SYNTHESIS, CHARACTERIZATION AND NONLINEAR OPTICAL PROPERTIES OF Si/PVA-PEG NANOCOMPOSITES

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Si/PVA-PEG polymer nanocomposites wereprepared by solvent casting method. XRD studies revealed the encapsulation of silicon in polymer matrix. Further crystalline behaviour of silicon in the polymer nanocomposites has been investigated. The size and morphological structure have been analysed with SEM. SEM showed the formation of homogeneous between PVA and PEG. FTIR confirmed the presence of silicon and various vibrational bonding natures. Band gap and refractive index of composites have been calculated from optical studies. Z-Scan analysis has been carried out at 532 nm which reveals optical non linearity of Si/PVA-PEG.

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1. Introduction

Nonlinear optical materials exhibit the wide range of applications such as optical limiting optical switching, phase conjugation, optical storage and all optical computing. In whichSilicon-based composites have increased huge consideration because of their wide range appropriateness such as solar energy cells, lithium-ion battery[1], luminescent display devices[2], micro and integrated semiconductors[3], agriculture etc.Further silicon nanoclusters [4] were reported for unveiling excellent optical nonlinearity caused by size quantization. Woefully silicon possesses the poor mechanical strength and poor electrical conductivity[5]. To overcome this problem with silicon, it is made composite with polymers, So that superior performance could be attained in view optical nonlinearity.

Many scientists have reported that polymer nanocomposites ofPVA and PEGhave attracted more attention due to their optical properties and theability to produce hydroxyl group which leads to optical nonlinearity[6-10]. In this article the synthesis, characteristics and third order NLO properties of silicon/PVA-PEG nanocomposites are presented. In addition, the third order NLO property has been studied with z-scan analysis at 532 nm.

2. Experimental

Initially polymer colloids were prepared from PVA and PEG. 2 grams of PVA was added in 20 ml doubled distilled water and stirred for 8 hours at 70^{o}C. Followed by 0.4 ml of PEG was added with homogeneous mixture and the solution were maintained at sustained stirring for 1 hour. Further the purchased silicon nanoparticle with average size of 20 nm has been added to the homogeneous mixture. Ultrasonication was carried out on the polymer nanocomposites for 40 mins to disperse the silicon nanoparticles in polymer and to increase the tensile strength of

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Si/PVA-PEG nanocomposites[11-12]. The film of polymer nanocomposites was prepared by pouring the sonicated colloids into petri-dish and kept at room temperature for one week. Later the thick film of Si/PVA-PEG nanocomposites was peeled out for further characterization.

3. Results and discussion

3.1. XRD analysis

XRD analysis of the powder sample and film has been taken using BRUCKER ECO D8 ADVANCE diffractometer with Cu$K\alpha$1 radiation of 1.54059 Å .The XRD analysis of pure Si nanoparticles and Si/PVA-PEG polymer nanocomposites is shown in Fig(1). The peaks corresponding to the pure Si was observed at 28.28, 47.30, 55.15, 68.98 and 76.49 which is well agreed with standard profile (JCPDS No. 27-1402) possessing resemblance with the crystal planes of (1 1 1), (2 2 0), (3 1 1), (4 0 0) and (3 3 1) having cubic crystalline structure. The same peaks have also been noticed in Si/PVA-PEG nanocomposites with less intensity implying that the crystalline nature of Si is not affected in Si/PVA-PEG nanocomposies. The observation of less intensity in Si peaks at Si/PVA-PEG nanocomposites reveals the entire encapsulation of Si by polymer matrix [13]. The characteristic peak observed at 19.42 and 20.52 corresponding to the PVA [14] and Peak at 23.40 corresponding to the PEG [15].

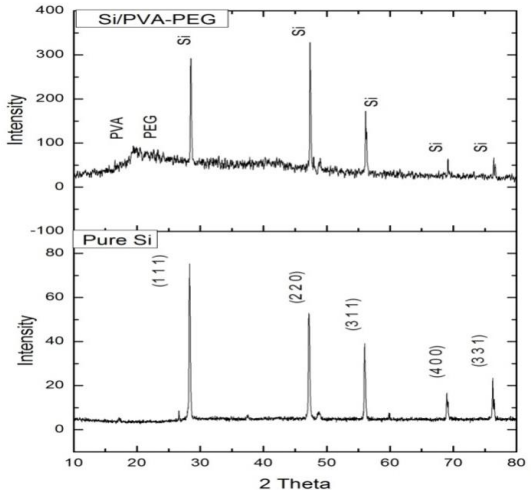


Fig.1.XRD pattern of (a) Pure Si (b) Si/PVA-PEG.

