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Spatial Variation of Local Field by the Ag Nanoparticle on the PANI Matrix: A Non Linear Optics (NLO) Perspective

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Abstract: The Ag-PANI nanocomposite was prepared using wet chemical synthesis method. The morphological and optical characterization studies were carried out using FE-SEM and UV-Visible spectrophotometer. The FTIR band peaks confirmed the presence of the polyaniline in the Ag-PANI nanocomposites. Variation of the optical characteristics of the Ag-PANI nanocomposites was studied while adding the PVA and acetonitrile. The non linear optical behaviour of Ag-PANI nanocomposite material was studied using the Z-scan measurement technique.

Key words: Nonlinear optics, Ag-PANI nanocomposite, nanostructure, nanocomposite, thin film

INTRODUCTION

The size dependent properties of low dimensional materials enable the development of new applications and the addition of flexibility in existing systems of various fields such as catalysis, sensors, optics, optoelectronics, microelectronics and so on (Wang *et al*., 2004).

Nanoparticles possess better and enhanced physical and chemical properties compared to their corresponding bulk materials. In particular Non Linear Optics (NLO) response of nanoparticles is a significant one in comparison with it s bulk form. This is not because of size effect but due to the interface and surface structure of the materials. These effects are useful for optical devices applications. Nanocomposite materials also possess very good Non Linear Optics (NLO) response and this property enables them to be used for optical switching devices (Wang *et al*., 2004). It is having the strong nonlinear effect due to dielectric/quantum confinement effects. Silver nanoparticles have been widely used due to their excellent physical and chemical properties. It exhibits new optical properties which were observed neither in molecules nor in bulk materials. Since they support surface plasmon at specific wavelength of light, the surface plasmons are driven into resonance (Sileikaite *et al*., 2006).

Silver nanoparticles incorporation in a polymer matrix modifies the refractive index of the structure due to the unique size dependent properties of metal particles at the nanoscale. The bulk conducting materials are opaque to a large range of electromagnetic spectrum due to damping of the impinging wave by conduction electrons inside the materials. Because of their small size absorption response is generally concentrated in a narrow peak at the surface plasmon frequency. This resonance depend not only a type of metal particles but its shape, size and optical property of the surrounding medium (Deng *et al*., 2008).

Polyaniline is the conducting polymer having non linear optical property. Among the various method of fabricating the nanocomposites materials, the famous and easy method of synthesis and simultaneous polymerization size reducing method was taken to fabricate the Ag-PANI nanocomposite material. Silver polymer nanocomposite materials are used for the ultra thin colour filters (Prosycevas *et al*., 2007). The Au:Ag nanocomposite polymer films having the nonlinear optical response to nanosecond laser pulses for near and off-resonant optical excitations. Its nonlinearity depends on the laser influence and sample composition (Karthikeyan *et al*., 2006). The Ag-polyaniline composite thin films are having the nonlinear optical property but it is not suitable for all optical applications. It is used for optical pulse compression and protecting sensor from high power laser pulses (Sezer *et al*., 2009).

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MATERIALS AND METHODS

Materials required: For the preparation of Ag-PANI nanocomposite, silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), BRIJ35, ammonium peroxodisulphate ($(NH_4)_2S_2O_8$), aniline monomer were used.

Sample preparation

Synthesis of Ag nanoparticle: For synthesis of silver nanoparticle, silver nitrate ($AgNO_3$) in various concentrations (0.05, 0.10 and 0.15 M) was used as precursor. For this precursor, sodium borohydrate ($NaBH_4$) was chosen as the reducing agent in the ratio of 1:2. For controlling and stabilizing the size of the particle, surfactant BRIJ35 was added. The precursor solution and surfactant mixture was kept in constant stirring for 20 min. Then surfactant was added drop by drop to reduce silver nitrate. The color of the solution changes to yellow. This confirmed the silver nanoparticle colloidal in the solution. Figure 1 explains the procedure for synthesis of silver nanoparticle.

The nanocomposite was synthesized by taking silver nanoparticle and aniline hydrochloride solution. To polymerize the mixture of solution ammonium peroxodisulphate was used as oxidizing agent to obtain Ag-PANI matrix. The ammonium peroxodisulphate was added drop by drop for 30 min. After adding the oxidizer, the solution is kept in constant stirring for 12 h at a temperature of 2-8°C. The color of the colloidal solution changes from yellow to pink and then blue, the final Ag-PANI matrix was seen in dark green colour. This colour confirms the formation of Ag-PANI matrix colloidal solution.

