of a local interaction between the radiation light and the sample. It is assumed that the susceptibility is a function of only the local intensity. But in this case, the focused CW laser beam is absorbed by the sample and immediately give rise to local heating followed by process of heat diffusion in the medium. The heat diffusion takes place and produced a spatial temperature distribution in the sample. The induced spatial temperature profile can differ significantly from the applied Gaussian laser intensity. As a result, a nonlocal interaction between the radiation light and the sample must be considered for analyzing the closed Z-scan measurement results [37,38].

Cuppo et al have reported that the thermal nonlinear phase shift under continuous laser illumination could be determined by the well-known closed Z-scan measurements based on the thermal lens model of Gordon et al. In their model, the induced thermal nonlinear effect in the medium is treated as an

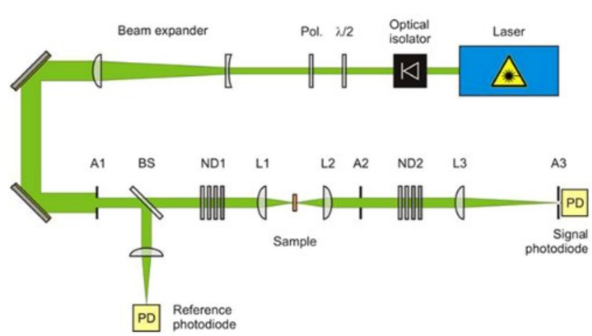

Figure 4. The closed Z-scan optical set up.

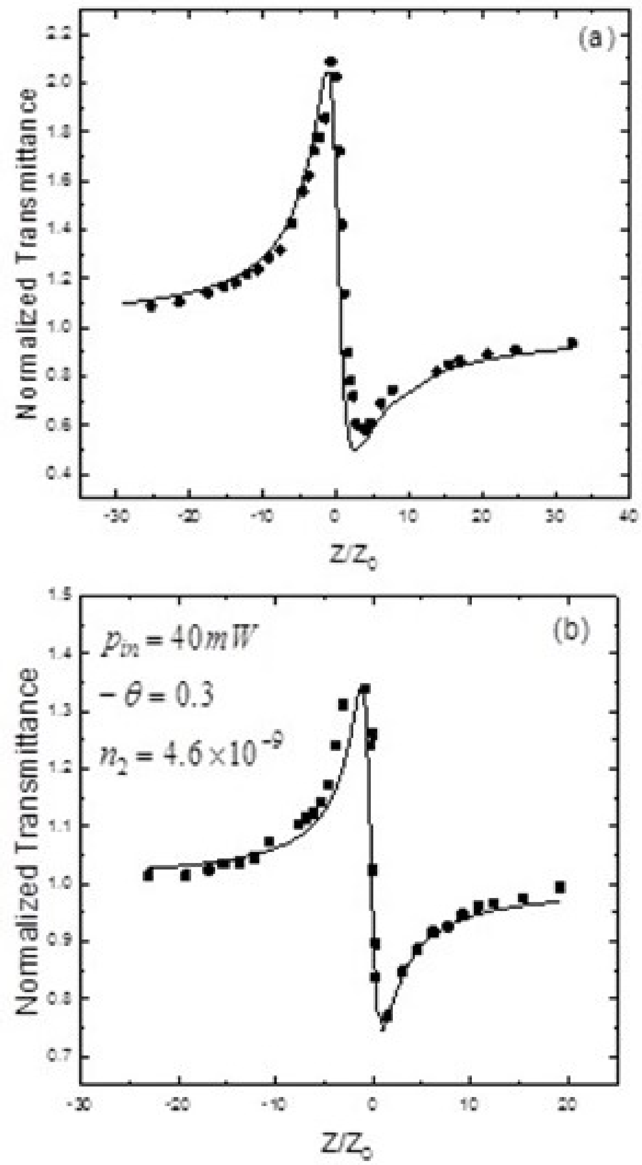

Figure 5. Experimental results of the normalized closed aperture Z-scan measurement of the (a) platinum nanoparticles and (b) gold nanoparticles in the water.

