

# Nonlinear Absorption and Scattering in Wide Band Gap Silver Sulfide Nanoparticles Colloid and Their Effects on the Optical Limiting

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**Abstract**—In this paper, we study the optical nonlinearities of Silver sulfide ( $\text{Ag}_2\text{S}$ ) nanostructures dispersed in the Dimethyl sulfoxide (DMSO) under exposure to 532 nm, 15 nanosecond (ns) pulsed laser irradiation. Ultraviolet–visible absorption spectrometry (UV-Vis), X-ray diffraction (XRD), and transmission electron microscopy (TEM) are used to characterize the obtained nanocrystal samples. The band gap energy of colloid is determined by analyzing the UV–Vis absorption spectra of the  $\text{Ag}_2\text{S}$  NPs using the band theory of semiconductors. Z-scan technique is used to characterize the optical nonlinear properties of the  $\text{Ag}_2\text{S}$  nanoparticles (NPs). Large enhancement of two photon absorption effect is observed with increase in concentration of the  $\text{Ag}_2\text{S}$  nanoparticles using open Z-scan measurements in the ns laser regime. The values of the nonlinear absorption coefficients are determined based on the local nonlinear responses including two photon absorption. The observed aperture dependence of the  $\text{Ag}_2\text{S}$  NP limiting performance indicates that the nonlinear scattering plays an important role in the limiting action of the sample. The concentration dependence of the optical limiting is also investigated. Our results demonstrate that the optical limiting threshold decreases with increasing the silver sulfide NPs in DMSO.

**Keywords**—Nanoscale materials, Silver sulfide nanoparticles, Nonlinear absorption, Nonlinear scattering, Optical limiting.

## I. INTRODUCTION

OPTICAL limiters have received significant attention during recent decades due to the ability to protect human eyes and sensors from intense laser pulses. This phenomenon can be caused by various nonlinear phenomena such as nonlinear absorption, nonlinear refraction, and nonlinear scattering. Any new materials fabricated are examined under different conditions with laser pulses of various energies, wavelengths and durations to understand the nonlinear physical properties [1]-[7]. Among the materials, semiconductor nanoparticles have presented good optical limiting performances due to the nonlinear properties such as nonlinear absorption, nonlinear refraction, nonlinear scattering and thermal nonlinear refraction [1]-[13]. Silver sulfide nanostructures are attractive due to their potential application in different devices such as resistive switching [14], photoelectrochemical cells [15], solar cells [15], and infrared photodetectors [16]. As shown by [13] the silver sulfide nanoparticles can be used as a low power optical limiter because they have exhibited large nonlinear thermo-optical response using CW lasers at 532 nm.

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In this work,  $\text{Ag}_2\text{S}$  NPs colloids at different concentrations of silver sulfide nanoparticles are synthesized by ns pulsed laser ablation of a silver plate in DMSO. We have used Z-scan method to measure the linear and nonlinear optical coefficients of the silver sulfide nanoparticles in nanosecond regime at 532 nm. The open Z-scan behaviours of the samples are investigated based on the local nonlinear responses including two photon absorption. The concentration dependence and aperture dependence of the optical limiting are also investigated.

## II. MATERIAL AND METHODS

Silver sulfide nanoparticles have been prepared by nanosecond pulsed laser ablation of highly pure silver target in the DMSO. The detailed of experimental procedure has been given in reference [17], [18]. The  $\text{Ag}_2\text{S}$  NPs colloids were denoted by A, B, C and D with the silver sulfide nanoparticle concentration of  $0.45 \times 10^{-4}$ ,  $0.87 \times 10^{-4}$ ,  $1.7 \times 10^{-4}$  and  $3.51 \times 10^{-4}$  Mol/L respectively. The prepared  $\text{Ag}_2\text{S}$  NPs colloids were studied using transmission electron microscopy, X-ray diffraction and a UV-Vis optical absorption spectrophotometer. A CW low power (100mW) diode-pumped Nd:YVO4 laser operating at a wavelength of 532nm was also used to measure the linear absorption coefficient of the  $\text{Ag}_2\text{S}$  NPs colloids. The nonlinear optical properties of the  $\text{Ag}_2\text{S}$  NPs colloids were studied by the Z-scan measurements using a 15-ns (FWHM) laser pulses irradiation at a wavelength of 532 nm. A similar optical geometry as given in Ref. 18 was used for nonlinear optical measurement. The beam was focused onto the samples (10mm cell) by using a lens with 50 cm focal length. The spot size in the focal region was  $65 \mu\text{m}$  ( $\text{HW}1/e^2\text{M}$ ).

