Influence of Surface Passivation by L-Arginine on Linear and Nonlinear Optical Properties of Ag-PVP Nanocomposite

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Abstract   We have investigated the effect of surface passivation using L- arginine on nonlinear optical responses, localized surface plasmon resonance(LSPR)and size of colloidal silvernano-particles (AgNPs) synthesized by chemical reduction method. The nonlinear optical responses of AgNPs embedded in the polyvinyl pyrrolidone (PVP) matrix were investigated using Z-Scan technique with wavelength 632 nm under the continuous wave (CW) regime. The surface plasmon resonance absorption peak of AgNPs showed a blue shift with an increase in L-arginine concentration. Transmission electron microscopy (TEM) analysis confirmed that the average size of AgNPs reduced from 10 nm to 6 nm as the concentration of L-Arginine increased from 1 mM to 5 mM. The sign of nonlinear refractive index (n_2) was found negative, which was of a self-defocusing nature and the magnitude was in the order of 10^{-4} cm^2/W. Very large third-order nonlinear susceptibility ($\chi^3 \sim 10^{-4}$ esu) was estimated. Both nonlinear refractive index and third-order nonlinear susceptibility were found to decrease as the concentration of L-arginine increased. Fourier Transform-Infared (FT-IR) studies revealed strong bonding between L-arginine functional groups and AgNPs. The X-ray diffraction study confirmed the formation of face-centred cubic (fcc) structured AgNPs. Based on the results, we have proposed that this material possesses a high potential for various optoelectronic device applications.

Keywords   L-arginine, Nonlinear refractive index, Nonlinear optical susceptibility, Silver nano-particles, Z-scan technique, AgNPs, Fourier transform infrared spectroscopy

1. Introduction

In recent years, nonlinear optical (NLO) properties of metal (Au, Ag, Pt, and Cu) nano-particles (MNP) embedded in adielectric matrix attracted great attention owing to their potential applications in catalysis, optical storage, photonics, sensors, optical switching, optical energy transportation, and thermal therapy [1-5]. AgNPsare of a very special class due to their potential applications in optics, catalysis, biological labeling, antibacterial applications, and surface enhanced Raman scattering (SERS) detection [6-12]. In the search of novel materials aiming atoptoelectronics device applications, thin films containing MNPs dispersed into the polymer matrix are very promising owing to the huge enhancement in the nonlinear refractive index (n_2) and third-order nonlinear susceptibility (χ^3) [13-17]. The investigations on χ^3 in the vicinity of LSPR of MNPs, specifically gold nano-particles embedded in various matrices, were carried out and huge third-order nonlinear susceptibility as large as $\chi^3 \approx 10^{-6}$ esu was found [18-20]. For AgNPs doped in the glass matrix, the magnitude of χ^3 in the order of 10^{-7} esu was obtained [21]. The large enhancement in the nonlinear optical responses is ascribed to the several factorssuch as SPR, size of the MNPs, effective refractive index of dielectric matrix, absorption coefficient, and mainly local field effects. However, for optoelectronic devices, which are based on the continuous wave (CW) laser operation or high repetition rates, the thermo-optic effect become dominant.

Numerous reports are available about the effect of surface passivation on the properties of MNPs, which would play a vital role in the applications such as biosensors [22], DNA/drug delivery [23], Imaging [24], bio diagnostic, and optoelectronics devices [25]. Common choice for MNPs surface modification is thiol-mediated binding of ligands

[26-27]. Aniline, long-chain amine carboxylic compounds have been used as stabilizers in the synthesis of MNPs [28]. Researchers have also studied the role of Poly-Vinyl Pyrrolidone (PVP), polyacrylate and polyacrylamide as protective agents, which can effectively alter shape, size, stability, and linear optical properties of AgNPs [29]. More recently, researchers have diverted attention to the binding of metal NPs with amino-acids [30]. Amino acids are inherently compatible, and one of the common amino acids is L-arginine, which has zwitterrionic structure. Upon functionalization of MNPs with L-arginine molecules, they can highly facilitate the interaction and hence have a potential to bring drastic changes in NLO properties. Joshi *et al.* (2004) reported the synthesis of L-lysine capped gold nano-particles [31]. Bhargava et.al (2005) reported the synthesis of gold nano-particles using the amino acids such asL-tyrosine, glycyl-L-tyrosine, and L-arginine as a reducing agent [32]. To the best of our knowledge, reports are not available on the use of L-arginine as a protective agent in the synthesis of AgNPs. Therefore, we have used L-arginine for surface modification in the synthesis of AgNPs.

Various methods such as degenerate four-wave mixing (DFWM), NLO interferometry, PPTFS (Pump-Probe technique of femtosecond spectroscopy), and VSD (Vectorial self-diffraction) have been used to measure NLO susceptibility and nonlinear refractive index [33, 21]. Among these, Z-scan method is extensively used because of its simplicity and accuracy. Further, this method gives not only real and imaginary part of third-order susceptibility but their respective sign too. Information on their sign is of great interest for applications in optoelectronic devices.

