Optical Limiting Properties of Colloids Enhanced by Gold Nanoparticles Based on Thermal Nonlinear Refraction

M. Eslamifar[a] and N. Mansour[*b]

[a]Physics Dept., Behbahan Khatam Al-Anbia University of Technology, Behbahan, Iran
[b]Physics Dept., Shahid Beheshti University, Tehran, Iran

[*]Corresponding author: n-mansour@sbu.ac.ir

ABSTRACT— In this work, thermo-optical properties of gold nanoparticle colloids are studied using continuous wave (CW) laser irradiation at 532 nm. The nanoparticle colloids are fabricated by 18 ns pulsed laser ablation of pure gold plate in the distilled water. The formation of the nanoparticles has been evidenced by optical absorption spectra and transmission electron microscopy. The nonlinear optical properties of gold nanoparticles colloids are investigated by closed Z-scan under irradiation of a low power CW laser. It will be shown that the thermal lens model is in excellent agreement with the experimental results of samples. The aperture-limitted optical limiters based on the nonlinear refraction of colloidal solution are presented. The tunability of limiting threshold of optical limiters can be accomplished by engineering of the experimental geometry.

KEYWORDS: Gold nanoparticles, Colloid, Thermo-optical properties, Nonlinear refraction, Optical limiter.

I. INTRODUCTION

With the extensive use of continuous wave (CW) lasers at power levels ranging from µW to kW in various applications, research on materials and devices for the protection of sensors and human eyes from intense optical beams has generated much interest in the development of optical limiting materials [1]-[2]. Optical limiting refers to a decrease in the optical transmittance of a material with increasing incident light intensity [2]. The optical limiting mechanisms can be caused by various nonlinear light-matter interactions, especially nonlinear absorption, nonlinear refraction and nonlinear scattering [3]. Under low power CW laser beam illumination, the form of optical nonlinearity exhibited by materials is predominantly refractive rather than absorptive [4] and convenient schemes based on nonlinear refraction have to be exploited for obtaining the limiting performance. Many materials such as organic dyes [5], phthalocyanines [6], liquid crystals [7], ferrosols [8] and In_2O_3 nanoparticles [9] are reported as good optical limiters under a low power laser irradiation due to the thermal nonlinear refractive properties.

In this paper, we report on the experimental investigation of the thermo-optic nonlinear response of colloids containing gold nanoparticles. Using the Z-scan technique, the behavior of the thermal nonlinear refractive index of colloids is studied. Observation of an asymmetrical configuration of the Z-scan measurements indicates that nonlinear refraction occurring in the AuNPs sample is related to process of nonlocal heat diffusion [1]. The results are analyzed based on nonlocal thermo-optic models [10]-[11]. It will be shown that the thin thermal lens model is in excellent agreement with the experimental results of the closed aperture Z-scan measurements of the sample. Fits have allowed extracting the value of nonlinear refractive index coefficient of the AuNP colloids. Thermo-optics coefficient of the colloids is obtained and reported. The application of nanoparticle colloids in designing low threshold optical limiters is demonstrated. The dependence of the threshold value on the aperture size and the distance between the sample and the aperture makes it suitable to optimize the threshold intensity of in optical limiting.