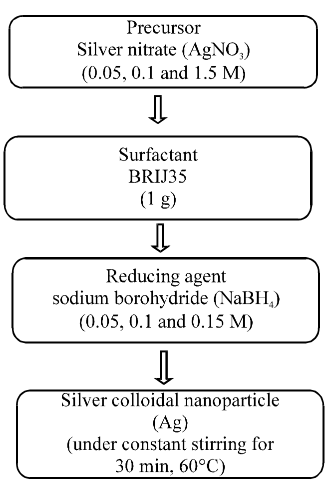

Fig. 1: Flow chart for synthesis silver nanoparticle

RESULTS AND DISCUSSION

Surface studies: The SEM micrographs of Ag-PANI nanocomposite material are shown in Fig. 2a and b. SEM images show well resolved grains with circular shaped dopant particles and particles are seen in uniform aggregate of polymer matrix. From the clouded materials it indicates the influence of strong composite morphology.

Structural characterization: The XRD pattern of Ag-PANI nanocomposite material was obtained for nanocomposites with 0.1 M of Ag and polyaniline combination is shown in Fig. 3. The obtained XRD pattern agrees with silver and polyaniline from the standard JCPDS card No. 03-0869 for polyaniline, JCPDS card No. 04-0783 for silver. The peak at 2θ values 27° corresponds to polyaniline peak and it also reveals the

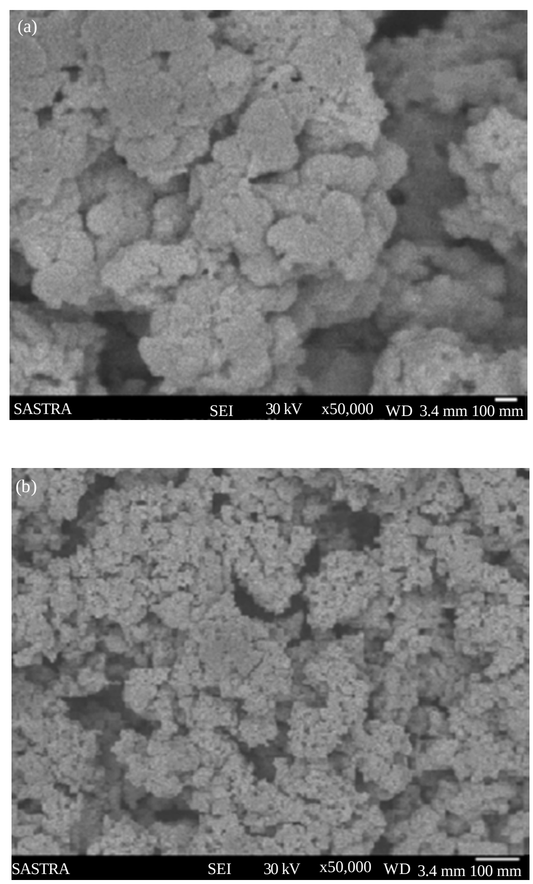

Fig. 2(a-b): SEM image for Ag-PANI nanocomposite material, (a) 100 nm and (b) 1 μm

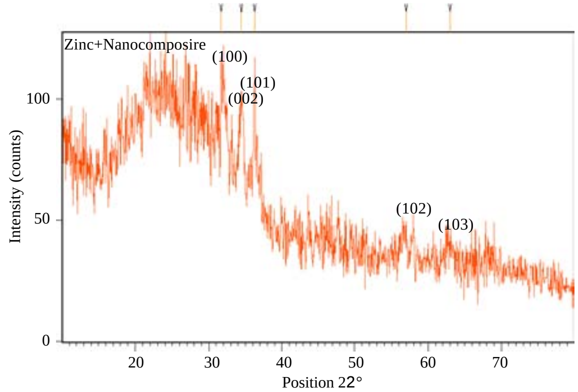

Fig. 3: XRD pattern of Ag-PANI nanocomposite material

sequential growth of polyaniline chain on the silver nanoparticles. From the corresponding JCPDS card No. 01-1164 it reveals that the obtained XRD pattern of Polyaniline-silver nanocomposite has characteristic peaks 27.89, 46.31, 67.58, 74.53 and 76.78°, representing Bragg's reflections from (111), (200), (220) and (311) planes of the face centered cubic lattice phase. The peak corresponding to 2θ value 46.31° reveal the crystalline nature of silver in planes (200), respectively.