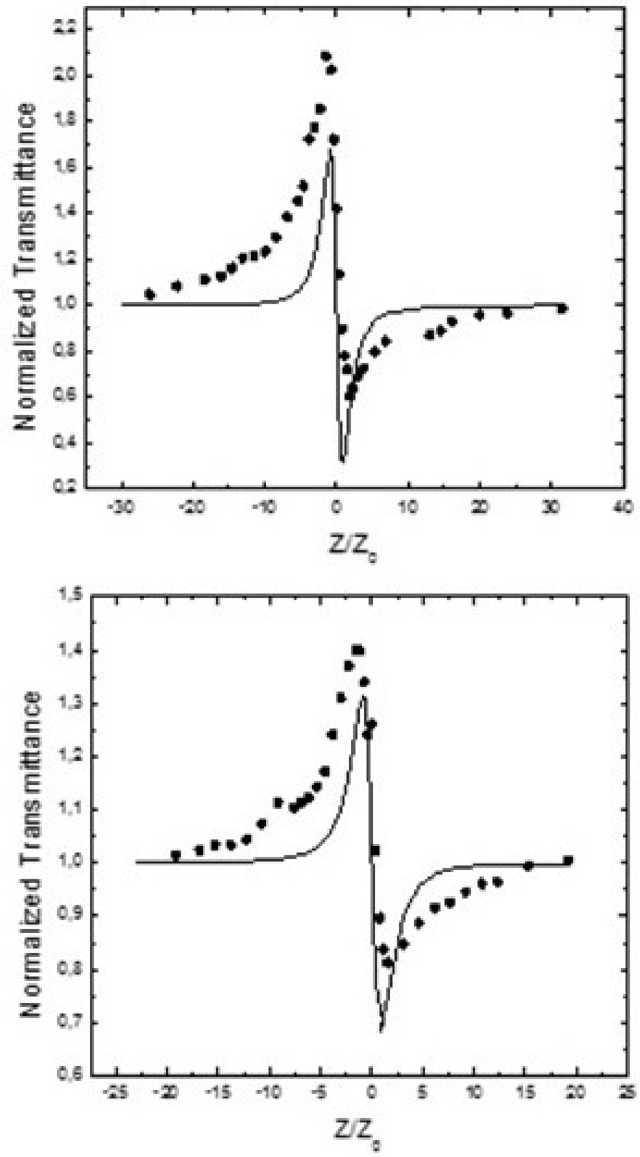

Figure 6. The solide curves are the fit using the phase shift calculation based on the Sheik-Bahae model.

ideal thin lens with the parabolic description of the temperature field. It is compared the goodness of the prediction of the model to the experimental data. In the parabolic model, the normalized transmittance for closed aperture Z-scan is [37] and [44]

$$T(\frac{Z}{Z_0},t) = \{1+\theta\frac{2\frac{Z}{Z_0}}{1+(\frac{Z}{Z_0})^2}+\theta^2\frac{1}{1+(\frac{Z}{Z_0})^2}\}^{-1} \qquad (2)$$

Where θ is the on-axis phase shift in the term of Rayleigh rang of the Gaussian beam $Z_0 = \pi\omega^2/\lambda$ with the beam waist ω and the laser wave length λ. The solid curve depicted in figures 5(a) and 5(b) is obtained from fitting by using Eq. (2). As indicated in this figure, the experimental closed aperture results deviate from prediction of the theoretical analysis. Using Eq. (2) to the fit the results of figures 5, the value of θ is determined. The thermal nonlinear refraction coefficient, n_2, of the gold and platinum nanoparticles can be obtained using the on-axis phase shift, θ, given by [37]:

$$n_2 = \frac{\theta}{kI_0L_{eff}} \qquad (3)$$

where I_0 is the on-axis irradiance at focus. The value n_2 of is obtained to be -4.6×10^{-8} cm^2/w and -0.108×10^{-8} cm^2/w respectively.

Our results show that the presence of the gold and platinum nanoparticles enhances optical and thermal properties of the colloids as summarized in the table 1. The measured value of nonlinear refraction coefficient of the gold nanoparticles

Table 1. Comparison of the optical and thermal properties of the PtNP and AuNP colloids.

Sample	Volume fraction %	α (cm^{-1})	n_2 (cm^2/w)
PtNPs	0.02×10^{-3}	0.16	-0.108$\times 10^{-8}$
AuNPs	0.45×10^{-3}	0.23	-4.6$\times 10^{-8}$

in water is compared with the recently reported values of nonlinear refraction coefficient of gold nanoparticles in different solvents [45, 46] and listed in table 2.Various studies have shown that changing the surrounding solvent can affect properties of colloidal metal nanoparticles such as stability and size distribution [47]. Compared to other solvents, castor oil and Chitosan present high polarity, very low vapor pressure and optical activity. They are transparent solvents in the visible region of spectrum and they improve the stability of colloids [48]. Hence, these unique physical and chemical properties of castor oil and Chitosan make them ideal candidates as a solvent for synthesis of metal nanoparticles. Comparison of our results shows that gold nanoparticles in castor oil and Chitosan show a higher nonlinear refractive index than water.

