Investigation of nonlinear optical properties of Ag nanoparticles

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ABSTRACT- In this research, Ag nanoparticles were prepared by using γ-radiation at concentration of 5.18×10^{-3} M and irradiated at different doses. A green laser was employed as excited source for measuring nonlinear refractive index and absorption coefficient. The measurements were done by z-scan method for both, closed and open aperture at temperature room. We deduced that with growth of size of Ag nanoparticles, nonlinear refractive index increased while absorption coefficient of samples decreased.

KEYWORDS: Optical properties, Nonlinear refractive index, Ag nanoparticles, Z-scan method.

I. INTRODUCTION

The study of the nonlinear optical properties of nanoparticles colloidal in solutions is an active field of research because of its many potential applications such as optical signal processing and optical communication devices[1-4]. The results of nanoscience are realized in nanotechnology as new materials and functional facilities. At present time nanophysics becomes one of the main growing directions of nanoscience [5]. Frequently, metallic nanoparticles show unique and considerably changed physical, chemical and biological properties compared to their macro scaled counterparts, due to their high surface-to-volume ratio. Thus, these nanoparticles have been the subject of substantial research in recent years [6, 7]. Metallic nanoparticles exhibit size and shape-dependent properties that are of interest for applications ranging from catalysts and sensing to optics, antibacterial activity and data storage [8, 9]. Metal nanoparticles can be prepared by two routes; the first one is a physical approach that utilizes several methods such as evaporation/ condensation and laser ablation. The second one is a chemical approach in which the metal ions in solution are reduced in conditions favoring the subsequent formation of small metal clusters or aggregations [10].

Z-scan method is a one of method for the determination of nonlinear refraction and absorption and has been widely used in material characterization because it provides both sign and magnitudes of real and imaginary parts of nonlinear susceptibility [11-15].

Many of the reported nonlinearities characterization of nanoparticles in dielectric materials was performed by the use of lasers at wavelengths close to the absorption maximum of the surface Plasmon resonance of nanoparticles [16]. However, in the present work we used a green laser beam for studying the effect of particle on nonlinearity properties of Ag solution. The nanoparticle size was controlled by γ radiation during sample preparation. The measurements were carried out for closed and open aperture configurations.

II. EXPERIMENTS

In the preparation of Ag nanoparticle, Silver nitrate, ($AgNO_3$, Aldrish-99%), Polyvinylpyrrolidone (PVP, MW 29,000 Aldrish), and isopropanol were used. The PVP solution was made by dissolving PVP powder in 50 ml deionized water at room temperature. In this case, the concentration of Ag nanoparticle was calculated to be 5.18×10^{-3} M.

The γ radiation (^{60}Co-rays) was used as an effective tool for the polymerization process and reducing agent. The sample was then irradiated with γ radiation at different doses i.e., 10, 20, 30, 40 and 50 kGy. The average diameters of Ag nanoparticles were measured using Nanophox Machine (Sympatec GmbH, D-38678) thus the relationship of particle size and γ irradiation dose was established. SEM images of Ag nanoparticles irradiated at doses of 10 and 20 kGy were prepared for confirmation the size and shape of the nanoparticles.

The linear refractive index and linear transmission coefficient were measured by using a conventional minimum deviation method and fiber optics spectrophotometer (Ocean Optics USB4000-FL). 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. 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.

III. 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. The particles size in the range of 30 to 54 nm can be controlled by irradiated γ radiation. The variation of the sizes with doses shows that with increasing of the dose, the size of the particles become smaller.

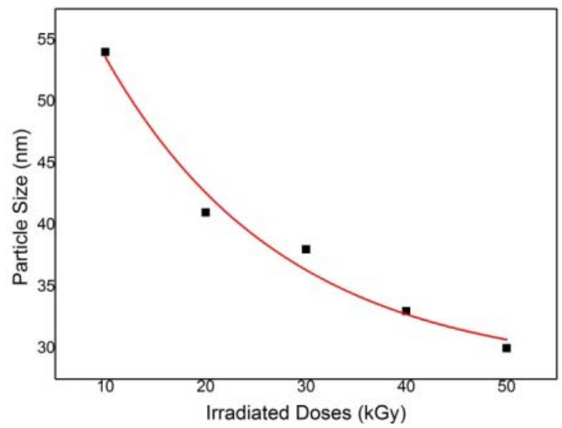

Fig. 1 The particle size at different doses of the Ag (5.18×10^{-3} M), S1; 10 kGy, S2; 20 kGy, S3; 30 kGy, S4; 40 kGy, S5; 50 kGy.