Optical characterization: The optical characterization of Ag-PANI nanocomposite material was carried out using UV-Visible spectrophotometer and absorption and transmittance of the nanocomposite materials are shown in Fig. 4 and 5.

Ag-PANI nanocomposite material: The optical characterization of Ag-PANI nanocomposite and Ag-PANI-PVA nanocomposite material was carried out using UV-VIS spectrometer. The absorption transmittance of the film is shown in Fig. 5.

The absorbance spectrum, confirmed the presence of silver PANI nanocomposite matrix at the wavelength of 289.33 nm. The spectrum shows a shift in peaks towards blue, which confirms the size of the composites in nanorange. The single peak confirms the presence of metal silver nanoparticle. In general the UV-absorbance peak of silver nanoparticle occurs at 450-400 nm. Here, the peak appears at 289.33 nm because of nanocomposite material nm and also the absorbance band at 300 reference the (Π-Π*) transition this confirms the presence of polyaniline polymer in the material.

Figure 5a and b shows the optical characterization of silver polyaniline and PVA nanocomposite material. In the

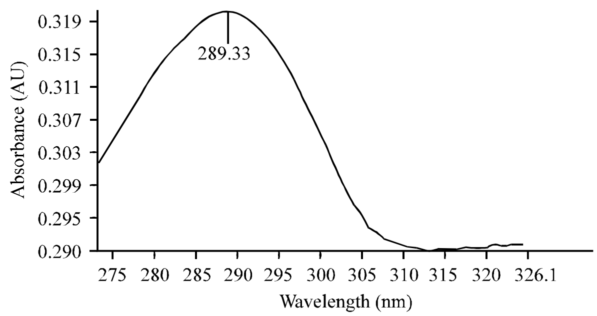

Fig. 4: UV-visible absorption spectra for Ag-PANI nanocomposite material

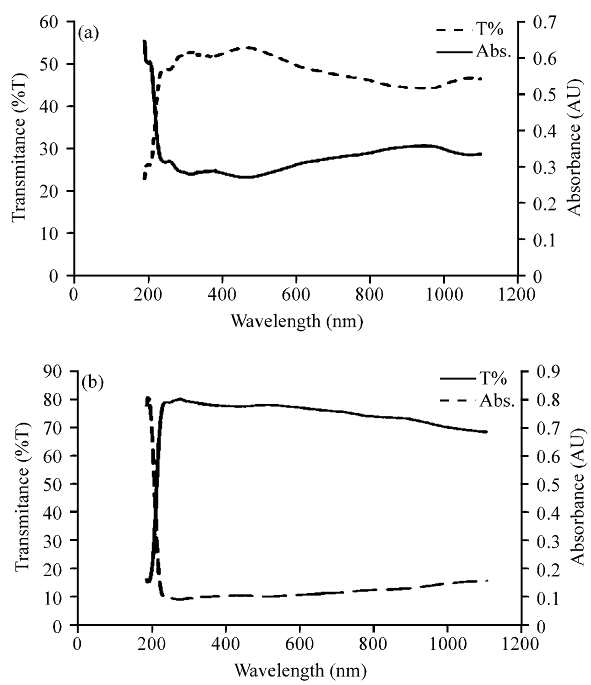

Fig. 5(a-b): Absorbance and transmittance spectra of, (a) Ag-PANI and (b) Ag-PANI-PVA nanocomposite

Ag-PANI nanocomposite material by adding PVA and acetonitrile in different concentration the changes in the optical properties varies linearly. Its behaves like transparent material as in Fig. 5b.

FTIR studies: From FTIR spectrum analysis, which in Fig. 6 describes the presence of C-N, N-H, C-H, amine functional group, conjugated bonds are confirmed. From this result formation of Ag/polyaniline nanocomposite material was confirmed. Table 1 gives the various functional and compound groups.

