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Research Article

Nonlinear-Optical and Fluorescent Properties of Ag Aqueous Colloid Prepared by Silver Nitrate Reduction

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The nonlinear-optical properties of metal Ag colloidal solutions, which were prepared by the reduction of silver nitrate, were investigated using Z-scan method. Under picosecond 532 nm excitation, the Ag colloidal solution exhibited negative nonlinear refractive index ($n_2 = -5.17 \times 10^{-4}\,\mathrm{cm^2/W}$) and reverse saturable absorption coefficient ($\beta = 4.32\,\mathrm{cm/GW}$). The data fitting result of optical limiting (OL) response of metal Ag colloidal solution indicated that the nonlinear absorption was attributed to two-photon absorption effect at 532 nm. Moreover, the fluorescence emission spectra of Ag colloidal solution were recorded under excitations at both 280 nm and 350 nm. Two fluorescence peaks, 336 nm and 543 nm for 280 nm excitation, while 544 nm and 694 nm for 350 nm excitation, were observed.

1. Introduction

Nanometer size noble metallic low-dimensional structures have received much attention in recent years due to their special electronic and optical properties [1–4]. As a typical kind of low-dimensional nanomaterials, metal nanoparticles exhibit a wide range of applications in many fields, such as in the labeling of biological molecules, biosensors, surface-enhanced Raman scattering, and even in commercial paintings and as local heat sources for targeted cancer tumor cell destruction [4, 5]. As promising materials with unique optical properties, the metal nanoparticles have many advantages in tunable photoluminescence spectra with narrow bandwidth, high quantum yield, large multiphoton absorption cross section and fast-response nonlinear refractive index. When the metal nanoparticles 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 [6]. Furthermore, it is proven that the nonlinear optical properties of organic materials can be enhanced by mixing with metal nanoparticles [7].

On the other hand, the nonlinear properties of metal nanoparticles can be modulated by varying the size and shape of them [8, 9]. From a fundamental research viewpoint, the absorption, scattering, and emission properties are inherently related to nanosizes of the metal particles and remain as the primary subject for research [10, 11]. Thus, the synthesis of nanoparticles with a tight control on their size and shape is a requirement for the achievement of many nanotechnology goals. Many efforts have been dedicated to achieve the goal and some unique techniques, such as laser ablation [12, 13], sonolysis method [14], and chemical method which were used DMF as the solvent and as a reducing agent [15], and so forth. However, for many cases, metal nanoparticles with various shapes and sizes dispersed in water rather than with certain shapes or sizes are widely used because of their higher stability, wider wavelength range for optical response, and easier for preparation [16].

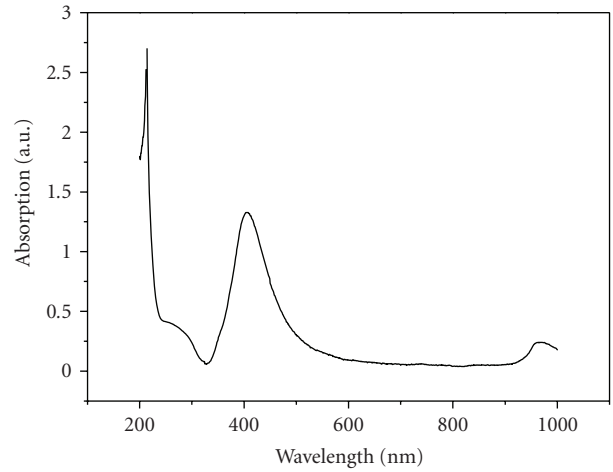
In this work, we presented our studies of nonlinear-optical and fluorescent properties of silver colloid, which was prepared by simple chemical reaction method. To our knowledge, this is the first study to evaluate the optical properties colloidal Ag particles prepared by using the silver-nitrate reduction method. The fluorescence emission spectra of Ag colloidal solution are recorded at 280 nm and 350 nm. The nonlinear refraction and nonlinear absorption

are investigated using the radiation of a 532 nm pulse laser with 10 Hz pulse repetition rate and 38 ps pulse duration. Furthermore, the two photon absorption induced optical limiting in Ag colloidal solution is demonstrated.

