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EFFECT OF PARTICLE SIZE ON NONLINEAR REFRACTION AND ABSORPTION OF Ag NANOPARTICLES

ESMAEIL SHAHRIARI, W. MAHMOOD MAT YUNUS
Department of Physics, Universiti Putra Malaysia, 43400UPM, Serdang, Selangor, Malaysia Tel

The nonlinear optical characteristics of silver nanofluid synthesized by γ-radiation technique at a concentration of 5.889×10^{-3} M were studied. The measurements were performed by a single Z-scan method using CW laser beam excitation wavelength of λ = 532 nm. The nonlinear refractive index and the nonlinear absorption of samples were determined for nanoparticle sizes ranging from 40.8 to 64.1 nm. It is shown that the nonlinear refraction of the samples caused by the thermal effect increased nonlinearly with particle size. However, the nonlinear absorption coefficient rapidly decreases up to the particle size of 52 nm and tends to increase for particle size greater than 52 nm. The third order nonlinear susceptibility of all series of samples is also calculated and discussed.

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1. Introduction

The investigation of the nonlinear optical properties of nanoparticles colloidal in solutions is an active field of research, which has many potential applications such as optical signal processing and optical communication devices [1-5]. Optical materials, which have large nonlinearities refractive index and small absorption coefficients (linear and nonlinear) are the goals in many optical limiting and optical photonic researches [6]. Metal nanofluid prepared by γ-radiation method has a particular advantage, such as the high homogeneity and small absorption coefficient. In addition, the particle size of metal nanofluid can be controlled by controlling the radiation dose and the exposure time.

Z-scan is a well-established method for the determination of nonlinear refraction and absorption and has been widely used in material characterization since it can provide not only the magnitudes of real and imaginary parts of nonlinear susceptibility, but also the sign of the real part [7-10]. In this method, the sample is scanned along the propagation path of a focus the Gaussian laser beam where the intensity of the transmission beam is measured at far-field of the experimental set up.

Most of the reported nonlinear characterization of nanoparticles in dielectric materials was performed using lasers at wavelengths close to the absorption maximum of the surface plasmon resonance of nanoparticles [11]. However, in the present work, we used a CW laser beam operated at 532 nm to study the effect of particle size on nonlinearity properties of Ag nanofluid. The effect of concentration on the nonlinear refraction coefficient of Au nanofluid in PVP has been recently published [12]. In addition the effect of particle size on the nonlinear refractive index of Au nanoparticle in PVA solution has been reported in our previous work for the particle size ranging from 7.0 nm to 18.7 nm [13]. The aim of the present paper is to report the effect of particle size on the nonlinear refractive index and nonlinear absorption coefficient of Ag nanofluid using a single beam z-scan experiment.

2. Experimental

In the preparation of Ag nanoparticle, 50 mg of silver nitrate, ($AgNO_3$, Aldrish-99%), 4 g polyvinylpyrrolidone (PVP, MW 29,000 Aldrish), and 1 ml isopropanol were used. The PVP and isopropanol were used as a colloidal stabilizer and radical scavenger of hydroxyl radical, respectively. The PVP solution was made by dissolving PVP powder in 50 ml deionized water at room temperature. The solution was magnetically stirred for 2 hours and was bubbled with nitrogen gas (99.5%) in order to remove oxygen. In this case, the concentration of Ag nano-particle was calculated to be 5.889×10^{-3} M. The sample was then irradiated with gamma radiation at different radiation doses (between 10 kGy and 50 kGy) to produce a sample with different nanoparticles sizes.

The linear refractive index and spectral absorbance of diluted samples were measured using the traditional minimum deviation method and an UV-Vis spectrophotometer (Shimadzu-UV1650PC). Furthermore, the linear absorption coefficient of the samples was measured by the conventional method on the basis of $\alpha = -(1/L)ln(I_o/I)$ in the linear regime of the experiment. For nonlinear properties measurements, a single beam Z-scan method with closed and open aperture arrangements was used to measure the nonlinear refractive and nonlinear absorption coefficients. The experiment was carried out at room temperature using a CW beam diode laser operated at 532 nm wavelength (Coherent Compass SDL-532-150T). The beam was focused to a small spot using a lens and the sample was moved along the z-axis by a motorized translational stage. At the focus point, the power output of the laser beam was measured to be 40 mW. The transmitted light in the far field passed through the aperture and the beam intensity was recorded by a photodiode detector. The laser beam waist ω_0 at the focus length was measured to be 24.4 μm and the Rayleigh length was found to satisfy the basic criteria of a z-scan experiment. A quartz optical cell containing the specimen solution was translated across the focal region along the z-axis direction. In order to extract the nonlinear refraction, the sample is moved through the focal point and the nonlinear transmission was measured as a function of the sample position with an aperture placed at the far field.