## III. RESULTS AND DISCUSSION

The UV–Vis absorption spectra of the  $\text{Ag}_2\text{S}$  NPs synthesized in DMSO at different concentrations of silver sulfide nanocrystals are shown in Fig. 1. The energy and the type of transition for the band gap energy of colloid are determined by analyzing the UV–Vis absorption spectra of the  $\text{Ag}_2\text{S}$  NPs using the band theory of semiconductors. The absorption coefficient for direct transition is written as [19].

$$\alpha = A(h\nu - E_g)^{1/2}/h \quad (1)$$

Moreover, for the indirect transition is written as:

$$\alpha = B(h\nu - E_g)^2/h\nu \quad (2)$$

where  $A$  and  $B$  are the absorption constants,  $h$  is Planck's constant,  $\nu$  is the frequency and  $E_g$  is band gap energy. The direct and indirect energy band gaps are obtained by extrapolating the linear part of the diagram of  $(\alpha h\nu)^2$  vs photon energy and  $(\alpha h\nu)^{1/2}$  versus photon energy, respectively (Figs. 2 and 3). We obtained the direct and indirect band gap energy to be 3.3 eV, 1.7 eV for Ag<sub>2</sub>S NPs. It is clear that the value of the indirect transition is smaller than the value calculated for the direct transition due to the phonon involvement in the optical absorption process.

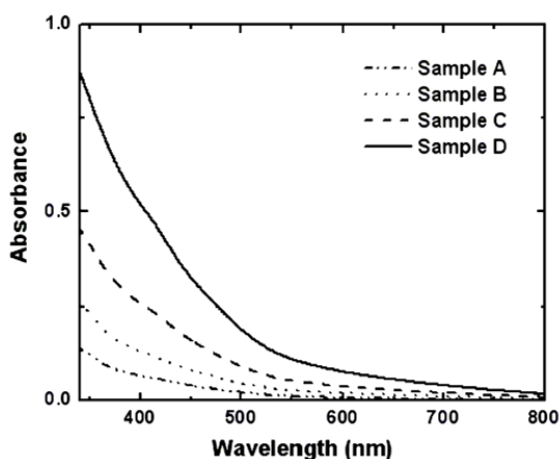


Fig. 1 The absorption spectra of the Ag<sub>2</sub>S NPs colloids at different concentrations

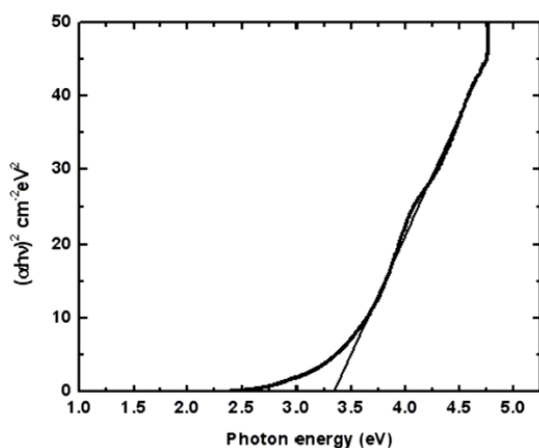


Fig. 2 The solid curve shows the plot of the  $(\alpha h\nu)^2$  of the Ag<sub>2</sub>S NPs and the solid line is the extrapolating of the linear part of the plot

Fig. 4 shows the XRD pattern of the Ag<sub>2</sub>S NPs film. The film shows highly crystalline structure with well-resolved diffraction peaks which are indexed as an  $\alpha$ -acanthite phase of Ag<sub>2</sub>S (JCPDS 14-0072). The TEM image of the Ag<sub>2</sub>S NPs colloid prepared in DMSO are presented in Fig. 5. The shape of the Ag<sub>2</sub>S NPs is spherical and the average Ag<sub>2</sub>S NPs radius is found to be about 4.5 nm. As shown in Fig. 6 the diffraction

pattern obtained by TEM also confirms the crystalline structure of the Ag<sub>2</sub>S NPs.

The linear absorption measurements of the Ag<sub>2</sub>S NPs colloids were performed under exposure to a low-power CW laser at the wavelength of 532 nm. Based on the beer-lambert law, the linear absorption coefficients are obtained for the colloids in range of (0.1-0.42) cm<sup>-1</sup>.