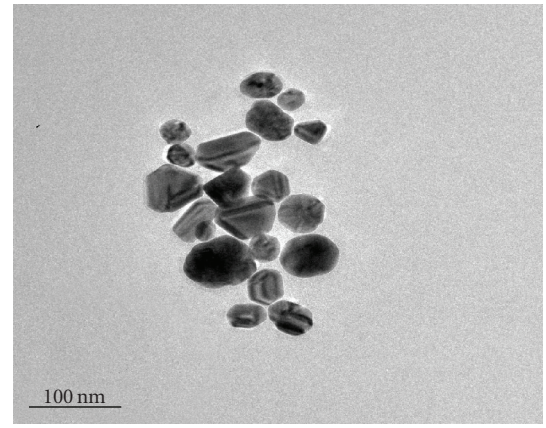
2. Experimental

Colloidal Ag nanoparticles were prepared in an aqueous solution by the reduction of silver nitrate with sodium citrate following the method reported by Lee and Meisel [16]. 36 mg of silver nitrate ($AgNO_3$) was added into 200 mL distilled water. The solution was heated to boiling and 4 mL of 1% trisodium citrate solution was added. The solution was boiled for one and half hours, and the gray Ag colloid was obtained after cooling at ambient. The surface plasma absorption spectrum of Ag nanoparticles is characterized by a strong absorption band in the visible region at 406 nm, as shown in Figure 1(a). Compared to [17], the shape of absorption spectrum is almost the same except for a small red shift for the absorption peak in their experiments (peak at 440 nm). This difference in the shape of the plasma band suggested the change in particle size. They determined that the average size of nanoparticles is about 60 nm, which should be a little larger than that in our experiments according to the red shift in absorption spectrum [18]. The TEM image of the prepared Ag nanoparticles is shown in Figure 1(b). From the picture, it can be seen that the shape of nanoparticles is irregular and the distribution of size in diameter was between 20 and 60 nm. The average size of nanoparticles is about 40 nm and it accords with the absorption spectrum. From the average size of the Ag nanoparticles, we can calculate that the concentration of Ag nanoparticles in colloid is 5×10^{-4} M. The intense absorption band in the visible wavelength range can be attributed to a so-called plasma resonance which occurs when the wavelength of light couples with the oscillation frequency of the conduction electrons. However, the precise wavelength of the plasma resonance depends on several parameters, among which particle size and shape, surface charge, and the nature of the environment are probably the most important [19]. For our case, optical properties of Ag nanoparticles in the visible range can be explained by the effect of the boundary conditions of the coherent electron oscillations and also due to the interband d → sp electronic transitions [20].

In this work, picosecond laser is adopted as the excitation source in Z-scan measurements in order to investigate nonlinear optical (NLO) properties of the Ag colloidal solution. Z-scan technique has been widely used to investigate the NLO properties of various kinds of optical materials [21]. The Z-scan experimental setup in our experiment was shown in Figure 2 and it was similar to [21]. In order to avoid inducing large linear absorption under a picosecond pulse Nd: YAG laser (Continuum Co. Ltd) at 532 nm, the concentration of Ag nanoparticles in colloid is distilled to 5×10^{-5} M in Z-scan experiments. Furthermore, the laser's repetition frequency was 10 Hz and the pulse duration was 38 picoseconds, respectively. The spot size at the focal point was 24.4 μm in radius and the Rayleigh length was



(a)



(b)

Figure 1: (a) Absorption spectrum of Ag colloidal solution; (b) TEM image of Ag nanoparticles.

3.5 mm. The focal length of the lens was 30 cm. The detector was a dual-channel joulemeter EPM2000 (Molectron Co. Ltd). Z-scan system is carefully calibrated by measuring the nonlinear refractive index of CS_2, and the mean error of the experimental data, mostly arising from the fluctuation of the laser power, is below 10%.

3. Results and Discussions

The synthesized colloidal silver nanoparticles are found to be photoluminescent. The fluorescence emission spectra of Ag colloidal solution (with a concentration of 5×10^{-4} M) are recorded on a Perkin-Elmer LS 55. Figure 3(a) presented the photoluminescence of fresh-prepared gray Ag sol under the excitation of 280 nm, which exhibited a sharp and strong peak near 336 nm and a broadened band between 460–700 nm. Photo-induced luminescence process includes the excitation of electron-holes pair, relaxation of the excited electron, and recombination of electrons and holes. It is well known that the fluorescence spectra from metal

