



# Biosynthesis of Silver Nanoparticles Using *Coriandrum Sativum* Leaf Extract and Their Application in Nonlinear Optics

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We present a simple and eco-friendly biosynthesis of silver nanoparticles using *Coriandrum sativum* leaf extract as reducing agent. The aqueous silver ions when exposed to leaf extract were reduced and resulted in silver nanoparticles whose average size is 26 nm. The silver nanoparticles were characterized by UV-Visible, X-ray diffraction (XRD), Fourier transform infra-red spectroscopy (FT-IR) and transmission electron microscopy (TEM) techniques. Nonlinear optical properties of silver nanoparticles were studied using Z-scan technique with 6 ns pulse duration at 532 nm. The nonlinear refractive index and third-order susceptibility  $|\chi^3|$  were measured to be  $\sim 6.0 \times 10^{-13} \text{ cm}^2/\text{W}$  and  $1.38 \times 10^{-9} \text{ esu}$ , respectively. Silver nanoparticles were found to exhibit strong reverse saturable absorption (RSA). RSA was identified as the main mechanism responsible for optical limiting.

## 1. INTRODUCTION

The synthesis of metal and semiconductor nanoparticles has attracted considerable attention from physicists, chemists, materials scientists, and engineers owing to their potential applications in catalysis,<sup>1</sup> biosensing,<sup>2</sup> recording media,<sup>3</sup> and optoelectronics.<sup>4</sup> Metal and semiconductor nanostructures of different sizes and shapes<sup>5</sup> can now be routinely synthesized by means of various chemical and physical methods. Their performance depends critically on their size, shape, and composition. Though numerous chemical methods are available for metal nanoparticles synthesis, copious reactants and starting materials are used in these reactions that are toxic and potentially hazardous. Increasing environmental concerns over chemical synthesis routes have resulted in attempts to develop bio-mimetic approaches. One of them is the synthesis using plant extracts eliminating the elaborate process of maintaining the microbial culture and often found to be kinetically favourable than other bioprocesses. Bio-molecules as reducing agents are found to have a significant advantage over their counterparts as protecting agents.<sup>6</sup> Environmentally benign nanoparticles synthesis procedures do not use any toxic chemicals in the synthesis protocols. In these aspects synthetic methods based on naturally occurring biomaterials provide an alternative means for obtaining these nanoparticles.

During recent times several groups have achieved success in the synthesis of Ag, Au, and Pd nanoparticles using extracts obtained from unicellular organisms like bacteria<sup>7–10</sup> and fungi<sup>11–13</sup> as well as extracts from plant parts, e.g., geranium leaves,<sup>14</sup> lemon grass<sup>15</sup> neem leaves,<sup>16</sup> aloe vera,<sup>17</sup> and several others.<sup>18–22</sup> The spectacular success in this field has opened up the prospect of developing bio-inspired methods of synthesis of metal nanoparticles with tailor-made structural properties. Among the various bio-reductants, *Coriandrum sativum* leaves extract was chosen for the present study since they have minerals and vitamin contents including calcium, phosphorus, iron, carotene, thiamine, riboflavin, and niacin. They also contain sodium and oxalic acid. Techniques using citrate reduction or reduction by plant extracts are all termed as green synthesis methods. To distinguish from others we refer to our method as biosynthesis. Silver nanoparticles have an advantage over other metal nanoparticles (e.g., gold and copper) because the surface plasmon resonance energy of Ag is located far from the interband transition energy. The Ag nanoparticles-contained composites are investigated for the nonlinear optical effects solely based on the surface plasmon contribution. In situ growth of metal nanoparticles in polymer films and their nonlinear optical properties have been reported by our group.<sup>23</sup> The advantage of this method is the use of the aqueous medium for the fabrication process, employment of the polymer itself as the reducing agent, mild thermal annealing for generating

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the metal, and in situ generation of the nanoparticles inside the polymer matrix which serves as the stabilizer as well.

