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Electrospun polymer nanofibers decorated with Ag/Au nanoparticles — A smart material with enhanced nonlinearity

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ABSTRACT

Functionalization of the surface and interior of nanofibers with nanoparticles by electrospinning process is an efficient fabrication technique for a wide variety of nanoparticle embedded materials. In the present study, it was aimed to compare the third order nonlinear absorption coefficient of the Ag/Au nanoparticles incorporated nanofibers with the casted films of Casein/Polyvinyl pyrrolidone (CAN/PVP) Au/Ag nanocomposites as well as CAN/PVP blend. Linear optical studies and morphological analysis of the CAN/PVP Au/Ag nanocomposite films and nanofibers confirms the efficient distribution of nanoparticles into the matrix. Open aperture Z-scan measurements at 532 nm, 5 ns laser pulses exposed that nanofibers with Au/Ag nanoparticles exhibited higher two photon absorption coefficient than its nanocomposite solution. This augmentation is correlated with the morphology of nanofibers and electric field enhancement of Au/Ag nanoparticles into the matrix. Optical limiting performance of the prepared CAN/PVP Au/Ag nanocomposites and nanofibers offer a better result than the CAN/PVP blend due to the nonlinear absorption of the nanoparticles in resonant and nonresonant regime, thus making it suitable for various optical limiting applications.

1. Introduction

Polymer nanofibers have been of great interest for potential applications in nano/micro devices owing to their novel optoelectronic properties, high surface to volume ratio and porosity [1]. Fabrication of 1D-polymer based nanomaterials by methods such as nanolithography, electrospinning, chemical synthesis etc. have been reported [2]. Electrospinning serves to be a versatile, cost-effective technique for the production of nanofibers with high aspect ratio and controllable diameters. These nanofibers can range from nanometers to microns and they can be produced by changing the processing parameters [3]. In this technique, nanofibrous composite mats are fabricated by the application of a strong electric force to a jetting polymer solution or melt and these fibers can be used as nanocatalysts, nanoelectronic devices, sensors in biomedical and pharmaceutical fields etc. [4–6]. Nanofibers can be functionalized by incorporating dye molecules, noble metal nanoparticles, quantum dots. Functionalized polymer nanofibers are good candidates for manipulating, generating and propagating light at the nanoscale and are found to be suitable for applications such as wave guides, light sources, sensors etc. [7,8]. Natural polymers have better biocompatibility and biodegradability, whereas synthetic polymers possess good mechanical strength such as stiffness, flexibility and good optical behaviour. CAN is a water soluble protein at

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a pH of 7-8 with possessing a number of favorable characteristics such as heat resistance, hydrophobicity, and biocompatibility. PVP is also a water soluble synthetic polymer with distinctive combination of extra ordinary chemical and physical properties. Because of the complete miscibility of these two polymes blending approach is desirable to get the beneficial effects of these two materials.

Noble metal nanoparticles of gold and silver show size and shape dependent optical and electronic properties. They strongly absorb visible light and it is a result of collective oscillations of conduction electrons over the whole volume of the nanoparticles are excited in the surface of metal, commonly referred to as surface plasmon resonance (SPR). When these nanoparticles are exposed to high intense laser pulses, nonlinearexcitation happens. Usually these nanoparticles show an increase in transmission, known as saturable absorption at the plasmon resonance frequency owing to the bleaching of ground state absorption. At high intensities, switching over from saturable absorption to reverse saturable absorption, leads to a decrease in transmission in these plasmonic nanoparticles [9–11]. Studies are mostly limited to the investigation of nonlinear optical properties of these plasmonic nanoparticles dispersed in solutions or embedded in polymers, glass hosts etc. [12]. Assembling silver nanoparticles in polymer nanofiber can produce a high density of hotspots which are regions of enhanced electric field. In addition, the morphology of nanofibers can trap light thereby enhancing the lightmatter interaction. Large scale PVP nanofiber film, containing aligned gold nanorod was fabricated through electrospinning technique with anisotropically enhanced nonlinear optical properties [13]. Quiros et al. reported the fabrication of silver, copper and zinc doped PVP nanofibers by electrospinning [14].

The nonlinearity of Ag/Au nanoparticles assembled in nanofibers PVA/PVP thin films doped with Ag/Au nanoparticles were prepared for application in optical devices by enhancing the nonlinear application coefficient [15]. Nanofibers can effectively trap and scatter light depending on their aspect ratio leading to enhanced light-matter interaction. Electrospun polymer nanofibers functionalized with quantum dots, noble metal nanoparticles and dye molecules are reported to be an efficient platform to propagate and modulate light [7]. Embedding Au nanoparticles in Rhodamine 6 G molecule doped polyacrylamidenanofibers lead to enhanced fluorescence intensity [16]. Nonlinear photoluminescence is reported to be enhanced in fluorescent dye doped PMMA nanofibers [17]. Aligning metal nanoparticles in nanofibers can create large density of hot spots. The role of aligning metal nanoparticles in nanofibers in determining the effective nonlinearity of the medium is less explored as far as to our knowledge. In this work we compared the nonlinear absorption of Ag/Au nanoparticles incorporated nanofibers with the casted films of CAN/PVP Au/Ag nanocomposites as well as CAN/PVP blend with an aim to understand the effect of packing and confining metal Nanoparticles in nanofibers whose size is of the order of wavelength of light.

