Ultrafast Nonlinear Optical Absorption of Silver Nanoparticles

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Abstract : Two photon absorption mechanism of silver nanoparticles in water system is studied using femtosecond z-scan technique. The value of nonlinear absorption coefficient is calculated to be 1.5×10^{-11} cm/W, which is found to be independent of the ageing period of the sample. The major source of the optical nonlinearity is originated from hot electron contribution which is devoid of the spectral dispersion of surface Plasmon resonance in non-resonant interaction regime.

***Key words* – metal nanoparticles, surface Plasmon resonance, z-scan, two-photon absorption**

I. INTRODUCTION

Metal nanoparticle acts as a role model system to tailor the strong coupling of light with matter in nano-meter dimension. The collective oscillation of free electrons in confined region results in resonant electric field enhancement known as surface plasmon resonance (SPR) which boost all linear and nonlinear optical properties, which makes them promising candidates for ultrafast optical switching, optical limiting and optical communication applications [1,2]. Dielectric field confinement and its impact on optical nonlinearities can be carefully manipulated by suitably controlling the nanoparticle size, its filling factor, shape and dielectric nature properties of host medium [3, 4,5].

In the family of metal nanoparticles, silver(Ag) nanoparticles has gained a special attention due to its spectral non- degeneracy of the SPR absorption with respect to the interband transition threshold; thus allowing the selective excitation of SPR band in Ag nanoparticle system. In the presented work, we have investigated the optical nonlinearities of silver nanoparticles prepared via chemical method. Silver nitrate and trisodium citrate were used as starting materials for the preparation of silver nanoparticles.. Briefly, 100 ml of 0.002 M silver nitrate solution was heated to boil. To this particular heated solution 10 mL of 1 % trisodium citrate was added drop by drop. During the process, solutions were mixed vigorously and heated until change of color to yellow, which is an indication of nucleation of silver nano-colloidal system [6].

II. EXPERIMENTAL RESULTS

The linear absorption spectrum of the sample is characterized using a UV-VIS absorption spectrometer; the corresponding absorption spectrum is shown in the inset of figure 1. a, b, c and d respectively. The indicated absorption spectra are recorded during the ageing period of the sample. The absorption spectrum of the sample shows an absorption band around 420 nm, which is a typical signature of surface Plasmon resonance in Ag nanoparticles. A femtosecond z-scan experiment has been employed to study the nonlinear optical absorption in silver nanoparticles. . In principal one measures the transmission change as a function of intensity, which is otherwise called as an open aperture z-scan. A Ti: Sapphire laser (wavelength λ=800nm, pulse duration τ=80fs, repetition rate 1 kHz) was used as excitation source. In the utilized experimental configuration, the sample is translated along the focussed laser beam direction. As the sample is away from the focal point, the nanoparticle system is subjected to low intensity excitation corresponding to a linear optical regime. As it approaches the focal point of the lens, the excitation intensity increases hence the nonlinearity pre-dominates [7,8].

The characteristic open aperture z-scan signals measured are shown figure 1.a, 1.b, 1.c and 1.d respectively; where the signals 1.a, 1.b, 1.c and 1.d denotes the characteristic z-scan signals measured during the ageing period of the sample. The measured z-scan curve clearly shows a transmission decrease (or an induced absorption) at the focal point, were the laser peak intensity is measured to be of 1.1×10^{11} $Wcm^{-2.}$. It is observed that the magnitude of the induced absorption is found be slightly increased during the ageing period of the sample. By looking at the absorption spectra of the sample (inset figure 1.a) shows a surface Plasmon resonance around 400 nm, thus exciting the nanoparticle system with 800 nm pump wavelength clearly enhance probably of the two-photon absorption process. Under 800 nm excitation, the presence of SPR band promotes absorption of two-photons simultaneously. In-order explain the induced absorption, a theoretical model involving the two-photon absorption mechanism is invoked. The transmission decrease due to the two-photon absorption can be theoretically explained by

$$T(Z) = \sum_{m=0}^{m=\infty} \left[\frac{-\beta I_{0}L_{eff}}{1+Z^2/Z_0^2}\right] \Big/ (1+m)^{1.5}$$