Nonlinear optical (NLO) materials are essential for high speed optical network systems dealing with a large amount of data. In particular, organic third-order NLO materials such as  $\pi$  conjugated polymers are powerful candidates for developing photonic devices, due to their fast response and easy chemical modification in comparison to the inorganic systems. Due to the local field enhancement with surface plasmon resonance, larger third-order nonlinearity of composite films has been observed in the presence of metal nanoparticles.<sup>24,25</sup> These materials with large nonlinearities have been considered to be good candidates for all optical and electronic devices.<sup>26</sup> The surface plasmon resonance (SPR), which plays an important role in enhancing the optical nonlinearities, can be altered by changing the size, shape, and volume of the particle. From the practical point of view, these metal composites can be optimized to meet the requirements of the optical device operation. Lasers with high intensity output pose a major problem to the safety to the sensors and human eye due to laser induced damage. It is therefore essential to develop a device that exhibits a linear transmittance at lower input fluencies and a damped transmission above it. These devices are termed as optical limiters. Our endeavour is to develop eco-friendly methods for synthesis of Ag nanoparticles and study their nonlinear optical, optical limiting characteristics. We also attempt to contrast the results obtained using this technique with those reported previously where the synthesis was through organic routes.<sup>27</sup> In this paper we report, for the first time to the best of our knowledge, biosynthesis of the Ag nanoparticles using *Coriandrum sativum* leaf extract as a reducing agent and demonstrate that this method yields faster and stable silver nanoparticles compared to other methods. We also present the nonlinear optical and optical limiting properties of these nanoparticles studied using nanosecond pulses at 532 nm. Our studies reveal that the silver nanoparticles demonstrate comparable or superior nonlinearities to that of nanoparticles synthesised by chemical routes.<sup>28–36</sup>

## 2. EXPERIMENTAL DETAILS

### 2.1. Biosynthesis of Silver Nanoparticles Using *Coriandrum Sativum* Leaf Extract Preparation of Leaf Extract:

A 20 gm of home-grown fresh leaves were washed thoroughly with double distilled water (DDW) and added to 100 ml of boiled sterile DDW for 5 minutes and filtered. The extract was stored at 4 °C for further experiments. The filtrate is used as reducing and stabilising agent for 1 mM of  $\text{AgNO}_3$  ( $\text{AgNO}_3$ , 99.99%, Sigma-Aldrich).

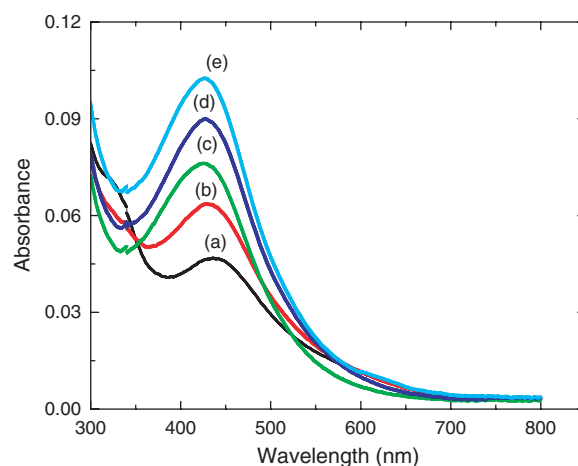
In a typical synthesis of silver (Ag) nanoparticles the leaf extract (1.5 ml) was added to 30 ml of  $10^{-3}$  M  $\text{AgNO}_3$  (99.99%) aqueous solution and kept at 33 °C. The experiment was done in triplicate for reproducibility. After 10 minutes the colour of the solution changed from colourless to yellow indicating the formation of Ag nanoparticles. The bio-reduced Ag nanoparticles solution was collected and monitored by periodic sampling of aliquots (5 ml) of aqueous component and measuring UV-visible spectra of the solution. The nanoparticles solution was diluted to 10 times with Millipore<sup>TM</sup> water to avoid errors due to high optical density of the solution.