3. Results and discussion

Fig. 1 shows the relationship between the particle size and the irradiation level of γ-radiation. It explains that increasing the irradiation dose made the particle size smaller. This result shows that the γ-radiation technique is the effective tool for controlling the nanoparticle sizes even in a small range (i.e. 40 nm to 65 nm). The linear optical absorption of the diluted samples measured using an UV-vis spectrophotometer (Shimadzu-UV1650PC) is displayed in Fig. 2. It shows that in general for the visible region, $\lambda < 700$ nm the large particle size sample gives a higher optical absorption value and shifts towards longer wavelengths when the particles become small.

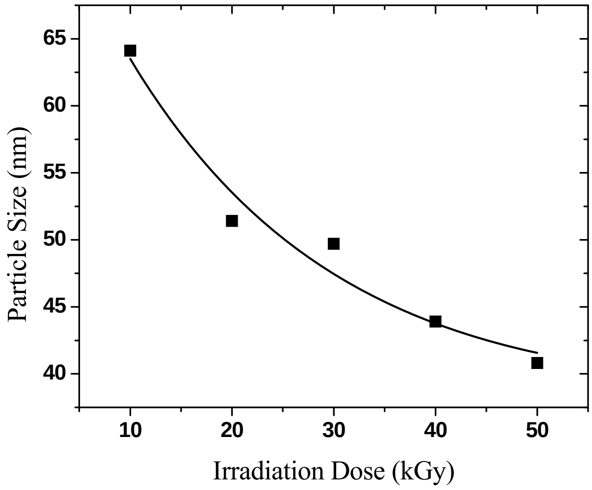

Fig. 1. Variation of particle size of Ag nanofluid (5.889×10^{-3} M) at different doses of radiation

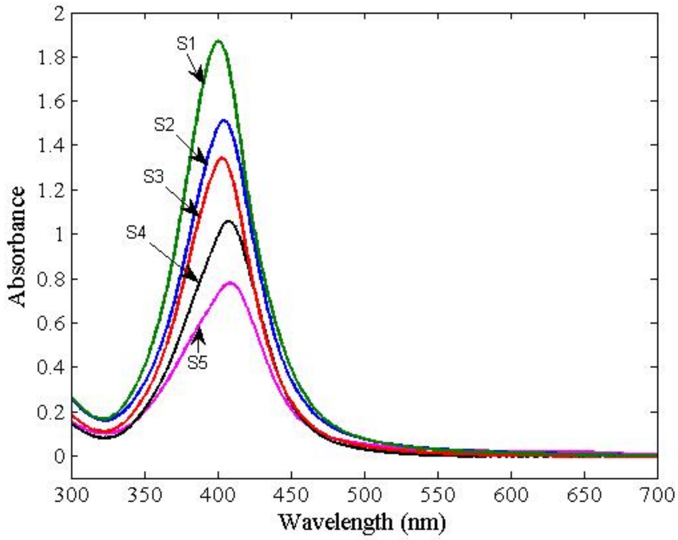

Fig. 2. Spectral absorbance of the five nanofluids diluted samples S1, S2, S3, S4, and S5.

The closed and open aperture Z-scan curves for Ag nanofluid prepared using γ-radiation at doses 10, 20, 30, 40 and 50 kGy which quoted as S1, S2, S3, S4, and S5, respectively are shown in Figs. 3 to 7. The symbols represent the experimental data while the solid lines are theoretical fits to the closed aperture and open aperture z- scan equations. For the case where only the nonlinear refraction is present in the sample, the normalized peak and valley (ΔT_{p-v}) curve are a perfect symmetry and can be used to calculate the nonlinear refractive index of the nanofluid using a simple relationship proposed by Sheik Bahae et. al [14]

$$n_2 = \Delta\phi_0 \lambda / 2\pi I_0 L_{eff} \quad (1)$$

where λ is the wavelength of the laser light, I_0 is the peak intensity within the sample. The $\Delta\phi_0$ and L_{eff} are the nonlinear phase shift and the effective thickness given by the following relations [14, 15]

$$\Delta\phi_0 = \frac{\Delta T_{p-v}}{0.406(1-S)^{0.25}} \tag{2}$$

$$L_{eff} = [1-\exp(-\alpha_0 L)]/\alpha_0 \tag{3}$$

here, L, S and α are sample thickness, aperture linear transmittance and linear absorption coefficient at wavelength λ, respectively. However, if the sample has a nonlinear refractive index and nonlinear absorption properties, the normalized transmission curve of closed aperture data does not show a perfect symmetry curve. This phenomenon can be clearly seen in Figs. 5, 6 and 7 where the closed aperture data (open circle) shows a suppressed peak and enhanced valley. In Figs. 3 and 4, the suppressed peaks and enhanced valleys are not too obvious due to the small nonlinear absorption present in these two samples.