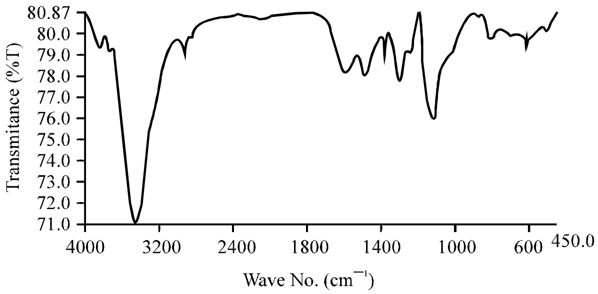

Fig. 6: FTIR spectrum of Ag-PANI nanocomposite

Figure 7 shows the structure, it has amine groups, C-N stretching with aromatic ring and Conjugated bond from property.

Z-scan technique: Figure 8 shows the non-linear absorption peak of Ag-PANI nanocomposite materials. The nonlinear absorption is observed at 532 nm. At this resonant wavelength there is no local field enhancement within the particle. In this excitation levels the data denotes characteristic saturable absorption. The Z scan instrument is an open aperture method. For inducing the non linearity in the Ag-PANI nanocomposite material the energy required is 60 μJ and at the point of 60 micro joules it gets saturated. This effect was observed due to the availability of the surface plasmon resonance in metal nanoparticle and also the Π-Π* transition PANI polymer matrix incorporated in to the silver metal particle. The Ag-PANI matrix can be used for the optical limiting and filtering applications.

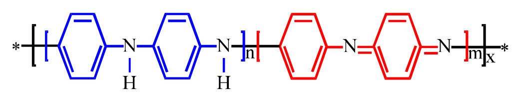

Fig. 7: Polyaniline structure

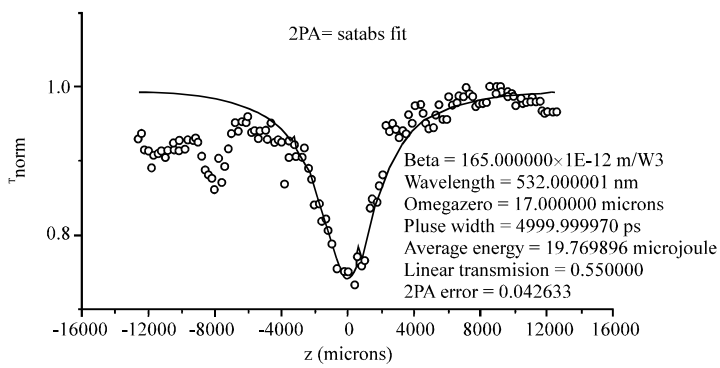

Fig. 8: Non linear absorption peak of Ag-PANI nanocomposite materials

Table 1: FTIR spectrum confirmation table

Functional groups and range	Sample characteristics range	Note	Conformation of polyaniline
C-N stretching /2200-2040 cm^{-1}	2091.88 cm^{-1}	This range refers the appearing the C-N stretching. it is attached with aromatic ring it is a strong vibration	From the polyaniline structure the C-N stretching is attached to the aromatic ring.
Amine groups/3700-3500 cm^{-1}	3447.5 cm^{-1}	The range refers the appearing a amine group in the nanocomposite material. As with amines an amide produces 0-2 N-H absorption depending on its type. (N-H (1 amine) 2 bands.	In polyaniline also two N-H groups are available…
C-C stretching/Conjugated bond/1585-1625 cm^{-1}	1591.06 cm^{-1}	This is C-C stretching. its range refers the conjugated bond also	From the polyaniline property refers that it has the conjugated bond

CONCLUSION

In summary Ag-PANI nanocomposite material was synthesized using the wet chemical method. The matrix was characterized using SEM, XRD and UV-visible spectrophotometer. For measuring the materials non linear property, the open aperture Z-scan measurement was used. The XRD analysis confirmed the presence of silver nanoparticles and polyaniline in the prepared nanocomposite. The UV-visible and FTIR studies confirmed the availability of silver and polyaniline in nanocomposite materials. The addition of silver with polyaniline polymer matrix leads to increase of linear and nonlinear optical properties. Using the Z-scan measurement the sign of nonlinearity was characterized in the nanocomposite material. The sign of nonlinearity depends on the sample composition and input laser influence. Hence, the confirmation of nonlinearity in these materials can be used to develop Ag/polyaniline matrix based optical limiting application.

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