## 3. UV-VISIBLE ABSORBANCE SPECTROSCOPY

UV-visible spectroscopy analysis was carried out on an a JASCO UV-visible absorption spectrophotometer with a resolution of 1 nm between 300 and 900 nm possessing a scanning speed of 300 nm/min. Equivalent amounts of the suspension (0.5 ml) were diluted in a constant volume of de-ionized water (5 ml) and subsequently analyzed at room temperature. The progress of the reaction between metal ions and the leaf extracts were monitored by UV-visible spectra of Ag nanoparticles in aqueous solution with different reaction times are shown in Figure 1. It was observed that the peak blue shifted in the absorption spectrum from 440 nm to 427 nm with increasing reaction time from 10 min to 30 min and the peak centered at 427 nm for 30, 40 and 60 minute samples. The reduction of silver ions and the formation of stable nanoparticles occurred rapidly within an hour of reaction, making it one of the fastest bio-reducing methods to produce Ag nanostructures reported till date.<sup>14, 15, 18, 19</sup>

## 4. X-RAY DIFFRACTION STUDIES

A thin film of the Ag nanoparticles was made by dipping a glass plate in the solution and carried out the X-ray studies. The diffraction pattern was recorded by  $\text{Co-K}\alpha 1$  radiation with a wavelength of 1.78 Å. The scanning was done in the region of 20° to 90° for  $2\theta$  at 0.02°/min and the time constant was 2 s. The crystalline nature of Ag nanoparticles was confirmed from the X-ray diffraction analysis. Figure 2 shows the XRD pattern with the diffraction peaks at 44.50, 52.20 and 76.7 corresponding to the (111), (200) and (220) facets of the face centred cubic crystal structure. The broadening of the Bragg peaks indicates the formation of nanoparticles. In addition to the Bragg peaks representative of fcc silver nanocrystals, additional, and yet unassigned, peaks were also observed suggesting that the crystallization of bio-organic phase occurs on the surface of the silver nanoparticles.



**Fig. 1.** UV-visible spectra recorded as a function of time of reaction of an aqueous solution of  $10^{-3}$  M  $\text{AgNO}_3$  with the *Coriandrum sativum* leaf extract (a) 10 min (b) 20 min (c) 30 min (d) 40 min and (e) 60 min.

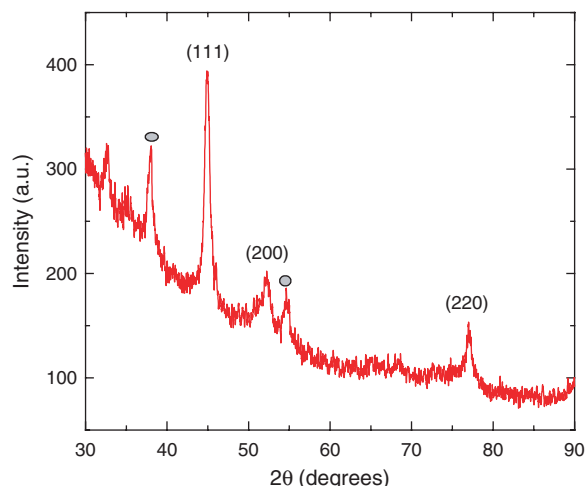


Fig. 2. XRD pattern of as synthesized silver nanoparticles.

## 5. FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

For FTIR measurements, the Ag nanoparticles solution was centrifuged at 10,000 rpm for 30 min. The pellet was washed three times with 20 ml of de-ionized water to get rid of the free proteins/ enzymes that are not capping the silver nanoparticles. The samples were dried and grinded with KBr pellets and analyzed on a JASCO FT/IR-5300 model in the diffuse reflectance mode operating at a resolution of  $4\text{ cm}^{-1}$ . Figure 3 shows the FTIR spectra of aqueous silver nanoparticles prepared from the *Coriandrum sativum* leaf extract. The peaks near  $3430\text{ cm}^{-1}$  and near  $2920\text{ cm}^{-1}$  were assigned to O–H stretching and aldehydic C–H stretching, respectively. The weaker band at  $1635\text{ cm}^{-1}$  corresponds to amide I, arising due to carbonyl stretch in proteins. The peak at  $1038\text{ cm}^{-1}$  corresponds to C–N stretching vibrations of the amine. IR spectroscopic study confirmed that the carbonyl group form amino acid residues and proteins has the stronger ability to bind metal indicating that the proteins could possibly form a layer covering the metal nanoparticles (i.e., capping of silver nanoparticles) to prevent agglomeration and thereby stabilize the medium. This suggests that the biological molecules could