The objective of this work is to synthesize silver nano-particles in colloidal form with various concentrations of the stabilizer (L-arginine) followed by its dispersion into PVP matrix to fabricate thin films by spin coating method and to study the effect of L-arginine concentration on SPR, size of AgNPs, nonlinear refractive index, and third-order NLO susceptibility.

2. Experimental Section

2.1. Chemicals

Analytical grade chemicals, i.e. Silver nitrate ($AgNO_3$, 99.999% purity), sodium borohydride ($NaBH_4$, 98% purity), L-arginine (99% purity), and PVP (MW 10000) were purchased from Sigma-Aldrich and used without further purification. De-ionized water was used in thesynthesis process. L-arginine was used as a stabilizing agent and $NaBH_4$ was used as a reducing agent.

2.2. Synthesis of L-Arginine Passivated Silver Nano-Colloids

Stock solutions of 1 mM silver nitrate ($AgNo_3$), 2 mM sodium borohydride ($NaBH_4$) were prepared. L-arginine solutions with 1, 2.5, and 5 mM concentrations were

prepared separately by dissolving appropriate amount in de-ionized water. All solutions were kept in ice-bath for 20 minutes. In three separate 200 ml volumetric flasks, 20 ml doubled distilled water, 10 ml $NaBH_4$, and 5 ml L-arginine solutions were taken and stirred at 50°C for 20 minutes. Silver nano-colloidal solution was obtained by drop wise addition of 5 ml silver precursor into the above mixture. The solution turned dark violet in colour in 10 minutes indicating the formation of silver nano-particles, which were stable for a duration of 3 months.

2.3. Fabrication of Thin Films

PVP solution was prepared by dissolving PVP powder (15 wt%) into 100 ml doubled distilled water and was stirred for 1 h at 40°C. An appropriate amount of silvercolloidal solution and PVP solution wasmixed,and the solution was further stirred for 1 hour to get ahomogeneous viscous mixture. This mixture was used to fabricate thin films by spin coating method. Prepared thin films were used in the Z-scan measurement to study their NLO properties and for other characterizations.

2.4. Characterisation

UV-vis spectrophotometer (Black-C-SR-50, Stellarnet, USA) was used to record absorption and transmission spectra in the spectral range 190 -1000 nm. Average size and shape of AgNPs were determined by TEM using theJEM-2100F (make- JEOL, Japan) andhaving a point-to-point resolution of 0.19 nm. Powder XRD spectra recorded using Rigaku rotating anode (H-3R) diffractometer (MiniFlex II) with irradiation from Kα line of copper (λ=1.5418 Å) and angle 2θ, ranging from 20 to 80°C was used. FT-IR spectra were obtained with the instrument, having the hyperion microscope with a vertex 80 FT-IR system -3000 (Maker - Bruker, Germany) in the range of 450-7500 cm^{-1}.

2.5. Measurements of Nonlinear Optical Properties

Nonlinear optical responses, i.e, nonlinear refractive index and third-order nonlinear optical susceptibility were investigated by Z-scan technique with the He-Ne laser (λ = 632 nm) under CW regime.

3. Results and Discussion

3.1. UV-Visible Study

Fig.1 depicts UV-Visible absorption spectra of L-arginine stabilized colloidal AgNPs prepared by reducing silver nitrate with sodium borohydride in the wavelength range 300 − 600 nm. Generally, AgNPs exhibit a surface plasmon resonance absorption peak in the range of 380 − 430nm. A characteristic plasmon band due to resonance phenomenon of free electrons in the conduction band of silver nano-particles is observed at 405, 395, and 391 nm for 1 mM, 2.5 mM, and 5 mM L-arginine concentration respectively.

This explains the blue shift in the optical absorption peak as the concentration of L-arginine (stabilizing agent) increases. The shift towards lower wavelength side (blue shift) also indicates that size of AgNPs is reducing as the concentration of stabilizer is increasing. Further, it is well noted from absorption spectra that the intensity of absorption is decreased with an increase of the L-arginine concentration, which is attributed to a decrease in the concentration of AgNPs and their size as well [34-35].
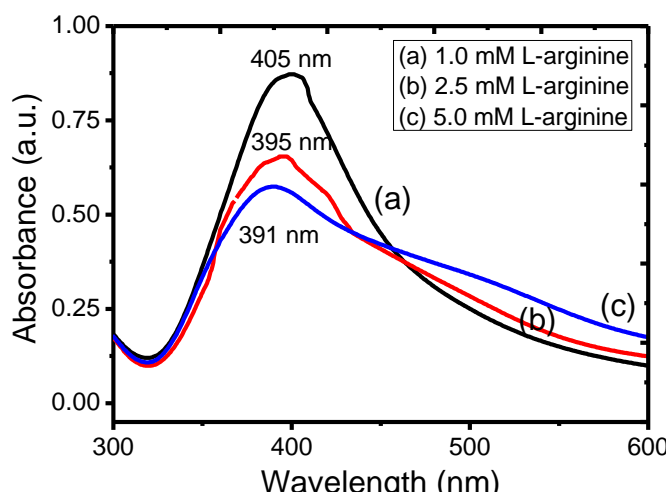

