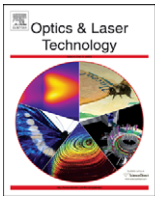
Optics & Laser Technology 42 (2010) 783–789

Contents lists available at ScienceDirect

Optics & Laser Technology

journal homepage: www.elsevier.com/locate/optlastec



# The effect of concentration on the thermo-optical properties of colloidal silver nanoparticles

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ARTICLE INFO

*Article history:*
Received 2 September 2009
Received in revised form
18 November 2009
Accepted 10 December 2009
Available online 4 January 2010

*Keywords:*
Silver nanoparticles
Thermo-optical properties
Nonlinear refraction

ABSTRACT

The thermo-optical properties of colloidal silver nanoparticles (AgNPs) are investigated under a low power laser irradiation at 532 nm. Colloidal AgNPs are synthesized by nanosecond pulsed laser ablation of a pure silver plate in distilled water. The morphology and size of the AgNPs are determined by transmission electron microscopy. Closed Z-scan measurements reveal that nonlocal thermo-optic process is responsible for the nonlinear refractive index of colloid containing different concentrations of silver nanoparticles. The Z-scan behavior of the nanoparticle samples has been investigated based on a nonlocal thermo-optic process and it is shown that the aberrant thermal lens model is in excellent agreement with the experimental results. Z-scan measurement fits have allowed the values of nonlinear refractive index ($n_2$) and thermo-optic coefficients ($dn/dt$) to be determined at different concentrations of silver nanoparticles. Large enhancement factors were measured for values of $n_2$ and $dn/dt$ of the colloids at higher silver nanoparticle volume fraction. Our results suggest that nonlocal thermal nonlinear processes will play an important role in the development of photonic applications involving metal nanoparticle colloids.

## 1. Introduction

The interest in the thermo-optic properties of colloidal metal nanoparticles has grown due to the wide range of applications in different fields such as photonics devices [1–3], chemical and biomolecular sensing [4–8], photo-thermal therapy [9] and cooling systems [10], where a temperature change within and around metal nanoparticles may alter the characteristics of their functionality. This may lead to a large spatial nonlocality of the refractive index changes of the medium. The thermal lens phenomenon has been shown to contribute significantly to the nonlinear optical response of composite media containing metal nanoparticles [11–13]. Large enhancement factors were observed for thermal nonlinear refractive index and thermo-optic coefficients of the colloid due to the presence of gold nanoparticles [12]. Recent works predicted and observed optical nonlocal effects exploiting the thermal nonlinearity in dye materials [14,15], polymers [16–18], $In_2O_3$ [19], phthalocyanines [20,21] and organic materials [22], when using long-lasting pulses and CW laser irradiation. The widespread applications of CW laser technology in many different areas ranging from optical communication [23], optical storage [24], to environmental monitoring [25] and thermotherapy [26] justifies the investigation of the interaction of the laser radiation with appropriate media.

Thermal lensing occurs as energy absorbed from a Gaussian laser beam produces heating in an absorbing medium about the beam axis. A radially dependent temperature distribution is created which in turn produces a refractive index change by the factor$dn/dT$, the change of refractive index with temperature. The thermal lens effect was first reported by Gordon et al. [27] and an expression for the focal length of the lensing medium was derived. The Gaussian laser beam is treated as a line heat source, and the temperature rise distribution in the sample is given by terms of exponential integral. This temperature is approximated by expanding integrals in a power series, to terms in $r^2$. Therefore, the thermal lens could be treated as an ideal thin lens. Later, Cuppo et al. [28] reported that the thermal nonlinear phase shift under continuous laser illumination could be determined by the well known Z-scan technique. They have presented the closed Z-scan formalism based on the thermal thin lens effect. However, the change in the temperature, and as a result the change in the refractive index, may not be parabolic and thus the thermal lens cannot be treated as a perfect thin lens. Sheldon et al. [29] reported that the thermal lens model based on the aberrant nature is more accurate than predictions made by the model based on the parabolic nature. Then he used a diffraction theory to find the intensity change at the center of the laser beam in far field. This model was further modified and discussed by Shen

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doi:10.1016/j.optlastec.2009.12.003

et al. [30]. Falconieri [31] has presented a model for calculation of the Z-scan signal induced by thermal nonlinearities using the aberrant thermal lens effect.

In this work, we report the experimental investigation of the thermo-optic nonlinear response of colloids containing different concentrations of silver nanoparticles. The colloidal nanoparticle samples were synthesized by nanosecond pulsed laser ablation of a pure silver plate in the distilled water. The sample containing AgNPs was characterized by linear absorption spectroscopy and transmission electron microscopy (TEM). Using the Z-scan technique, the behavior of the thermal nonlinear refractive index of colloid was studied at different concentrations of silver nanoparticles. Observation of an asymmetrical configuration of the Z-scan data indicates that nonlinear refraction occurring in the AgNPs samples are related to the thermo-optic process [32]. We have investigated the Z-scan behavior of the samples based on nonlocal thermo-optic models [27–31]. It will be shown that the aberrant thermal lens model is in excellent agreement with the experimental results of the closed aperture Z-scan measurements of the sample. Fits have allowed the values of nonlinear refractive index coefficient of the AgNP colloids to be determined at different concentrations. The thermo-optic coefficients of the colloids are obtained.

