Open-aperture Z-scan and optical limiting of plasmonic silver-polymer system

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The present study reports the green synthesis of silver nanoparticles using *Mimosa pudica* as reducing agent. The formation of silver nanoparticles was confirmed by UV-Vis absorption spectroscopy and Transmission Electron Microscopy. The average particle size of the synthesised material is about 16 nm and are almost spherical in shape. Nonlinear optical absorption properties of synthesized "Green" AgNP-PVA were investigated using open-aperture Z-scan technique at 532 nm and it can be used to study the optical limiting property. The adopted green-synthetic approach is very much cost-effective.

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Keywords: Silver nanoparticles, Green synthesis, Mimosa pudica, Open-aperture Z-scan, Nonlinear absorption coefficient, Optical limiting

1. Introduction

Noble metal nanoparticles (MNPs) have received much attraction owing to their enhanced third order nonlinear optical properties near the surface plasmon resonance (SPR) [1]. Various physical and chemical methods have been reported to synthesize silver nanoparticles (AgNPs). Among these, the most common method is the chemical approach which includes reduction of metal precursor. The plant-assisted synthesis of nanoparticles is more advantageous since they avoid the tedious process of maintaining the cell culture and can be simply scaled-up for the MNPs synthesis [2,3]. Moreover, plant extracts are low-cost and eco benign, and have been exploited recently for "green" developing nanomaterials with interesting optical and biological properties [4,5,6].

Mimosa pudica (*touch-me-not-plant*) is a sensitive ayurvedic medicinal herb [3]. Owing to its pharmacological activities, it invites attention of the researchers worldwide. It has been previously reported that the constituents of *Mimosa pudica* are alkaloids, non-protein amino acids (mimosine), flavonoids, C-glycosides, steroidal sapogenins, fatty acids, unsaturated sterols, tri-terpenoids, tannins and essential oils. This plant has several anti-asthmatic, antidepressant, aphrodisiac and analgesic properties. Various parts of this plant have been traditionally used for the treatment of several diseases like skin diseases, high blood pressure, diarrhoea, insomnia, tumour, gynaecological disorders and several urogenital infections [3]. *Mimosa pudica* leaf extract assisted synthesis of Cu, Co, Ni and Ag nanoparticles were already reported [3,7].

Herein we report the green synthesis of AgNPs using *Mimosa pudica* leaf extract at room temperature. Nonlinear optical properties of AgNP-PVA were also evaluated using open-aperture Z-Scan technique.

2. Experimental

2.1. Synthesis of *Mimosa pudica* leaf extract

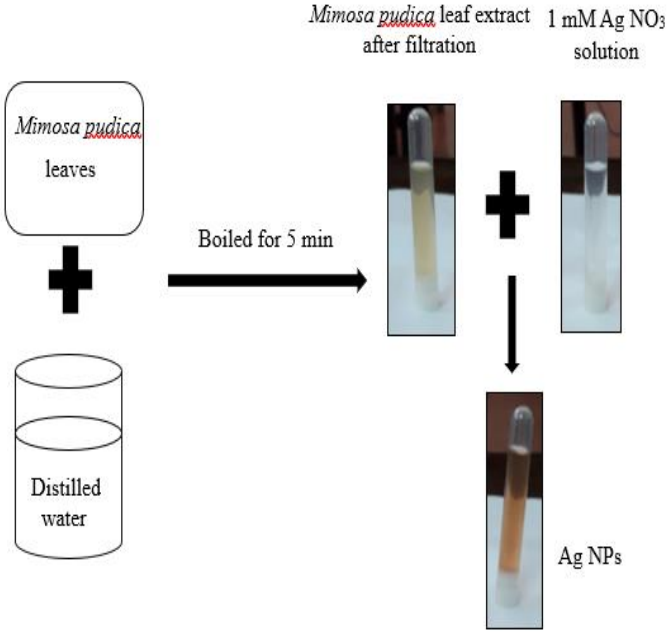
Mimosa pudica leaf extract was prepared using the same method as described in Ref. [8]. Fresh leaves of *Mimosa pudica* were collected from nearby places (Chengannur, Kerala, India) which were cleaned and completely dried at sunshade. About 1 g of the dried *Mimosa pudica* leaves dispersed in 100 mL distilled water and were boiled for 5 minutes. The resulting solution was then filtered out using Whatman No. 1 filter paper and kept it for further use.