In this work, we fabricated nanofibers of CAN/PVP blend by electrospinning. We functionalize these nanofibers by incorporating Ag /Au Nanoparticles with an aim to make it a smart material for nonlinear application. Assembling and confining silver/gold Nanoparticles in nanofibers whose size is of the order of wavelength of light can efficiently trap and scatter leading to enhanced light-matter interaction. Thus, we also investigated the non-linear absorption of these functionalized polymer nanofibers and compared it with that of Au/Ag nanoparticles dispersed in solution.

2. Experimental

The experimental procedure has been subdivided into three parts. Preparation of CAN/PVP blends, nanofibers and its Au/Ag nanocomposites as well as Z-scan experimental technique for nonlinear optical studies.

2.1. Preparation of CAN/PVP blend and its Au/Ag nanocomposite films

Casein (CAN, $\overline{M}_w$ = 2060 g/mol), polyvinyl pyrrolidone (PVP, $\overline{M}_w$ = 360,000 g/mol) Silver nitrate ($AgNO_3$), Chlaurauric acid ($HAuCl_4$), Trisodium citrate and Sodium borohydride were purchased from sigma Aldrich (purity, ≈ 99 %). The chemicals were used without further purification and Milli Q water is used as a solvent.

The solutions of CAN and PVP were prepared by dissolving powdered chemicals to a concentration of 3 wt% in water and stirred at room temperature for 1 h. The prepared solution of CAN and PVP were mixed homogeneously at a weight ratio of 30:70 and casted into a petridish using the solution casting method for the preparation of CAN/PVP blend films. The petridish was allowed to stay in hot air oven at 40 °C for 5 h for the evaporation of solvent. Au/Ag nanoparticles were prepared by our earlier reported method [18,19]. Nanocomposites obtained by dissolving 0.15 wt% of Au/Ag nanoparticles in homogeneous blend solution of CAN/PVP followed by solvent evaporation of casted solution into the petridish.

2.2. Preparation of CAN/PVP nanofibers and composite nanofibers with Au/Ag nanoparticles

Electrospinning technique is carried out to fabricate the nanofiber and composite nanofibers of CAN/PVP blend. PVP of 15 % (w/v) is dissolved in water ethanol mixture (4:1). CAN/PVP at 30:70 weight ratio (by the appropriate weight of CAN) was taken for the preparation of nanofibers. The solution was taken in a 5 ml syringe attached to a needle tip of 0.3 mm inner diameter. A power supply of 23 kV was applied for the fiber formation. The needle tip to collector distance is 15 cm and the flow rate is maintained at 0.6 ml/h. The negative terminal of the power supply was connected to a collector which was covered by an aluminium foil. The schematic representation of electrospinning process is shown in Fig. 1. Au/Ag nanoparticles (0.15 wt %) was electrospun into nanofibers by keeping the processing parameters except the flow rate as mentioned above procedure. The flow rate was adjusted due to the increased conductivity and improved attraction towards the target (Table 1).

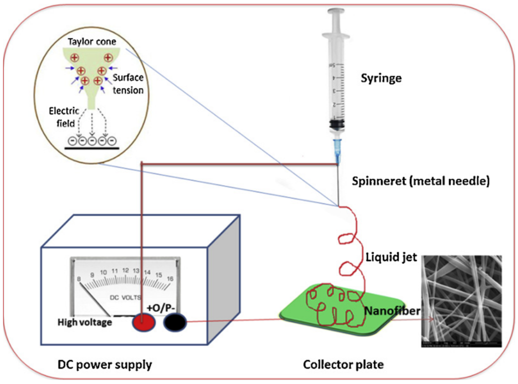

Fig. 1. Schematic representation of electrospinnig process.

Table 1
Experimental parameters used for the fabrication of nanofiber and composite nanofibers.

Sample code	Applied voltage (kV)	Flow rate
CAN/PVP	23	0.6 ml/h
CAN/PVP/Au	23	0.3 ml/h
CAN/PVP/Ag	23	0.1 ml/h

2.3. Z-scan technique

The third order nonlinear optical(NLO) properties of the prepared samples were investigated by open- aperture (OA) Z-scan technique. Laser pulses of 5 ns duration, 532 nm wavelength and 10 Hz repetition rate from a Q-switched, frequency doubled Nd: YAG laser was used for the characterization. The laser pulses were divided into two. One part was focused into the sample taken in a 1 mm thick quartz cuvette. The other part was used as the reference signal. The propagation direction of the laser beam which is optically exciting the sample is considered as z- axis. Maximum fluence will be obtained at the focal point ($z = 0$). This will symmetrically decrease towards either direction on the z-axis. The transmitted energy at the far field was measured for different sample positions using the detector (Rj7620, Lase Probe). All the samples were dispersed in water so that the linear transmission is nearly 80 %. The energy of the input laser pulses was nearly 85 μJ. An analytical method was employed to determine the effective two-photon absorption coefficient.