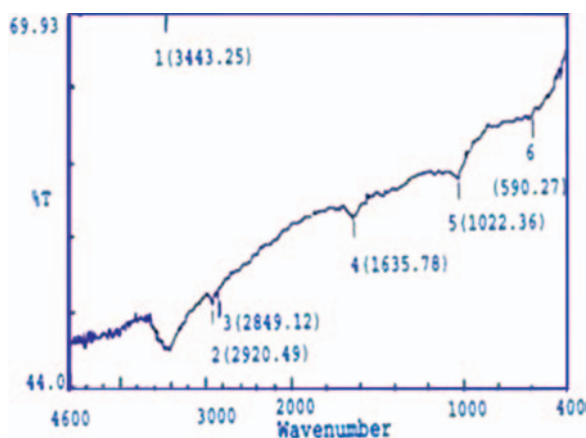


Fig. 3. FT-IR spectrum recorded by making KBr disc with as synthesized silver nanoparticles prepared from the *Coriandrum sativum* extract.

possibly perform dual functions of formation and stabilization of silver nanoparticles in the aqueous medium.

## 6. TRANSMISSION ELECTRON MICROSCOPY (TEM)

TEM technique was employed to visualize the size and shape of Ag nanoparticles. The 200 kV Ultra High Resolution Transmission Electron Microscope (JEOL-2010) has been used. TEM grids were prepared by placing a drop of the particle solution on a carbon-coated copper grid and drying under lamp. Figure 4(a) shows the typical bright-field TEM micrograph of the synthesised Ag nanoparticles. It is observed that most of the Ag nanoparticles were spherical in shape. A few agglomerated silver nanoparticles were also observed in some places, thereby indicating possible sedimentation at a later time. Figure 4(b) shows the histogram taken from a large number of micrographs. It is evident that there is variation in particle sizes and the average size estimated was 26 nm and the particles size ranged from 8 nm to 75 nm. Figure 4(c) corresponds to high resolution lattice image form one such particle. The lattice spacing confirms the Ag (111) planes. Figure 4(d) represents a selected area electron diffraction (SAED) form a cluster of silver particles. Very interestingly, all the Ag particles have single orientation.

## 7. NONLINEAR OPTICAL STUDIES

The nonlinear optical properties were measured by the Z-scan technique, with a frequency-doubled, Q-switched Nd:YAG (Spectra Physics, INDI 40) laser, delivering 6 ns laser pulses at 532 nm and a repetition rate of 10 Hz. Nonlinear absorption and refraction of the Ag nanoparticles in solution are studied by carrying out the open and closed aperture Z-scan measurements. The general set up used in these experiments has been described elsewhere.<sup>37</sup> Briefly, in a typical Z-scan experimental set up, a laser beam with a transverse Gaussian profile was focused using a lens. The sample in a 1 mm thick cell was then translated along the propagation direction of the focused beam. At the focal point, the sample experiences greatest intensity, which will gradually decrease in either direction from the focus. An f/40 configuration was used for our present studies. The thickness of the sample was chosen such that it was smaller than the Rayleigh range of the focused beam, which was nearly 3 mm. Apertures are introduced in the path for beam shaping and calibrated neutral density filters were used to vary the laser intensity. The data was recorded by scanning the cell across the focus and collecting the data through a SRS boxcar averager (model SR250), the output of which is given to a personal computer with an analog-to-digital (ADC) card.