2.2. Synthesis of PVA doped with silver nanoparticles (AgNP-PVA)

For the preparation of AgNPs, we have followed the synthetic strategy adopted by Thomas et al. [7] with slight modifications. All commercially available solvents and reagents for synthesis were of reagent grade and used as received without further purification. About 50 mL of 1 mM aqueous $AgNO_3$ solution was mixed with 10 mL of *Mimosa pudica* leaf extract at room temperature. Colourless solution turned to yellow and then to orange-brown after thoroughly mixing it for about 120 minutes which indicates the

formation of AgNPs. The schematic representation of the synthesis is shown in Scheme 1. Phyto-synthesized AgNPs were then incorporated with 5 wt % PVA solution to obtain AgNP-PVA.

AgNPs synthesized using *Mimosa pudica* as reducing agent were characterized by UV-Visible (UV-Vis) absorption spectroscopy. UV-Vis absorption spectrum was recorded using a Shimadzu UV-1800 UV-Vis spectrophotometer. The size and morphology of AgNPs were examined by transmission electron microscopy (JEOL, JEM 2100 model instrument).



Scheme 1. Synthesis approach of AgNPs (color online)

A highly sensitive single-beam Z-scan experiment based on spatial beam distortion was used for nonlinear optical studies of the prepared sample. A Q-switched Nd:YAG laser (Spectra Physics LAB -1760, 532nm, 7ns, 10 Hz) was used as the excitation source. Sample was taken in a 1 mm thick cell and moved along the z-axis through the focal point of a lens of focal length 20 cm. An energy ratio meter (Rjp7620 Laser probe Corp) having two identical pyroelectric detectors heads (Rjp 735) was used for the simultaneous measurement of transmitted beam energy, reference beam energy and the ratio of beam energies. Calibration of Z-scan set-up was done using Carbon disulfide (CS_2) (Ottokemie).

3. Result and discussion

Mechanism behind the formation of AgNPs was already discussed in ref. [4]. AgNPs absorb radiation in the range of 380-450 nm owing to the excitation of surface plasmon vibrations (SPR). This is accountable for the yellow-brown colour of AgNPs in different media [9]. *Mimosa pudica* leaf extract mediated AgNPs shows colour change from yellow to orange brown indicating the formation of AgNPs. Fig. 1 displays the colour change during the formation of AgNPs.

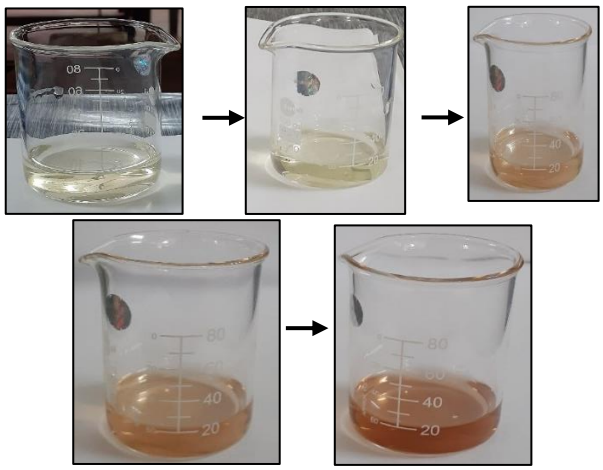


Fig. 1. Colour change during the formation of AgNPs (color online)

UV-Vis absorption spectrum of AgNP-PVA is shown in Fig. 2. A strong absorption peak at 437 nm originates from the surface plasmon resonance of AgNPs dispersed in PVA matrix.