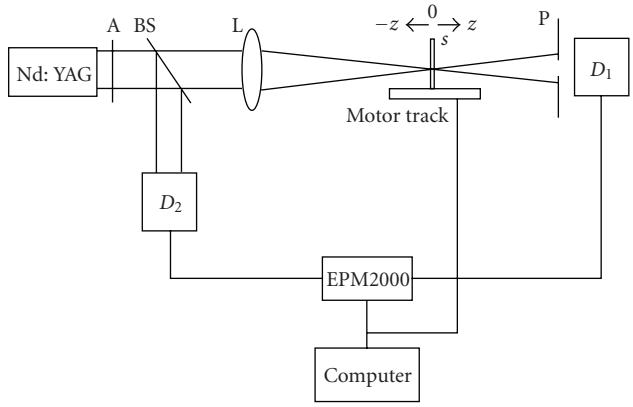


Figure 2: Schematic diagram of Z-scan experimental setup. A: attenuator, BS: beam splitter, L: lens, P: aperture, and S: sample.

nanoparticles vary with different shapes and structures. The experimental result in our case is similar to that in [22], which discusses some of these problems by investigating the photoluminescence of Ag sol with a regulated change of their granularity and concentration. However, Zhao et al. [17] reported the photoluminescence spectra of Ag nanoparticles prepared by citrate reduction, 532 nm laser ablation, and 248 nm laser ablation, respectively, which are much different from those in our case. Complementary to bulk metal, nanoparticles have large surface and a more complex system, and their luminescence often reflects the interaction that affects electron-hole recombination. In most cases, the involvement of silver clusters in the vicinity of the surface in the luminescence process is hypothesized to be important. Charge silver congeries can also be important for the origin of photoluminescence [22, 23]. However, it is still unclear what mechanisms and structural or environmental factors are responsible for the emission signals [24]. Figure 3(b) shows the emission spectrum excited at 350 nm, and two fluorescence peaks are observed (peak at 350 nm, which comes from the excitation light itself, are not included). The first peak in visible wavelength region takes place at 544 nm, while the other peak takes place at 694 nm. The wavelength of the main peak (694 nm) is longer than that under 280 nm's excitation, and it can be easily attributed to the longer excitation wavelength. On the other hand, compared to the broad emission band between 460–700 nm under 350 nm's excitation, the peak at 694 nm is much sharper. This can be explained by the inhomogeneous size of the nanoparticles in Ag aqueous colloid. The smaller nanoparticles can absorb the photons with higher energy (which is manifested as a blue shift in the absorption spectrum) [18]. Then they can be excited to a higher energy level and eventually emit the fluorescence with shorter wavelength when they are back to the ground state. The sharper peak for the longer wavelength's excitation indicates that the nanoparticles with bigger size have a large ratio among the nanoparticles.

Figures 4(a), 4(b), and 4(c) show Z-scan experimental data for closed-aperture (CA) curve, open-aperture (OA) curve, and closed aperture curve divided by open aperture

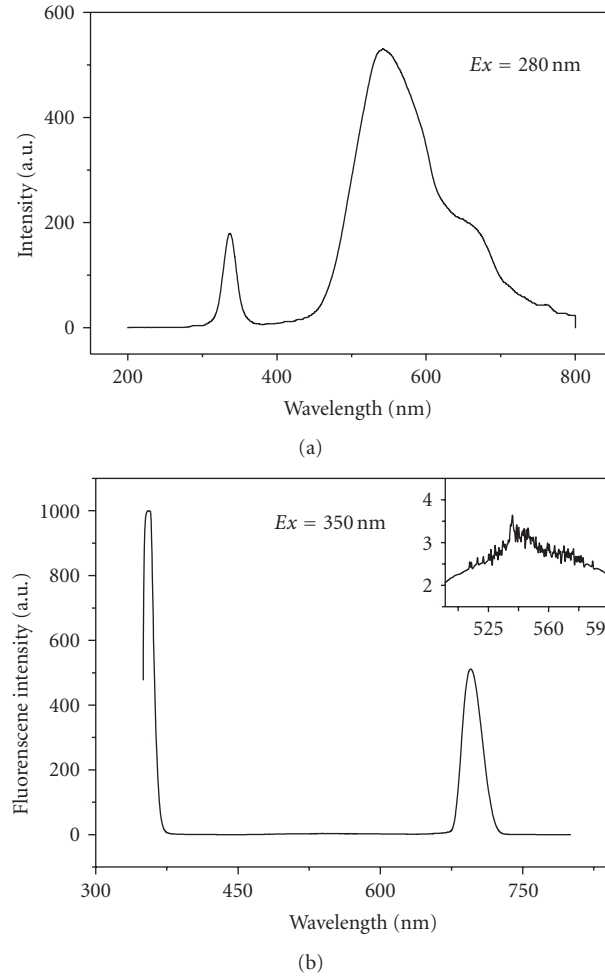


Figure 3: Fluorescence emission spectra of Ag colloidal solution under the excitation of (a) 280 nm and (b) 350 nm.