For obtaining the nonlinear coefficients ( $\beta_{\text{eff}}$  and nonlinear refractive index  $n_2$ ) from Z-scan data we used equation (1) to fit the open aperture data and equations (2) and (3) for the closed aperture data.

$$T_{OA(2PA)} = 1 - \left( \frac{\beta_{\text{eff}} I_{00} L_{\text{eff}}}{2\sqrt{2} \left[ 1 + \left( \frac{z}{z_0} \right)^2 \right]} \right) \quad (1)$$

where  $z$  is the sample position,  $z_0 = \pi \omega_0^2 / \lambda$  is the Rayleigh range;  $\omega_0$  is the beam waist at the focal point ( $Z = 0$ ),  $\lambda$  is the laser

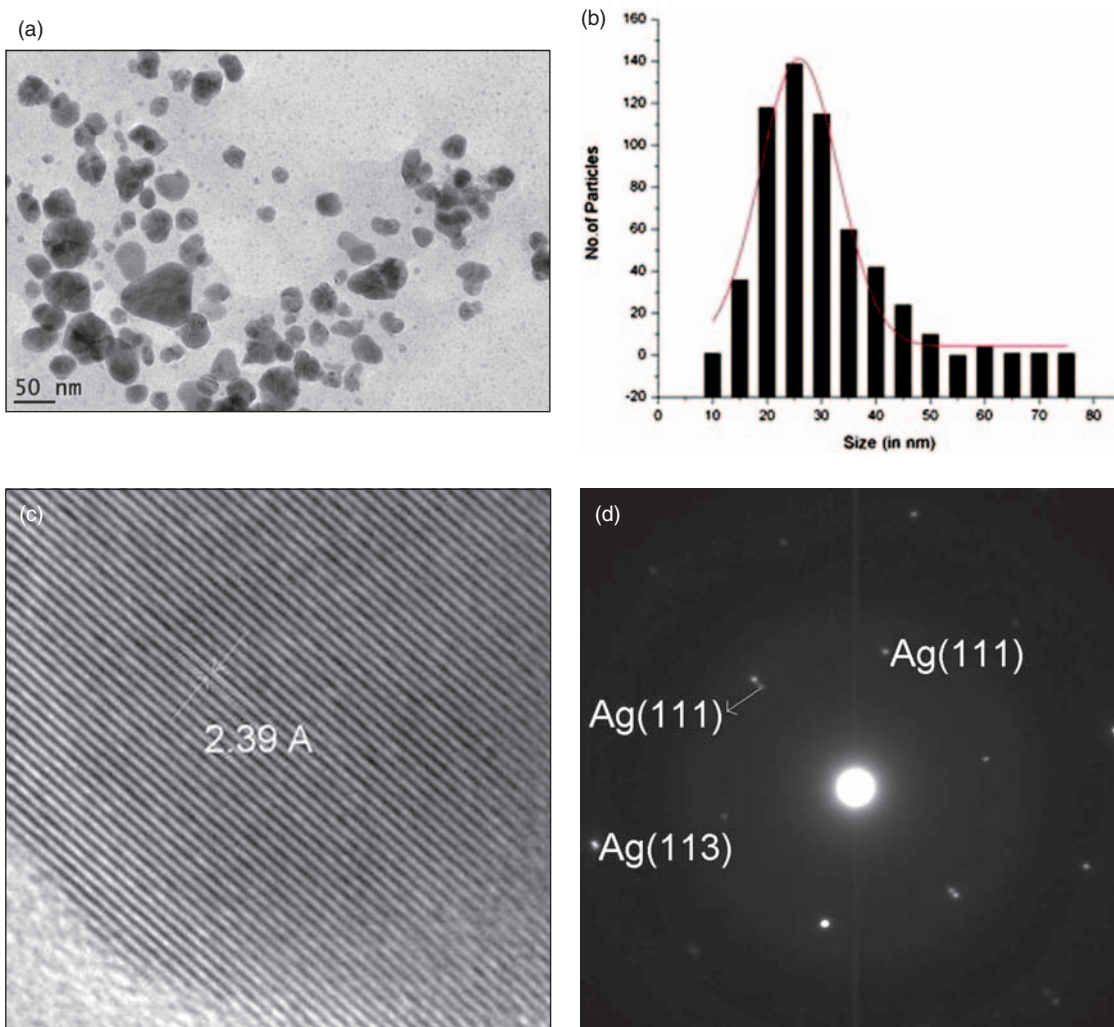


Fig. 4. (a) A typical bright field TEM image of bio reduced silver nanoparticles. (b) Histogram of the Ag nanoparticles. (c) Lattice spacing. (d) SAED pattern.