Table 2. Comparison of the optical and thermal properties of the AuNPs in different solvents.

Sample	Volume fraction %	n_2 (cm^2/w)
AuNPs in chitosan	0.58×10^{-7}	-34$\times 10^{-8}$
AuNPs in castor oil	1.4×10^{-7}	-16.1$\times 10^{-8}$

4. Conclusion

In summary, we report a systematic investigation on the thrmo-optics nonlinearity of colloids containing of gold and platinum nanoparticles. The colloidal solution are synthesized by nanosecond pulsed laser ablation of gold and platinum plates in distilled water. The thermo-optical nonlinear properties are investigated by Z-scan technique. Analyses based on nonlocal thermal process (the parabolic temperature field approximation) are reported for the experimental closed Z-scan results and are found in excellent agreement with the model. The value of nonlinear refractive index is evaluated. Our results show that the presence of nanoparticles results in a nonlinear refractive index in the colloids. This is useful in fabrication of photonic devices by using of metal nanoparticles in colloids.

Conflict of interest statement:
The authors declare that they have no conflict of interest.

References

[1] L. W. Tutt and A. Kost. *Nature*, **356**:225, 1992.

[2] W. Ji, H. J. Du, S. H. Tang, and S. Shi. *Journal of the Optical Society of America B*, **12**:876, 1995.

[3] J. Staromlynska, T. J. Mckay, and P. Wilson. *Journal of Applied Physics*, **88**:1726, 2000.

[4] I. H. El-Sayed, X. Huang, and M. A. El-Sayed. *Cancer Letters*, **239**:129, 2006.

[5] S. M. You, J. H. Kim, and K. H. Kim. *Applied Physics Letters*, **83**:3374, 2003.

[6] R. Karimzadeh and N. Mansour. *Physica Status Solidi B*, **247**:365, 2010.

[7] Z. Mao, L. Qiao, F. He, Y. Liao, C. Wang, and Y. Cheng. *Chinese Optics Letters*, **7**:949, 2009.

[8] R. F. Souza, M. A. R. C. Alencar, C. M. Nascimento, M. G. A. Da Silva, M. R. Meneghetti, and J. M. Hickmann. *SPIE Conference Procedings*, **6323**:63231T, 2006.

[9] T. Jia, T. He, P. Li, Y. Mo, and Y. Cui. *Optics and Laser Technology*, **40**:936, 2008.

[10] M. Q. Zhu, L. Q. Wang, G. J. Exarhos, and A. D. Q. Li. *Journal of the American Chemical Society*, **126**:2656, 2004.

[11] L. Francois, M. Mostafavi, J. Belloni, J. F. Delouis, J. Delaire, and P. Feneyrou. *The Journal of Physical Chemistry B*, **104**:6133, 2000.

[12] V. Joudrier, P. Bourdon, F. Hache, and C. Flytzanis. *Applied Physics B*, **67**:627, 1998.

[13] W. Jia, E. P. Douglas, F. Guo, and W. Sun. *Applied Physics Letters*, **85**:6326, 2004.

[14] S. Qu, C. Du, Y. Song, Y. Wang, Y. Gao, S. Liu, Y. Li, and D. Zhu. *Chemical Physics Letters*, **356**:403, 2002.

[15] N. Venkatram, D. N. Rao, and M. Akundi. *Optics Express*, **13**:867, 2005.

[16] Y. P. Sun, J. E. Riggs, H. W. Rollins, and R. Guduru. *The Journal of Physical Chemistry B*, **103**:77, 1999.

[17] Y. Gao, Y. Wang, Y. Song, Y. Li, S. Qu, H. Liu, B. Dong, and J. Zu. *Optics Communications*, **223**:103, 2003.

[18] R. B. Martin, M. J. Meziani, P. Pathak, J. E. Riggs, D. E. Cook, S. Perera, and Y. P. Sun. *Optical Materials*, **29**:788, 2007.

[19] T. Tsuji, K. Iryo, Y. Nishimura, and M. Tsuji. *Journal of Photochemistry and Photobiology A: Chemistry*, **145**:201, 2001.

[20] T. Tsuji, Y. Tsuboi, N. Kitamura, and M. Tsuji. *Applied Surface Science*, **229**:365, 2004.

