# Nonlinear optical properties and thermal lensing of PVA doped with green synthesized Ag-Cu nanoparticles

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Ag-Cu nanoparticles were synthesized by the reduction of Ag and Cu ions in aqueous solution using *Mimosa pudica* as reducing agent. Nonlinear optical response of the PVA doped with Ag-Cu nanoparticles (Ag-CuNPs@PVA) was studied using open-aperture Z-scan technique. Ag-CuNPs@PVA showed higher nonlinear absorption than that of Ag NPs and Cu NPs alongside a better optical limiting property as revealed in nonlinear transmission studies. Nonlinear studies thus indicate Ag-CuNPs@PVA as an efficient material for photonic applications. Further, investigations on thermal diffusivity of the PVA doped with Ag-Cu nanoparticles using a dual beam mode match experimental set-up have revealed an enhanced thermal diffusivity for the sample.

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## 1. Introduction

Metallic nanoparticles exhibit unique properties that are extremely different from their bulk materials, and find application in catalysis, sensors, electronic devices, optical data storage, energy, ultrafast data communication etc. [1-4]. Bimetallic nanoparticles, either as alloys or as core-shell structures show improved catalytic, optical, electronic, biological and magnetic properties compared to their monometallic counterparts [1-3,5-8]. Due to the high third order nonlinearity, core-shell nanoparticles possess large nonlinear optical properties which provide better applications in optical limiting, optical switching etc. [9]. In core-shell nanostructured regime, silver and copper have received more attention owing to their remarkable potential in optical, electronic, biological, catalysis and sensing applications [9]. The core-shell nanostructures are most commonly synthesized using the techniques of micro emulsion, epitaxial growth, microwave irradiation, electrochemical de-alloying, multi-step reduction, solvothermal, polyol process etc. [1, 6]. However high costs, difficult synthetic routes etc. limit the use of many of these techniques to a certain extent [1]. Hence simple, inexpensive processes for the growth of metallic core-shell nanostructures are highly significant [1]. In green synthesis technique, phyto-chemicals present in the extract act as both bio reducing and capping agents [10]

Herein a simple, eco-friendly method was adopted for the preparation of poly vinyl alcohol (PVA) doped with silver-copper nanoparticles (Ag-CuNPs@PVA) in aqueous solution using *Mimosa pudica* as reducing agent. We demonstrate that the successive reduction of silver (Ag) and copper (Cu) salts can lead to the formation of silver-copper nanoparticles (Ag-CuNPs), which show remarkable nonlinear optical properties. Although, the nonlinear optical (NLO) properties and thermal lensing of metallic nanostructures are reported in previous studies, those of *Mimosa pudica* mediated Ag-CuNPs has not yet been reported. We had already reported the nonlinear optical properties of AgNP-PVA and CuNP using *Mimosa pudica* extract [11,12]. This work is an extension to the work previously reported by J. John et al. [11]. To evaluate the third order nonlinear optical properties and thermal diffusivity, we have used open-aperture Z-scan and dual beam mode matched thermal lens techniques, respectively. A higher thermal diffusivity value was obtained for the *Mimosa pudica* mediated Ag-CuNPs which was evaluated for the first time.

## 2. Experimental

### 2.1. Synthesis of PVA doped with Ag-Cu nanoparticles (Ag-CuNPs@PVA)

Leaf extract of *Mimosa pudica* was prepared by adopting the procedure of J. John et al. [12]. Silver nitrate and Copper sulphate solutions (1 mM) were used as the metal salt precursors. Aqueous solutions of these metal salts were mixed in 1:1 ($AgNO_3$:$CuSO_4$) molar ratio. To the above solution an equal volume of extract solution was added and the ensuing reduction was allowed to proceed at

room temperature. Ag-CuNPs@PVA was prepared by incorporating Ag-CuNPs with 5 wt% PVA solution in water. Silver nitrate and Copper sulphate were purchased from Himedia Laboratories. All samples were prepared using distilled water.