II. EXPERIMENTAL DETAILS

Gold nanoparticle colloids have been synthesized by nanosecond pulsed laser ablation of highly pure gold target in distilled water. The laser ablation of gold was carried out using a second-harmonic radiation of Q-switched Nd: YAG laser. The laser generated 18 ns (full-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 a gold plate placed inside a 10 mm cell. The spatial profile of the laser pulse was Gaussian, with 300µm (FW1/ e^2M) beam waist at the target. The gold sample was irradiated with the laser fluence level of about 200 J/cm^2 for two hours. The volume fraction of the AuNPs is 1.86×10^{-4}. Optical absorption spectra are recorded at room temperature using an ultraviolet/visible (UV-vis) spectrophotometer with wavelengths range of the 400 to 900 nm. Transmission electron microscopy (TEM) is carried out to determine the size distribution and shape of nanoparticles. A continuous wave low power (100mW) diode-pumped Nd: YVO_4 laser operating at wavelength of 532nm is also used to measure the linear absorption coefficient of the colloids. The nonlinear optical properties of the AuNP colloids were studied by transmittance and Z-scan measurements using the low power laser at wavelength of 532 nm. For Z-scan measurement, the optical geometry used in this work is similar to given in [12]. An attenuator and a beam splitter were used to control the power of the laser beam. The beam was focused onto sample (5 mm cell) by using a lens with 50 cm focal length. The spot size in the focal region was 50µm (HW1/e^2M). A diaphragm located before the output power detector, is used to control the cross section of the beam coming out of the sample. The sample is positioned at the focus. At different laser input power, the corresponding output power is measured. When the laser power changed, the far-field profile shows intensity variation which is recorded through the aperture.

III. RESULTS AND DISCUSSION

Figure 1 shows UV-vis absorption spectrum of the colloids prepared by laser ablation of a gold plate immersed in the water. One can observe that the AuNPs exhibit typical surface Plasmon absorption (SPA) peak about 525 nm [13].

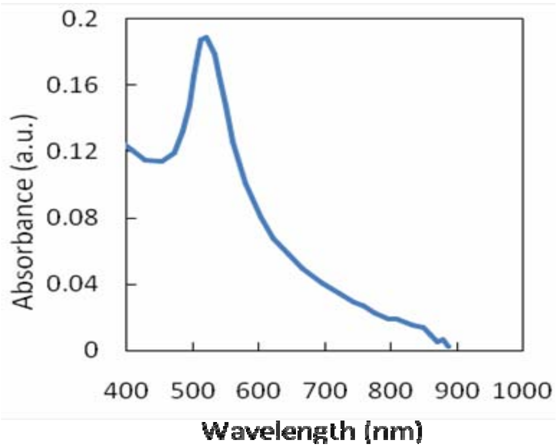


Fig. **1** Absorption spectrum of the AuNP colloids obtained by laser ablation of a gold plate in the water.

The shape and size distribution of the gold nanoparticles are studied by TEM and the measurements conducted just after laser ablation. The TEM image and size distribution of AuNP colloids have been reported [12]. Average AuNPs radius is found to be about 7nm, with a standard deviation of 5nm. Observation of the SPA peak around 520-530 nm are agreement with the presence of small 3-30 nm gold nanoparticles in the solution. Figure 2 shows transmission measurements of the water (♦) and the AuNP colloid (■), under exposure to low power laser at 532 nm. Up to the applied laser of 90 mW, we have not measured any nonlinear absorption in the sample. The solid curves are fitted based on linear absorption theory (Beer’s Law) and the absorption coefficients of the water and the AuNP colloids are measured to be 0.11 cm^{-1}, 0.54 cm^{-1} at the applied wavelength of 532 nm, respectively. We have also experimentally investigated the nonlinear absorption process of the water and the AuNPs using the open Z-scan measurements. The results do not show any nonlinear absorption in the both medium.

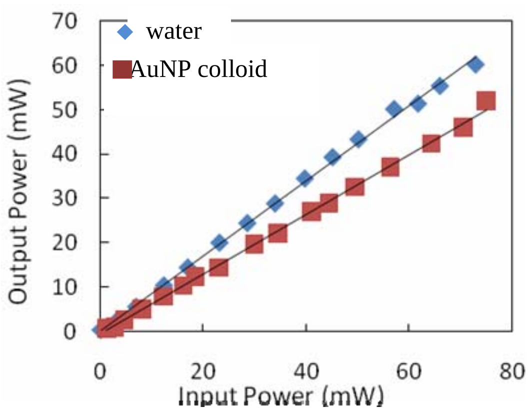


Fig. 2. Transmittance measurements of the water and the AuNP colloids.