(CA/OA) curve of the silver aqueous colloid. The non-symmetrical closed aperture Z-scan curve in Figure 4(a) indicated that the nonlinear absorption existed, so the nonlinear refractive index under 532 nm excitation, with division of corresponding open aperture Z-scan curves, could be obtained as shown in Figure 4(c). The shape of the CA/OA Z-scan curve exhibits negative value for the nonlinear refractive index n_2, that is, self-defocusing. A mode-locked Nd:YAG laser (PY61C-10, Continuum) was used as the light source. In this measurement, the input energy was 1 μJ, corresponding to the optical intensity of 2.83×10^9 W/cm^2 at the focus point. The solid line in Figure 4(a) is theoretically fit according to [21]

$$T(z, s = 1) = \sum \frac{[-q_0(z,0)]^m}{(m+1)^{3/2}}, \quad (q_0(z,0) < 1), \qquad (1)$$

where $q_0(z,0) = \beta I_0 L_{\text{eff}}/(1 + z^2/z_0^2)$, $L_{\text{eff}} = [1 - \exp(-\alpha L)]/\alpha$, $z_0 = k\omega_0^2/2$, β is the nonlinear absorption coefficient, I_0 is the intensity of the laser beam at focus $z = 0$, $L_{\text{eff}} = [1 - \exp(-\alpha L)]/\alpha$ is the effective thickness of the sample, α is the linear absorption coefficient, and L is the thickness of the