Figure 1. Absorption spectra of Silver nano-colloids with (a) 1 mM (b) 2.5 mM (c) 5 mM L-arginine concentration

The effect of the blue shift in LSPR on nonlinearity is explained by Palpant *et.al* (1998) [36]. They reported blue shift in the localized surface plasmon resonance (LSPR) with decreasing particle size. They applied Time-dependant local-density-approximation (TDLDA) theory for calculations and found good agreement. They explained the effect as follows: the metal nano-particle cluster has two regions; inner core and outer shell. The blue shift with decreasing size is due to the screening effects, due to polarisable inner medium, that vanishes at theouter shell of the particles. Alvarez *et.al* [37] also found similar results. However, De *et.al* [38] do not attribute the blue shift of LSPR to the size effect. They have explained that the blue shift of LSPR is due to the electron transfer to the Ag cluster from hydrogen in reducing atmosphere, filling up its 5*s* band. The increase of s-electron density gives rise to the increasing of the Fermi energy and thus plasma frequency.

3.2. Structural and Morphological Study

Fig.2 illustrates X-ray diffraction spectra (X-RD) of AgNPs embedded in the PVP matrix. The diffraction peaks at $2\theta \approx 38.11°$, $44.27°$, $64.42°$, and $77.47°$ indexed to the (111), (200), (220), and (311) planes of face-centered cubic crystal structure of silver respectively. The intensity of all peaks matched with JCPDS data given in the literature (PDF card No- 040783). The line broadening of the X-ray diffraction peak is mainly due to small particle size. The broad peak (hump) around $2\theta = 25°$ suggests the existence of PVP [39]. From full-width at half maximum (FWHM) of diffraction peaks, the average size of AgNPsis estimated

using Debye-Scherrer equation $2R = 0.9\lambda/\beta \cos\theta$ [40], where 2R is the size (diameter) of QD, β is full-width half maxima (FWHM) of XRD peak in radians, θ is thediffraction angle, and λ is wavelength of X-ray (1.540598Å).
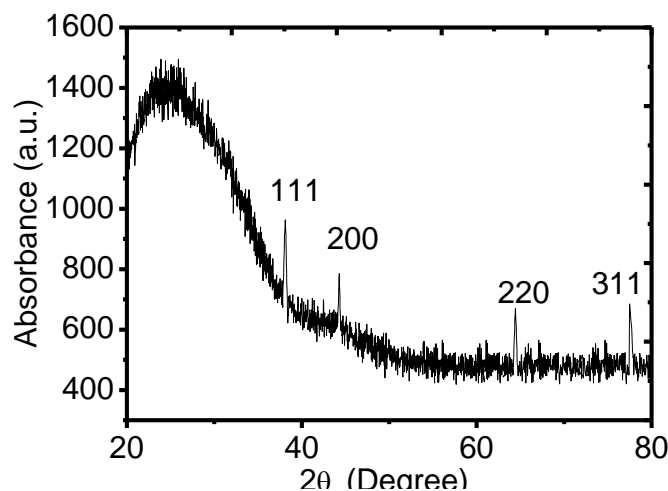

Figure 2. X-RD spectra of Ag-PVP thin film

The average size estimated using the above equation are 13, 10, and 8 nm for 1, 2.5, and 5 mM L-arginine concentration respectively, which is consistent with the sizes obtained from TEM analysis. From TEM images, the sizes are found as 10, 9 and 6 nm for 1, 2.5, and 5mM L-arginine concentration respectively. Fig.3(a) shows TEM image of AgNPs stabilized in 1mM L-arginine and 3(b) shows corresponding particle size distribution. Fig. 3(c) represents TEM image of AgNPs stabilized in 5mM L-arginine and 3(d) represents corresponding particle size histograms. In fig. 3(e), the Selected Area of Electron Diffraction (SAED) pattern is shown.

The structural and morphological study, supported by TEM analysis, confirmed that the size of AgNPs decreased as the stabilizer concentration increased from 1mM to 5mM. The literature reports indicate that the stabilizer concentration has a significant influence on the particles size. Murray and co-workers [41] have reported that different sized gold nano-particles have been synthesized by changing the concentration of the stabilizer (Hexanethiolate) and found that size of nano-particles reduces as the concentration of the stablizer increases. However, Sardar *et.al. (2011)* have observed contradictory results. They have found that the size of gold nanoparticles increased from 2.6 to 4.3 nm as the stabilizer concentration increased [42].