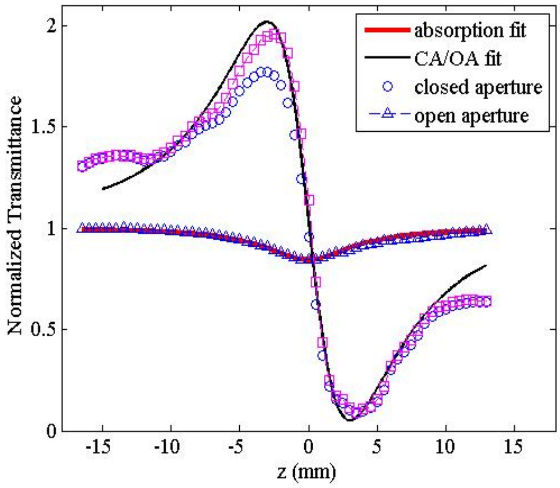

Fig. 3. Normalized Z-scan transmittance curves of the Ag nanoparticle at concentration of 5.889×10^{-3} M irradiated with 10 kGy dose. The solid lines are the theoretical fit to the experimental data.

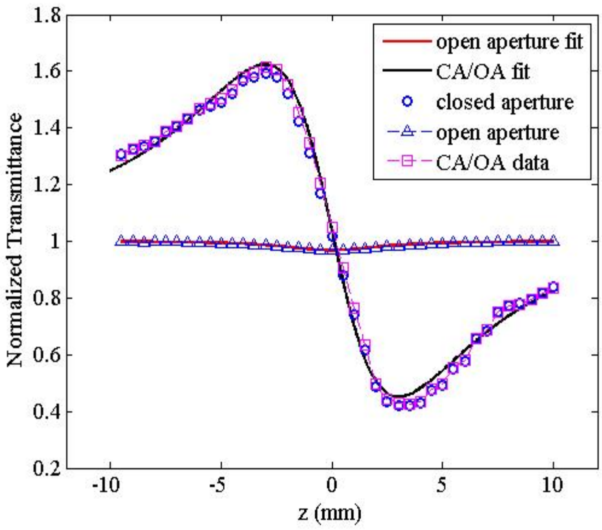

Fig. 4. Normalized Z-scan transmittance curves of the Ag nanoparticle at concentration of 5.889×10^{-3} M irradiated with 20 kGy dose. The solid lines are the theoretical fit to the experimental data.

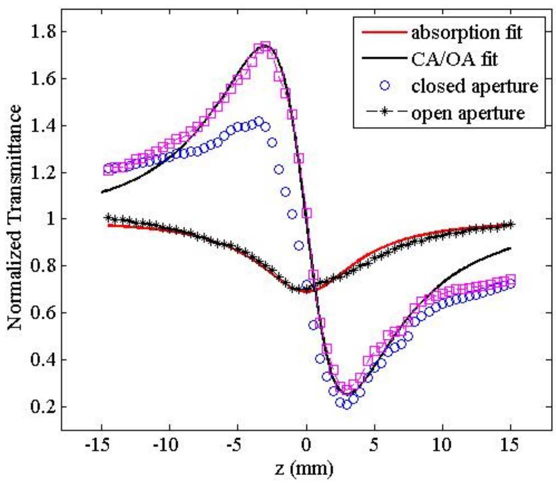

Fig. 5. Normalized Z-scan transmittance curves of the Ag nanoparticle at concentration of 5.889×10^{-3} M irradiated with 30 kGy dose. The solid lines are the theoretical fit to the experimental data.