3. Results and discussion

3.1. Linear optical studies of polymer blends and nanocomposites

To monitor the formation of CAN/PVPAg/Au nanocomposites, UV–vis absorption spectroscopy were performed (Fig. 2). These spectra indicate that the SPR peak is observed at 414 nm in the spectrum of CAN/PVP/Ag film while the SPR phenomenon is

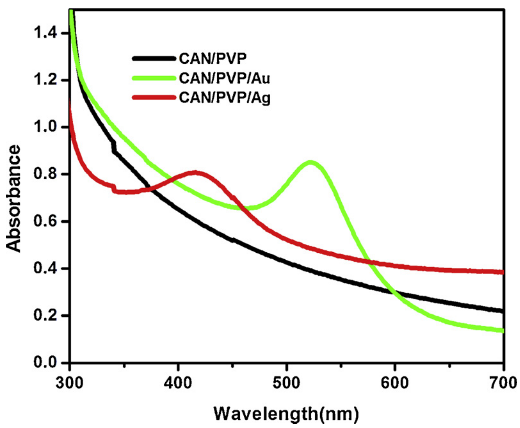

Fig. 2. UV–vis absorption spectra of CAN/PVP and its Au/Ag nanocomposite films.

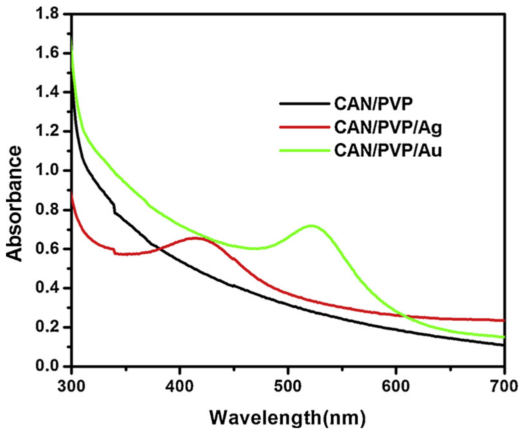

Fig. 3. UV–vis absorption spectra CAN/PVP nanofiber and its Au/Ag composite nanofibers.

indicated by the peak at 520 nm in the case of CAN/PVP/Au film. These observations establish the presence of Ag/Au nanoparticles into the polymer matrix.

UV–Visible absorption spectroscopy was performed for CAN/PVP, CAN/PVP/Ag and CAN/PVP/Au nanofibers as shown in Fig. 3. The linear absorption spectra of nanocomposite fibres showed peaks at 421 nm and 530 nm corresponding to CAN/PVP Ag and Au nanofibers respectively. These absorption bands match the characteristic SPR band of Ag and Au nanoparticles [20,21], which were absent in the nanofibers of CAN/PVP which did not contain metal nanoparticles. This established the effective incorporation of nanoparticles into the nanofiber matrix.

3.2. Morphology of nanofibers and films

SEM analysis was carried out on CAN/PVPand CAN/PVP/Ag and CAN/PVP/Au films. The SEM images of the three polymer samples taken are presented in Fig. 5. It can be seen that CAN/PVP film is non continuous and there are substantial pores as well as a few flaps at the cross section of the film, as shown in Fig. 4(a).This indicates superior air permeability through the film. SEM image of CAN/PVP/Ag nanocomposite is given in Fig. 4(b) and (c) shows the surface morphology of the CAN/PVP/Aunanocomposite. Ag nanoparticles can be seen incorporated in the CAN/PVP matrix and Au nanoparticles are present in the CAN/PVP/Au nanocomposite.

The characteristic surface morphology, alignment and diameter of the CAN/PVP and CAN/PVP/Au and CAN/PVP/Ag nanofibers were carried out using SEM analysis.

The SEM images of nanofibers and the size distribution graph of CAN/PVP, CAN/PVP/Ag and CAN/PVP/Au are shown in Fig. 5(a–c). SEM micrograph of polymer blend nanofibers (Fig. 5(a) shows continuous nanofibers without any defects. The morphology of composite nanofibers confirms the incorporation of metal nanoparticles into the polymer matrix. There is a difference in the size of composite nanofibers compared with the neat polymer. This reduction in the diameter of composite nanofibers is due to increased conductivity produced in the solution by the presence of metal nanoparticles. The surface charge of the polymer jet was increased by this electrical conductivity and thus stronger stretching forces were imposed to the jet resulting in ultrafine nanofibers. This phenomenon is similar to that of the reported nanofibers of PLA/CNC, PVP/CNC/$AgNO_3$, Ag Nanoparticles and nisin incorporated 50:50 blend of PDLLA/PEO [22–24]. There is also a distribution of metal nanoparticles onto the surface of the prepared nanofibers. The average diameters of CAN/PVP-4, CAN/PVP-4/Au and CAN/PVP-4/Ag nanofibers are 254 nm, 232 nm and 224 nm respectively.

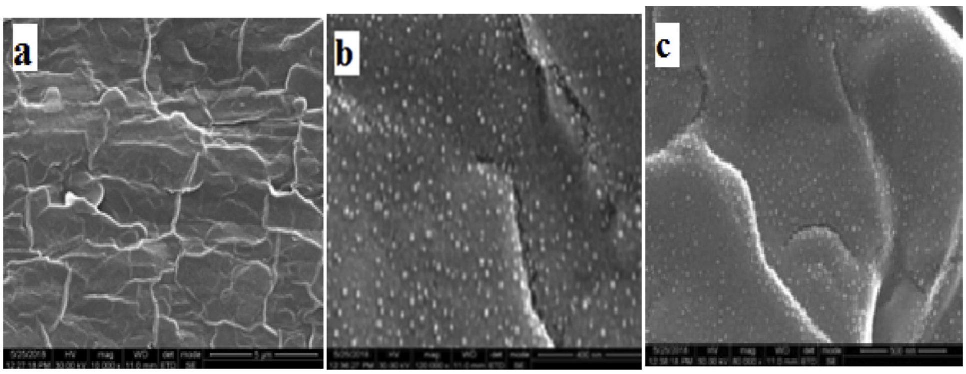

Fig. 4. SEM Micrographs of (a) CAN/PVP(10000X) (b) CAN/PVP/Ag(12000X) and (c) CAN/PVP/Au (10000X).