3.3. FTIR Study

Fig. 4 Exhibits Fourier Transform infra-red spectra (FT-IR) of silver nano-colloids stabilized in the L-arginine prepared by reducing silver nitrate with sodium borohydride. The spectra reveal the interaction of silver nano-particles with L-arginine functional groups. It is observed that the intensity of different peaks reduces with an increase in L-arginine concentration suggesting the formation of strong bonding between AgNPs and L-arginine functional groups. This results in the formation of smaller size particles for higher

L-arginine concentration. This, in turn, reduces χ^3.

Peaks in the highest energy region, i.e. 3800 cm^{-1} to 2700 cm^{-1}, are called hydrogen region peaks. The bands from wavenumber 3782 cm^{-1} to 3595 cm^{-1} appeared in the spectra,are mainly due to C-Hstretching absorption, which indicates the presence of water in the samples.Protonated amino acid (L-arginine) shows true C=O stretching at higher frequency 1720 cm^{-1}, which is shifted to 1722 cm^{-1}. The peak at 1666 cm^{-1} is assigned to N-H bending vibration. The carboxylate stretching mode of CO group, which usually gives a transition peak at 1600 cm^{-1}, is shifted to 1592 cm^{-1} due to its attachment to the AgNPs. The two medium bands at 1485 cm and 1442 cm are present because of symmetric NH$_3^+$ deformational vibration. Due to stretching of CNH group, a band is appeared at 704 cm^{-1}. The bending vibration of COO and COH group, yielded the band at 631 cm^{-1}. The rocking motion of theNH$_2$ group produces a band at 449 cm^{-1} which is slightly shifted to 441cm^{-1}. The shift in the band positions, as discussed above, indicates the strong bonding between L-arginine and AgNPs [43-45].
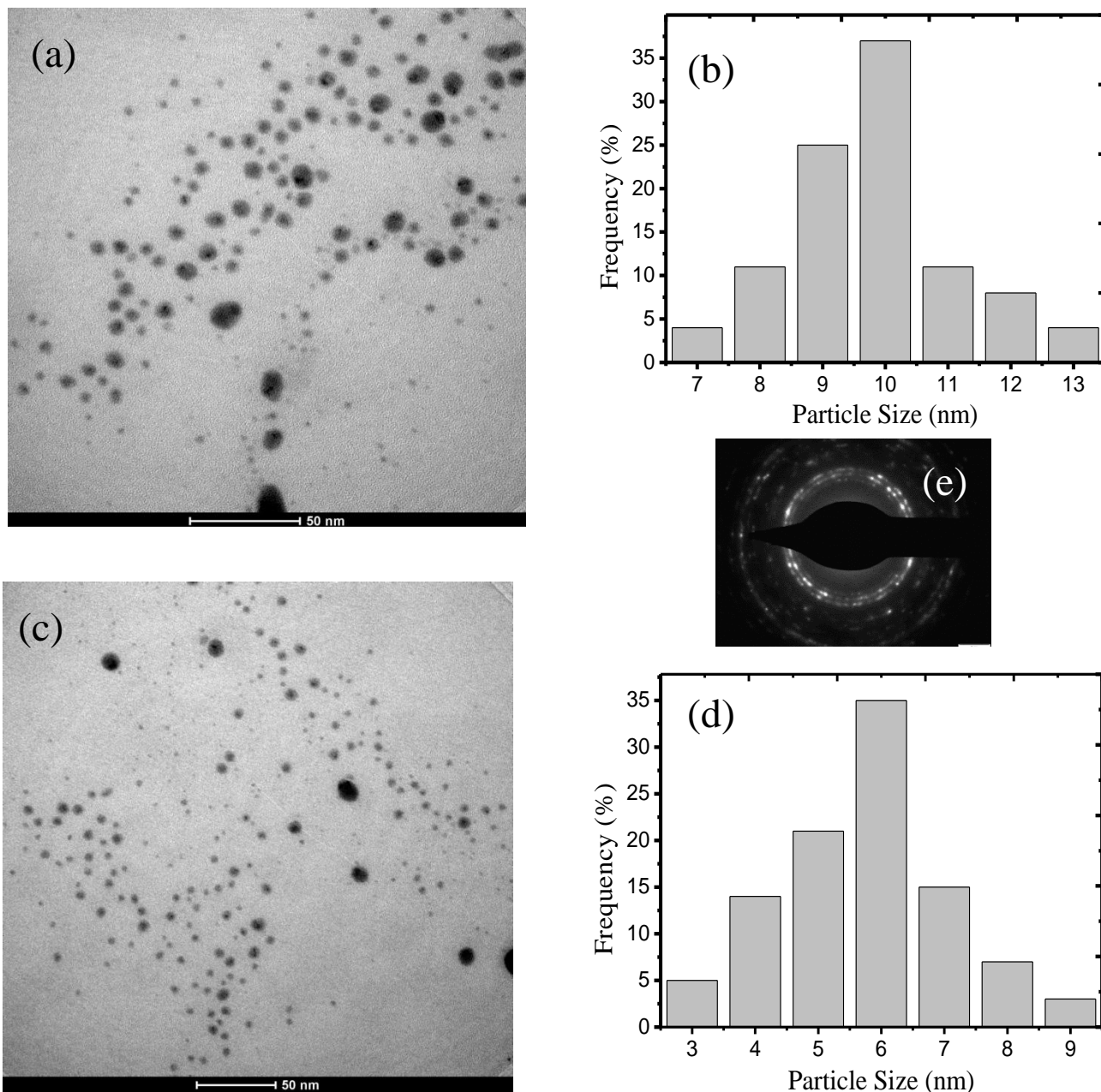