## 2. Experimental

### 2.1. The fabrication of silver nanoparticles

Silver nanoparticle colloids have been prepared by nanosecond pulsed laser ablation of highly pure silver target in distilled water. The laser ablation of silver was carried out using a Q-switched Nd:YAG laser operating at its fundamental wavelength of 1064 nm. The laser generated 18 ns (FWHM) pulses with a repetition rate of 1 Hz. The laser beam was focused by a 50 cm focal length lens on the surface of a silver plate placed inside a 10 mm cell. The spatial profile of the laser pulse was Gaussian, with a 300 μm (FW1/$e^2M$) beam waist at the target. The silver sample was irradiated with a laser fluence level of about 30 J/cm$^2$ for 1 h. The AgNP colloids were denoted by A, B, C, D and E with the silver nanoparticle volume fraction of $0.5\times10^{-6}$, $1.1\times10^{-6}$, $2.2\times10^{-6}$, $4.3\times10^{-6}$ and $8.7\times10^{-6}$, respectively. The volume fraction, $v$, of the nanoparticles is defined by

$$v=\frac{V_S}{V_S+V_L} \tag{1}$$

where $V_S$ is the volume of the particles and $V_L$ is the volume of the water. The volume of the nanoparticles is $V_S=m/\rho$, where $\rho$ is the silver mass density and $m$ is the mass of particles dispersed in the liquid. The prepared AgNP colloids were studied using a transmission electron microscopy (TEM), and an UV–vis optical absorption spectrophotometer. A continuous wave low power (100 mW) diode-pumped Nd:YVO$_4$ laser operating at wavelength of 532 nm is also used to measure the linear absorption coefficient of the colloid.

### 2.2. The nonlinear measurements

The nonlinear optical properties of the AgNP colloids were studied by transmittance and the Z-scan measurements using a continuous wave low power (100 mW) diode-pumped Nd:YVO$_4$ laser operating at wavelength of 532 nm. For Z-scan measurement, the optical geometry used in this work is shown in Fig. 1. An attenuator and a beam splitter were used to control the power of the laser beam. The beam was focused onto the sample (5 mm cell) by using a lens with 50 cm focal length. The spot size in the focal region was 50 μm (HW1/$e^2M$). In our experiment, the condition $\pi\omega_0^2/\lambda > L$ was satisfied, so that the sample could be considered as a thin medium, where $\pi\omega_0^2/\lambda$ is the Rayleigh range, $L$ the thickness of the sample and $\lambda$ the free wavelength of the beam. A diaphragm located before the output power detector, was used to dissociate the nonlinear absorption from the nonlinear refractive effect. The nanoparticle-containing cell was moved using a translation system along the propagation direction ($z$-axis) through the focusing area. At the focal point, the sample experiences maximum laser power, which will gradually decrease in either direction from the focus.

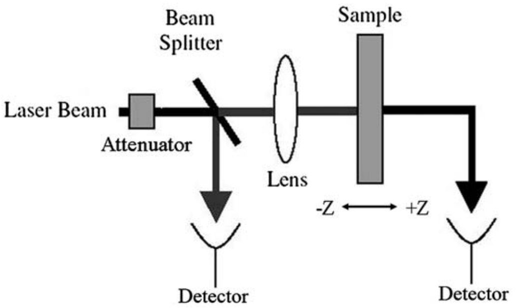

**Fig. 1.** Optical geometry used to characterize optical nonlinearity of the AgNP colloids.

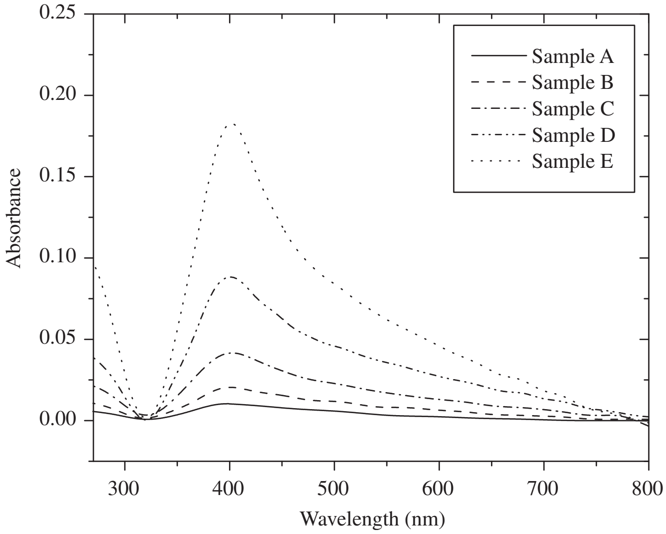

**Fig. 2.** Compare absorption spectrum of the colloids at different concentrations of silver nanoparticle.

## 3. Experimental results and discussion

Fig. 2 shows UV–vis absorption spectrum of the colloids containing different concentrations of silver nanoparticles prepared by laser ablation of a silver plate immersed in water. One can see that the AgNP samples show a surface plasmon absorption band about 400 nm in the UV–vis region of the spectrum [33,34]. Note that the surface plasmon (SP) absorbance of the colloids at wavelength of 532 nm increases by increasing the AgNPs concentration.

The shape and size distribution of the AgNPs were studied by TEM and the measurements conducted just after laser ablation. The TEM image and size distribution of AgNP colloids prepared in water are presented in Fig. 3. Average AgNPs radius is found to be about 9 nm, with a standard deviation of 3 nm.