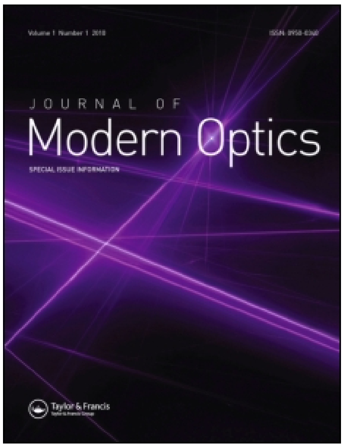

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Tingchao He[a]; Zhipeng Cai[a]; Pengwei Li[a]; Yongguang Cheng[a]; Yujun Mo[a]
[a] Institute of Optics & Photoelectronic Technology, Henan University, Kaifeng, P.R. China

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Third-order nonlinear response of Ag/methyl orange composite thin films

Tingchao He, Zhipeng Cai, Pengwei Li, Yongguang Cheng and Yujun Mo*
Institute of Optics & Photoelectronic Technology, Henan University, Kaifeng, P.R. China; College of Physics and Information Optic-electronics, Henan University, Kaifeng, P.R. China

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The large third-order nonlinearities of metal nanocluster doped oxide matrix composite films have been investigated widely, but there is very little literature reporting third-order nonlinearity of metal nanoparticle doped azobenzene molecule thin films induced by picosecond laser pulses. This paper has investigated the third-order nonlinearity of colloidal Ag and methyl orange composite films using the Z-scan technique with 38 ps pulses at 532 nm apart from the surface plasma resonance frequency of composite film. Large and negative third-order nonlinearity was observed. The mechanism responsible for the process of nonlinear refraction was discussed in terms of the enhancement of the local field effect, which was confirmed by using the SERS technique. At the end, the figures of merit were evaluated and the results showed that this material would be valuable in the application of all-optical devices.

Keywords: third-order nonlinearity; methyl orange; colloidal Ag; Z-scan; SERS; figures of merit

1. Introduction

Recently, there has been growing interest in nanocomposite films. When the Au, Ag and Cu nanocluster are embedded in dielectric matrices, the films will exhibit specific optical absorption and large third-order nonlinearity, which have great potential application in nonlinear optical devices. Nanoparticles show strong surface plasma resonance, which occurs in the UV-visible to near-IR region, depending on the metal species, shape and dielectric medium. In previous studies, nanosized metal clusters were embedded in dielectric matrices with low dielectric constant and small optical nonlinearities, such as SiO_2 and Al_2O_3 [1,2]. Also, when nanosized metal clusters are embedded in oxides with high dielectric constant and large dielectric matrices, such as $BaTiO_3$ and $LiNbO_3$, they show large third-order nonlinearity [3]. In very recent years, nonlinear optical properties of metal nanoparticle doped organic thin films have been investigated [4]. There has been growing interest in the third-order nonlinearity of azo-dye materials for their large $\chi^{(3)}$ value, which are interesting for application in

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*Corresponding author. Email: moyj@263.net

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optical-limiting and optical switching applications. However, optical nonlinearities of metal nanoparticle doped azobenzene molecule thin films have been rarely reported on up to now. In this paper, the off-resonant third-order nonlinearity of methyl orange (MO) and colloidal Ag composite films are investigated using the Z-scan technique with picosecond laser pulses.

Most of the investigation into nonlinear-optical characterization of metal nanoparticles in dielectric materials was performed by the use of lasers with wavelengths close to the absorption maximum of the surface plasma resonance of nanoparticles. For Ag and Au nanoparticles prepared by chemical methods, when the nanoparticles are small, the surface plasma resonance is located in the 410–420 and 550 nm regions, respectively. Whereas, when the aggregation of nanoparticles increases, it will broaden the plasma resonance peak and will give rise to a spectral feature at longer wavelengths [5]. It is obvious that the third-order nonlinear response of metal nanoparticles exhibits the largest cubic nonlinearity under the conditions of resonance excitation, which is due to the strengthening of the local field at surface plasma resonance frequencies. Until now, the largest third-order nonlinearity (10^{-6} esu) by pulse laser excitation was observed in Au–Al_2O_3 composite films [1].