Figure 3.   (a) TEM image of Ag nano-particles stabilised in 1mM L-arginine, (b) corresponding particle size distribution, (c) TEM image of Ag Nano-particles stabilised in 5mM L-arginine, (d) represents corresponding particle size histogrames and (e) SAED pattern
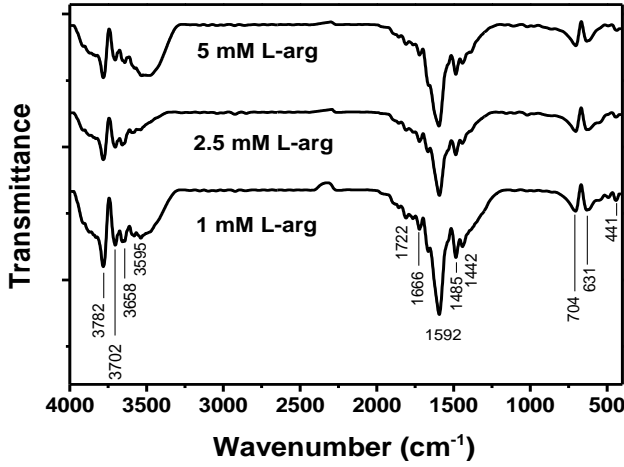
Figure 4. FTIR spectra of silver nano colloids stabilised in 1, 2.5 and 5 mM L-arginine

3.4. Nonlinear Optical (NLO) Study

NLO properties of L-arginine stabilized AgNPs embedded in the PVP polymer matrix were investigated by using single beam Z-Scan technique [46-47]. Fig.5 shows the schematic diagram of the experimental setup of the Z-scan technique. The He-Ne laser with wavelength 632 nm was used as anexcitation source under CW regime.
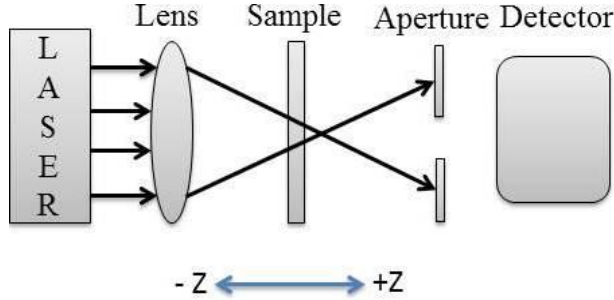

Figure 5. Experimental Z-scan setup for closed aperture measurements

In this technique, the transmittance of a tightlyfocused Guassian beam through a finite aperture in the far field is measured by thedetector as a function of sample position Z along the focal plane. Spatial beam broadening or narrowing in the far field takes place due to nonlinear refraction of the thin film. Therefore, the thin film receives different intensity of light at each position of the sample, which resulted in a change in the fraction of light that passed through the aperture as the sample position was moved along the focal plane. The position of the peak and valley depended on the sign of the nonlinear phase shift. For positive phase shift, the peak would trail the valley and self-focusing occurred. If the phase shift was negative, the valley would trail the peak and self-defocusing occured. If the sample is considered thin compared to the Rayleigh length of the beam ($L < Z_0$), the maximum nonlinear phase-shift can be evaluated from the peak to the valley variation of the transmittance curve. Knowing the incident laser power, one can estimate the nonlinear refractive index (n_2). It is possible to measure the

nonlinear absorption by removing the aperture in the far field. In the open-aperture Z-scan experiments, the curves are symmetric with respect to the focal point, where they exhibit a minimum transmittance in the case of reverse saturable absorption and a maximum for the saturable absorption. If the materials exhibit both nonlinear refraction and absorption properties, one can obtain a pure nonlinear refractive index (n_2) by dividing the closed aperture data by the open aperture data [48].

