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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 (Ag_2S) 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 Ag_2S NPs using the band theory of semiconductors. Z-scan technique is used to characterize the optical nonlinear properties of the Ag_2S nanoparticles (NPs). Large enhancement of two photon absorption effect is observed with increase in concentration of the Ag_2S 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 Ag_2S 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 liming 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, wavelenghts 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, Ag_2S 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 liming 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 Ag_2S NPs colloids were denoted by A, B, C and D with the silver sulfide nanoparticle concentration of 0.45×10^{-4}, 0.87×10^{-4}, 1.7×10^{-4} and 3.51×10^{-4} Mol/L respectively. The prepared Ag_2S 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 Ag_2S NPs colloids. The nonlinear optical properties of the Ag_2S 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 µm ($HW1/e^2M$).

III. Results and Discussion

The UV–Vis absorption spectra of the Ag_2S 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 Ag_2S NPs using the band theory of semiconductors. The absorption coefficient for direct transition is written as [19].

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

Moreover, for the indirect transition is written as:

$$\alpha = B(h\upsilon - E_g)^2/h\upsilon \qquad (2)$$

where A and B are the absorption constants, h is Plank's constant, υ 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 $(\alpha h\upsilon)^2$ vs photon energy and $(\alpha h\upsilon)^{1/2}$ 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_2S 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.

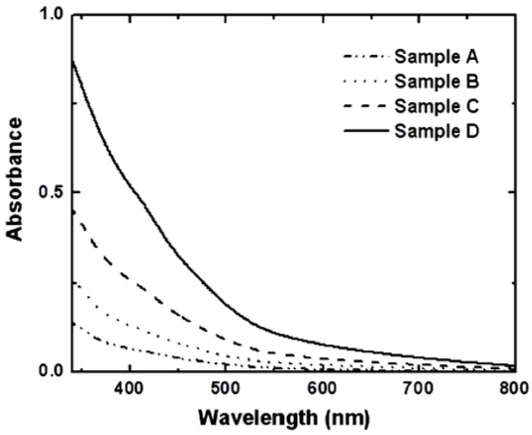

Fig. 1 The absorption spectra of the Ag_2S NPs colloids at different concentrations

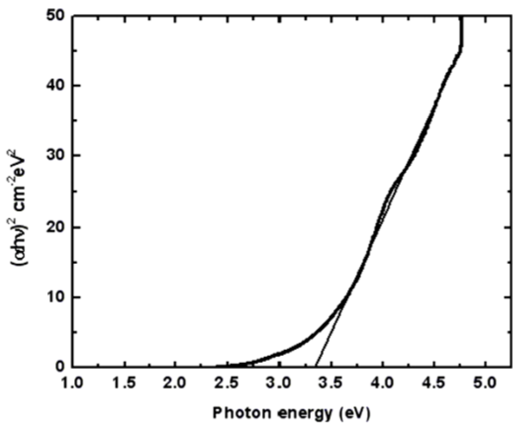

Fig. 2 The solid curve shows the plot of the $(\alpha h\upsilon)^2$ of the Ag_2S NPs and the solid line is the extrapolating of the linear part of the plot

Fig. 4 shows the XRD pattern of the Ag_2S NPs film. The film shows highly crystalline structure with well-resolved diffraction peaks which are indexed as an α-acanthite phase of Ag_2S (JCPDS 14-0072). The TEM image of the Ag_2S NPs colloid prepared in DMSO are presented in Fig. 5. The shape of the Ag_2S NPs is spherical and the average Ag_2S 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_2S NPs.

The linear absorption measurements of the Ag_2S 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^{-1}.

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_2S NPs colloid with the silver sulfide nanoparticle concentration of 3.5×10^{-4} 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_2S 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_2S NPs in the medium causes the observation of nonlinearities such as nonlinear absorption and scattering.

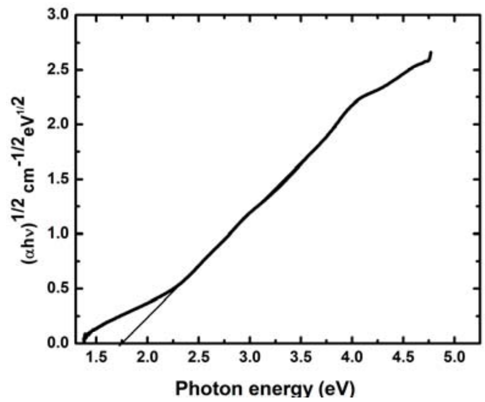

Fig. 3 The solid curve shows the plot of the $(\alpha h\upsilon)^{1/2}$ of the Ag_2S NPs and the solid line is the extrapolating of the linear part of the plot