Though the materials exhibit larger third-order nonlinearity than that observed apart from the resonant frequency region, the Stegeman conditions are not fulfilled because of large linear absorption when operating near resonant frequencies [4]. In order for third-order nonlinear materials to be useful in optical signal processing devices it must satisfy two conditions, the Stegeman conditions. The first is that the effect of linear absorption must be weak compared to the effect of nonlinearity. This needs the figure of merit $W = \Delta n/(a\lambda) > 1$, where $\Delta n = n_2 I$ is the induced index change, a is the linear absorption (expressed in units of inverse length) and λ is the wavelength of light (units of length). The other is that the effect of two-photon absorption must be weak compared to the nonlinear effect. This needs the figure of merit $T = (\beta\lambda)/|\gamma| < 1$, where β is the two-photon absorption coefficient (cm W^{-1}) [6]. At the same time, it should be taken into account that the nonlinear optical materials must work at the wavelengths of the most common lasers, such as Nd:YAG ($\lambda = 1064$ or 532 nm) from the viewpoint of possible practical application of these composite materials. It will be useful to investigate the third-order nonlinearity of composite materials for the consideration of application [7].

MO is an important azobenzene molecule, and there have been many reports about the nonlinear optical characteristic and its optical storage, most of which has been investigated by CW laser as excitation source [8–11]. Though the third-order nonlinearity of materials using a CW laser is large, it is not applicable for high-bandwidth optical signal processing due to the long excitation and relaxation times [6].

The Z-scan technique is a simple and effective tool for us to measure the nonlinear properties and has been used widely in material characterization for nearly 20 years. It provides not only the magnitudes of the real part and imaginary part of the nonlinear susceptibility, but also the sign of the real part [12]. Both nonlinear refraction and nonlinear absorption in solid and liquid samples can be rapidly measured by the Z-scan technique, which utilizes self-focusing or self-defocusing phenomena in optical nonlinear materials [13–16].

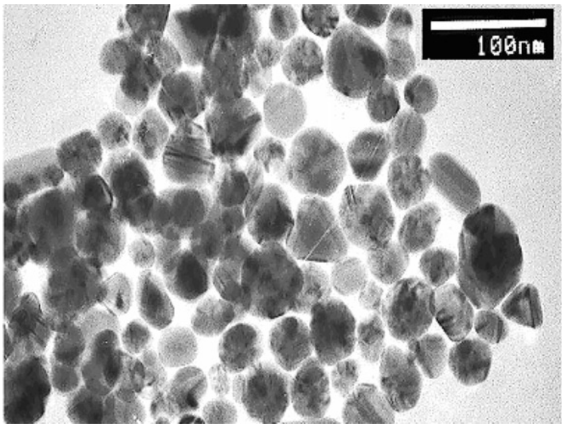

Figure 1. TEM image of colloid Ag solution.

2. Experimental

The colloidal silver nanoparticles were prepared by the method proposed by Lee and Meisel [17]. The concentration of nanoparticles was 10^{-3} M. The TEM image of colloidal silver nanoparticles is shown in Figure 1, from which it is known that most of the Ag clusters are spherical with diameters ranging from 20 to 50 nm.

The Ag/MO film was prepared as follows: MO and PVA (the quality ratio of MO to PVA is 1:10) were dissolved separately in distilled water. The solution of MO and PVA was mixed completely with equal volume. The mixed solution was added to a colloid solution of silver nanoparticles with equal volume. Then the obtained solution was stirred for 40 min and some solution was spread by spin-coating on clear optical glass. The last step consisted of drying the samples under vacuum at 40°C for 40 min and the morphology of the cross-section by scanning electron microscopy revealed a 4 μm thickness of the films.

Figure 2(*a*) shows the linear absorption spectrum of colloid Ag solution with its peak at 420 nm and methyl orange aqueous solution (10^{-4} M) with its peak at 467 nm. The linear absorption spectrum of the composite film with its peak at 448 nm is shown in Figure 2(*b*). All the absorption spectra are measured by an UV–VIS–NIR spectrophotometer (Type: Varian Cary 5000). The absorption of glass substrate was eliminated from the absorption spectrum. As compared to the absorption peak of colloid Ag solution and methyl orange aqueous solution, the absorption peak of composite film shifts by 28 and 19 nm, respectively.