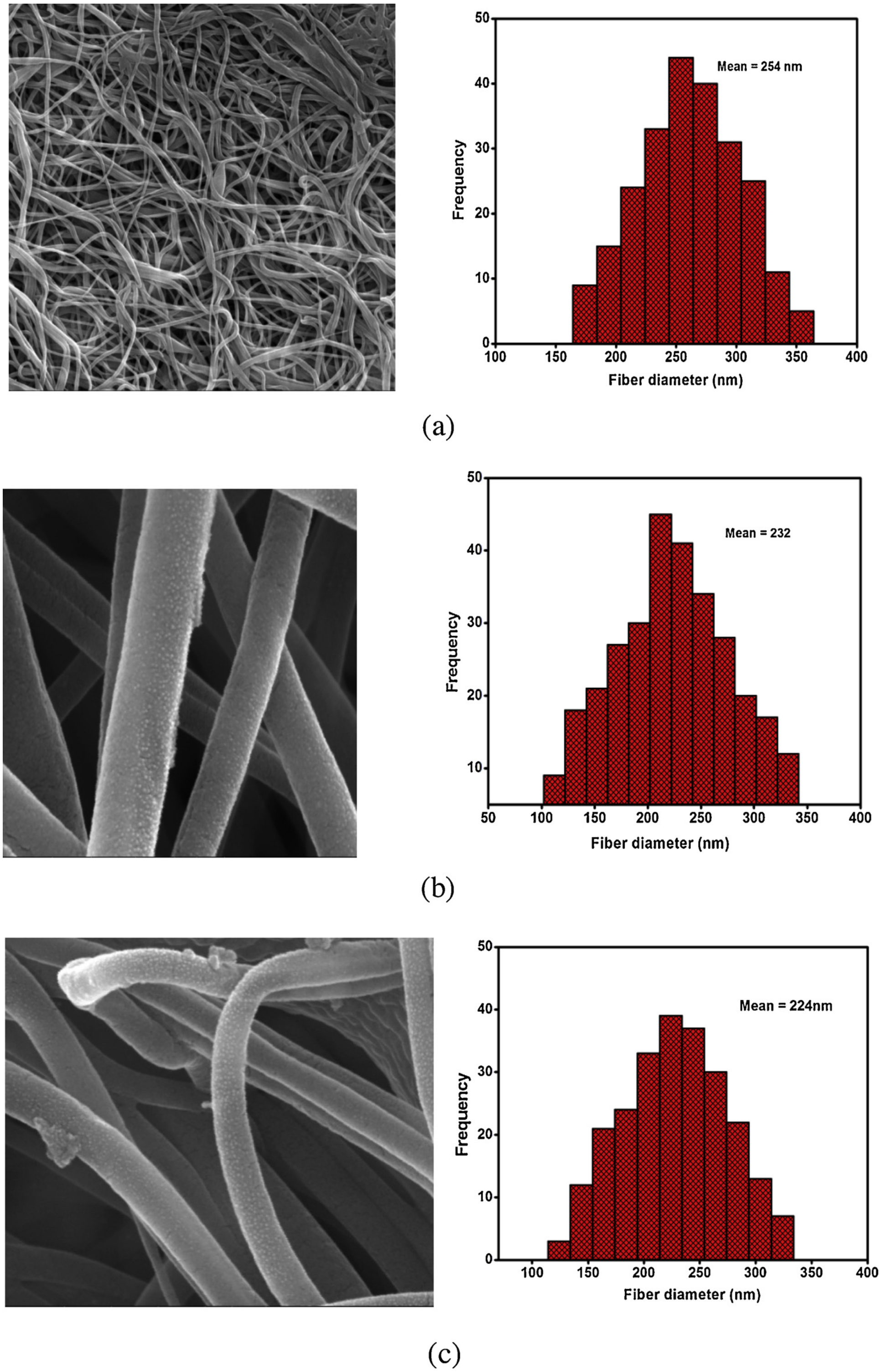

Fig. 5. SEM images and size distribution of nanofibers of (a) CAN/PVP (b) CAN/PVP/Au and (c) CAN/PVP/Ag.