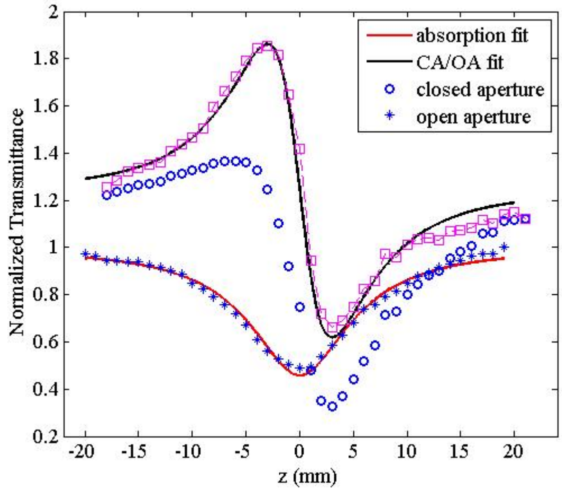

Fig. 6. Normalized Z-scan transmittance curves of the Ag nanoparticle at concentration of 5.889×10^{-3} M irradiated with 40 kGy dose. The solid lines are the theoretical fit to the experimental data.

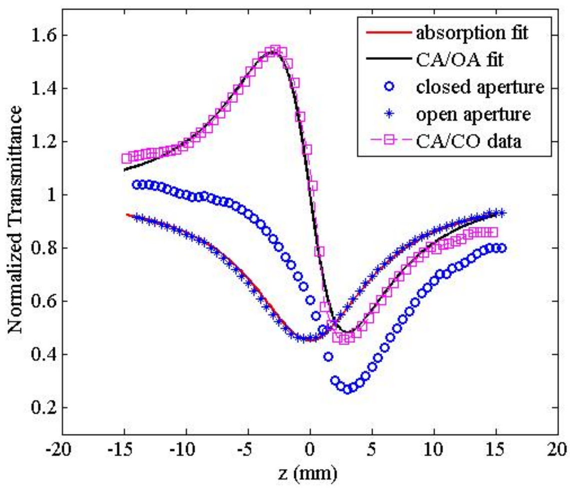

Fig. 7. Normalized Z-scan transmittance curves of the Ag nanoparticle at 5.889×10^{-3} M irradiated with 50 kGy dose. The solid lines are the theoretical fit to the experimental data.

The nonlinear absorption coefficient β (cm/W) can be obtained from a best fitting performed on the experimental data of the open aperture measurement using a well known equation used by Sheik Bahae [14,15]

$$T(z,s=1)=\sum_{m=0}^{\infty}\frac{[-\beta I_0 L_{eff}/(1+z/z_0)]^m}{(m+1)^{3/2}} \tag{4}$$

where $T(z,s=1)$ is the normalized transmittance for the open aperture (OA) with z_0 being the Rayleigh range. In the present work, the nonlinear refractive index and nonlinear absorption coefficient were analyzed by normalizing the closed aperture signals to the open aperture signals as shown in Fig. 3 to 7 (open square).

The nonlinear refractive index n_2 and nonlinear absorption coefficient β were used to calculate the real and imaginary parts of the third-order nonlinear optical susceptibility χ^3 [16, 17] according to the following relations.

$$\mathrm{Re}\,\chi^3(esu)=10^{-4}\frac{\varepsilon_0 c^2 n_0^2}{\pi}n_2(cm^2W^{-1}) \tag{5}$$

$$\mathrm{Im}\,\chi^3(esu)=10^{-2}\frac{\varepsilon_0 c^2 n_0^2\lambda}{4\pi^2}\beta(cmW^{-1}) \tag{6}$$

where ε_0 is the vacuum permittivity and c is the light velocity in the vacuum. The values of linear refractive index n_o was measured using a minimum deviation method. Thus the absolute value of the third-order nonlinear optical susceptibility was calculated as.

$$\left|\chi^3\right|=\left[(\mathrm{Re}(\chi^3))^2+(\mathrm{Im}(\chi^3))^2\right]^{1/2} \tag{7}$$

The values of the nonlinear refraction coefficient n_2 (cm^2/W), nonlinear absorption coefficient β (cm/W), and the third order nonlinear susceptibility obtained for the present samples are completely listed in Table 1. The values of $\Delta n_o = n_2 I_o$ are also included in Table 1.

Table 1. The nonlinear optical parameters measured for Ag nanofluid at concentration of 5.889×10^{-3} M and irradiated at different doses.