The difference between normalized peak-valley transmittance (ΔT_{p-v}) can be directly measured by this technique based on equations given in [46-47]. The change in normalized peak-valley transmittance is given by

$$\Delta T_{p-v} = 0.406 (1-s)^{0.25} |\Delta \phi_0| \qquad (1)$$

where $S = 1 - \exp\left(\dfrac{-2r_a^2}{w_a^2} \right)$ is linear aperture

transmittance, where r_a is aperture radius and $\omega_a = 22$ μm is the beam waist.The maximum nonlinear phase shift $\Delta \phi_0$ can be obtained by the following equation:

$$n_2 = \frac{\Delta \phi_0 \lambda}{2\pi L_{ff} I_0} \qquad (2)$$

where the linear aperture transmittance $s = 0.3$, λ is the wavelength of source (632 nm), I_0 is the intensity of a laser beam (13.16 MW/m²) at focus z = 0, $L_{eff} = 1 - e^{\alpha L / \alpha}$ is the effective length of the sample and L is the thickness of the sample, α is the linear absorption coefficient [49]. In our experimental setup, a low power (13.16 mW) laser beam was focused by using aconvex lens with a focal length of 20 cm. The spot size at the focus was determined using CCD camera (Thorlab, BC106-VIS) and was found to be 44 μm (beam waist, ω=22 μm and Rayleigh range, z_0=2.4 mm).

The real and imaginary parts of the third-order NLO susceptibility (χ^3) were estimated based on the nonlinear refractive index (n_2),

$$\mathrm{Re}\,\chi^3 (esu) = 10^{-4} \frac{n_0^2 c^2 \varepsilon_0}{\pi} n_2 \ (\mathrm{cm}^2/\mathrm{W}) \qquad (3)$$

Where, ε_0 is the permittivity of vacuum, n_0 is the linear refractive index, c is the velocity of light in a vacuum. The absolute value of the third-order NLO susceptibility is a calculation from the real and imaginary values.

The normalized transmittance is plotted against the sample position. Fig.6 shows the closed aperture normalized transmittance curves of Ag-PVP thin film. The solid lines indicate the theoretical fits.
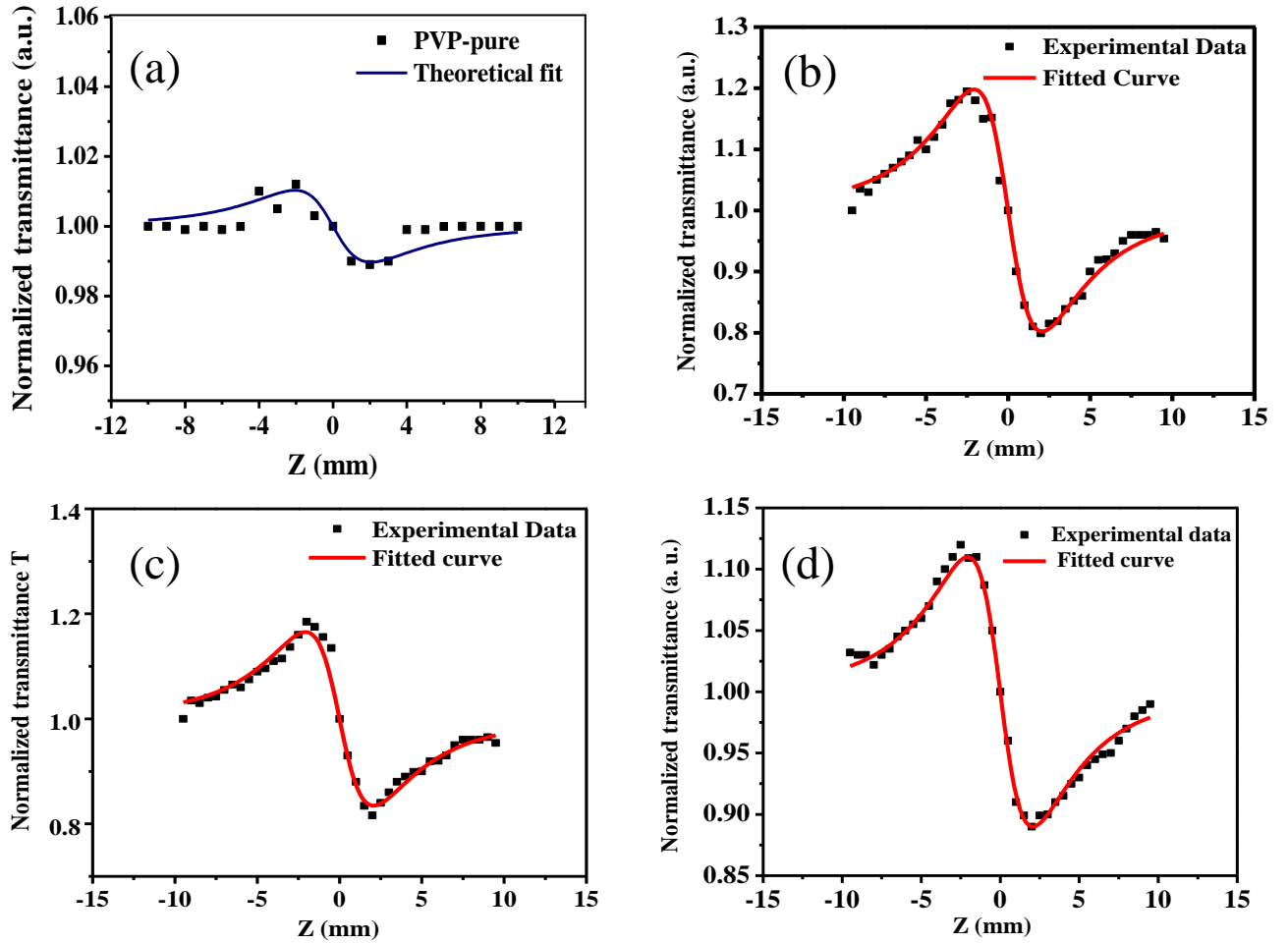
Figure 6. Closed aperture Z-scan curves of Ag-PVP nanocomposite for (a) Pure PVP (b) 1 mM (c) 2.5 mM (d) 5 mM L-arginine concentration

