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The Optical Nonlinearity of Au and Ag Nanoparticle Prepared by the γ-Radiation Method

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Abstract: Problem statement: The third order nonlinear optical properties of metal nanoparticles have been of interest in physical chemistry, medical diagnostics and optical devices. Gold colloidal nanoparticles are responsible for the brilliant reds seen in stained glass windows and silver particles are typically yellow. The purpose of the study was to determine the nonlinear refraction and absorption coefficient of the Au and Ag nanoparticles in PVP solution. **Approach:** The samples were prepared by γ-radiation method and the nonlinear optical properties of the composites were investigated using a single beam Z-scan technique with a beam power of 40 mW and operated at wavelength of 532 nm. The measurements were carried out for both Open and closed aperture Z-scan arrangements. **Results:** For both Au/PVP and Ag/PVP samples the results exhibited reverse saturable absorption. The closed aperture Z-scan of the nano-fluid samples revealed self-defocusing effect while the open aperture Z-scan of the samples show a reversible saturable absorption. **Conclusion:** The Z-scan measurement showed that silver and gold nano-fluid prepared by gamma radiation exhibited large thermal nonlinear refractive index n_2 as -8.78×10^{-7} and -2.478×10^{-6} cm^2/W, respectively. We have also investigated nonlinear absorption of these samples and we found a large value of nonlinear absorption for Ag nanoparticle and a weak absorption for Au nanoparticle. In conclusion, the experimental result shows a good nonlinear refractive index at low laser power in which encouraging for possible applications in nonlinear optical devices.

Key words: Z-scan, metal nanoparticles, optical properties

INTRODUCTION

Colloidal solutions containing metal nanoparticles can be prepared by different methods, such as laser ablation method (Ganeev *et al*., 2004) and chemical reaction method (Henglein and Giersig, 1999; Lee and Meisel, 1982). Lately, in situ synthesis technique has been developed to prepare noble metal colloidal solution with well-dispersion and high concentration (Karthikeyan *et al*., 2006). There are many literatures reporting the nonlinear optical response of metal colloids, but nonlinear optical parameters of colloidal metals vary at various stages of aggregation. Because the aggregation of colloidal metals can be excluded in the solid state, therefore it will be more valuable to investigate the optical nonlinearity of metal nanoparticles.

The z-scan measurement technique (Sheik-Bahae *et al*., 1989; 1990) is often used for measuring the strength of the Kerr nonlinearity (i.e., the magnitude of the nonlinear index n_2) and thermal nonlinearity effect of an optical material. Essentially, a sample of the material under investigation is moved through the focus of a laser beam and the beam radius (or the on-axis intensity) is measured at some point behind the focus as a function of the sample position. These quantities are affected by the self-focusing effect. If the nonlinear refractive index is positive and the sample is placed behind the focus, self-focusing reduces the beam divergence and thus increases the detector signal. If the sample is moved to the left-hand side of the focus and the stronger divergence after the focus decreases the detector signal. From the measured dependence of the detector signal on the sample position, it is possible to calculate the magnitude of the nonlinear index. Nonlinear absorption due to two-photon absorption, can also affect the measured signal. This, however, can be measured separately by recording the power of the whole transmitted beam. With these data, the measurement of nonlinearity can be corrected.

In present work, we presented our studies of nonlinear optical properties of Au and Ag nanoparticles

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doped in Polyvinylpyrrolidone (PVP) solution, in which Au and Ag nanoparticles were prepared by γ-radiation method. We investigated the nonlinear refraction and nonlinear absorption using CW laser beam excitation of 532 nm.

MATERIALS AND METHODS

Silver nitrate, $AgNO_3$ (Aldrish-99%), polyvinylpyrrolidone, PVP (MW 29,000 Aldrish), Citrate trisodium (Fluke 95%) isopropanol were used for preparing Ag nano-fluid sample. The PVP and isopropanol were used as a colloidal stabilizer and radical scavenger of hydroxyl radical respectively. The PVP solutions were made by dissolving PVP powder in deionized water at room temperature. The solution was magnetically stirred for 2 h and was bubbled with nitrogen gas (99.5%) in order to remove oxygen.