The open-aperture Z-scan experiment was performed with the nanosecond laser at wavelength of 532 nm. Fig. 7 shows the nanosecond open-aperture Z-scan measurement for the Ag<sub>2</sub>S NPs colloid with the silver sulfide nanoparticle concentration of 3.5 × 10<sup>-4</sup> Mol/L. The measurement result is analyzed through the process of the two photon absorption using the procedure of [20] and the solid line shows the fit. The extracted values for linear and nonlinear absorption coefficients are presented in Table I. The results in the nanosecond time domain show that the presence of the Ag<sub>2</sub>S NPs enhances the optical properties of the medium. We have also experimentally investigated nonlinear absorption and refraction of DMSO using the closed- and open-aperture Z-scan experiments by nanosecond pulsed laser at 532 nm. The measurements do not show any nonlinearity for the DMSO in the nanosecond regime. This means that the presence of the Ag<sub>2</sub>S NPs in the medium causes the observation of nonlinearities such as nonlinear absorption and scattering.

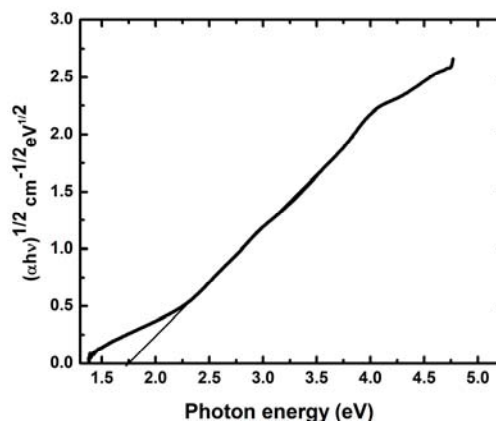


Fig. 3 The solid curve shows the plot of the  $(\alpha h\nu)^{1/2}$  of the Ag<sub>2</sub>S NPs and the solid line is the extrapolating of the linear part of the plot

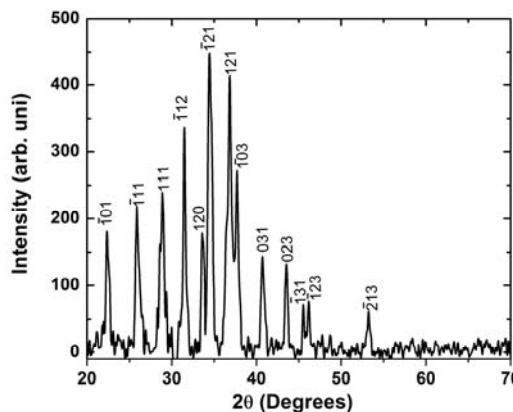


Fig. 4 The XRD pattern of Ag<sub>2</sub>S NPs

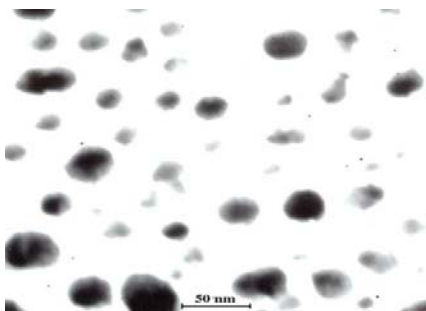


Fig. 5 The TEM image of the Ag<sub>2</sub>S NPs colloid

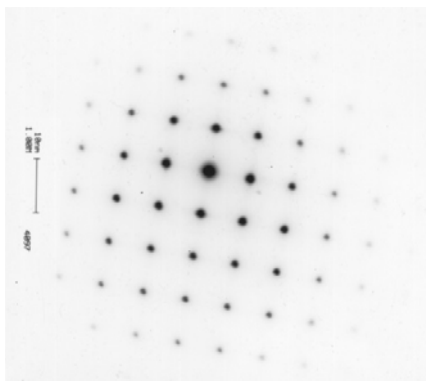


Fig. 6 The electron diffraction pattern of the Ag<sub>2</sub>S NPs obtained by TEM

TABLE I  
 THE MEASURED VALUE OF LINEAR AND NONLINEAR OPTICAL COEFFICIENTS  
 OF THE Ag<sub>2</sub>S NPs IN DMSO WITH DIFFERENT CONCENTRATIONS

Sample	Concentration (mol/L)	$\alpha$ (cm <sup>-1</sup> )	$\beta$ (cm/GW)
A	$0.45 \times 10^{-4}$	0.10	12.5
B	$0.87 \times 10^{-4}$	0.16	23.0
C	$1.70 \times 10^{-4}$	0.23	47.1
D	$3.51 \times 10^{-4}$	0.42	90.2

The optical limiting effect of the colloids was investigated under exposure to nanosecond laser at 532 nm. Fig. 8 demonstrates the optical limiting properties of the Ag<sub>2</sub>S NPs when different diaphragm sizes are used before the output detector. Considering the applied laser beam diameter to be about 3mm at the diaphragm position, it is not expected that changing the aperture size from 4 to 14mm (open aperture) should appreciably change the transmitted energy for a two-photon absorption process.

