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Size-dependent nonlinear optical properties and thermal lens in silver nanoparticles

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ABSTRACT

We have investigated the nonlinear response of the silver nanoparticle samples in a low-power regime of electromagnetic field based on nonlocal thermo-optic models. In this work, the experimental investigation of the thermo-optic nonlinear response of Ag colloids containing different size of silver nanoparticles is reported. The colloidal nanoparticle samples were synthesized by nanosecond pulsed laser ablation of Ag bulk in acetone. The sample containing Ag was characterized by linear absorption spectroscopy and transmission electron microscopy. Using the z-scan technique, the behavior of thermal nonlinear refractive index of colloid was studied at different concentrations of silver nanoparticles. Observation of asymmetrical configurations of the z-scan data indicates that nonlinear refraction occurring in the Ag samples is related to the thermo-optical process. The optical limiting here is due to nonlinear refraction of the samples arising from thermal lens formation under low-power CW excitation. When the laser power is low, the self-defocusing effect is mainly dominated by surface plasmon resonance effect. Results show that with increasing concentration of nanoparticles in acetone, the nonlinear refractive index increases while the threshold power of optical limiting decreases.

1. Introduction

Recently, metal nanoparticles (NPs) suspended in a solution have attracted much attention. Due to their small size, nanomaterials exhibit novel properties which largely differ from the bulk materials. The new emergent properties include quantum size effect, nonlinear optical properties, and so on. Nonlinear optical properties (NLOs) are of those significant properties, which are enhanced remarkably with respect to the relative bulk materials, due not only to their atomic scale structures, but also their interface and surface structures [1]. The nanomaterials have extensive applications in civil and industrial areas. For example, they can be used as microelectronic materials, bacteriostatic materials, catalytic materials, or magnetic recording materials [2,3]. They even have potential applications in DNA detection and photodetection [4,5]. Silver NPs, a noble metallic nanomaterial, can be used as antibacterial materials, antistatic materials, cryogenic superconducting materials, biosensor materials, etc. [6–8]. In the electronic industry, there are growing demands for decreasing the thickness of conductive films and the width of printed circuits. It is thus required that the diameter of silver NPs in the conductive paste is small [9]. As catalytic materials, the catalytic activity of silver NPs is dependent on their size, structure, shape, size distribution, and chemical–physical environment [10,11].

The production of these particles in the liquid is used in several ways. Methods consist of chemical, electrical, and pulsed laser ablation (PLA). Evidence shows that the latter method is superior to other methods. Indeed, laser ablation in liquids, which consist of the pulverization of a solid target in liquid ambience, gives a unique opportunity to solve the toxicity problems. In contrast to chemical nanofabrication methods, laser ablation can be performed in a clean, well-controlled environment, such as deionized water, giving rise to the production of ultrapure nanomaterials. The use of these particles decreases toxicity risks, which are especially important in biosensing and imaging applications [12–14]. In addition, laser pulse energy, wavelength, spot size, and pulse width are useful parameters to control the size and morphology of NPs produced by the PLA method [15–21].

Optical limiting performance will be enhanced by coupling two or more of the NLO mechanisms for NLO behavior of nanoparticles. The thermal lens model (TLM), which considerably predates the z-scan technique, can be successfully used to interpret z-scan experiment [22–26]. In this case, the sample is considered as a weakly absorbing medium, where energy absorbed from the laser beam is immediately converted into heat. The nonlinearity arises from the dependence of the refractive indices on temperature. Due

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Table 1
Features of nanoparticles in acetone.

Sample	1	2	3
Laser fluence (J/cm^2)	14	18	22
SPR peak position (nm)	398	466	476
TEM average size (nm)	16.77	26.76	32.24

to the diffusion of heat, the spatial temperature profile can differ significantly from the laser intensity profile; hence the mechanisms is nonlocal [27].The thermal lens phenomenon has been shown to contribute significantly to the NLO response of composite media containing metal NPs.

At the beginning of this paper, the production of silver nanoparticles by laser ablation method is described and their characteristics are investigated. In this experiment, we used ultraviolet visible near-infrared (UV-VIS-NIR) spectroscopy and TEM analysis. Then single z-scan method is employed to investigate the NLO properties of samples. The z-scan method was proposed by Sheik-Bahae elegant method for determining the sign and magnitude of the nonlinear refractive index n_2 in 1989 [28,29]. Also, we calculated the thermal lens effect and refractive index for Ag nanoparticles. The manuscript is organized as follows. Following the introduction in Section 1, in Section 2, the experimental set-up is presented. Section 3 is devoted to results and discussion, and finally Section 4 includes conclusion.