In the Z-scan technique, the transmittance of a tightly focused Gaussian beam through a finite aperture in the far field is measured by a detector, which is a function of the sample position z with respect to the focal plane. Since the nonlinear refraction of the film causes a spatial beam broadening or narrowing in the far field, light intensity irradiated on the sample is different at each position, which results in the changed fraction of light that passes through the aperture as the sample position moves. A typical peak–valley (valley–peak) transmittance curve is obtained when the nonlinear refractive index of the medium is negative (positive). Removing the aperture in the far field, it is possible to perform

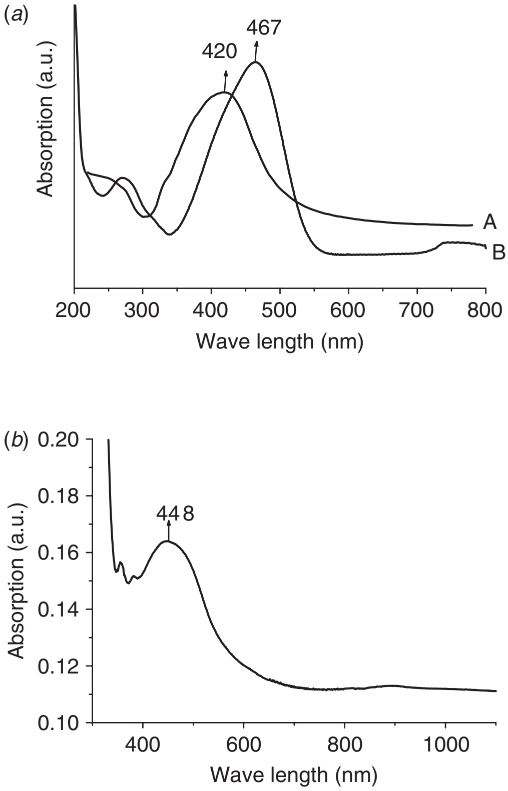

Figure 2. UV-Visible-NIR absorption spectrum of: (*a*) curve A – colloid Ag solution, curve B – methyl orange aqueous solution (10^{-4} M); (*b*) Ag/methyl orange composite film.

nonlinear absorption measurements. In the open aperture Z-scan experiments, the curves are symmetric with respect to the focal point ($z=0$), where they exhibit a minimum transmittance in the case of reverse saturable absorption and a maximum for the saturable absorption. If the materials exhibit both nonlinear refraction and absorption properties we can obtain a pure third-order nonlinear refractive index by dividing the closed aperture data by the open aperture data [12].

Figure 3 is the schematic diagram of the Z-scan experiment set-up in which autocontrol and processing system was adopted. The excitation source was a mode-locked Nd:YAG laser (PY61- 10, Continnum), with a pulse duration of 38 ps (HW/eM) and a repetition frequency of 10 Hz. 532 nm wavelength was used for excitation in the experiment. The detector was a dual-channel energy meter (EPM2000). The excitation light passed through a neutral attenuator A and then was split into two beams with equal energy. One beam entered channel D_2 to monitor the fluctuation of the laser energy, and the other was focused onto the sample by a lens with 26 cm focal length. The spot size at the focal point for 532 nm was 26.4 μm (FW/e^2W) in diameter. As the sample moves along a motor track near the focal point, the transmitted light changing with excitation intensity was recorded by detector D_1. The data from the two channels were input into a computer for processing.

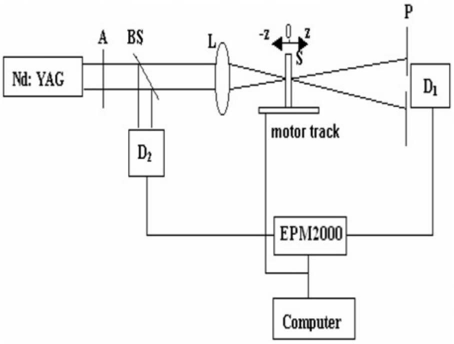

Figure 3. Schematic diagram of Z-scan experiment set-up: A, Attenuator; BS, Beam splitter; L, Lens; P, Aperture; S, Sample; D_1, D_2, Detector.

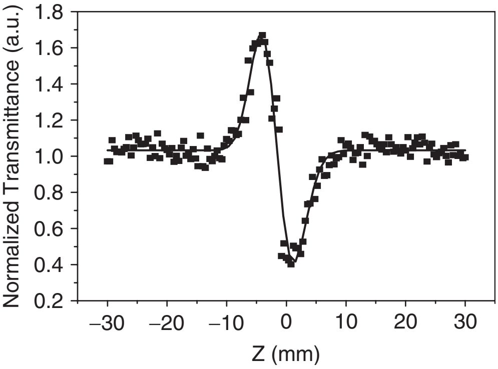

Figure 4. Z-scan data of Ag/MO composite film for 532 nm excitation.

An aperture P was placed before D_1 for the closed aperture experiment. When it was for the open aperture measurement, P was replaced by a lens to collect all the light into D_1.