[21] P. V. Kazakevich, A. V. Simakin, V. V. Voronov, and G. A. Shafeev. *Applied Surface Science*, **252**:4373, 2006.

[22] T. Tsuji, K. Iryo, N. Watanabe, and M. Tsuji. *Applied Surface Science*, **202**:80, 2002.

[23] C. H. Bae, S. H. Nam, and S. M. Park. *Applied Surface Science*, **197-198**:628, 2002.

[24] Y. H. Chen and C. S. Yeh. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **197**:133, 2002.

[25] A. Pyatenko, K. Shimokawa, M. Yamaguchi, O. Nishimura, and M. Suzuki. *Applied Physics A*, **79**:803, 2004.

[26] A. V. Kabashin, M. Meunier, C. Kingston, and J. H. T. Luong. *The Journal of Physical Chemistry B*, **107**:4527, 2003.

[27] W. T. Nichols, T. Sasaki, and N. Koshizaki. *Journal of Applied Physics*, **100**:114911, 2006.

[28] T. Tsuji, T. Hamagami, T. Kawamura, J. Yamaki, and M. Tsuji. *Applied Surface Science*, **243**:214, 2005.

[29] T. Sasaki, Y. Shimizu, and N. Koshizaki. *Journal of Photochemistry and Photobiology A: Chemistry*, **182**:335, 2006.

[30] R. A. Ganeev, A. I. Ryasnyanskiy, and T. Usmanov. *Optics Communications*, **272**:242, 2007.

[31] K. V. Anikin, N. N. Melnik, A. V. Simakin, G. A. Shafeev, V. V. Voronov, and A. G. Vitukknovsky. *Chemical Physics Letters*, **366**:357, 2002.

[32] A. A. Ruth and J. A. Young. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **279**:121, 2006.

[33] R. Karimzadeh, H. Aleali, and N. Mansour. *Optics Communications*, **284**:2370, 2011.

[34] Y. P. Rakovich, M. V. Artemyev, A. G. Rolo, M. I. Vasilevskiy, and M. J. M. Gomes. *Physica Status Solidi B*, **224**:319, 2001.

[35] B. Yu, Y. Gu, Y. Mao, C. Zhu, and F. Gan. *Journal of Nonlinear Optical Physics and Materials*, **9**:117, 2000.

[36] K. Sendhil, C. Vijayan, and M. P. Kothiyal. *Optics and Laser Technology*, **38**:512, 2006.

[37] F. L. S. A. Cuppo, A. M. Figueiredo Neto, S. L. Gomez, and P. Palffy-Muhoray. *The Journal of the Optical Society of America B*, **19**:1342, 2002.

[38] J. P. Gordon, R. C. C. Leite, R. S. Moore, S. P. S. Porto, and J. R. Whinnery. *Journal of Applied Physics*, **36**:3, 1965.

[39] H. Aleali and N Mansour. *Journal of sciences, Islamic Repablic of Iran*, **21**:273, 2010.

[40] O. Muller, V. Pichot, L. Merlat, and D. Spitzer. *Scienctificreports*, **9**:519, 2019.

[41] B. Karmakar, K. Rademann, and A. L. Stepanov. *Glass Nanocomposites, Synthesis, Properties and Applications*. Elsevier, 1th edition, 2016.

[42] S. J. Sheldon, L. V. Knight, and J. M. Thorne. *Applied Optics*, **21**:1663, 1982.

[43] M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan, and E. W. Van Stryland. *IEEE Journal of Quantum Electronics*, **26**:760, 1990.

[44] C. A. Carter and J. M. Harris. *Applied Optics*, **23**:476, 1984.

[45] M. Tajdidzadeh, A. B. Zakaria, Z. Abidin Talib, A. S. Gene, and S. Shirzadi. *Journal of Nanomaterials*, **2017**:1, 2017.

[46] R. F. Souza, M. A. R. C. Alencar, E. Da Silva, and M. R. Meneghtti. *Applied Physics Letters*, **92**:201902, 2008.

[47] R. M. Talaki, A. Irajizad, and S. M. Mahdavi. *Applied Physics A*, **84**:215, 2006.

[48] E. C. da Silva, M. G. A. da Silva, S. M. P. Meneghetti, G. Machado, M. A. R. C. Alencar, J. M. Hickmann, and M. R. Meneghetti. *Journal of Nanoparticle Research*, **10**:201, 2008.