Table 1. Calculated Values of (n_2) and $\left|\chi^3\right|$ Measured for Ag-PVP Thin Film at Different Concentration of L-Arginine and Pure PVP

L-arginine concentration (mM)	Average size of AgNPs	$\Delta\phi_0$	(n_2) (cm²/W) $\times 10^{-4}$	Re χ^3(esu) $\times 10^{-4}$	$\left|\chi^3\right|$ (esu)$\times 10^{-4}$
1	10 nm	-1.145	-5.58	2.56	2.56
2.5	9 nm	-1.051	-4.8	2.20	2.20
5	6 nm	-0.655	-3.16	1.45	1.45
Pure PVP			-1.26×10^{-6}		2.56×10^{-6}

Transmittance curve shows that the peak is followed by a valley indicating a negative nonlinear refraction. The negative phase shift and negative sign of nonlinear refractive index suggest the self-defocusing phenomenon. The symmetrical closed aperture Z-scan curve indicates nonlinear absorption that is negligible, and we could not find any nonlinear absorption process. This suggests that, in our samples, nonlinear refraction dominates thus masking absorption completely. Hence, the imaginary part of third-order nonlinear optical susceptibility (Im χ^3) is zero.

From the peak-valley variation of the transmittance curve (ΔT_{p-v}), it is possible to calculate the maximum nonlinear phase shift ($\Delta\phi_0$) that can be used to find the nonlinear refractive index (n_2), by knowing the incident laser power. Nonlinear absorption measurements can be done by removing aperture in the far field.

The nonlinear refractive index (n_2) and third-order nonlinear susceptibility (χ^3) are calculated for various

concentrations of L-arginineand are listed in Table 1. We have also taken Z-scan measurements for pure PVP to estimate the nonlinear refractive index (n_2) and (χ^3). It is found that (n_2) and (χ^3) for pure PVP are in the order of 10^{-6} cm^2/W and 10^{-6} esu, respectively, whereas for composite thin films, (n_2) and (χ^3) are found in the range of 10^{-4}.

R. A. ganeev et.al [50] studied AgNPs in various media such as ethanol, ethylene glycol, and water, and measured χ^3 as high as 10^{-8} esu. Numerous results are reported by A. L. Stepanov [33]. Nonlinear optical responses of AuNPs in various matrices such as SiO_2, TiO_2, and Al_2O_3 are studied and third-order nonlinear susceptibility (χ^3) as large as 10^{-7} esu and nonlinear refractive index (n_2) up to 10^{-8} have been obtained. We have estimated huge enhancement in $\chi^3 \approx 10^{-4}$ esu and $n_2 \approx 10^{-4}$ cm^2/W.

Table 1 reveals that the nonlinear refractive index (n_2) and third-order NLO susceptibility (χ^3) decreased linearly with an increase in the L-arginine concentration. This may be due to the decrease in the particle size (as confirmed from TEM images) as the L-arginine concentration increases. Similar results were obtained by E. Shahriari et. al. [49] while studying the effect of concentration and particle size of gold nano-particles on the nonlinear refractive index, and found that n_2 decreased as the particle size/Au concentrationis reduced. In our sample, χ^3 is reducing with the particles size. This effect is explained by Fukumi et.al [51]. They demonstrated that χ^3 is proportional to the fourth power of particle radius, volume fraction of the metal colloid particles, and third-order susceptibility of the metal particles only, (χ_m^3). Aggregation of the sample also leads to the increase of the nonlinear optical response. R. A.Ganeev et.al (2005) found that χ^3 is increased from 10^{-15} esu to 10^{-14} esu, and n_2 is increased from 1.43×10^{-11} to 16.0×10^{-11} when aggregation rate of silver nano-particles was increased from 0 to 0.80. In our case, TEM images (fig.3) show small agglomeration for 1mM L-arginine concentration, and as the L-arginine concentration increased to 5 mM, well separated smaller AgNPs are formed [21, 50]. This can be another reason why χ^3 is decreasing with increasing L-arginine concentration.