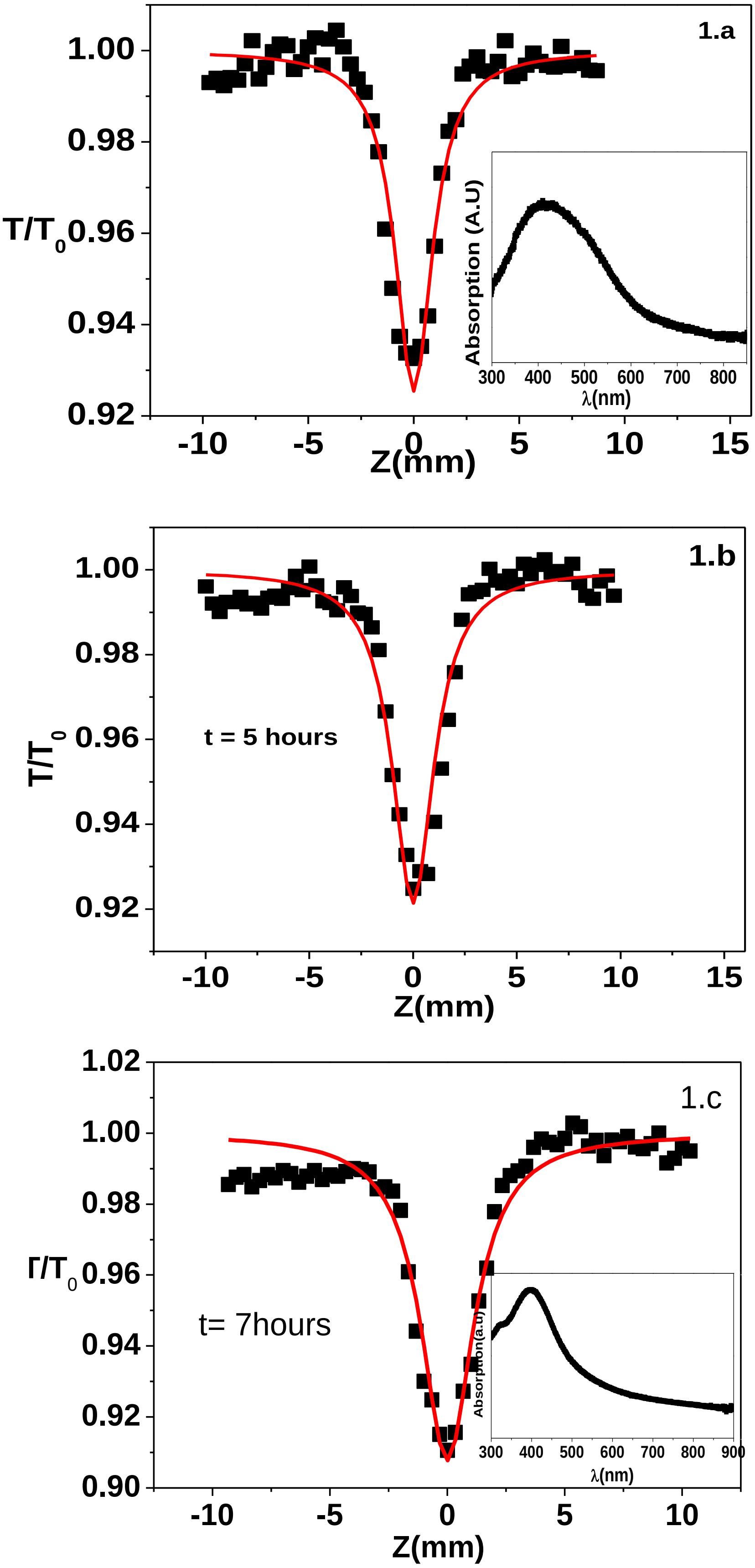

Figure 1.a, b and c . represents the open aperture z-scan signal measured during the aging period of the sample 2 hours, 5 hours and 7 hours respectively. Here the dark squares experimental data points and the red continuous line represents the theoretical calculation