3.2. Vibrational Studies

FTIR spectrum of the Si/PEG-PVA polymer nanocomposites has been carried out with Spectrum TWO PERKIN ELMER apparatus ranging from 4000 cm^{-1} to 400 cm^{-1}. An FTIR peak of Si/PVA-PEG nanocompsites is shown in the Fig (2) to examine the reaction between Si and PVA-PEG polymer matrix. In FTIR spectra, the peaks at 3400 cm^{-1} and 1645 cm^{-1} were concomitant with -OH stretching and -OH bending vibrations respectively. The peaks at 1405 cm^{-1} and 1348 cm^{-1} were attributed to the $-CH_2$ stretching and C-C- stretching vibrations respectively. [16] Besides peaks around 1098 cm^{-1}, 895 cm^{-1} and 468 cm^{-1} were caused, respectively, by Si-O-Si asymmetrical stretching, Si-O-Si symmetrical stretching and bending vibrations. The stretching vibration corresponds to the C-C-O bonds of PEG was observed at 842 cm^{-1} [17-20]. The peak which were observed at 1249 indicating the presence of Si-C vibration [21].

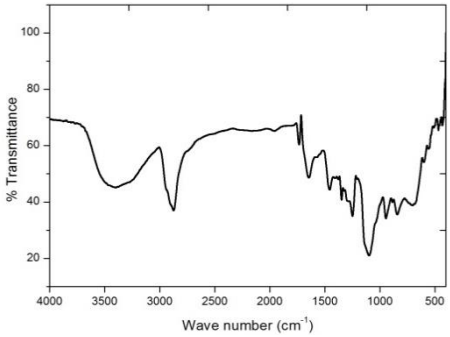
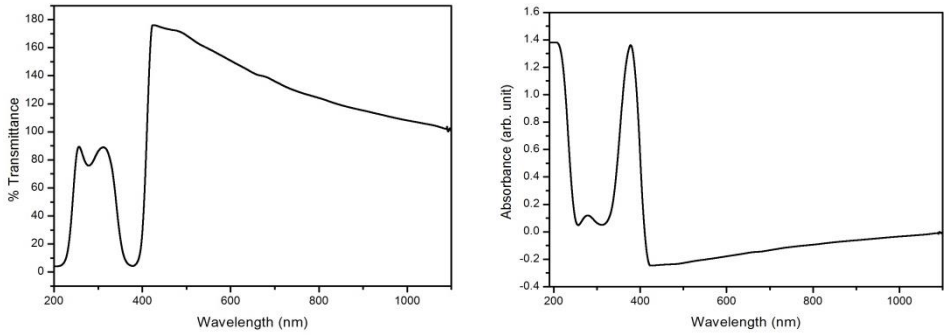


Fig.2.FTIR spectrum of Si/PVA-PEG.

3.3. Optical Studies

Optical studies of the prepared were recorded with Lambda PERKIN ELMER ranging from 190 nm to 1100 nm. Fig (3) shows the transmittance, absorbance and Tauc plot of Si/PVA-PEG nanocomposites observed with the help of UV-Vis spectroscopy. From Fig. 4a it is observed that the title compound possesses the maximum transparency in the visible and infra-red region. The Tauc plot was drawn between $(\alpha h\vartheta)^{1/2}$ versus photon energy $(\hbar\vartheta)$ and the corresponding optical band gap are shown in Figure 3.c. The optical band gap value of title compound has been noted as 2.97 eV and the value is a bit higher than the reported value of silicon nanoparticles which varied between 1.23 eV to 1.3 eV[22]. Due to the poor concentration of silicon in nanocomposites and amorphous nature of polymer caused increase in optical band gap of the Si/PVA-PEG nanocomposites. In addition, carrier interaction in valence band and conduction band was decreased due to the high concentration of PVA-PEG compared to silicon in composites which causes increase in optical band gap.



a) *b)*

Fig.3. (a) Optical transmission and (b) absorption spectrum of Si/PVA-PEG.