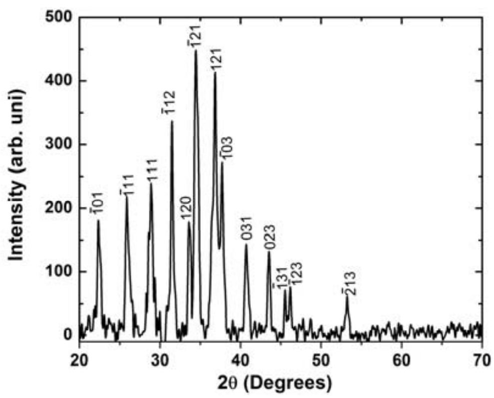

Fig. 4 The XRD pattern of Ag2S NPs

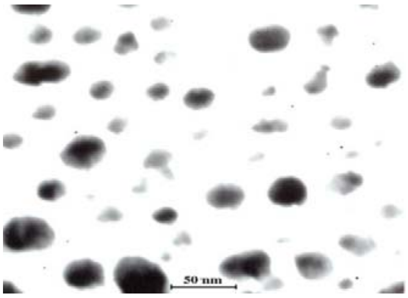

Fig. 5 The TEM image of the Ag2S NPs colloid

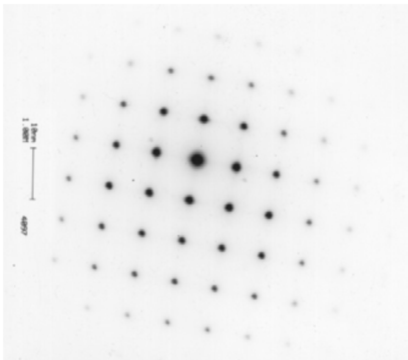

Fig. 6 The electron diffraction pattern of the Ag_2S NPs obtained by TEM

TABLE I
THE MEASURED VALUE OF LINEAR AND NONLINEAR OPTICAL COEFFICIENTS OF THE AG_2S NPS IN DMSO WITH DIFFERENT CONCENTRATIONS

Sample	Concentration (mol /L)	α (cm^{-1})	β (cm/GW)
A	0.45×10^{-4}	0.10	12.5
B	0.87×10^{-4}	0.16	23.0
C	1.70×10^{-4}	0.23	47.1
D	3.51×10^{-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_2S 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_2S NPs. The Ag_2S 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_2S 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_2S nanoparticles. Hence, the desirable threshold limiting power can be achieved by changing the nanoparticle concentration. These suggest that Ag_2S colloid could be a very promising nonlinear medium for nonlinear photonics devices in ns time regime.

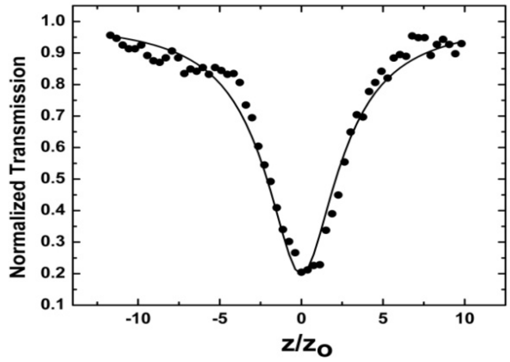

Fig. 7 Open-aperture Z-scan measurement of the sample A using ns pulsed laser at 532 nm. The solid curve is the theoretical fit for the two-photon absorption process

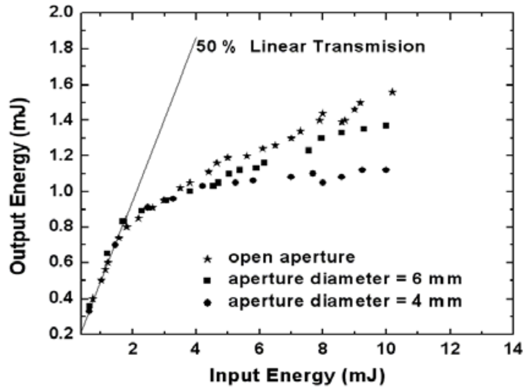

Fig. 8 Optical limiting performances of the Ag_2S NPs colloid at different aperture diameter using ns pulsed laser at 532 nm

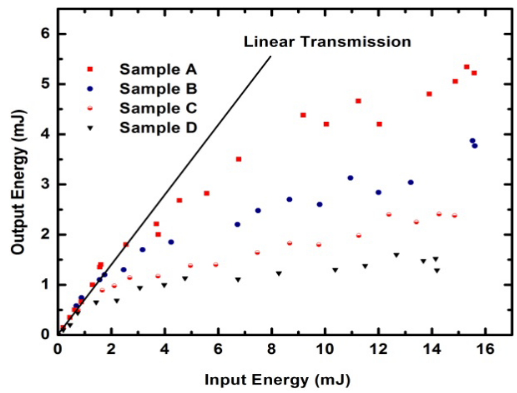

Fig. 9 Optical limiting performances of the Ag_2S NPs colloids at different concentrations using ns pulsed laser at 532

IV. CONCLUSION

The XRD result of the prepared Ag_2S NPs shows that a pure monoclinic α-phase Ag_2S 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_2S 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_2S colloid was due to the nonlinear scattering effect. The strong optical limiting effects at the different concentrations of Ag_2S 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_2S nanoparticles in DMSO. The excellent nonlinear optical performance of the Ag_2S 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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