### 2.2. Nonlinear optical measurements

Z Scan technique, introduced by Sheik Bahae, is a simple and powerful tool in evaluating the nonlinear optical properties. A Q-switched Nd:YAG laser (Spectra Physics lab-1760), delivering 7 ns laser pulses at 532 nm and a repetition rate of 10 Hz was used as the light source for investigating the nonlinear optical properties of the bimetallic nanoparticles. Sample Ag-CuNPs@PVA was taken in a 1 mm thick cell. It was moved along the propagation direction through the focal point of a lens of focal length of 20 cm. The thickness of the sample was chosen in such a way that the Rayleigh length be greater than its thickness (1 mm). Energies of transmitted beam and reference beam were simultaneously measured using an energy ratiometer (Rjp7620 Laser probe Corp) and the Z-scan set-up was calibrated using $CS_2$. Open aperture Z-scan method was used to determine the nonlinear absorption of the prepared sample. Changes in the transmittance values are recorded carefully without an aperture to get nonlinear absorption coefficient of the sample. Generally, Z-scan traces (with open aperture) are symmetric with respect to focus.

Dual beam mode match thermal lens technique was used to evaluate the thermo-optic properties of Ag-CuNPs@PVA In the dual beam mode matched thermal lens technique, a 532 nm diode pumped solid state laser was used as the pump source and a He-Ne laser as the probe beam. Two beams were focussed into the sample so that the beam areas were same at the sample plane, resulting in a mode matched thermal lens configuration [12, 13].

## 3. Results and discussion

Absorption spectrum of Ag-CuNPs@PVA is shown in Fig. 1. Two different absorption peaks one at 460 nm and the other at 519 nm appear in the visible region. This is due to the surface plasmon resonance of both AgNPs and CuNPs, respectively. Existence of two peaks at 460 nm and 519 nm demonstrates that the NPs do not form alloy and they hold their individuality [14]. For alloy NPs, a single surface plasmon band occurs in between the SPR peak of Ag and Cu, as reported for Au-Cu and Au-Ag nanosystems [14].

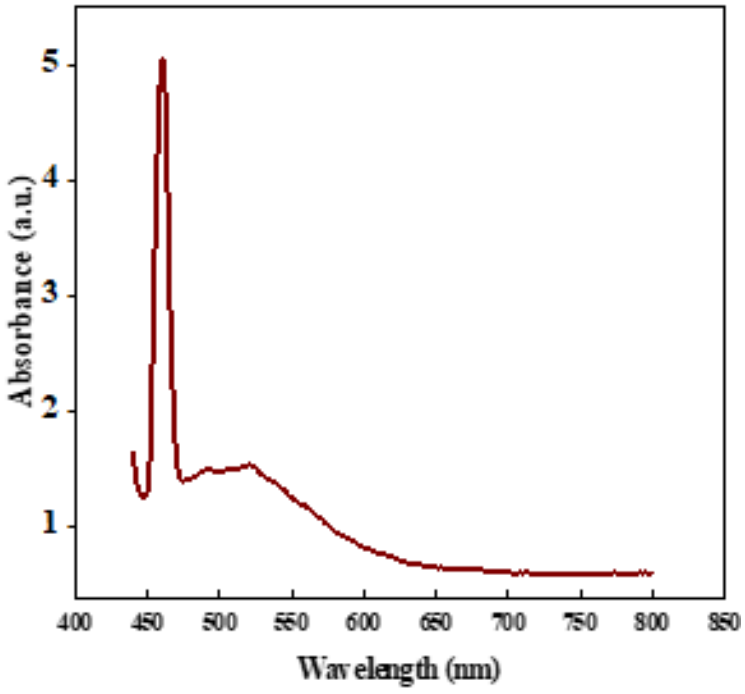


*Fig. 1. Absorption spectrum of Ag-CuNPs@PVA (color online)*

Typical TEM image of green synthesized Ag-CuNPs@PVA is shown in Fig. 2. Particles are nearly spherical with dimensions in the nanometer scale. The d spacing in the red square (1) measured through FFT pattern corresponds to Cu (111) d spacing, and the d spacing measured in the green square (2) is close to d spacing of Ag (111)). These results are consistent with the previously reported works [6].