The scattered light of normal Raman scattering (NRS) and surface enhanced Raman scattering (SERS) spectra were collected by a Raman spectrometer (type: Renishaw RM-1000). The excitation wavelength was 632.8 nm, the spectral resolution was estimated at $2.5\,\mathrm{cm}^{-1}$, the power reaching the sample was 5 mW; at 180°C a back scattering configuration with a 20× lens was used and the integrated time was 10 s × 1.

3. Results and discussion

The third-order nonlinear refractive index n_2 of composite film was evaluated by the measurements of the Z-scan. Figure 4 shows the closed aperture experiment data of the films for $\lambda = 532$ nm. The solid line is the theoretical fit according to Equation (1) [12]

$$T(z, \Delta\Phi_0) = 1 - 4\Delta\Phi_0\chi/[\chi^2 + 9][\chi^2 + 1], \tag{1}$$

where $\chi = z/z_0$, $z_0 = k\omega_0^2/2$ is the diffraction length of the beam, $k = 2\pi/\lambda$ is the vector and λ is the laser wavelength, all in free space.

The peak followed by a valley-normalized transmittance obtained from the closed aperture curves (the dots) indicates that the sign of the refraction nonlinearity is negative, i.e. self-defocusing. It also can be seen in the Z-scan curve that the distance between the peak and valley ($\Delta T_{\mathrm{p-v}}$) is about 6.1 mm as compared to $1.7Z_0$, which indicates that the nonlinear effect is a third-order nonlinear response.

The difference between normalized peak and valley transmittance $\Delta T_{\mathrm{p-v}}$ denoting T_{p}–T_{v} can be directly measured by the Z-scan technique [12]. The variation of this quantity as a function of $|\Delta\Phi_0|$ is given by

$$\Delta T_{\mathrm{pv}} = 0.406(1-s)^{0.25}|\Delta\Phi_0|, \tag{2}$$

where $s = 1 - \exp(-2r_0^2/\omega_0^2)$ is the aperture linear transmittance with r_0 denoting the aperture radius and ω_0 (HW/e^{2}M) denoting beam radius at the aperture in the linear region. $\Delta\Phi_0$ can be obtained from Equation (3):

$$\Delta\Phi_0 = kL_{\mathrm{eff}}\gamma I_0 = (2\pi/\lambda)L_{\mathrm{eff}}\gamma I_0, \tag{3}$$

where I_0 is the intensity of the laser beam at focus $z=0$, $L_{\mathrm{eff}} = [1 - \exp(-aL)]/a$ is the effective thickness of the sample, a is is the linear absorption coefficient and L is the thickness of the sample. Then the nonlinear refractive index γ can be evaluated utilizing Equations (2) and (3). The third-order nonlinear refractive index γ ($\mathrm{m^2\,w^{-1}}$) is connected with n_2 (esu) by Equation (4)

$$n_2(\mathrm{esu}) = (cn_0/40\pi)\gamma\ (\mathrm{m^2\,w^{-1}}), \tag{4}$$

where γ ($\mathrm{m^2\,w^{-1}}$) and n_2 (esu) both denote the third-order nonlinear refractive index in a different units system.

For Ag/MO composite film, the laser intensity at the focus was $2.47\,\mathrm{GW\,cm^{-2}}$. In our experiment, the aperture linear transmittance is 0.3. The third-order nonlinear refractive index was calculated as $\gamma = -8.67 \times 10^{-11}\,\mathrm{cm^{-2}\,w^{-1}}$ (or 3.10×10^{-8} esu) in our experiment under 532 nm excitation.

The nonresonant third-order nonlinearity of MO/PVA thin films attributed to electronic nonlinearity was investigated in our previous work [18]. Electronic nonlinearities arise from either population redistribution or distortion of electronic clouds. A molecule undergoes a transition from the ground state to the excitation after absorbing a photon. The dipole moment of the molecule changes during such a transition [6]. The cubic nonlinear refractive index of Ag/MO composite film obtained in our experiment is 20 times larger than that of MO doped PVA thin films [18], and it is 10^3 times larger than that of methyl orange solution [19]. It is obvious that the third-order nonlinearity of the Ag/MO composite thin film does not merely result from electric nonlinearity.