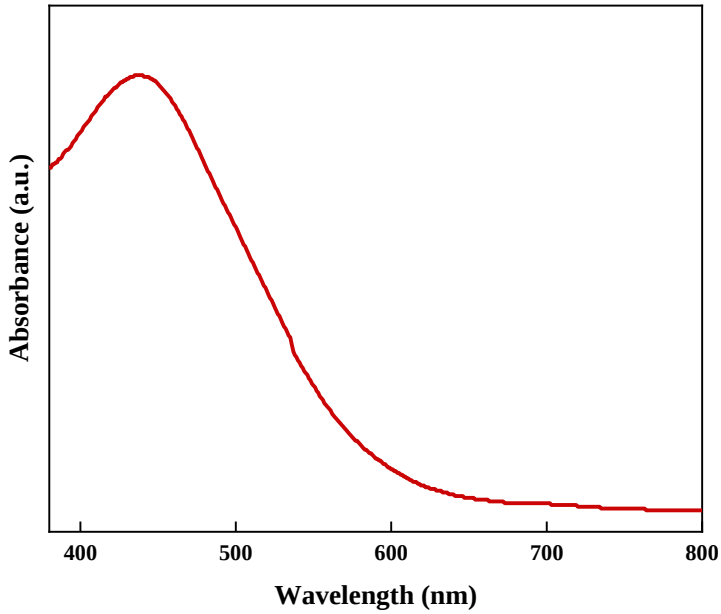
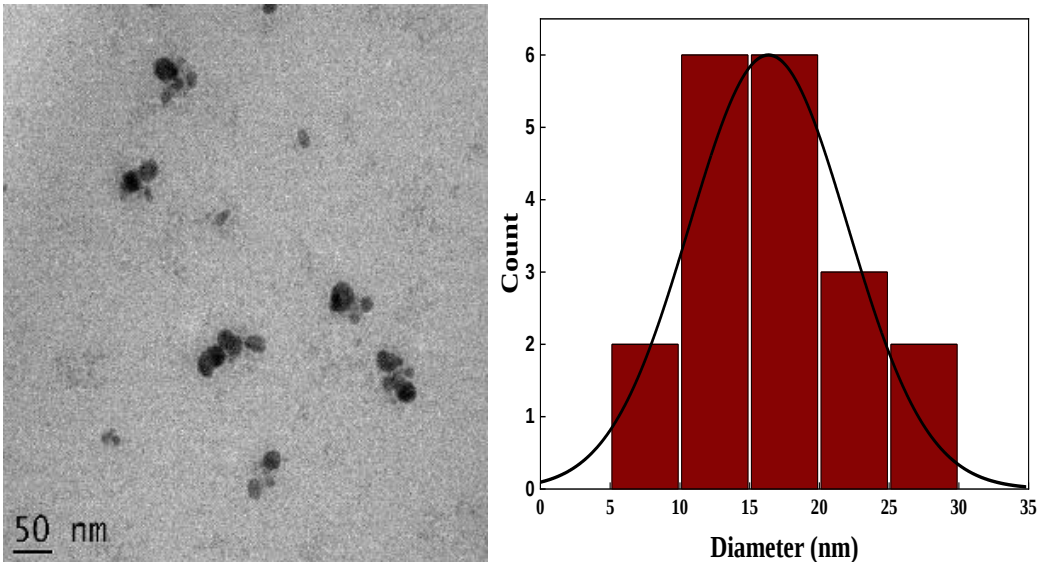


Fig. 2. UV-Vis absorption spectrum of AgNP-PVA (color online)

Typical TEM image of AgNP-PVA synthesized using *Mimosa pudica* extract as reducing agent is shown in Fig. 3. The particles are almost spherical in shape. Fig. 3 (b) reveals the histogram of the particle size distribution of AgNP-PVA. The average size of the particles was found to be around 16 nm.



(a) *(b)*

Fig. 3. TEM image of (a) AgNP-PVA and (b) Histogram of the particle size distribution of AgNP-PVA (color online)

Single beam Z-scan technique was used to study the nonlinear optical properties of AgNP-PVA. The origin of nonlinear optical absorption can be ascribed to various processes like two photon absorption (TPA) or multiphoton absorption, inter-band transition, intraband transition, excited state absorption and nonlinear scattering. In AgNPs, SPR lies below the inter-band transition thresholds d → p and p → s from occupied p states to unoccupied s states. For inter-band transitions to occur, energy of the photon must be greater than the gap energy (4 eV for Ag) [10]. The excitation wavelength used in the present Z-scan experiment is 532 nm (2.33 eV), which is smaller than the band gap energy 4.0 eV. Hence, the probable transition may be through TPA process. Therefore, the observed reverse saturable absorption (RSA) process in the present study is due to this TPA process. A small mismatch between the conduction band gap energy of AgNPs and the total energy of the two photons will be compensated by phonon-assisted excitation [2].

For an open-aperture Z-scan, normalized transmittance is given by:

$$T(z) = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{\frac{3}{2}}} \quad (1)$$

where

$$q_0(r,t) = \frac{\beta I_0(t) L_{eff}}{(1+\frac{z^2}{z_0^2})} \quad (2)$$

The effective length of the medium, L_{eff} in equation (2) is related to linear absorption coefficient $\propto_0$ and the thickness of the sample (l) and is given by:

$$L_{eff} = \frac{1-e^{-\propto_0 l}}{\propto_0} \quad (3)$$

Nonlinear absorption coefficient β is related to the imaginary part of third order nonlinear susceptibility ($Im(\chi^3)$) by the relation:

$$Im(\chi^3)(esu) = 10^{-2} \frac{\varepsilon_0 n_0^2 c^2 \beta(^{cm}/_W)}{2\pi\omega} \quad (4)$$

where ε_0 is the permittivity of free space, n_0 is the linear refractive index, ω is the excitation frequency, c is the velocity of light in vacuum and β is the nonlinear absorption coefficient in cm/W [11].