The linear optical transmissions of the samples measured by using fiber optics spectrophotometer are displayed in Fig. 2.

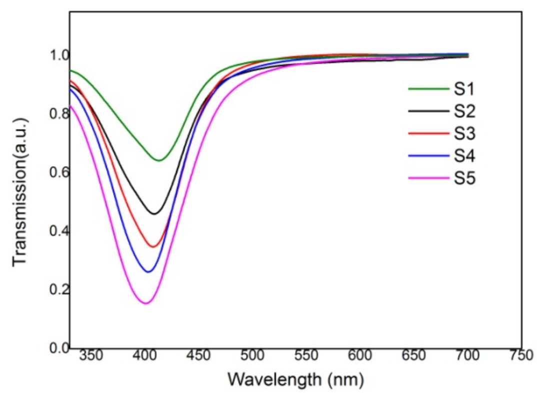

Fig. 2 Transmission spectrum of the Ag nanoparticle at the concentration of 5.18×10^{-3} M radiated at different dose: S1; 10 kGy, S2; 20 kGy, S3; 30 kGy, S4; 40 kGy, S5; 50 kGy.

The linear absorption coefficient of samples can be extracted from transmissions data by using Beer-Lambert low which is noted as:

$$\alpha = \frac{1}{d}\ln T \tag{1}$$

where α is linear absorption coefficient, d is thickness of sample and T is optical transmission.

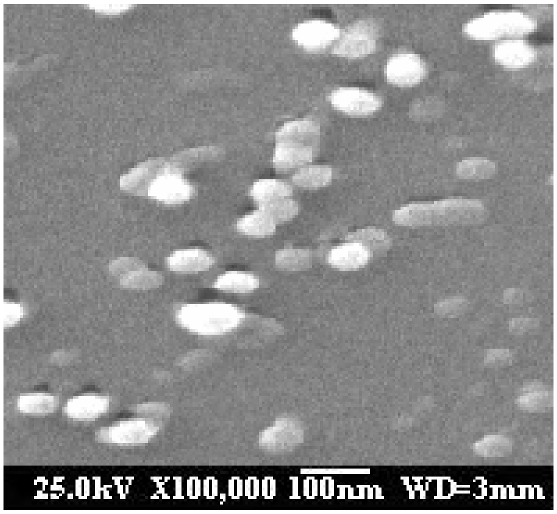

Fig. 3 SEM images Of Ag nanoparticles for: a) 54 nm and b) 41 nm.

The SEM image of Ag nanoparticles irradiated at doses of 10 kGy (54 nm) and 20kGy (41 nm) shown in Fig. 3. As can be seen, the shape of particles almost unique. These images confirm that the measurements of the Nanophox and SEM images are in good agreement in sizes.

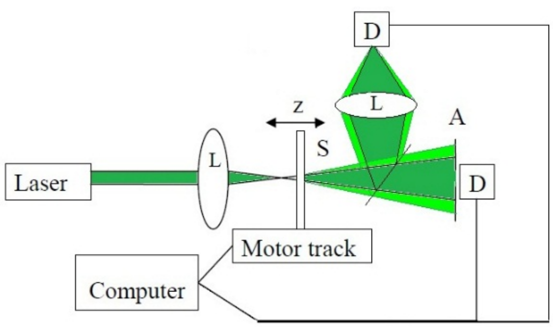

Fig. 4 Schematic diagram of a single beam Z-scan experiment setup: L, Lens; S, Sample; A, Aperture; D, Detector.

Figure 4 shows the schematic diagram of a single beam z-scan experiment with closed and open aperture arrangements was used to measure the nonlinear refractive and nonlinear absorption coefficients. The experiments were performed using a 532 nm laser beam from a diode laser. 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 50 mW. The transmitted light in the far field passed through the aperture and the beam intensity was recorded by a photodiode detector, D.

Table 1 The nonlinear optical parameters measured for Ag nanoparticle at 5.18×10^{-3} M radiated at different doses.

Nanoparticle samples	Average particle size (nm)	n_2 (cm^2/W) $\times10^{-8}$	β (2PA) (cm/W) $\times10^{-4}$
S1	54	-8.57	2.51
S2	41	-6.89	14.6
S3	38	-5.69	21.1
S4	33	-5.13	65.2
S5	30	-4.17	66.9

A. *Closed z-scan experiment*

The closed aperture z-scan curves for Ag nanoparticle prepared by γ radiation at doses 20 kGy is typically shown in Fig. 5. The circle symbols represent the experimental data while the solid lines are theoretical fits to the closed aperture z- scan Equations.