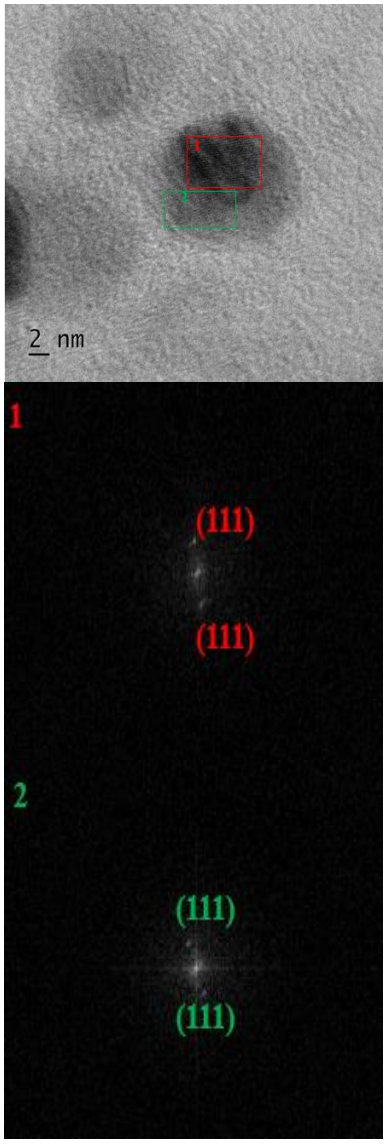


*Fig. 2. TEM image of Ag-CuNPs@PVA (Fig 2 above). FFT pattern of CuNPs (Fig 1 below) and AgNPs (color online)*

The unique optical properties of metallic nanoparticles make them an excellent candidate in various applications such as nonlinear optical processes, thermal lensing etc. [9]. Z scan technique is a simple and effective method to find the nonlinear optical properties of a sample [15] Generally, transmittance of nonlinear optical materials arises from various processes like two or three photon absorption, excited state absorption, saturated and reverse saturated absorption, free carrier absorption, interband and intraband transitions nonlinear refraction and nonlinear scattering [9,13]. Open-aperture Z-scan measurements were carried out to determine the nonlinear absorption coefficient [16].

For open aperture Z-scan, the transmittance

$$T_{OA} = 1 - \left(\frac{\beta I L_{eff}}{2\sqrt{2}\ [1+(\frac{z}{z_0})^2]}\right) \qquad (1)$$

where $z_0 = \frac{k\omega_0^2}{2}$ is the diffraction length of the beam, $k = \frac{2\Pi}{\lambda}$ is the wave factor, $\omega_0$ is the beam waist radius at the focal point, $L_{eff} = \frac{1-\exp(-\alpha L)}{\alpha}$ is the effective length of the nonlinear medium, L is the sample thickness, and $I_0$ is on-axis irradiance at focus.

The imaginary part of the third order nonlinear susceptibility $\chi^3$ of the nanoparticles can be estimated by the relation:

$$Im(\chi^3) = \frac{\lambda \varepsilon_0 n_0^2 c\beta}{4\pi} \text{ x } 9 \text{ x } 10^8 \text{ esu} \qquad (2)$$

where $n_0$ is the linear refractive index of the nanoparticles, $\varepsilon_0$ is the permittivity of free space, c is the velocity of light in vacuum, $\lambda$ is the wavelength of the light used.

Using open-aperture Z-scan analysis, nonlinear absorption coefficient $\beta$ was measured for the prepared sample. Data are analyzed according to the procedure described by Sheik-Bahae et.al [17]. The solid line in the transmittance curves in Fig. 3 is the theoretical fit to the experimental data.