Based on Maxwell theory [14], the formula for calculating the effective thermal conductivity of AuNP colloids is given by

$$K_{eff} = K_L\left(1+\frac{3(\gamma-1)\nu}{(\gamma+2)-(\gamma-1)\nu}\right) \tag{1}$$

with $\gamma = K_S/K_L$. In these equations, K_L is the thermal conductivity of the liquid, K_s is the thermal conductivity of the nanoparticles, ν is the particle volume fraction. Using Eq. (1) and thermal parameters reported from literature for gold and the water [15], the effective thermal conductivity of AuNP colloids is calculated and listed in Table 1. We used in our calculation the values: $K_L = 0.6\text{W/mK}$ and $K_s = 317\text{W/mK}$. The closed aperture Z-scan technique permitted us to measure the value of the thermal nonlinear refractive index of the AuNP colloids. 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. When the sample experiences different intensities at different positions, the recording of transmission as a function of z coordinate provides accurate information about the presence nonlinear refraction effect. Figure 3 shows the normalized transmittance of Z-scan measurements as a function of distance from the focus of the Gaussian beam for the colloids. Applied incident laser power is about 47mW. The Z-scan results of the AuNP colloids show an asymmetric peak followed by valley, typical of negative nonlinearity for refractive index. This asymmetric nature of 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 [1]. The pure liquid of the water does not show any closed Z-scan signal for the applied laser power up to about 50mW.

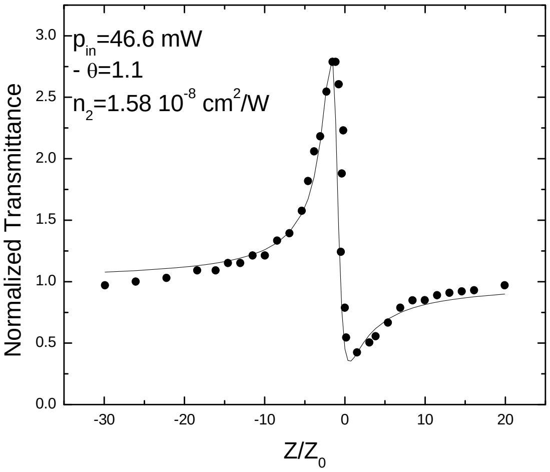


Fig. 3. Shows experimental results of the normalized closed aperture Z-scan measurement of the AuNPs dispersed in the water. The solid curve is the fit using phase shift calculation based on the thermal thin lens model Eq. (2).

Our experimental results for the closed Z-scan measurement of AuNP colloids [Fig. 4] cannot be explained with the Sheik-Bahae formalism [16]. 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 AuNP colloids and immediately give rise to the local heating followed by process of heat diffusion in the medium. The heat diffusion takes place and produces 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 as has been reported by Cuppo et al [10].

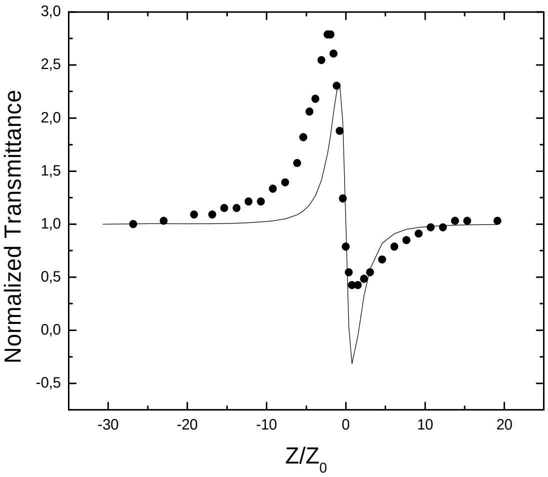


Fig. 4. Shows experimental results of the normalized closed aperture Z-scan measurement of the AuNPsdispered in the water. The solid curve is the fit using phase shift calculation based on the Sheik-Bahae model.