3.3. TEM analysis

TEM analysis was carried out for CAN/PVP/Ag and CAN/PVP/Aunanocomposites and the images of these polymer film obtained at two different magnifications are given in Figs. 6 and 7. The TEM image is another evidence to confirm the presence of Au/Ag

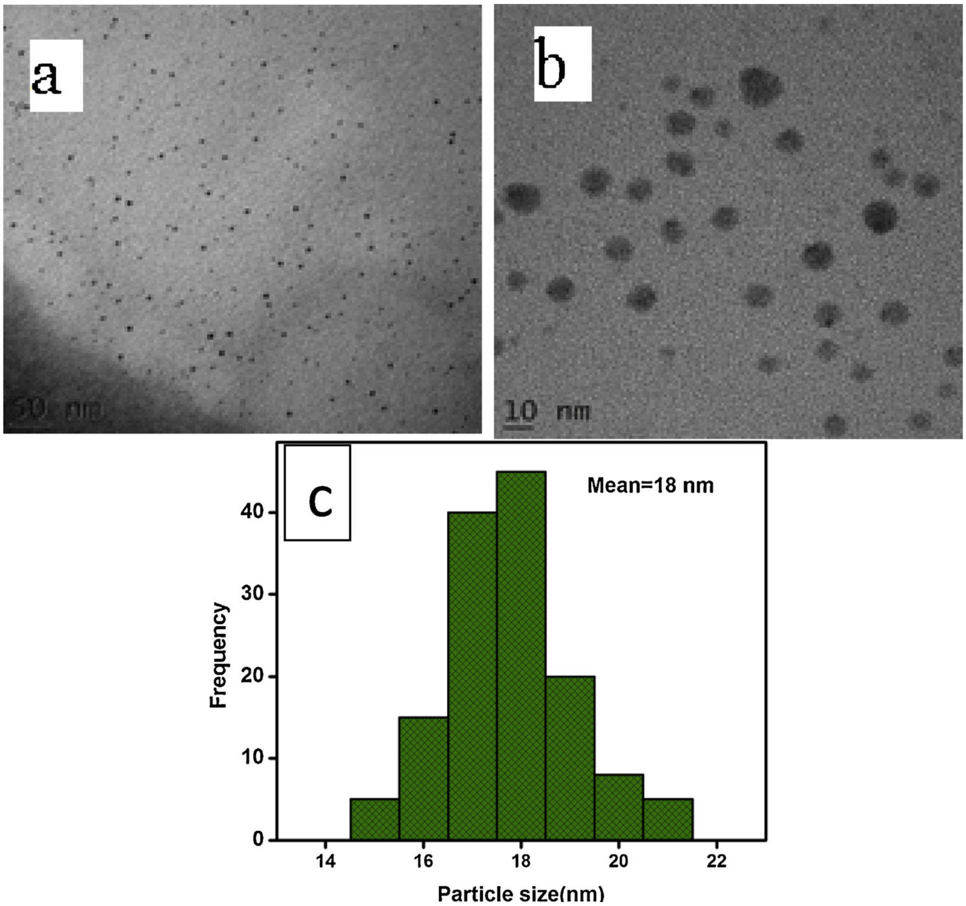

Fig. 6. TEM images of CAN/PVP/Ag at (a) lower and (b) higher magnification(c) particle size distribution graph.

nanoparticles in the CAN/PVP blend matrix. Further, the average size of Au nanoparticles in the nanocomposite is found to be 18 − 20 nm and Ag nanoparticles is found to be 7 − 9 nm

TEM analysis of CAN/PVP/Ag nanofibers (Fig. 8) were carried out and the image of the composite nanofibers confirms the presence of spherical Ag nanoparticles on the nanofibers with an average diameter of 7 nm.

3.4. Nonlinear optical properties of polymer nanocomposites

With an aim to understand the effect of assembling Ag/Au nanoparticles in polymer matrix on determining the third order nonlinearity, we performed OA Z-scan experiment.

Fig. 9 represents the OA Z-scan curves of CAN/PVP, CAN/PVP/Ag and CAN/PVP/Au. The nonlinear absorption in these nanocomposites is due to two major contributions, one is due to the saturable absorption resulting from the bleaching of the ground state absorption and the other is due to reverse saturable absorption resulting from the inter-band and intra-band excited state absorption. So, the effective nonlinear absorption coefficient is given by:

$$\alpha(I) = \frac{\alpha_0}{1 + \left(^{I}/_{I_s}\right)} + \beta I$$

where, α_0 is the linear absorption coefficient at the excitation wavelength, I is the incident laser intensity, I_s is the saturation intensity and β is the effective nonlinear absorption coefficient. By determining the best-fit for OA-Z scan curves, β can be determined.

The comparative studies of the third order optical properties of the samples were done and the 2PA values are displayed in Table 2

When the two photon coefficients of the polymer samples are compared, we found that β_{eff} values are greater for the nanocomposites with Ag/Au Nanoparticles than those for the pure blend. The assembly of Au/Ag Nanoparticles showed enhanced third order nonlinearity in CAN/PVP film. Au/Ag Nanoparticles are known to generate large local electric fields because of its inherent SPR and hence the incorporation of such metal Nanoparticles in a polymer can significantly alter the linear and nonlinear optical properties of the latter. This can be attributed to the large optical polarization associated with the nanocomposites and it showed an enhanced nonlinearity compared to the pure polymer blend. Among the nanocomposites containing the noble metal nanoparticles,