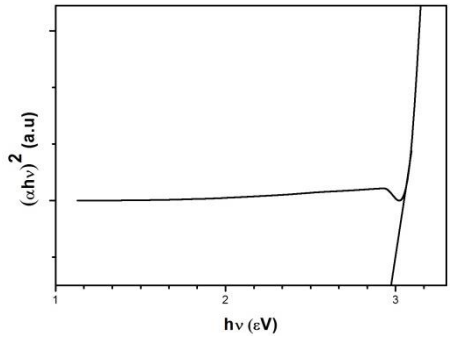


Fig.4. Plot between hνvs. $(\alpha h\upsilon)^{2}$.

3.4. SEM Analysis

SEM analysis was studied with the help of EVO-18 CAREL ZEISS instrument. The Fig (4) showed the morphological studies of Si/PVA-PEG nanocomposites by FE-SEM. As shown in the Fig (5a, b), functionalized polymer nanocomposites had irregular and huge size particles with average particle size 98 nm. From this figure (4) it was observed that Si nanoparticles are fully surrounded by PVA and PEG. In addition, there is no separation of phase identified between PVA and PEG indicating the formation of homogeneous polymer phase. At the interface, Si nanoparticle aggregates homogeneously, and the PVA-PEG and Silicon integrate well due to the infiltration of the polymer at 70°C.

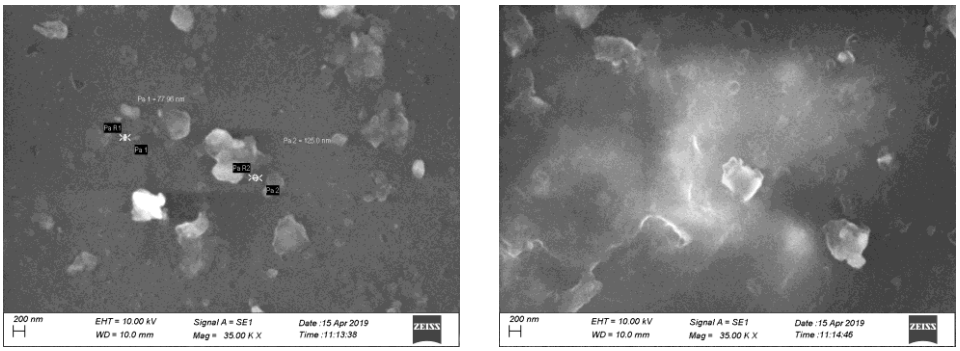


Fig.5. SEM picture of Si/PVA-PEG.

3.5. Third Harmonic Generation

Z-scan data has been taken with semiconductor continuous wave laser of wavelength and power output of 532 nm and 100mW respectively and the convex lens of focal length f = 103 mm. Incident beam with the intensity of I_0 = 3.47 kW/cm^2 made to fall on the sample and photo detector was used to analyse the transmitted beam. The light powers, transmitted over the example, were estimated as a component of sample position in the z-axis concerning the central plane either through a closed aperture or open aperture so as to determine the nonlinear refraction and absorption coefficients.

Third-order nonlinear refractive index (n_2), absorption coefficient (β), real and imaginary of third order optical susceptibility (χ^3) of the Si/PVA-PEG nanocomposites has been determined. Z-scan transmittance curve of title sample in closed aperture and open aperture has been shown in Fig. 6.The nonlinear absorption coefficient β was computed from the mathematical relationship $\beta = 2\sqrt{2\Delta T}/I_0 L_{eff}$ where, ΔT indicates the normalized transmittance value of the sample at position Z.The aperture linear transmittance was enumerated using the following formula $S = 1 - \exp\left(-2r_a^2/w_a^2\right)$where r_a and ω_a represent radius of the aperture and radius of the laser spot.The third order nonlinear refractive index (n_2) was calculated from $n_2 = \Delta\phi_0/KL_{eff}I_0$ here, $\Delta\emptyset_o$ is the on-axis phase shift, k=2π/λ, L_{eff} is effective thickness and I_0 is the intensity of the incident beam at Z = 0Effective thickness of the sample was calculated from $L_{eff} = -1 - e^{-\alpha L}/\alpha$ here α is the linear absorption coefficient and it was calculated using the following expression $\alpha = 2.303\log(1/T)/t$. ΔT_{P-V} is a peak valley normalized transmittance and it is a measurable quantity for the sample from the closed aperture Z-scan data. Positive value of ΔT_{P-V} indicates two photon absorption takes place in the sample. The variation of this term as a function of on-phase-shift |Δϕ0| and is given as $\Delta T_{P-V} = 0406(1-S)^{0.25}\left|\Delta\Phi_0\right|$. The nonlinear refractive index value has been calculated by using the relation $n_2 = \Delta\Phi_0\lambda/2\pi L_{eff}I_0$. The obtained positive value of n_2 = 5.56×10^{-10} (cm^2/W) represents the spatial soliton wave propagates with the uniform transverse