Nano-Fluid samples	Average particle size (nm)	n_2(cm^2/W) $\times10^{-8}$	β(cm/W) $\times10^{-3}$	Δn_o $x10^{-4}$	Re($\chi^{(3)}$) $\times10^{-6}$	Im($\chi^{(3)}$) $\times10^{-7}$	$\left\|\chi^{(3)}\right\|$ $\times10^{-6}$
S1	64.1	-9.57	0.951	-4.08	-5.88	2.47	5.889
S2	51.3	-8.89	0.176	-3.79	-5.47	4.61	5.480
S3	48.7	-7.69	2.51	-3.28	-4.47	6.61	4.822
S4	43.9	-7.13	7.22	-3.04	-4.43	19.0	4.830
S5	40.8	-6.17	7.99	-2.63	-3.88	21.3	4.433

The effects of particles size on nonlinear refractive and nonlinear absorption are shown in Figs. 8 and 9, respectively. The nonlinear refractive index increases nonlinearly with the increasing of particle size while the nonlinear absorption coefficient decreases rapidly from 7.99 x 10^{-5}cm/W (40.8 nm) to 1.76 x 10^{-5}cm/W (51.3 nm). However, for particle size greater than 52 nm the nonlinear absorption coefficient tends to increase with the particle size. The increasing of nonlinear refractive index with particle size is due to the decreasing number of particle in the medium as well as increasing the ratio of linear absorption to thermal diffusivity of the medium, α/D (D is thermal diffusivity). Considering the effective thermal nonlinearity of the medium written as [18]

$$n_2^{th} = \left(\frac{dn}{dT}\right)\frac{\omega_0^2\alpha}{4\kappa} \tag{8}$$

where thermal conductivity of the medium can be written as $\kappa = (\rho C_p)D$. In the present work the thermal diffusivity of all samples was measured using double beam thermal lens method where the results show that the value of α/D increases with the increasing of particle size. Thus for small changes of ρC_p and dn/dT, the nonlinear refractive index will solely depend on the ratio of α/D. This explains the variation of the n_2 with particle sizes of our experimental results shown in Fig. 8 which is nonlinearly increasing with particle sizes. In Fig. 9, rapidly decreasing the nonlinear absorption coefficient with particle size was attributed by a large number of particles that accommodate in a volume if the particles become smaller. Since the Re(χ^3) and Im(χ^3) were calculated using Eqs. 5 and 6, therefore the variation of Re(χ^3) and Im(χ^3) will follow the same trend as n_2 and β.

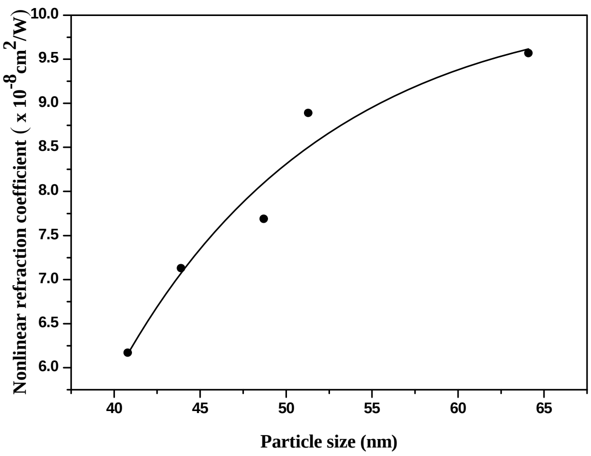

Fig. 8. Nonlinear refraction coefficient plotted as a function of particle size for Ag nanofluid at concentration of 5.889×10⁻³ M.

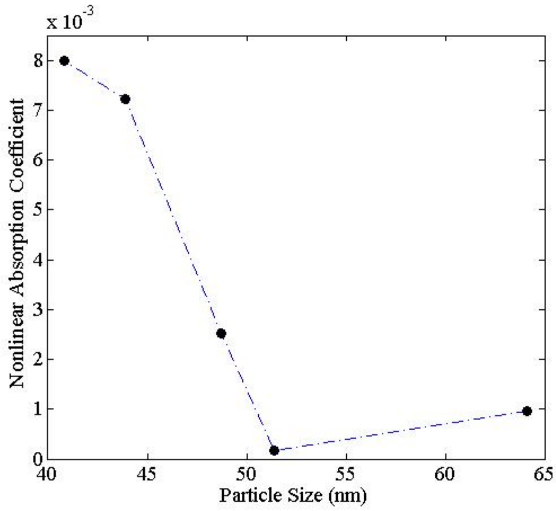

Fig. 9. Nonlinear absorption coefficent plotted as a function of particle size for Ag nanofluid at concentration of 5.889×10⁻³ M.

4. Conclusion

The nonlinear refractive index, n_2 and nonlinear absorption coefficients, β of Ag nanofluids at a concentration of 5.889×10^{-3} M were successful measured for the particle sizes ranging from 40.8 to 64.1 nm. The variations of nonlinear coefficients of samples as the particle size increase were notified. The third-order nonlinear optical susceptibilities were also calculated using the measured values of n_2 and β and it shows a significant third order nonlinear response. The sign of the nonlinear refractive index was found to be negative and the magnitude was in the order of 10^{-8} cm2/W.

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