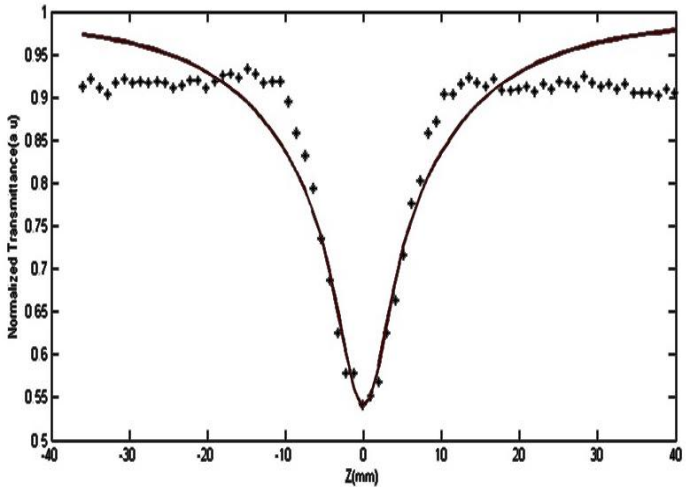


*Fig. 3. Open-aperture Z-scan curve of Ag-CuNPs@PVA*

The nonlinear absorption coefficient of Ag-Cu NPs is found to be β = 41.8 cm/GW and the imaginary part of the third order nonlinear susceptibility is Im ($\chi^3$) = 1.62 x $10^{-10}$ esu. In the case of Ag-CuNPs@PVA, β = 60.5 cm/GW and Im ($\chi^3$) = 2.20 x $10^{-10}$ esu. Both samples show reverse saturable absorption (RSA) due to two-photon absorption mechanism. Table 1 shows the nonlinear absorption coefficient β and Im($\chi^3$) of different nanosystems and it is seen that nonlinear absorption of Ag-Cu NPs@PVA is higher than that of silver and copper nanoparticles.

Various optical processes that may occur in metal nanoclusters involve interband transitions, intraband transitions and induced thermal scattering of light (ITS). Depending on the size, surrounding medium, excitation wavelength and the energy adsorbed by the nanoparticles, laser pulses can cause one or more of these effects in the system, which may eventually lead to optical limiting [18]. An ideal optical limiter is considered by its linear transmission under a threshold value of laser power. It must keep a constant value for transmittance beyond the threshold power. Ideal characteristic of an optical limiter is that there is a decrease in the value of transmittance with increase in input laser intensity. Limiting curve is not linear in the case of a real optical limiter [19]. Optical limiting response of the "green" synthesized Ag-CuNPs@PVA is shown in Fig. 4. Optical limiting threshold for copper nanoparticles is 237 MW/cm$^2$ and that of silver nanoparticles is 242 MW/cm$^2$ [12, 21]. Lower limiting threshold value (118 MW/cm$^2$) of Ag-CuNPs@PVA in suspension shows that the present material can be used as an efficient optical limiter.

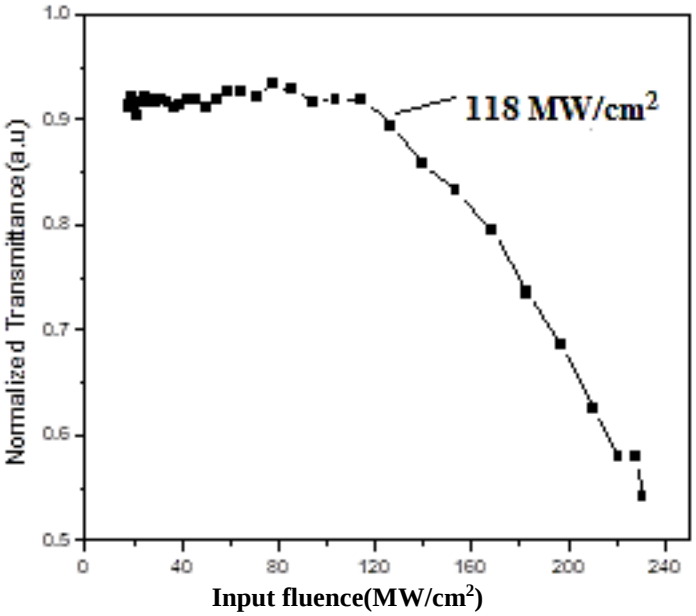


*Fig. 4. Optical limiting curve of Ag-CuNPs@PVA*

*Table 1. Nonlinear absorption coefficient β and Im($\chi^3$) of different nanosystems*

| **Sample** | **β (cm/GW)** | **Im ($\chi^3$) (esu)** | **Ref** |
|---|---|---|---|
| Ni-Ag NPs | 7 | - | [18] |
| Fe-Ag NPs | 6 | - | [18] |
| AgNPs | 1.7 | - | [18] |
| Au-Ag NPs | ~1.5 x $10^6$ | - | [20] |
| Cu@Ag core-shell NPs | -6.63 x $10^{-5}$ | 2.93 x $10^{-11}$ | [9] |
| CuNPs | 33.7 | 1.24 × $10^{-10}$ | [12] |
| AgNPs | 28.4 | 1.79 x $10^{-10}$ | [21] |
| Ag-Cu Nanoparticles | 41.8 | 1.62 x $10^{-10}$ | Present work |
| Ag-CuNPs@PVA | 60.5 | 2.20 x $10^{-10}$ | Present work |

The principle behind dual beam mode match thermal lensing technique used to measure the thermal diffusivity is that a laser beam can make a refractive index gradient [22]. Fig. 5 shows the thermal lensing of Ag-Cu NPs in solution.