A nonlinear optical response of metal particles embedded in the matrix is based on the following effects [52]: (a) intraband transitions that originate in the filled conduction band state near the Fermi level. The effective value of χ^3 is smallest in magnitude and inversely proportional to the cube root of the particle radius,(b) Interband transitions from the valence band to empty the conduction band occurs. For nano-particles in the range of 5 – 15 nm, interband nonlinearity near LSPR is 100 times greater than intraband nonlinearity and is also independent of the nano-particlessize, (c) electrons in the conduction band absorb a photon and get heated, yielding what is called hot electrons. The hot

electron transitions are particularly strong and can be dominant in the metal cluster. This transition produces χ^3 with a magnitude 10 to 10^4 times as high as intraband transitions. All the above transitions have a picosecond response time.

Moreover, in the CW laser regime, the nonlinear optical response of AgNPs in the dielectric matrix is caused by thermal-induced nonlinearity, indicating a temporal variation of refractive index due to nonlinear absorption in the medium and to non-radiative relaxation down to the ground state. This thermal pulse leads to the generation of acoustic waves that change the density of medium, followed by a variation of refractive index of the medium [50, 52-53]. In our experiments, thermal nonlinearity is mainlycontributing as we used a CW laser. Opticalnonlinearity of the composite thin films constitutes thermal and electronic nonlinearity. Irradiation of samples (thin films) with CW laser causes thermal nonlinearity domination, whereas irradiation with pulsed laser having low repetition rateelectronic nonlinearity dominates the optical nonlinear phenomenon. Thermal nonlinearity can be suppressed by replacing CW laser with pulsed laser.

The origin of the huge enhancement in nonlinear optical responses has been explained by several authors. K. Dolgaleva et. al. [54] predicted the ten fold enhancement in nonlinear optical responses as due to local field effects. The enhancement is specially hugein the metal-dielectric nanocomposite materials due to the combined effect of surface plasma resonances and the local field effect. In the metal-dielectric composite, surface plasmon excitations are localized in the small nano-region called hot-spots. Electromagnetic energy accumulated in the hot-spots associated with localized plasmons led to local fields that can exceed the intensity of applied field by four or five times in magnitude [55-57]. The high local fields in the hot-spots resulted in a huge enhancement in nonlinear optical responses. Local field factor also became dependent on the dielectric constant (ϵ_d) of dielectrichost matrix as thelocal field factor (f) takes the form of f = $3\epsilon_d$/i ϵ_2 near SPR. Therefore, the matrix with a larger dielectric constant makes the composite gain the larger value of f, and SPR peak also shifts due to the energy dependence of dielectric constant. Hence, metal particles embedded in a composite matrix usually have larger optical nonlinear responses near their individual SPR. Specifically, third-order nonlinear optical susceptibility (χ^3) becomes proportinal to the fourth power of the local field factor under the condition of low metal concentration [58-61]. Finally, the huge enhancement in the nonlinear optical responses of AgNPs embedded into PVP matrix is due to the LSPR, thermo-optic effect, and the local field factor.

4. Conclusions

In conclusion, highly stable AgNPs were synthesized using L-arginine as a stabilizer by chemical reduction method and dispersed into the PVP matrix. The effect of the

L-arginine concentration on LSPR, the size of AgNPs, nonlinear refractive index, and the hird-order NLO susceptibility were studied. A sizable enhancement in the magnitude of nonlinear refractive index (n_2) in the order of 10^{-4} cm^{2}w^{-1} and third-order NLO susceptibility (χ^3) in the order of 10^{-4} esu wasdetected. The magnitude of n_2 and χ^3 was found to decreasewith an increase in the concentration of L-arginine. The negative sign of n_2 indicates a self-defocusing phenomenon of Ag-PVP nano-composite. The enhancement of n_2 and χ^3 in the composite film was due to the combined effect of SPR, thermo-optical phenomenonand local field factor. No nonlinear absorption was observed in all samples. The average size of AgNPs, as analysed by TEM, was found to decreasefrom 10 nm to 6 nm with anincrease in the L-arginine concentration from 1mM to 5 mM. X-RD study confirmed the presence of fcc structuredof AgNPs in thin films. The blue shift in the SPR peak position wasobserved. The strong bonding between AuNPs and L-arginine functional groups was confirmed from FT-IR study. These results demonstrate that our study has good potential in optoelectronic device applications.

ACKNOWLEDGEMENTS

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