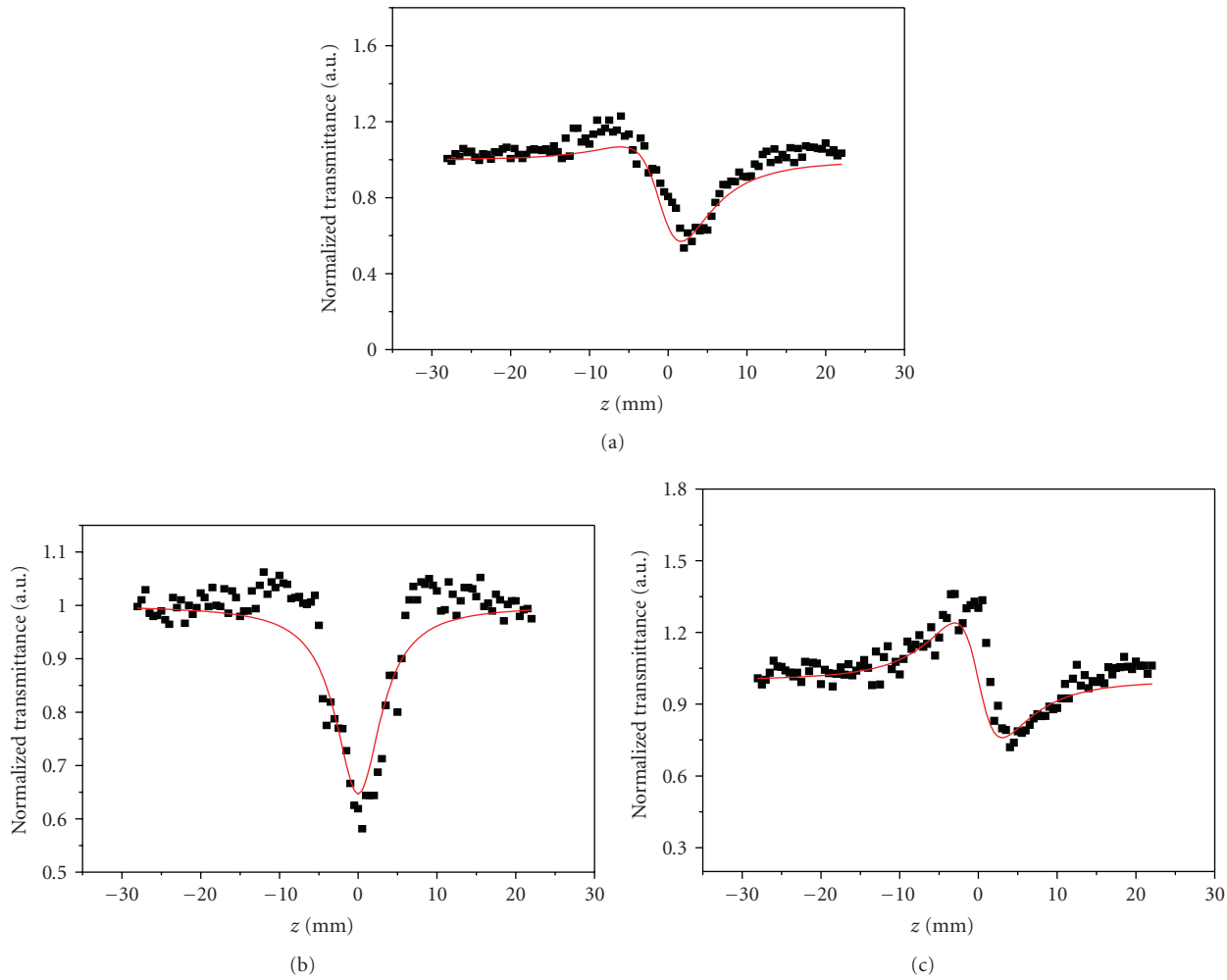


Figure 4: Z-scan experimental data for Ag colloid under picosecond 532 nm excitation: (a) CA curve, (b) OA curve, and (c) CA/OA curve.

sample. In the experiment, $\alpha = 0.2$ and $L_{\text{eff}} = 0.81$ mm. From the theoretical fit result, the nonlinear absorption coefficient was obtained to be 4.32 cm/GW.

The nonlinear refractive index n_2 of the solution is given by [21]

$$n_2 = \frac{\Delta T_{p-v}\lambda}{0.406 \cdot (1-s)^{0.25} \cdot 2\pi \cdot L_{\text{eff}} I_0}, \tag{2}$$

where λ is the wavelength of the pump laser, ΔT_{p-v} is the difference between normalized peak and valley transmittance, and the value of ΔT_{p-v} can be obtained to be 0.5 through the best theoretical fit from the results of the Z-scan curve as shown in Figure 4(c). s is the aperture linear transmittance, I_0 is the intensity of the laser beam at focus $z = 0$. The aperture linear transmittance was $s = 0.40$. And then the third-order nonlinear refractive index is calculated to be -5.17×10^{-14} cm^2/W (or -1.64×10^{-11} esu). This nonlinear refractive index contains the contribution of solvent. However, the nonlinear refraction in the pure water is much smaller than that of Ag colloid, so the contribution of solvent was negligible [25].

The third-order nonlinearity observed is not induced by thermal effect within the pulse temporal width. Firstly, the electronic nonlinearities arise very rapidly (within the 38 ps pulse duration). However, the responding time scale of thermal nonlinearities which arise from density changes in the materials is very large [26, 27]. If we estimate the propagating speed of acoustic wave in the material to be in the order of 3×103 m/s, the time to propagate a distance equal to the beam radius at focus is about 9 ns at 532 nm excitation. This time scale is about 230 times longer than the pulse width. Secondly, thermal heating induced by a single laser pulse can only last for a certain period of 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 repetition rate of several 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} m^2/s to 6×10^{-7} m^2/s.

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. Furthermore, the nonlinear refraction induced by thermal effects is estimated, which results from linear absorption. The value of it can be calculated by [21]

$$\Delta n = \frac{(dn/dT)}{\Delta T} \approx \left(\frac{dn}{dT}\right)\left(\frac{I\tau\alpha}{\rho c}\right), \quad (3)$$

where τ is duration of laser pulses, c is the specific heat of sample, α is coefficient of linear absorption, and I is the laser intensity irradiated on the sample. Under the picosecond excitation, Δn from thermal contribution was calculated to be in order of 2.25×10^{-6}, much smaller than the $\Delta n_0 = n_2 I_0 = 1.46 \times 10^{-4}$ obtained from picoseconds Z-scan measurement, so the thermal effect should be negligible. Reference [28] reported the nonlinear refraction of silver nanoparticles in ethylene glycol at 532 nm was studied using the Z-scan technique with an 8 ns laser and showed negative nonlinear refraction ($n_2 = 8.96 \times 10^{-11}$ esu), which should be induced by the larger thermal effect in nanosecond excitation regime.