As shown in Fig. 8, it is clear here that the transmitted energy decreases with decreasing diaphragm size. This aperture dependence indicates that the nonlinear scattering may play an important role in the observed optical limiting performance of the Ag<sub>2</sub>S NPs. The Ag<sub>2</sub>S NPs may enhance the absorption of laser light by the two-photon absorption process and induce a very high rise in the temperature of the sample, which leads to the formation of scattering centres. Fig. 9 shows the optical limiting properties of the Ag<sub>2</sub>S NPs dispersed in DMSO at different concentrations. As it is clear in this figure the limiting threshold decreases with increase in concentration of the Ag<sub>2</sub>S nanoparticles. Hence, the desirable

threshold limiting power can be achieved by changing the nanoparticle concentration. These suggest that Ag<sub>2</sub>S colloid could be a very promising nonlinear medium for nonlinear photonics devices in ns time regime.

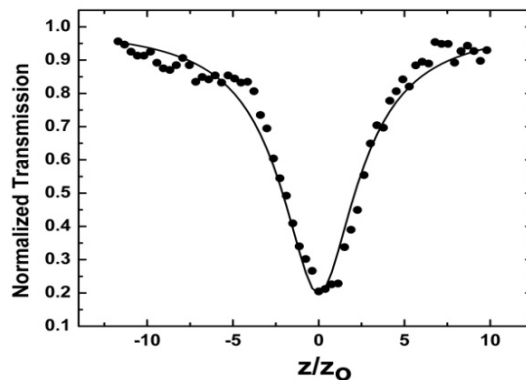


Fig. 7 Open-aperture Z-scan measurement of the sample A using ns pulsed laser at 532 nm. The solid curve is the theoretical fit for the two-photon absorption process

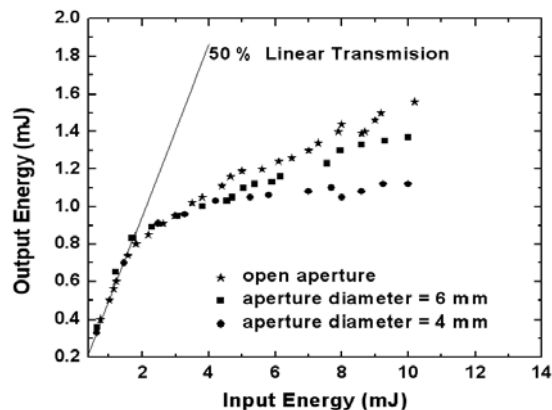


Fig. 8 Optical limiting performances of the Ag<sub>2</sub>S NPs colloid at different aperture diameter using ns pulsed laser at 532 nm

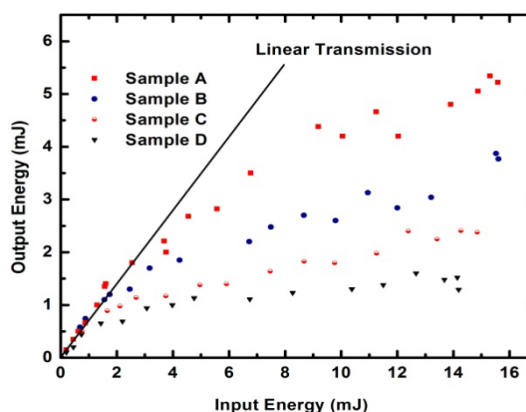


Fig. 9 Optical limiting performances of the Ag<sub>2</sub>S NPs colloids at different concentrations using ns pulsed laser at 532

#### IV. CONCLUSION

The XRD result of the prepared Ag<sub>2</sub>S NPs shows that a pure monoclinic  $\alpha$ -phase Ag<sub>2</sub>S has been obtained. The electron

diffraction of the colloid confirmed the crystalline structure of the NPs. The values of the direct and indirect band gap energy of the NPs were determined. The optical nonlinear properties of the Ag<sub>2</sub>S NPs colloid were investigated using a nanosecond pulsed laser irradiation at 532 nm. The nonlinear absorption coefficients were measured for the colloids using open Z-scan method. The values of the nonlinear absorption coefficients of samples with different concentrations are within the range of 12.5-90.2 cm/GW. The aperture-dependence of the optical limiting of the Ag<sub>2</sub>S colloid was due to the nonlinear scattering effect. The strong optical limiting effects at the different concentrations of Ag<sub>2</sub>S NPs were observed with the nanosecond pulsed laser at 532. Our results show that the limiting threshold decreases with increase in concentration of the Ag<sub>2</sub>S nanoparticles in DMSO. The excellent nonlinear optical performance of the Ag<sub>2</sub>S NPs colloid under exposure to ns pulsed laser make it an ideal candidate in photonics device fabrication such as optical limiters.

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