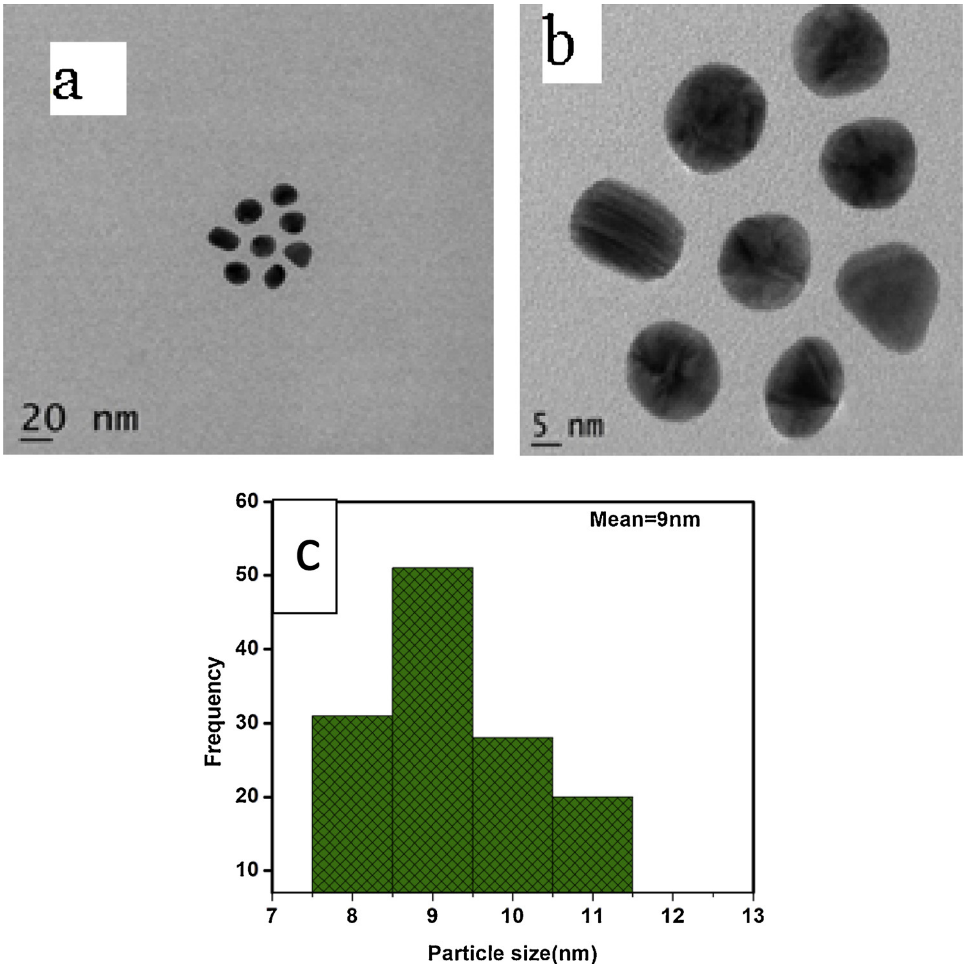

Fig. 7. TEM images of CAN/PVP/Au at (a) lower and (b) higher magnification (c) particle size distribution graph.

Ag containing nanocomposites showed enhanced nonlinear absorption compared to nanocomposites with Au nanoparticles, attributed to the higher extinction coefficient of Ag nanoparticles. It has been reported plasmon band bleaching was observed by Au decorated graphene nanocomposites and Ag and Au nanostructures [25,26]. Wang et al. reported highly efficient photon to plasman conversion (~70 %) achieved when the electromagnetic field of the confined wave guiding modes overlap with the plasmonic modes of metal Nanoparticles [27]. It has been reported that the addition of Ag nanoclusters and nanoparticles into the oxyfluoride glass host matrix showed enhanced nonlinear absorption indices at 480 nm ns laser pulses due to both nonsaturated and saturated nonlinear absorption [12].

OA Z-scan studies were carried out in the CAN/PVP, CAN/PVP/Au, CAN/PVP/Ag nanofibers. The results obtained are given in Fig. 10. These results show that nanofibers had an enhanced nonlinearity compared to the polymer matrix. This can be understood by considering the increased scattering and prolonged path lengths in nanofibers, thereby leading to efficient light matter interactions when compared to that in polymer matrices. Excitation by laser pulses can lead to plasmonic oscillations in metal nanoparticles and therefore, the composite nanofibers show an enhanced nonlinearity when compared to the nanofiber of CAN/PVP. It has been reported that the polymer nanofibers can be functionalised with quantum dots, noble metal Nanoparticles, dye molecules etc. [14,28,29]. These nanofibers serve as a platform for propagating and modulating light. Yu et al. reported 17-fold enhanced fluorescence intensity of Rhodamine 6 G molecules doped in Au- polyacrylamide nanofibers [30]. High and sensitive optoelectronic responses have been reported in Ag nanoparticles doped poly (p-phenylenevinylene) nanofibers [7]. Nonlinear photoluminescence enhancement has been reported by Chang et al. in fluorescent dye doped PMMA nanofibers [17]. Their reports indicate that the enhanced photoluminescence in nanofibers is because of the increase in the scattering of light, prolonged path lengths and multiple light absorption in PMMA nanofiber scaffolds. Light scattering is found to be highly sensitive to fiber diameter and less sensitive to aspect ratio. Our results of OA Z-scan studies show that composites nanofibers show an enhanced nonlinearity compared to the neat nanofiber. This is because of the presence of nanoparticles which can provide high density of "hot spots" in nanofibers which refers to the regions of highly enhanced local electromagnetic field. CAN/PVP/Ag shows highest value among the composite nanofibers due to the presence of Ag nanoparticles with SPR absorption band away from the excitation wavelength of the laser.