At present, the reverse saturable absorption (RSA) properties of optical materials are at the forefront of research. Materials with large RSA can effectively limit the throughput energy of incident light. Since the solution showed pronounced reverse saturable absorption behavior, the research was extended to optical limiting, which was a practical application based on reverse saturable absorption. Figure 5 shows the optical limiting curve for Ag colloidal solution (with a concentration of 5×10^{-5} M) under 38 ps laser pulse. At very low incident fluence, the output fluence of the solution increases linearly as the incident fluence increases with a coefficient 0.64 (which is also in accord with the linear transmittance at 532 nm) obeying the Beer-Lambert law. However, at high incident fluence, the transmittance of the solution decreases with increasing input fluence and a nonlinear relationship is observed between the output and input fluence, suggesting that the Ag aqueous colloid has obvious optical limiting property. With a further increase in the incident fluence, the transmitted fluence of solutions reaches a plateau.

The NLO mechanisms for optical limiting can be two-photon absorption (TPA) or RSA. Generally, TPA can be yielded in principle under the laser irradiation of picosecond or shorter pulses. RSA can be achieved on nanosecond or longer pulses, rather than a picosecond time scale, because of the different excited-state lifetimes involved in a multilevel energy process [29]. In this work, the solution is excited by the laser with 38 ps pulse width at 532 nm. Therefore, we consider that the optical limiting property of the solution may mainly originate from TPA. Using Boggess' theory model, if the beam has a Gausian transverse distribution in the medium, the TPA-induced transmittance change will be [30]

$$T(I_0) = \frac{I(L)}{I_0} = \frac{[\ln(1 + I_0 L\beta)]}{I_0 L\beta}, \quad (4)$$

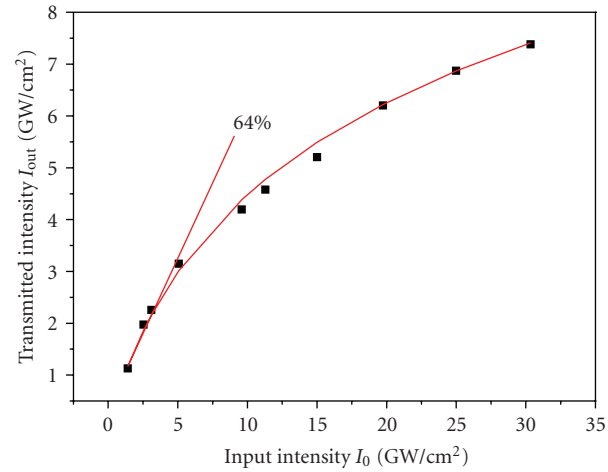


Figure 5: Optical limiting curve for Ag colloidal solution under 38 ps laser pulse.

where I_0 is the incident intensity, L is the thickness of the solution sample, and β is the TPA coefficient of the solution [31]. That equation should be an appropriate theoretical approach to fit the corresponding experimental data. In Figure 5, the solid curve is given by (4) by using the best-fitting parameter of $\beta = 4.1$ cm/GW. It is obvious that there is a good agreement between the theoretical prediction and the nonlinear absorption coefficient obtained from OA Z-scan experiment, which further confirms that the optical limiting behavior in Ag colloidal solution is induced by TPA effect. Zeng et al. [32] also reported the two-photon absorption-induced optical limiting response of silver nanoparticles. However, they prepared the nanoparticles by a focused femtosecond laser irradiation in a 5 mM $AgNO_3$ solution in the presence of TiO_2 sol. The nonlinearity was attributed to the absorption-induced nonlinear scattering of silver particles under fs laser's irradiation. Again, Wang et al. [33] reported the optical limiting response of an azobenzene liquid crystal polymer which originated from two-photon absorption. They revealed that though the polymer has a linear absorption coefficient of $\alpha_0 = 4.6\,\text{cm}^{-1}$ at 532 nm, the two-photon absorption can be presented by use of the Q-switched (10 ns) second-harmonic generation Nd:YAG pulse laser.

4. Conclusion

In conclusion, the nonlinear refraction, nonlinear absorption and optical limiting property of Ag colloidal solution, which was prepared by the reduction of silver nitrate, have been investigated under the irradiation of 38 ps laser pulse at 532 nm. The value of nonlinear absorption is determined to be 4.32 cm/GW. From the experimental conditions and theory fit results, we attribute the nonlinear absorption and optical limiting property o to TPA effect at 532 nm. Meanwhile, under both the excitation at 280 nm and 350 nm, two fluorescence peaks are observed in the Ag colloidal solution.

Acknowledgments

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