In their model, the induced thermal nonlinear effect in the medium is treated as an ideal thin lens with the parabolic description of the temperature field. In the parabolic model, the normalized transmittance for closed aperture Z-scan is [10]:

$$T\left(z/z_0,t\right)=\left(1+\theta\frac{2z/z_0}{1+\left(z/z_0\right)^2}+\theta^2\frac{1}{1+\left(z/z_0\right)^2}\right)^{-1} \tag{2}$$

where $\theta=(dn/dT)\alpha PL_{eff}/\lambda K_{eff}$ is the on-axis phase shift, α is the absorption coefficient of the sample, $L_{eff}=[1-\exp(-\alpha L)]/\alpha$ is the sample effective length, L is the sample length, dn/dT is the thermo-optic coefficient of the medium, K_{eff} is the thermal conductivity of nanoparticle colloids and $z_0=\pi\omega_0^2/\lambda$ is the Rayleigh range of the Gaussian beam with the beam waist ω_0 and the laser wavelength λ. The solid curve depicted in Fig.3 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 fit the results of Fig. 3, the value of θ is determined. The thermal nonlinear refraction coefficient, n_2, and thermo-optic coefficient, dn/dT, of the AuNPs can be obtained using the on-axis phase shift, θ, given by [10]:

$$n_2=\frac{\theta}{kI_0L_{eff}} \tag{3}$$

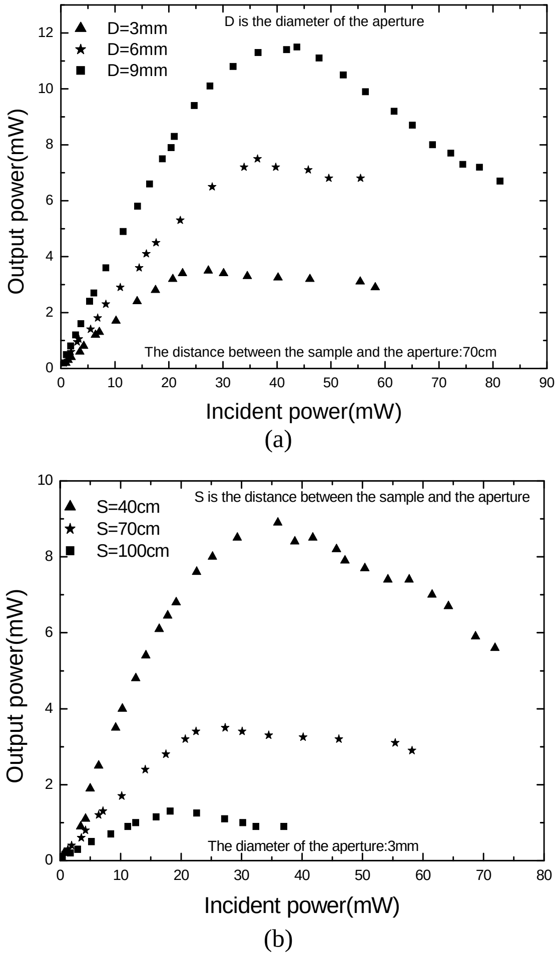
$$\frac{dn}{dT}=-\frac{\lambda K_{eff}}{\alpha PL_{eff}}\theta \tag{4}$$

where I_0 is the on-axis irradiance at focus. The values n_2 and thermo-optic coefficient of the colloid are obtained to be -1.58×10^{-8}cm^2/W and $-0.32\times10^{-4}\,K^{-1}$, respectively. Our results show that the presence of the gold nanoparticles increases optical and thermal properties of the colloids as summarized in Table 1.

Table. 1 Optical and thermal properties of the colloids.

volume fraction (%)	α (cm^{-1})	k_{eff} (W/mK)	dn/dT (K^{-1})	n_2 (cm^2/W)
0	0.11	0.6	-	-
1.86×10^{-4}	0.54	0.600003	-0.32×10^{-4}	-1.58×10^{-8}

The optical limiting properties of the AuNPs dispersed in the water are studied using low power CW laser light at 532 nm. Figures 5(a) and 5(b) exhibit the optical limiting experimental results of the sample. As it is clearly shown in the figures, the transmitted power increases linearly with the incident power (for the low power range) and then reaches the maximum. When the incident power is further increased, the transmitted power will decrease and tend to approach a steady value. The limiting threshold defined as the maximum transmitted power at fixed diameter and position of the aperture.