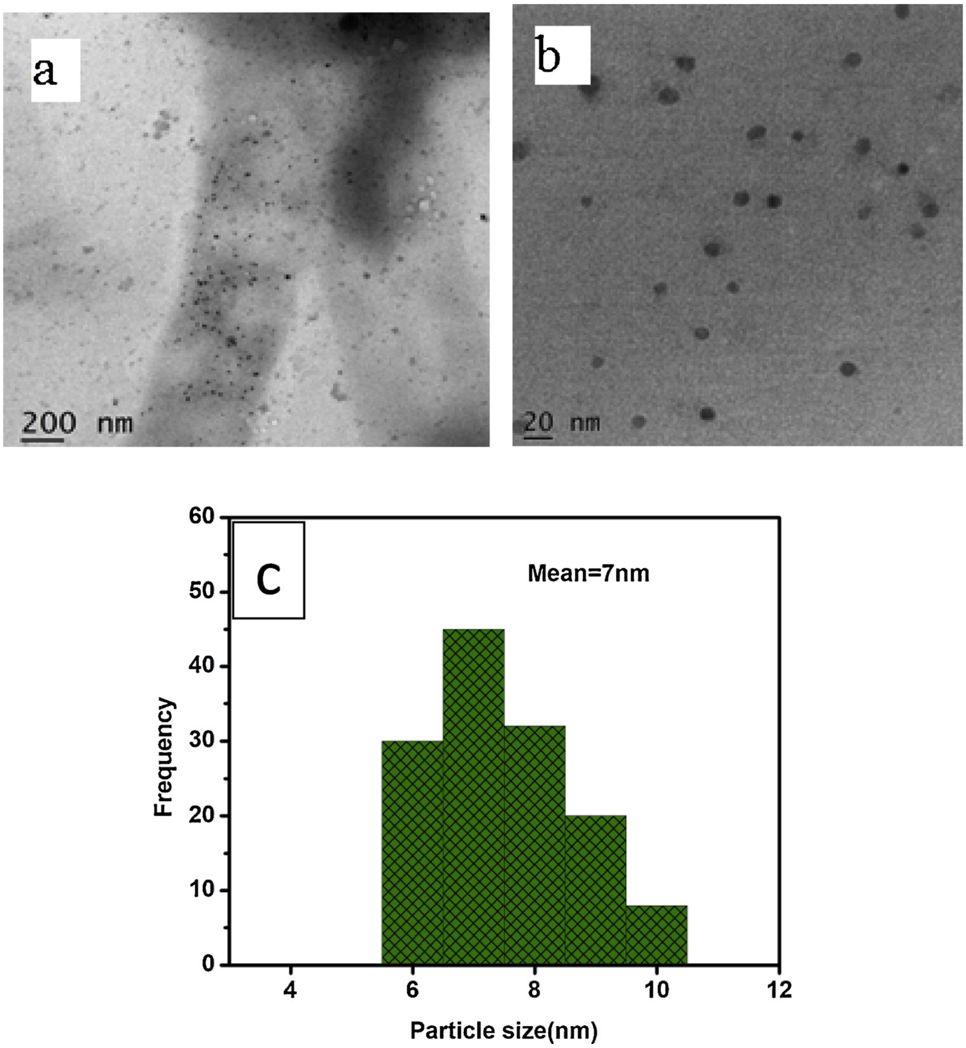

Fig. 8. (a) TEM images of CAN/PVP/Agnanofibers. (b) Magnified image of Ag nanoparticles on the nanofibers (Particle size distribution graph).

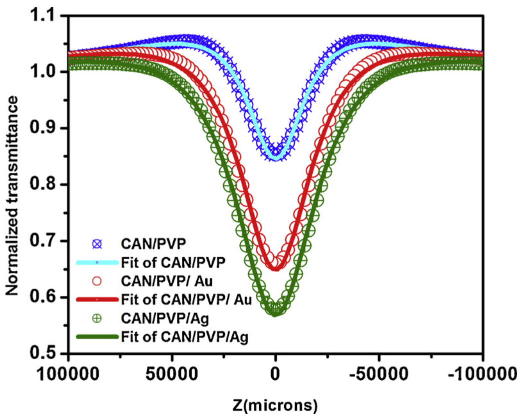

Fig. 9. OA Z-scan curves of CAN/PVP, CAN/PVP/Au and CAN/PVP/Ag films.

Optical limiters are the materials that strongly attenuate (decrease) optical beams at high intensities while exhibiting transmittance at low intensities. An optical limiter with fast response speeds, high linear transmission, stability and high optical damage has been used for the optical limiting applications in photonic or optoelectronic devices. Optical limiting properties also depend on the

Table 2
Effective two- photon absorption coefficient (β_{eff}) and optical limiting threshold calculated for CAN/PVP polymer blend, CAN/PVP/Au and CAN/PVP/Agnanocomposites.