γ-Radiation (^{60}Co-rays) was used as an effective tool for polymerization process and reducing agent. Silver nitrate (AgNO3) at concentration of 4.709×10^{-3}M was added into 4 mg PVP solution and isopropanol. The mixture was then irradiated with γ-radiation at doses of 30 kGy. In this process, γ-irradiation produces hydrated electrons that reduce the silver ions to silver atoms, which then aggregated and suspended in the solution. A similar procedure was applied for preparing Au nano-fluid sample. In this case $HAuCl_4.3H_2O$ at concentration of 5.886×10^{-4} M and 2.5 g PVP was used. The average diameters of Ag and Au nanoparticles were measured using nanophox machine (Sympatec GmbH, D-38678) and the particles size were recorded as 33.5 and 36.2 nm, respectively.

Figure 1 shows the schematic diagram of a single beam Z-scan experiment used in the present measurement for closed aperture. The open aperture experimental set up has been previously discussed (Shahriari and Yunus, 2010). The experiments were performed using a 532 nm laser beam from Laser-diode (Coherent Compass SDL-532-150T). The beam was focused to a small spot using a lens and the sample was moved along a z-axis by a motorized translational stage. The transmitted light in the far field passed through the aperture and the beam intensity was recorded by a detector D. The laser beam waist ω_0 at the focus length was measured to be 24.4 μm and the Raleigh length was found to satisfy the basic criteria of the z-scan experiment. The linear absorption spectra for both samples were measured using UV-Vis spectrophotometer (Shimadzu-UV1650PC).

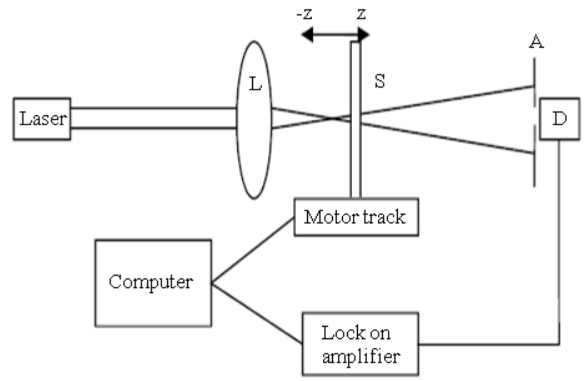

Fig. 1: Schematic diagram of a single beam Z-scan experiment setup: (L) Lens; (S) Sample; (A) Aperture; (D) Detector

RESULTS

Figure 2 and 3 show the linear absorption spectra for Ag and Au nano-fluid. The peaks show the surface plasmon resonance absorptions which are located at 520 and 410 nm, respectively.

Figure 4 and 5 show the typical transmittance curves obtained for Au and Ag nano-fluids prepared by γ-radiation from ^{60}Co source. The laser intensity was measured to be $I_0 = 4.27\times10^3$ W/cm^2 and the aperture size was 0.2. These peak-valley curves indicate that the nonlinear refractive index of the medium is negative. The third order nonlinear refractive index, n_2 was calculated using a similar method to the one as reported by Sheik-Bahae *et al*. (1990) and Wang *et al*. (1994) i.e.:

$$n_2 = \frac{\Delta\phi_o}{kL_{eff}I_o} \quad (1)$$

Where:

k = $2\pi/\lambda$ is the wave factor
I_0 = The beam intensity
L_{eff} = $(1-\exp(-\alpha L))/\alpha$ is the effective thickness of the sample
α_0 = The linear absorption of the medium
L = The thickness of the sample

The linear absorption coefficient α was obtained from the absorption spectra Fig. 2 and 3. The $\Delta\phi_o$ was calculated from the experimental data of the normalized peak to valley transmittance, ΔT_{p-v} given as:

$$\Delta T_{p-v} \approx 0.406(1-s)^{0.25}|\Delta\phi_o| \quad (2)$$

where, s is the aperture linear transmittance and taken to be 0.2 for the present experiment. The solid line in Fig. 4 is the calculated value using analytical equation proposed by Liao *et al*. (1997); (1998):

$$T(z,\Delta\phi) = 1 - \frac{4\Delta\phi_o x}{(x^2+1)(x^2+9)} \quad (3)$$

where, $x = z/z_0$.

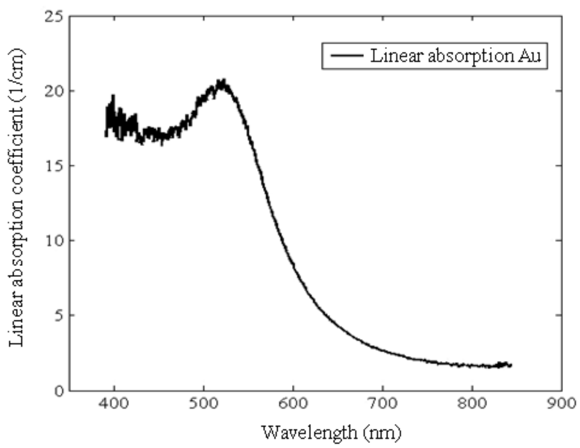

Fig. 2: Linear absorption coefficient Au/PVP nano-fluid at concentration of 5.886×10^{-4} M. The average particle size is 36.2 nm