wavelength,  $I_{oo}$  is the intensity on the sample at focus; effective path lengths in the sample of length  $L$  is given as  $L_{\text{eff}} = \frac{1-e^{-\alpha_0 L}}{\alpha_0}$

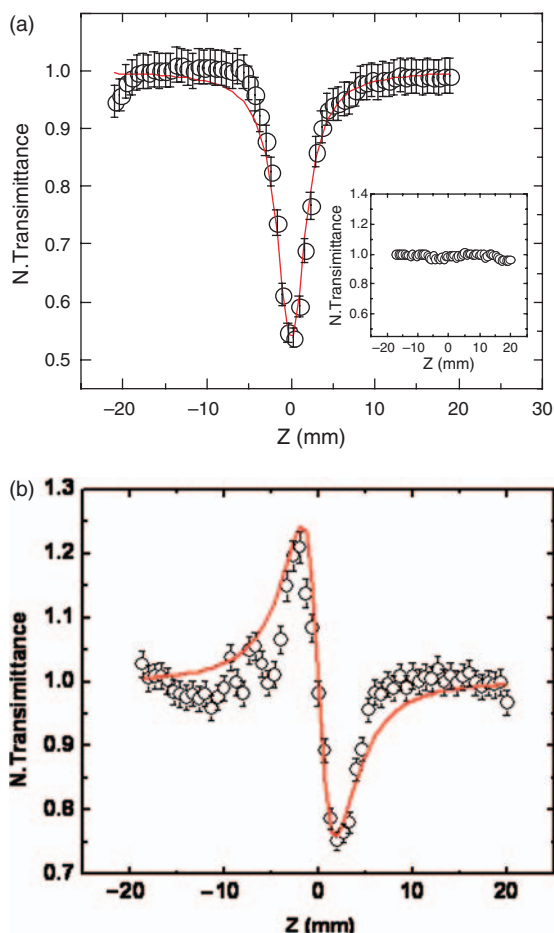
$$T_{CA} = 1 - \frac{4\Delta\Phi_0(z/z_0)}{[1 + (z/z_0)^2][9 + (z/z_0)^2]} \quad (2)$$

where  $\Delta\phi_0$  is the phase change of laser beam due to the nonlinear refraction.  $\Delta\phi_0$  value was estimated from the theoretical fits to experimental data. Nonlinear refractive index,  $n_2$  was calculated from

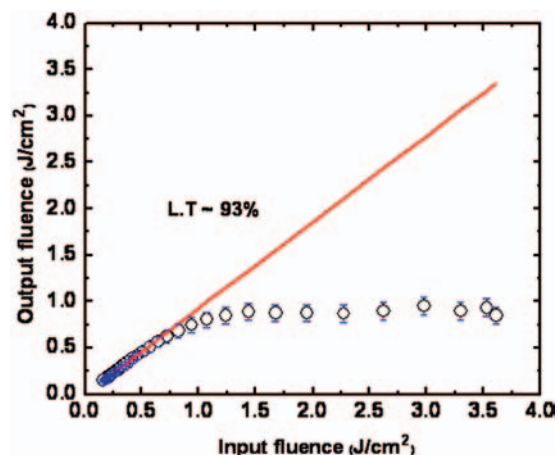
$$n_2(\text{cm}^2\text{W}^{-1}) = \frac{|\Delta\Phi_0|\lambda}{2\pi I_{00}L_{\text{eff}}} \quad (3)$$