(a)

(b)

Fig. 5. Optical limiting behavior of the colloids. (a) Optical limiting properties of the AuNP colloids for different diameters of the aperture D. (b) Optical limiting properties of the AuNP colloids for different positions of the aperture S.

The results show that the limiting threshold increases linearly with increase diameter of the aperture, but decreases linearly with increase distance between the sample and the aperture. Hence, the desirable threshold can be achieved by varying these two parameters.

The limiting action response time, t, is given by [17]:

$$t \approx \frac{\left(\rho_{eff} C_{eff}\right)\omega_0^2}{K_{eff}} \tag{5}$$

where ρ_{eff}, the effective mass density and C_{eff}, the effective heat capacity of the colloids can be calculated by [18]:

$$\rho_{eff} = \rho_s \nu + \rho_L \left(1-\nu\right) \tag{6}$$

and

$$C_{eff} = C_s \phi_W + C_L \left(1-\phi_W\right) \tag{7}$$

where ρ_S is the mass density of particles, ρ_L is the mass density of liquid, C_S is the heat capacity of particles, C_L is the heat capacity of liquid and ϕ_W is the mass fraction of the particles. The calculated value of limiting action response time is about 17ms.

In low power laser irradiation, one of the dominant mechanisms for material limiting performance has been reported as the nonlinear self defocusing due to the nonlocal heat effect [5] and [9]. It seems laser light scattering may also play important contributions in limiting response of nanoparticle colloidal systems. However, light absorption by the nanoparticles may cause local heating, thermal diffusion and convection [19]-[20]. Our experimental results show that the nonlinear self defocusing plays major role in optical limiting action of AuNPs dispersed in the water.

IV. CONCLUSION

We have investigated the thermo-optical nonlinearities of colloids containing gold nanoparticles using the Z-scan technique. The colloidal solution are fabricated by nanosecond pulsed laser ablation of a gold plate in distilled water. 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 values of nonlinear refractive index and thermo-optic coefficients are evaluated. The observed self defocusing effect in the AuNPs can be used to fabricate an optical limiter. The limiting threshold can be improved with change in the experimental geometry, e.g. the aperture size and position behind the sample. Our results suggest that the thermal nonlinear refraction will play an important role in development of photonic applications involving metal nanoparticle colloids.

REFERENCES

[1] K. Sendhil, C. Vijayan and M.P. Kothiyal, “Low-threshold optical power limiting of cw laser illumination based on nonlinear refraction in zinc tetraphenyl porphrin,” Opt. Laser Technol. Vol. 38, pp. 512-515, 2006.

[2] K. Jamshidi-Ghaleh and N. Mansour, “Nonlinear absorption and optical limiting in Duran glass induced by 800 nm femtosecond laser pulses,” J. Phys. D: Appl. Phys. Vol. 40, pp. 366-369, 2007.

[3] L.W. Tutt and T.F. Boggess, “A review of optical limiting mechanisms and devices using organics, fullerenes, semiconductors and other materials,” Prog. Quantum Electron. Vol. 17, pp. 299-338, 1993.

[4] R. Karimzadeh, H. Aleali, and N. Mansour, “Thermal nonlinear refraction properties of Ag_2S semiconductor nanocrystals with its application as a low power optical limiter,” Opt. Commun. Vol. 284, pp. 2370-2375, 2011.

[5] R.K. Rekha and A. Ramalingam, “Nonlinear characteristic and optical limiting effect of oil red O azo dye in liquid and solid media,” J. Mod. Opt. Vol. 56, pp. 1096-1102, 2009.

[6] K. Sathiyamoorthy, C. Vijayan, and M.P. Kothiyal, “Low power optical limiting in CIAI-Phthalocyanine due to self defocusing and self phase modulation effects,” Opt. Mater. Vol. 31, pp. 79-86, 2008.

[7] I.C. Khoo, R.R. Michael, and G.M. Finn, “Self- phase modulation and optical limiting of a low power CO_2 laser with a nematic liquid-crystal film,” Appl. Phys. Lett. Vol. 52, pp. 2108-2110, 1988.