2. Experimental set-up

Silver nanoparticles were produced by PLA of an Ag plate in acetone. The Ag plate was cleaned ultrasonically in alcohol, acetone, and deionized water before the experiments. Nanoparticles were prepared using the fundamental harmonic of a Nd:YAG laser operating at 1064 nm. Laser pulse width was 7 ns with 10 Hz repetition rate. The laser beam of 2 mm in diameter was focused using an 80 mm focal length lens. The laser pulse hit the target at 1 cm depth in acetone. Pure silver target was ablated for 4 min at a laser beam energy density of 14, 18, and 22 J/cm^2 to obtain three samples of silver nanoparticle in acetone with different sizes. Detail about the sample preparation is presented in Table 1 and suspensions are shown in Fig. 1. Transmission electron microscopy (TEM; Philips EM 208) and UV–Vis–NIR absorption spectrophotometer (PG Instruments Ltd) were used to characterize the samples. TEM images were obtained by placing a drop of the concentrated suspension on a carbon-coated copper grid and absorption spectrum was recorded when suspensions were in a 10 mm path quartz cells at room temperature.

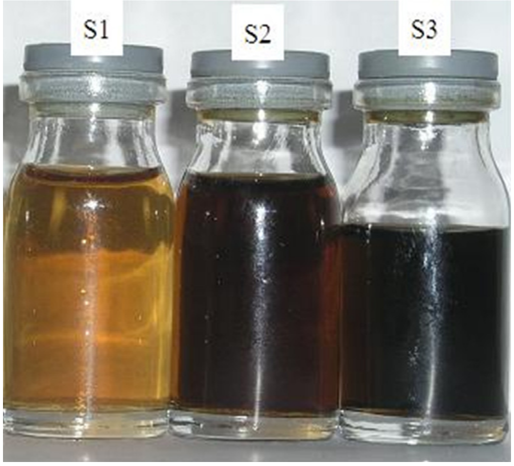

Fig. 1. Produced Ag nanoparticles with laser ablation in acetone.

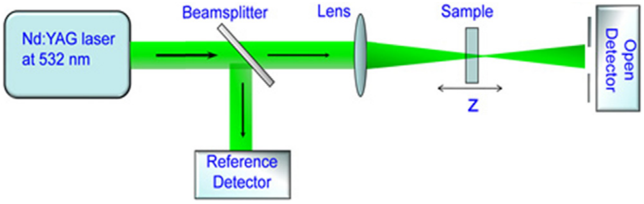

Fig. 2. Schematic diagram of z-scan experimental setup.

After characterizing NPs, optical limiting and close z-scan experiments were carried out to study their nonlinear optical properties. Indeed, the nonlinear optical properties of Ag nanoparticles were studied by means of transmittance and close z-scan measurements using a 120 mW continuous-wave diode pump laser operating at 532 nm wavelength. The experimental setup is presented in Fig. 2. A beam splitter was used to control the power of the laser beam. The 1 mm diameter beam was focused onto the sample in 1 mm thickness quartz cell by using a 6.5 mm focal length lens. The cell was moved in the *z*-direction by using a translation system along the propagation direction through the focusing area. Detector 1 was used to control the input power and detector 2 was used to measure the output power. The diameter of the apertures was 0.5 and 0.8 mm in this experiment.

3. Result and discussion

3.1. Nanoparticle characterization

Nanoparticle (NP) suspensions are shown in Fig. 1. From samples 1 to 3, the color of suspensions is changed from light brown to dark brown. This is due to variation of size and concentrations of NPs in acetone. It seems that samples 2 and 3 are close to each other since their color is similar.

The absorbance of suspended Ag nanoparticles prepared by PLA in acetone was measured in the 200–1100 nm wavelength range with respect to acetone absorption as the baseline. Fig. 3 presents optical absorption spectra of Ag nanoparticle solutions. They demonstrate a visible absorption peak from the SPR absorption of Ag nanoparticles at 400–480 nm. Shifts in the position of SPR peak may represent varying particle size. The shift towards longer wavelength (red shift) of the prepared nanoparticle thus indicates increased particle size [30]. Absorption spectra showed that the particle size of silver nanoparticles increased with increasing laser pulse fluence. This phenomenon was also confirmed in the particle size distribution obtained from the TEM image. Fig. 3 also shows that the shape of the plasmon band depended on the laser wavelength. The plasmon bands are more broadened in the red spectral region. The difference in the shape of the plasmon bands indicated the change in particle size under different laser wavelengths [31]. Increasing the intensity of absorption peaks confirms that with

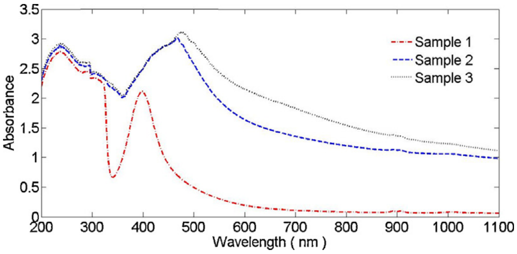

Fig. 3. Absorbance spectrum of Au nanoparticles suspension in acetone.