The nonlinear refractive index of the nanoparticle using the simple relation proposed by Sheikh-Bahaei [17]:

$$n_2 = \frac{\Delta\varphi_0 \lambda}{2\pi I_0 L_{eff}} \tag{2}$$

where λ is the wavelength of the laser light, I_0 is the peak intensity within the sample, $\Delta\varphi_0$ is the nonlinear phase shift and L_{eff} is the effective thickness given by the following relations [17,18]:

$$\Delta\varphi_0 = \frac{\Delta T_{p-v}}{0.406\left(1-S\right)^{0.25}} \tag{3}$$

$$L_{eff} = \left[1-\exp\left(-\alpha_0 L\right)\right]/\alpha_0 \tag{4}$$

Here, S is the aperture linear transmittance, L is the thickness of the sample and α is the linear absorption coefficient at wavelength, λ.

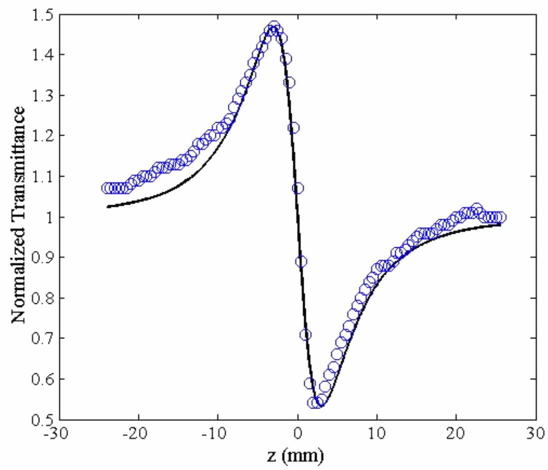

Fig. 5 Normalized z-scan transmittance curves of the Ag nanoparticle at 5.18×10^{-3} M irradiated with 20 kGy dose for closed aperture. The solid lines are the theoretical fit to the experimental data.

The nonlinear refractive index n_2 obtained for the present samples were calculated and listed in Table 1.

Majles Ara *et al.* measured nonlinear refractive index of Ag and Au particles using the moire deflectometry with a CW He–Ne laser at wavelength of 632.8 nm [19]. Regard to their experimental results, they obtained the nonlinear refractive index of Ag and Au nanoparticles at power of 50 mW are 1.8×10^{-7} and 1×10^{-8} (cm^2W^{-1}).

Mashayekh and Dorranian by using the z-scan technique investigated the nonlinear response of the Ag nanoparticle samples were synthesized by nanosecond pulsed laser ablation [20]. They reported optical nonlinear properties of NPs are strongly influenced by their size and concentration. They extracted n_2 in range of 1.9×10^{-7} to 5.1×10^{-7}(cm^2/W) which are in agreement with our results 0.86×10^{-7} to 0.42×10^{-7} (cm^2/W).

The effects of particles size on nonlinear refractive is shown in Fig. 6. In this figure, increasing of nonlinear refractive index with particle size is due to the increases of 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 can be written as [21]:

$$n_2^{th} = \left(\frac{dn}{dT}\right)\frac{\omega_0^2}{4\rho C_p}\left(\frac{\alpha}{D}\right) \quad (6)$$

where ρ is density of solution, Cp is specific heat capacity at pressure constant, dn/dT is temperature coefficient of refractive index and ω_0 is beam waste of laser at focal point. For the case of small changes of ρCp and dn/dT, the nonlinear refractive index will solely depend on the ratio of α/D. In previous work [22, 23] the thermal diffusivity of Ag nanoparticles was measured and showed that an increasing with the growth of particle sizes. Furthermore, there was increasing in linear absorption coefficient with increasing of particle size as shown in Fig. 2. The obtained values of α/D become bigger by increasing the particle size. Then, according to the equation (6) n_2^{th} must be increased.