Thermal diffusivity D is estimated using the relation [23]:

$$D = \frac{w^2}{4t_c} \tag{3}$$

where w is the beam radius at the sample position and $t_c$ is the characteristic time constant.

With fitting parameter θ = -4.784 and $t_c$ = 0.059 s, the value of thermal diffusivity D is found to be 1.09 x$10^{-7}$ m$^2$/s. Negative value of θ shows that the sample expands on heating. Table 2 shows the thermal diffusivity values of various metallic and bimetallic nanosystems. Thermal diffusivity of Ag-CuNPs@PVA show slight variation in value when compared with CuNPs and AgNPs.

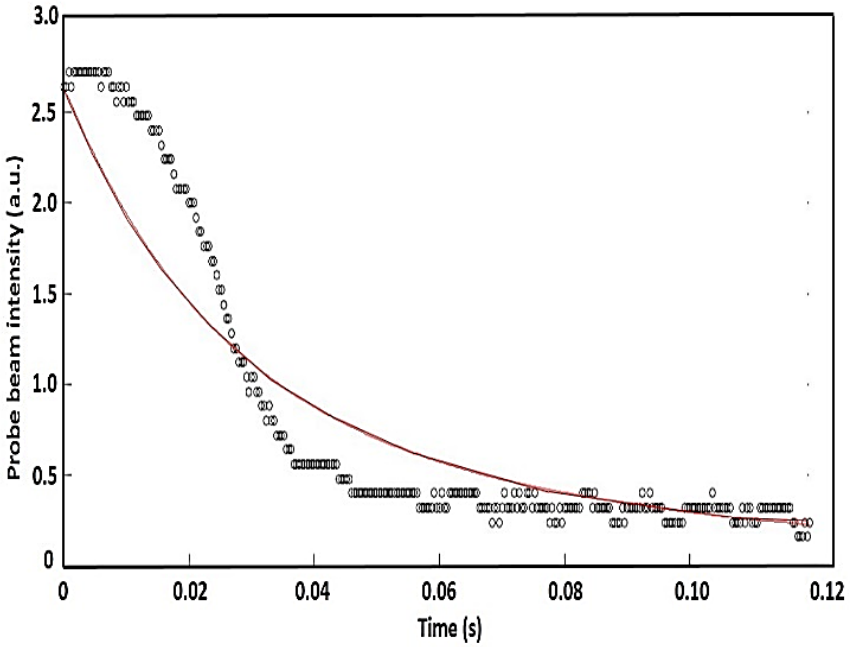


*Fig. 5. Thermal lensing curve of Ag-CuNPs@PVA (color online)*

*Table 2. Thermal diffusivity values of different metallic and bimetallic nanosystems*

| Sample | $t_c$ (s) | Θ | D ($m^2/s$) x$10^{-7}$ | Ref |
|---|---|---|---|---|
| AuNPs | 0.00349 | 0.11962 | 1.182 | [24] |
| PdNPs | 0.00359 | 1.12914 | 1.114 | [24] |
| Au-Pd NPs | 0.23803 | 0.00312 | 1.282 | [24] |
| Au-Ag NPs | 0.00187 | 0.5578 | 2.139 | [25] |
| AgNPs | 0.057 | -4.077 | 1.13 | [21] |
| CuNPs | 0.052 | -2.754 | 1.231 | [12] |
| Ag-Cu NPs | 0.051 | -2.816 | 1.251 | Present work |
| Ag-CuNPs @PVA | 0.059 | -4.784 | 1.091 | Present work |

## 4. Conclusions

A simple eco-friendly method has been developed for synthesizing Ag-CuNPs@PVA whose nonlinear properties have been successfully investigated. The results indicate significant nonlinear optical properties for the synthesized Ag-CuNPs@PVA making it a worthy candidate for nonlinear thermal applications. Ag-CuNPs@PVA nanoparticle increases the nonlinear absorption resulting in an enhancement of optical limiting property. Thermal diffusivity studies further show that Ag-CuNPs@PVA improve heat diffusion in the base liquid more efficiently than their individual counterparts.

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