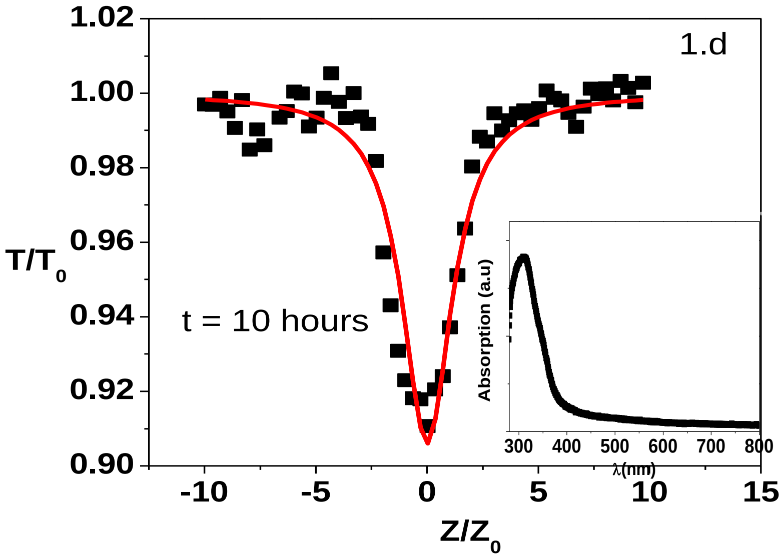

Figure 1.d. represents the open aperture z-scan signal measured during the aging period of the sample of 10 hours. Here the dark squares experimental data points and the red continuous line represents the theoretical calculation

where β, I_0, L_{eff} and Z_0 represents the two-photon absorption coefficient, the laser peak intensity, effective sample length and Rayleigh range of the laser pump beam respectively. In this case, the chosen values of effective sample length and the Rayleigh range are 1mm and 6.5×10^{-3} cm respectively. The comparison between the theoretical studies (the red continuous line) with the experimental data points indicates a pure two-photon absorption in the selected spectral excitation region. The estimated value of the two-photon absorption is found to be 1.51×10^{-11} cm/W.

III. RESULTS AND DISCUSSION

Using 800nm as excitation wavelength with plasmon band peaked at 400 nm allows one to excite the sample in its transparency regime. Resulting nonlinearity is instantaneous in nature. As demanded by the selection rules for optical transition in the non-resonant regime, measurements at low intensity values do not show any nonlinear transmission change. Measurements at high intensities showed very strong optical nonlinearity (figure 1.a,b &c full points) an indication of positive nonlinearity and corresponding absorption increase is explained as a two-photon absorption process. Upon excitation of femtosecond laser pulses, in near infra-red spectral range, it is the conduction electrons which will contribute to over all nonlinear optical process. As pointed out by the work of Hamanaka et al., an increase in temperature of conduction electron system through non-radiative energy relaxation process drastically influence dielectric constant of the nanoparticle which is represented as $\varepsilon\left(\omega, T_e, T_l\right) = \left[1 - \frac{\omega^2{}_p(T_l)}{\omega^2 - i\gamma(T_e, T_l)\omega}\right]$ which acts as source of nonlinearity generally where T_e ,T_l corresponds to the electron and lattice temperature change immediately after laser excitation [2, 8, 9,10,11,12]. In general under femtosecond laser pulse excitation, the optical nonlinearity of the metallic nanoparticles is mainly dominated by a hot electron contribution, which results in a positive nonlinearity. In the present scenario, where the spectral excitation falls in the non-resonant regime, in which the spectral gap between the pump wavelength with respect to the SPR absorption is calculated to be 2.5 eV. Hence the contribution due to the dielectric field enhancement due to the SPR resonance is completely negligible. Hence the sign of the optical nonlinearity is found to be completely devoid of the dispersion effects due to the SPR resonance. It can be also inferred from our studies that the spectral tuning of pump wavelength in the near resonant regime of the SPR will drastically changes the nature of the nonlinear absorption from two-photon absorption to the saturable absorption.

III. CONCLUSION

The absorptive optical nonlinearities in silver nanoparticles in water system is investigated using femtosecond laser pulses. In the investigated excitation regime, the absorptive nonlinearity is found to be originated from two-photon absorption process. The estimated value of the two-photon absorption process is found to be slightly increased during the cause of the ageing period of the sample. In the non-resonant interaction regime, the optical nonlinearity is found to be originating the hot electron contribution. The observed two-photon absorption in metallic nanocomposite system makes them perfect candidate for all optical switching and optical limiting applications.

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