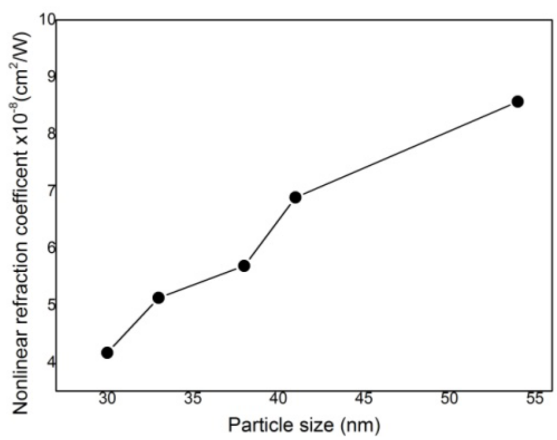

Fig. 6 Nonlinear refraction coefficient plotted as a function of particle size for Ag nanoparticle at concentration 5.18×10^{-3} M.

B. *Open z-scan experiment*

The open aperture z-scan curves for Ag nanoparticle prepared by γ radiation at doses 20 kGy is typically shown in Fig. 7. The symbols represent the experimental data while the solid lines are theoretical fits to the open aperture z- scan Equations.

The nonlinear absorption coefficient β (cm/W) can be obtained from the best fitting performed on the experimental data of the open aperture measurement using the well-known equation used by [17]

$$T(z,s=1)=\sum_{m=0}^{\infty}\frac{\left[-\beta I_0 L_{eff}/\left(1+z/z_0\right)\right]^m}{\left(m+1\right)^{3/2}} \quad (5)$$

where $T(z,s=1)$ is the normalized transmittance for the open aperture (OA) with z_0 being the Rayleigh range. The nonlinear absorption coefficient β obtained for the present samples were calculated and listed in table 1.

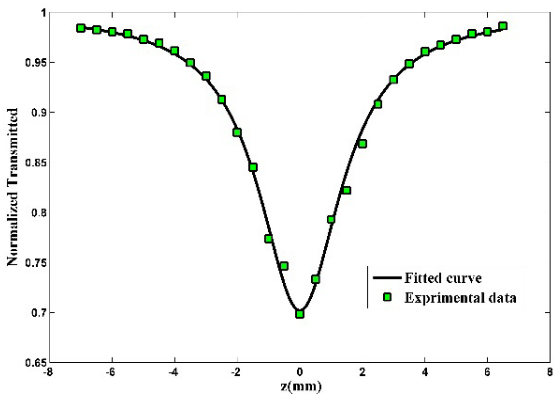

Fig. 7 Normalized z-scan transmittance curves of the Ag nanoparticle at 5.18×10^{-3} M irradiated with 20 kGy dose for open aperture. The solid lines are the theoretical fit to the experimental data.

Shahriari *et al.* obtained the nonlinear absorption coefficients of Ag nanofluid to be 5.8×10^{-3}, 4.5×10^{-3} and 3.2×10^{-3} cm/W for different sizes [24]. Our results β are comparable with these results and exactly are same in order.

The effects of particles size on nonlinear absorption coefficients shown in Fig. 8. In this figure, decreasing the nonlinear absorption coefficient with particles size attributed to large number of particles that will accommodate in a volume if the particles become smaller.

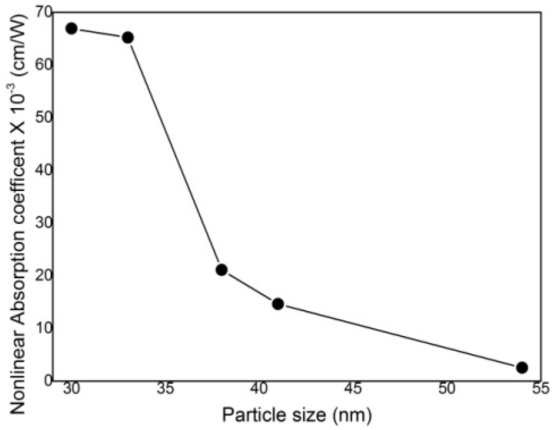

Fig. **8 N**onlinear absorption coefficent plotted as a function of particle size for Ag nanoparticle at 5.18×10^{-3} M.

IV. Conclusion

The nonlinear refractive index, n_2 and nonlinear absorption coefficients, β of Ag nanoparticles at concentration of 5.18×10^{-3} M were successful measured for the fluids with particle sizes. The variations of nonlinear coefficient of samples as particle sizes increase were notified. The sign of the nonlinear refractive index is found to be negative and the magnitude is in the order of 10^{-8} cm^2/W. The nonlinear absorption coefficient of Ag nanoparticles is decreased with increasing of particle sizes.

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