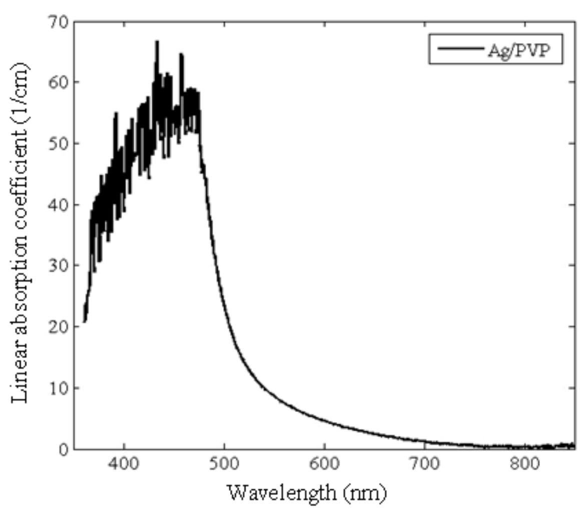

Fig. 3: Linear absorption coefficient Ag/PVP nano-fluid at concentration of 4.709×10^{-3} M. The average particle size is 33.5 nm

The nonlinear absorption was obtained by analyzing the experimental data using a well known nonlinear absorption equation proposed by Sheik-Bahae *et al.* (1990):

$$T(z) = \sum_{m=0}^{\infty} \left(\frac{\beta I_0 l_{eff}}{1 + z^2 / z_0^2} \right)^m (m+1)^{-3/2} \quad (4)$$

Where:

z_0 = $k\omega_0^2/2$ is the diffraction length of the beam

ω_o = the beam waist radius at the focal point

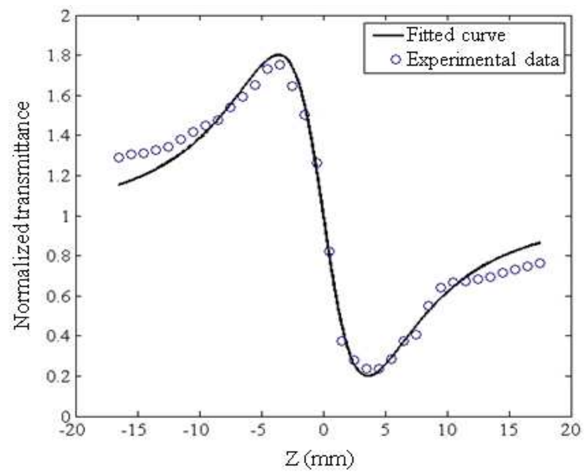

Fig. 4: Closed aperture experimental data of Au nano-fluid measured at concentration of 5.886×10^{-4} M. The average particle size is 36.2 nm. The solid line is the theoretical curve calculated using Eq. 3

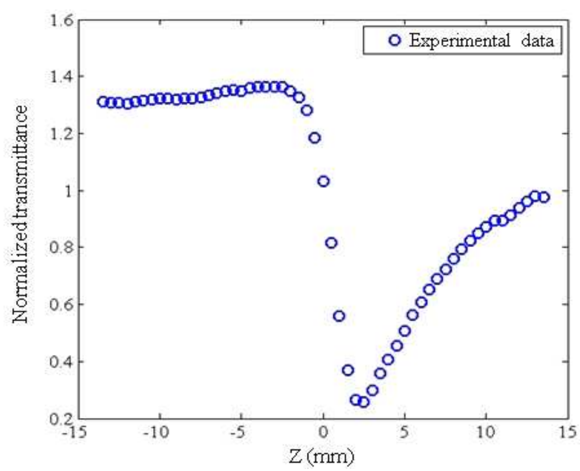

Fig. 5: Closed aperture experimental data of Ag nano-fluid measured at concentration of 4.709×10^{-3} M. The average particle size is 33.5 nm