In the present study, AgNPs were incorporated into the PVA. When NPs are incorporated into a host matrix, the third order susceptibility is given by the expression:

$$\chi^{(3)} = pf^2|f|^2\chi_m^{(3)} \quad (5)$$

where p is the volume fraction of NPs embedded in the host matrix, f is the local field enhancement and $\chi_m^{(3)}$ is the third-order nonlinear susceptibility of the metal clusters. The local field enhancement factor f is given by the following relation:

$$f = \frac{3\varepsilon_d}{\varepsilon_m + 2\varepsilon_d} \quad (6)$$

In equation (6), ε_d is the dielectric constant of the host matrix and ε_m is the dielectric constant of metallic particle [12].

When NPs were embedded into the host matrix (PVA), the host matrix is exposed to the improved electric field scattered by the MNPs. Therefore, the effective nonlinear polarization P of the host matrix (polymer) is given by:

$$P = \varepsilon_0 \chi^{(3)} E^{(3)} \quad (7)$$

where $E^{(3)}$ is the enhanced electric field.

The dielectric constant is strongly associated with the position of SPR of NPs which in turn depends on their size and shape. Hence, several parameters need to be tuned to fabricate nonlinear optical nanocomposites with high performance [13].

It has been reported that pure PVA did not show nonlinear absorptive property [14]. The incorporation of green synthesized AgNPs into PVA influences the optical polarization of PVA thereby increasing the third-order nonlinear optical response of PVA. Nonlinear optical absorption property of AgNP-PVA was evaluated using an open-aperture Z-scan technique with nanosecond pulses. The data were analysed using the same procedure as described by Bahae *et al*. [11].

Fig. 4 shows the normalized transmittance curve for the open-aperture Z-scan curve of AgNP-PVA at an excitation wavelength of 532 nm. Z-scan curve displays a valley at the focus Z=0. This shows that the AgNP-PVA sample possess positive nonlinearity for nonlinear optical absorption in the nanosecond regime. It was reported that the nonlinear absorption coefficient β for mimosine-based AgNP is 2.84 x 10^{-10} m/W [7]. In the present case, the value of β for AgNP-PVA is 6.2 x 10^{-10} m/W. The imaginary part of third order nonlinear susceptibility ($Im(\chi^3)$) was calculated from the nonlinear absorption coefficient β (in cm/GW) using equation (4) and is found to be 2.21 x 10^{-10} esu.

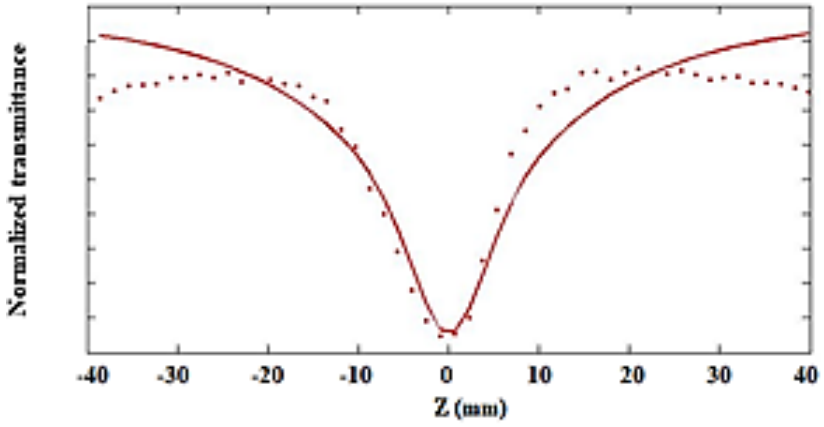


Fig. 4. Z-scan curve of AgNP-PVA (color online)

The nonlinear absorption coefficient β of the synthesized AgNP-PVA is in the order of 10^{-10} m/W and shows higher value than those reported for materials like coated Fe_2O_3-NPs and bare Fe_2O_3-NPs (10^{-11} m/W) [15], Pt-

PVA NCs (10^{-12} m/W) [16]. The values of β are comparable to the previously reported values of NPs: AgNPs stabilized by bovine serum albumin (10^{-10} m/W) [17], Ag-doped glass (10^{-10} m/W) [1], AgNPs (x 10^{-10} m/W) [7] and PtNP-PVP (10^{-10} m/W) [18]. The nonlinear absorption coefficient values of various similar systems were listed in Table 1.