Polymer code	β_{eff}(m/W)	Linear transmission	Limiting threshold J/m^2
CAN/PVP	11.3×10^{-11}	0.80	60
CAN/PVP/Au	27.4×10^{-11}	0.80	36
CAN/PVP-4/Ag3	38.6×10^{-11}	0.80	22

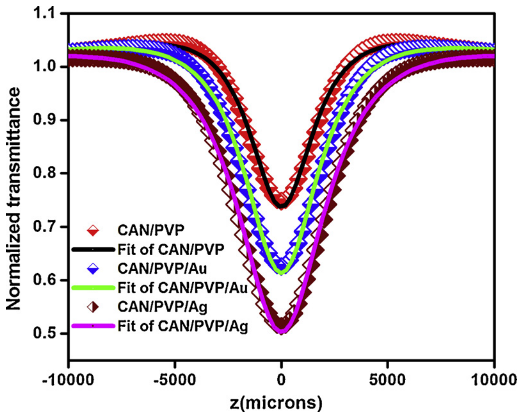

Fig. 10. OA Z-scan curves of nanofibers of CAN/PVP, CAN/PVP//Auand CAN/PVP/Ag.

reverse saturable absorption, mutiphoton absorption, excited state absorption, free carrier absorption and nonlinear scattering. It is a nonlinear phenomenon observed in the material when the input laser intensity (fluence) increases transmission of the medium decreases.The optical limiting plot of the synthesised polymer blend films CAN/PVPand its nanocomposites CAN/PVP/Au and CAN/PVP/Ag are depicted in Fig. 11

The optical limiting threshold values for the three samples are given in Table 2.It can be concluded from the data given in the above table that the optical limiting threshold was decreased significantly by the incorporation of Au/Ag nanoparticles in the CAN/PVP polymer blend. SPR absorption in the resonance and non-resonance regime are found to be the major contributor to the observed optical limiting. It is also noted that the optical limiting threshold gets lower values in Ag nanocomposites than in Au nanocomposite. The optical limiting plot of the three nanofibers of CAN/PVP and its nanocomposites CAN/PVP/Au and CAN/PVP/Ag are depicted in Fig. 12.

The comparative studies of the optical limiting threshold were done for the nanofibers and composite nanofibers and the values are listed in Table 3. It can be seen from the data that the β_{eff} and the limiting threshold values follow similar trend as observed in the polymer blend and its nanocomposites. Our results suggest that nanofiber morphology can enhance light matter interaction thereby leading to an increase in the effective nonlinear absorption coefficient and optical limiting threshold. Among all the polymer samples, Ag nanoparticles incorporated composite nanofiber film shows maximum enhancement in the values.

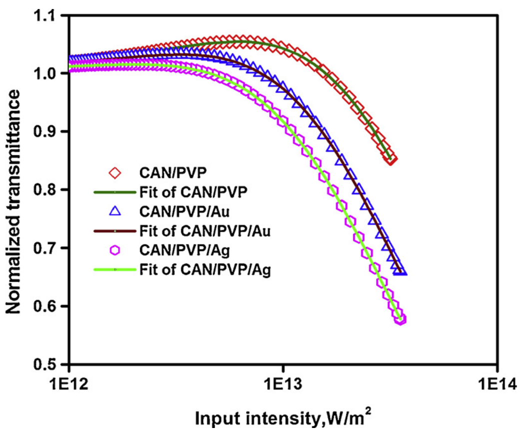

Fig. 11. Optical limiting of CAN/PVP, CAN/PVP/Au and CAN/PVP/Ag.

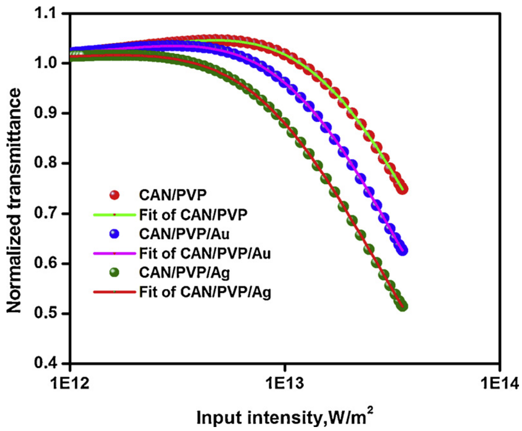

Fig. 12. Optical limiting of nanofibers of CAN/PVP, CAN/PVP/Au and CAN/PVP/Ag.

Table 3
Effective two- photon absorption coefficient (β_{eff}) and optical limiting threshold calculated for CAN/PVPnanofiber and CAN/PVP/Au, CAN/PVP/Ag composite nanofibers.

Polymer code	β_{eff}(m/W)	Linear transmission	Limiting threshold J/m^2
CAN/PVP	18.6×10^{-11}	0.80	37
CAN/PVP/Au	32×10^{-11}	0.80	23
CAN/PVP/Ag	51.7×10^{-11}	0.80	18

4. Conclusions

CAN/PVP blend Ag and Au nanocomposites and nanofibers were successfully formulated and evaluated by solution casting method and electrospinning technique. Linear absorption studies and morphological characterisation confirms the presence of nanoparticles in the prepared nanofibers. Nonlinear studies show that nanoparticles of Ag and Au functionalised nanofibers exhibits improved two-photon absorption coefficient and optical limiting properties when compared to the bare polymer and nanofibers. The overall results suggest that nonlinear optical properties were enhanced considerably by the modification of the polymer blend. Incorporation of Au and Ag nanoparticles on the polymer matrix enhances the application performance of these polymer films and nanofiber mats.

Conflicts of interest statement

The authors certify that they have NO affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.ijleo.2020.164180.

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