Figure 5(a) illustrates the open aperture data while Figure 5(b) shows the closed aperture data. Open circles are the experimental data and the solid curves are theoretical fits using Eq. (1) And (2). Absorption spectrum of Ag nanoparticles capped with the plant extract did not show any absorption in the UV-Vis region characteristic of bio-molecule to account for any kind of energy transfer or direct two photon absorption by the bio-molecule. Further, we have recorded and confirmed that the leaf extract did not exhibit any nonlinear absorption that is evident from the open aperture Z-scan data presented in the inset of Figure 5(a). We believe

that the nonlinear absorption observed in silver nanoparticles solution was mainly due to reverse saturable absorption (RSA). RSA can be attributed to either the excitations from SPR band to the free carrier band of nanoparticles or two-photon absorption. We have recorded open aperture Z-scan curves of Ag nanoparticles for different intensities ranging from 97.6 MW/cm<sup>2</sup> to 602 MW/cm<sup>2</sup>. The nonlinear coefficient ( $\beta_{\text{eff}}$ ) was fairly constant for all the intensities. We obtained  $\beta_{\text{eff}}$  to be  $\sim 72.5$  cm/GW, where  $\beta_{\text{eff}}$  is the effective nonlinear absorption coefficient incorporating both the excited state absorption and two-photon absorption. From  $\beta_{\text{eff}}$  values we estimated the imaginary part of  $\chi^{(3)}$ , which was  $1.38 \times 10^{-9}$  esu. By recording the closed aperture Z scan curves, we estimated the nonlinear refractive index ( $n_2$ ), real part of  $\chi^{(3)}$ , to be  $-6.0 \times 10^{-13}$  cm<sup>2</sup>/W and  $2.7 \times 10^{-11}$  esu, respectively. The magnitude of  $|\chi^{(3)}|$  (at 1 mM conc.) was calculated to be  $\sim 1.38 \times 10^{-9}$  esu. The values presented above include an error of  $\pm 10\%$  arising from the errors in estimation of beam waist at focus, fitting errors, neutral density filter calibration errors etc. Figure 6 shows the optical limiting curve of silver nanoparticles at 532 nm. The energy transmittance decreased with increasing input energy. The limiting threshold was  $\sim 1.80$  J/cm<sup>2</sup>. We did not observe any scattering



**Fig. 5.** (a) Open aperture Z-scan of bio-reduced silver nanoparticles (60 minutes reaction time) at 532 nm using 6 ns pulses. Inset shows open aperture Z-scan data for the leaf extract indicating no nonlinear absorption. (b) Closed aperture Z-scan of bio-reduced silver nanoparticles (60 minutes reaction time) at 532 nm using 6 ns pulses. Open circles represents the experimental data and solid line obtained from theoretical fit.



**Fig. 6.** Optical limiting curve of silver nanoparticles (60 minutes reaction time) at 532 nm using 6 ns pulses, open circles represents experimental data and solid line represents linear transmittance (L.T.).

from the nanoparticles suggesting that the limiting resulted from pure RSA. The absence of nonlinear scattering is largely due to the average particle size being  $\sim 25$  nm and nonlinearities much smaller in magnitude than the semiconducting counterparts to induce significant nonlinear scattering. The role of solvent should be also significant for inducing nonlinear scattering. Our experiments, accounted for both scattering and nonlinear absorption, evidently confirmed the absence of any nonlinear scattering. Further studies are in progress to control the nanoparticles size, enhance their nonlinearities, induce nonlinear scattering and thereby improve the limiting threshold.

## 8. CONCLUSION

In conclusion we introduce a simple, fast, and economical biological procedure to synthesize Ag nanoparticles using *Coriandrum sativum* leaf extract. We characterized these nanoparticles using TEM, XRD, and UV-visible, FTIR spectroscopic techniques. We measured the nonlinear refraction and absorption coefficients using Z-scan technique with ns laser pulses. The values of  $n_2$ ,  $\beta_{\text{eff}}$ , and  $|\chi^3|$  for silver nanoparticles (at 1 mM conc.) obtained through these measurements were  $-6 \times 10^{-13}$  cm<sup>2</sup>/W, 72.5 cm/GW, and  $1.38 \times 10^{-9}$  esu, respectively. The limiting threshold of the sample was  $\sim 1.80$  J/cm<sup>2</sup>. The optical nonlinearity of these silver nanoparticles was comparable or superior to those synthesized through other procedures.

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