The origin of asymmetries in the nonlinear curves may be due to the impurities present in the sample. The reasons for the impurities are that (i) sample used for the measurement is in the liquid phase and (ii) presence of various phytochemicals in the *Mimosa pudica* extract (such as mimosine) used for the reduction of NPs [19].

Table 1. Nonlinear absorption coefficient of various similar systems

Nanoparticles	**NLA coefficient β (m/W)**	**Ref**
Coated Fe_2O_3 NPs Bare Fe_2O_3 NPs	1.0 x 10^{-11} 0.82 x 10^{-11}	[15]
Pt-PVA	0.9-1.5 x 10^{-12}	[16]
Pt-PVP	3.2 x 10^{-10}	[18]
AgNPs dispersed in glass host	4.5x 10^{-10}	[1]
NF-RGO/ AgNPs at 0.1 M 0.3 M 0.5 M 1.0 M	 7.99 x 10^{-10} 7.99 x10^{-10} 7.99 x 10^{-10} 13.9 x 10^{-10}	[20]
AgNPs stabilized by the bovine serum albumin	8.836 x 10^{-10}	[17]
AgNPs	2.84 x 10^{-10}	[4]
AgNP-PVA	6.2 x 10^{-10}	Present study

To study the optical limiting property of AgNP-PVA, the nonlinear transmittance of AgNP-PVA is studied as a function of input fluence (MW/cm^2). Optical limiting behaviour of AgNP-PVA is shown in Fig. 5. Materials displaying NLO properties are of great interest, mainly those materials showing strong nonlinear absorption as an optical limiter [17]. Limiting threshold value of 163 MW/cm^2 for AgNP-PVA sample suggests the possibility of its application as an optical limiter.

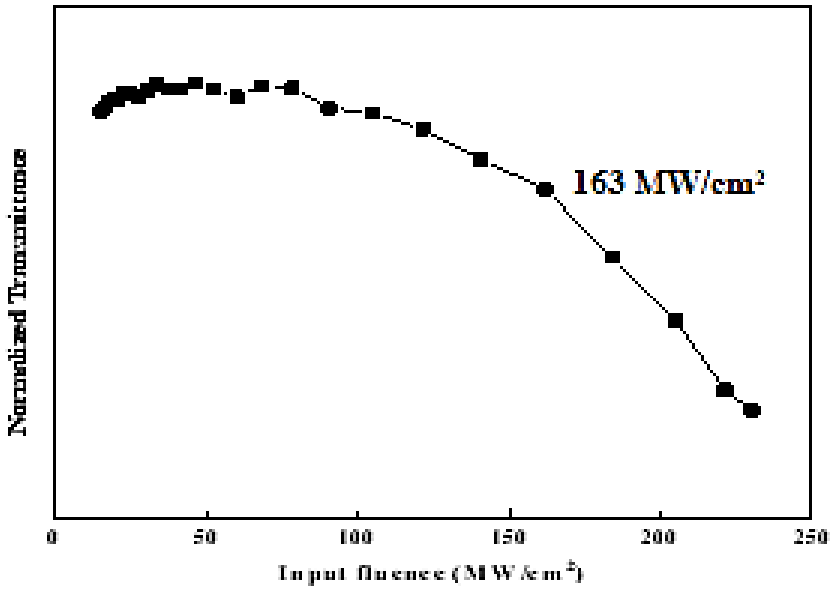


Fig. 5. Optical limiting curve of AgNP-PVA

4. Conclusion

Highly stable AgNPs were synthesized *via* green synthetic approach using *Mimosa pudica* leaf extract as reducing agent. The phyto-synthesized AgNPs shows characteristic peak at 437 nm which originates from the SPR band of AgNPs. Nonlinear optical absorption properties of AgNP-PVA sample were evaluated using single beam open-aperture Z-scan technique. The obtained nonlinear absorption coefficient is 62.0 cm/GW. Imaginary part of third order nonlinear susceptibility is found to be 2.21 x 10^{-10} esu. AgNP-PVA shows good optical limiting property with an optical limiting threshold value of 163 MW/cm^2. Hence, AgNP-PVA is a potential candidate for optoelectronic devices and applications.

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