[8] S. Pu, L. Yao, F. Guan, and M. Liu, “Threshold-tunable optical limiters based on nonlinear refraction in ferrosols,” Opt. Commun. Vol. 282, pp. 908-913, 2009.

[9] B. Yu, C. Zhu, F. Gan, and Y. Huang, “Optical limiting properties of In_2O_3 nanoparticles under cw laser illumination,” Opt. Mater. Vol. 7, pp. 103-107, 1997.

[10] F. Cuppo, A.M. FigueiredoNeto, S.L. Gomez, and P. Palffy-Muhoray, “Thermal-lens model compared with the Sheik-Bahae formalism in interpreting Z-scan experiments on Lyotropic liquid crystals,” J. Opt. Soc. Am. B, Vol. 19, pp. 1342-1348, 2002.

[11] J.P. Gordon, R.C.C. Leite, R.S. Moore, S.P.S. Porto, and J.R. Whinnery, “Long- Transient effects in lasers with inserted liquid samples,” J. Appl. Phys. Vol. 36, pp. 3-8, 1965.

[12] H. Aleali, L. Sarkhosh, M. Eslamifar, R. Karimzadeh, and N. Mansour, “Thermo-Optical properties of colloids enhanced by gold nanoparticles,” Jpn. Appl. Phys. Vol. 49, pp. 085002-085008, 2010.

[13] A.V. Kabashin, M. Meunier, C. Kingston, and J. H. T. Luong, “Fabrication and characterization of gold nanoparticles by femtosecond laser ablation in an aqueous solution of cyclodextrins,” J. Phys. Chem. B, Vol. 107, pp. 4527-4531, 2003.

[14] J. C. Maxwell, *A Treatise on Electrisity and Magnetism*, 2nd ed. Oxford Univ. Press, Cambridge, 1904.

[15] R.C. Weast, *Handbook of Chemistry and Physics*, 84th ed. CRC Press, Boca Raton, FL, 2004.

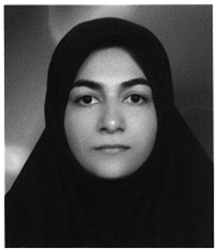
[16] M. Sheik-Bahae, A.A. Said, T.–H. Wei, D.J. Hagan, and E.W. Van Stryland, “Sensitive measurement of optical nonlinearities using a single beam,” IEEE J. Quantum Electron. Vol. 26, pp. 760-769, 1990.

[17] R.W. Boyd, *Nonlinear Optics*, Academic, New York, 2003.

[18] X. Zhang, H. Gu, and M. Fujii, “Effective thermal conductivity and thermal diffusivity of nanofluids containing spherical and cylindrical nanoparticles,” Exp. Therm. Fluid Sci. Vol. 3, pp. 593-599, 2007.

[19] R. Spill, W. Kohler, G. Lindenblatt, and W. Schaertl, “Thermal diffusion and soret feedback of gold-doped polyorganosiloxane nanospheres in toluene,” Phys. Rev. E, Vol. 62, pp. 8361-8368, 2000.

[20] W. Schaertl and C. Roos, “Convection and thermodiffusion of colloidal gold tracers by laser light scattering,” Phys. Rev. E, Vol. 60, pp. 2020-2028. 1999.



Mina Eslamifar was born in Behbahan, Khuzestan, Iran. She has received her B.Sc. and M.Sc. degrees in Physics from Shahid Beheshti University, Tehran, Iran in 1386 and 1388, respectively. Her research activities have been concentrated on the study of nonlinear optical processes in nanomaterials. She is a lecturer in Behbahan Khatam Al-Anbia University of Technology. She is a member of Iran Nanotechnology Initiative Council.

Nastaran Mansour is a professor at Physics Department of Shahid Beheshti University, Tehran, Iran. Her current research interests focus on the synthesis and characterization of structural and nonlinear optical properties of nanostructured materials obtained by laser ablation method.

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