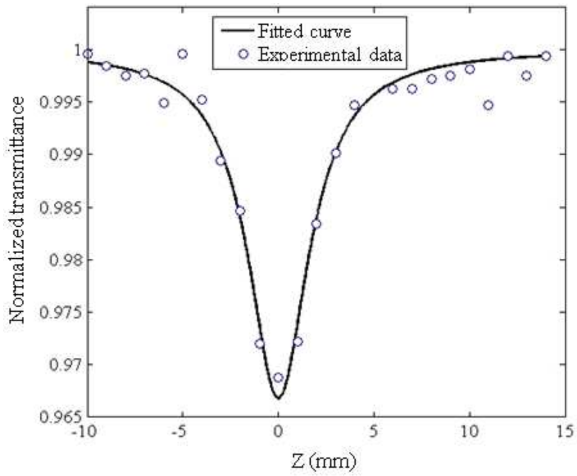

Fig. 6: Open aperture Z-scan curve for Au nanoparticle measured at a concentration of 5.886×10^{-4} M Solid line is the fitted curve using Eq. 4

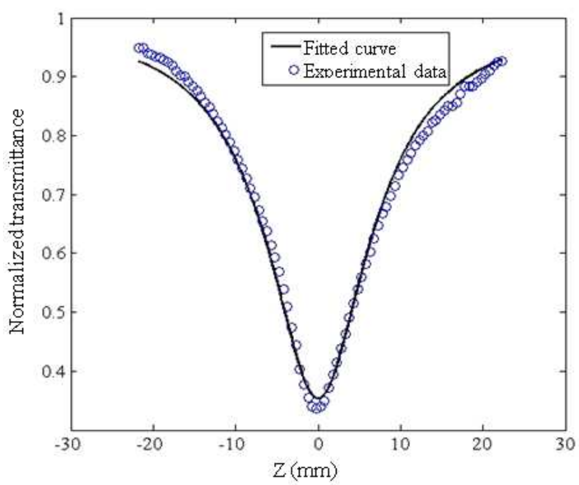

Fig. 7: Open aperture Z-scan curve for Ag nanoparticle measured at a concentration of 4.709×10^{-3}M Solid line is the fitted curve using Eq. 4

using the value of I_0 and s measured in the present work we obtained the value of non-linear refractive index n_2 for Au and Ag nano-fluid sample as-2.47×10^{-6} and -8.78×10^{-7} cm^2/W, respectively.

Figure 6 shows the open aperture z-scan experimental data of Au nanoparticle while Fig. 7 displays the experimental data for Ag nanoparticles. The solid lines in the Fig. 6 and 7 are theoretical fits based on nonlinear absorption phenomenon described by Eq. 4. Using the laser beam intensity at the focus point was as 4.27×10^{3} W/cm^2 we calculated the nonlinear absorption coefficient for these two types of samples. The values are listed in Table 1.

Table 1: Nonlinear optical properties of Au and Ag nano-fluid measured at 532 nm laser beam

Samples	Particle size (nm)	n_2 (cm^2/W)	β(cm/W)	α(cm-1)
Au/PVP	36.2	-2.478×10^{-6}	1.71×10^{-3}	19.110
Ag/PVP	33.5	-8.780×10^{-7}	1.88×10^{-1}	11.852

DISCUSSION

Whenever the sample has a nonlinear refractive index and high 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 Fig. 5 where the closed aperture data (open circle) shows a suppressed peak and enhanced valley. In Fig. 4, the suppressed peak and enhanced valley did not exist due to small nonlinear absorption coefficient of Au nano-fluid sample. For case in Fig. 5, the nonlinear refraction coefficient of the sample was obtained by dividing the Closed Aperture (CA) experimental data (Fig. 5) to the Open Aperture (OA) experimental data of Fig. 7. Thus ΔT_{p-v} measured from CA/OA fitted curve (not shown) was used to calculate the third order nonlinear refractive index of Ag nanofluids as listed in Table 1.

This result shows that the Ag nano-fluid with the particle size of 33.5 nm gives large values of nonlinear refractive index and nonlinear absorption while the Au nano-fluid with the particle size of 36.2 nm gives a large value of nonlinear refraction coefficient and weak nonlinear absorption coefficient.

CONCLUSION

The optical thermal nonlinear coefficient refractive index of Au and Ag solution were investigated by a single beam Z-scan technique. The Z-scan measurement shown that gold and silver nano-fluid prepared by gamma radiation exhibited large thermal nonlinear refractive index n_2 as -2.478×10^{-6} and -8.78×10^{-7} cm^2/W, respectively. The experimental data also confirmed the nonlinearity phenomenon was due self-defocusing process. We have also investigated nonlinear absorption of these materials and found a large value for Ag nanoparticle while a weak absorption for Au nanoparticle. The nonlinear behavior of these nanoparticles at low laser power made them good candidates for possible applications in nonlinear optical devices.

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