dimension because of an ideal harmony among diffraction and the self focusing which establishes the prepared nanocomposites suitable for optical switching devices. Real, Imaginary and absolute value of third order susceptibility values have been calculated by the substitution of n_2 and β and it is given as 2.5×10^{-08}esu.

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

$$\mathrm{Im}\,\chi^{(3)}(esu) = \frac{10^{-2}\varepsilon_0 C^2 n_0^2 \lambda\beta}{4\pi}(cm/W)$$

$$\left|\chi^{(3)}\right| = \left[\left(\mathrm{Re}(\chi^{(3)}\right)^2 + \left(\mathrm{Im}(\chi^{(3)}\right)^2\right]^{0.5}$$

Calculated values are tabulated in Table.1 Optical nonlinearity of the prepared nanocomposites originates due to the synergistic effect of charge transfer between PVA-PEG and silicon. The $\chi^{(3)}$ of the prepared the composite is comparable with porous silicon[4,23] and non linear response reveals the suitability of the Si/PVA-PEG composites for photonic applications[24].

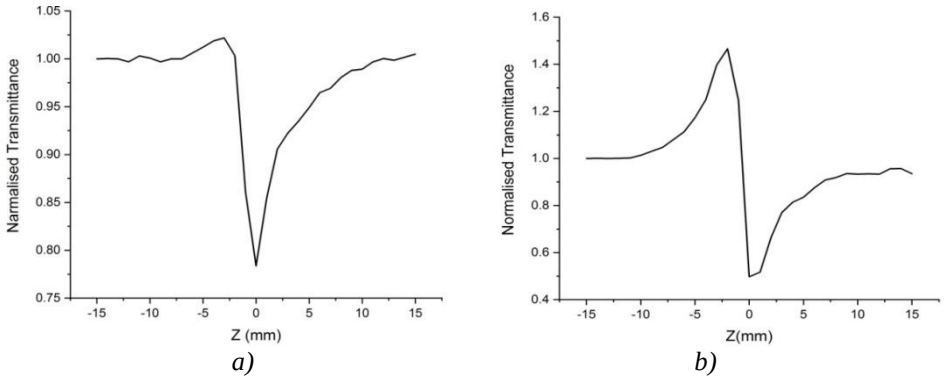


Fig.6. (a) Open aperture and (b) closed aperture Z-scan data of Si/PVA-PEG.

Table1. Z-scan measurement calculated values.

Parameters	**Value**
Laser beam wavelength	532 nm
Lens focal length	25 cm
Beam radius of the aperture	23 μm
Sample thickness	0.21 mm
Effective thickness (L_{eff})	$2.09\text{x}10^{-4}$
Linear Absorption co-efficient (α)	10
Non linear Absorption coefficient (β) cm/W	3.81×10^{-05}(cm/W)
Non linear refractive index (n_2) cm^2/W	5.56×10^{-10}
Real part of the third - order susceptibility Re ($\chi^{(3)}$) esu	1.8492×10^{-8}
Imaginary part of the third-order susceptibility Im ($\chi^{(3)}$) esu	1.6853×10^{-8}
Third order optical nonlinear susceptibility (($\chi^{(3)}$) esu	2.5×10^{-8}

4. Conclusions

The polymer composite of Si/PEG-PVA was successfully prepared by solvent casting method and thick film was obtained for characterization. The presence of cubic crystalline structure of silicon in polymer matrix was identified from XRD analysis. SEM analysis revealed agglomeration of particles with average size was found to be 98 nm. FTIR revealed the formation of hydroxyl bond with silicon which leads to the existence of optical nonlinearity in composite material. The optical study was carried out which reported large band gap value 2.97 eVdue to the reduction of carrier interaction between valence band and conduction band in silicon. Finally large value of third order non linear susceptibility was estimated which makes the title compound apt for photonic applications such optical switching and optical limiting devices.

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