The large third-order nonlinearity arises from the enhancement of the local field effect, which is evidenced by the SERS signal of the Ag/MO composite thin film. Surface enhanced Raman scattering (SERS) has long been recognized as a powerful analytical technique for adsorbates on surfaces. Briefly speaking, SERS refers to the observation of a Raman spectrum of certain molecules adsorbed on specially prepared metal surfaces, whose intensity exceeds by a factor of 10^5–10^6 what one expects on the basis of simple calculations. Although not all fine points of the enhancement mechanism have been

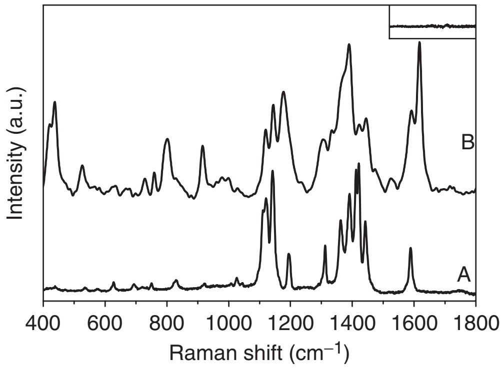

Figure 5. Curve A: NRS of MO powder. Curve B: SERS of the Ag/MO composite thin film; inset: NRS of MO-doped PVA thin film.

clarified, the majority view is that the largest contributor to the intensity amplification results from the electric field enhancement that occurs in the vicinity of metal nanoparticles that are illuminated with light resonant or near resonant with the localized surface-plasmon frequency of the metal structure [20]. In our experiment, the methyl orange molecules adsorbed on the surface of Ag nanoparticles. If the surface local field of the Ag nanoparticles increases, the SERS signal and third-order nonlinearity of methyl orange will both be enhanced. Figure 5 shows the NRS spectrum of MO powder and the SERS spectrum of the Ag/MO composite thin film. The inset in Figure 5 is the NRS spectrum of the MO-doped PVA thin film with 8 μm thickness, and the NRS signal is much weaker than the SERS signal of the Ag/MO composite thin film. Obviously, the Raman signal of MO molecules in the Ag/MO composite thin film is enhanced greatly, which indicates that the local field effect of the nanostructured Ag surface is enhanced greatly. Thus, the third-order nonlinearity of the Ag/MO composite thin film is enhanced greatly by the local field effect.

The third-order nonlinearity observed is not induced by the thermal effect within the pulse temporal width. On one hand, the electronic nonlinearities arise very rapidly (within the 38 ps pulse duration). Refractive index changes due to thermal nonlinearities arise due to density changes in the materials propagating with acoustic wave speed caused by heating [21]; if we estimate it to be on the order of $3 \times 10^3\ \mathrm{m\,s^{-1}}$, the time to propagate a distance equal to the beam radius at focus is about 9 ns at 532 nm excitation, about 230 times longer than the pulse width. On the other hand, thermal heating induced by a single laser pulse persists over some characteristic time t_c. As a result, when the time interval between consecutive laser pulses is shorter than t_c, the thermal effect increases. It is a common assumption that Z-scan measurements should be made with a repetition rate of a few Hertz in order to extract a nonlinear refractive index influenced by only electronic effects. The time scale of this cumulative process is given by $t_c = \omega^2/4D$, where ω is the beam waist and D is the thermal diffusion coefficient of the materials. Generally, the value of D ranges from 1×10^{-7} to $6 \times 10^{-7}\ \mathrm{m^2\,s^{-1}}$. The magnitude of the calculated t_c is within 10^{-3} s, which is much smaller than the time interval between consecutive laser pulses 0.1 s used in our experiment [22].

For practical use in ultra-fast all-optical switching devices, many considerations have been taken to investigate the effectiveness of nonlinear materials. Two figures of merit have to be satisfied for a 2π phase shift in order to evaluate the films for applications in such devices [6]:

$$W = \Delta n/(a\lambda) > 1, \quad T = (\beta\lambda)/|\gamma| < 1. \tag{5}$$

We obtained $W_{532} \approx 4.36$, $T_{532} = 0 < 1$ under 532 nm excitation. The large value of W, the small value of T and large optical nonlinearity, as well as the fast response time make the film promising for applications in all-optical switching technology.

4. Conclusion

The process of nonlinear refraction in Ag/MO composite film has been investigated experimentally. The value of the third-order nonlinear index was measured. It is shown that the nonlinear refraction in the Ag/MO composite film at 532 nm excitation is caused by the process of self-defocusing and that the probable mechanism is due to the local field effect. The figures of merit evaluated showed the film to be a valid candidate for ultra-fast all-optical switching devices.

Acknowledgements

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