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Evaluation of third order nonlinear optical properties of SiO_2/PVA-PEG Nanocomposites by Z-Scan Method

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SiO_2 nanoparticles was synthesized by sol-gel method and polymer nanocomposites by solvo-casting method. XRD and SEM analysis have revealed the size, morphological structure and formation of SiO_2/PVA-PEG polymer nanocomposites. The presence of hydrogen bond between SiO_2 and PVA-PEG was proved with the help of Fourier Transform Infra Red Spectroscopy (FTIR). Further UV-Vis studies were used to find the optical band gap and linear refractive index. Third order nonlinear optical properties such as two photon absorption, nonlinear refractive index and third order nonlinear susceptibility was evaluated for the title compound using Z-scan method. The estimated nonlinear optical properties of title compound proved the appropriateness of the sample for optical applications.

Keywords: Polymer Nanocomposites, XRD, Optical Studies, NLO

1 Introduction

Polymer materials are essential component in electronics, automotive, packaging, medical devices due to its flexibility, excellent mechanical properties and exhibit the good electrical conduction through charge transport[1-3]. Currently, composites of organic and inorganic molecules has been investigated and played prominent role in many applications and the hybrids of nanosized particles with standard matrix has manifested intense improvement in mechanical strength, optical, thermal stability, toughness and electrical properties[4-5]. As of late, the nanocomposites of silica with polymer grid is utilized to upgrade the optical and mechanical properties which has shown various applications, for example, non linear optical materials, reactant movement, sensors and subtilisin immobilization[6-12]. Addition of nanoparticles in to the polymer matrix exhibits effective roles in enhancing NLO properties. It is reported that the incorporation of semiconductor nanomaterials in polymer matrix can enhance the optical properties of polymer composite materials. In particular, the PVA/SiO_2 and PEG/SiO_2 nanocomposites have unveiled properties such as good thermal stability, biocompatibility, magnetic properties, optical properties, good electrochemical properties *etc.*[13-16]. Focus of this study was to synthesize membrane for third harmonic generation. To do this, PVA-PEG/SiO_2nanocomposites has been synthesized and its third harmonic generation has been analyzed using Z-scan analysis.

2 Experiment

Preparation of SiO_2 nanoparticles

SiO_2 nanoparticles were prepared from tetraethyl orthosilicate (TEOS) as a precursor and acetic acid. TEOS dissolved in double distilled water was added to acetic acid and stirred for 4 hr. Centrifugation has been carried out to the resultant sol and washed with ethanol in order to remove residue formed on the surface of SiO_2 NPs. Further it was calcinated at 600 °C for 2 hr to obtain SiO_2 nanoparticles.

Preparation of nanocomposites

Initially 2g of PVA was added to the 20 ml double distilled water maintained at 60 °C and stirred up to 6 h. Then 2 mol of PEG was added to the colloidal solution and further it was stirred for 1 hr. Now 0.3 g of SiO_2 was mixed with PVA/PEG solution and it was sonicated for 2 hr to minimize agglomeration of SiO_2 nanoparticles. Finally title compound was poured on petridish, dried in air and allowed to spread with equal density in all over the surface of petridish. It was allowed to dry in an open air. After one week, the resulting thick film of SiO_2-PVA-PEG nano-composites has been peel off from the petridish. Based on the trial and error method, it is confirmed that the 0.3 g of SiO_2 added PVA/PEG solution yielded good films.

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3 Results and Discussions

X-Ray Diffraction Analysis

X-ray diffraction analysis of the silica powder sample and SiO_2/PVA-PEG film was studied using BRUCKER ECO D8 ADVANCE diffract meter with Cu$K\alpha$1 radiation of 1.54059 Å. XRD Peaks of pure SiO_2 and SiO_2/PVA-PEG are shown in the Figs 1(a-b) The observed diffraction peaks at 20.7, 26.43, 30.89, 35.12, 39.16, 40.85, 42.34, 49.97, 54.01, 57.41, 60.38, 67.79 & 75.02 are well agreed with standard pattern of SiO_2, having similarity to the crystal planes of (100), (101), (220), (110), (102), (111), (200), (003), (202), (210), (211) & (203) (JCPDS card no. 46-1405). From this observation it is confirmed that pure SiO_2 nanoparticles possessed trigonal structure. By using Debye-Scherrer's formula the crystallite size has been calculated. The crystallite size of SiO_2 synthesized by sol-gel method is measured as 20 nm But, a few obvious modifications has been observed on the diffraction peaks of these SiO_2/ PVA-PEG at low bragg angles, with the look of a extensive height among 10° and 30° (Fig. 1.(b)) after polymerization. The presence of hydroxyl group in the PVA reacted with SiO_2 and PEG, therefore, affects the crystallinity of polymer nanocomposites[17]. This broad diffraction peak has shown the amorphous nature of polymer which confirms the formation of SiO_2/PVA-PEG nanocomposites by the simple chemical solution method. The peaks at 26.78° and 49.75°confirmed the presence of SiO_2 nanoparticles in the polymer matrix with low intensity showing the size reduction happened in SiO_2 nanoparticles.

SEM analysis

Morphological structure was studied using Field Emission Scanning Electron Microscope- EVO-18 CAREL ZEISS instrument. Figure 2, showed the morphology of SiO_2/PVA-PEG nanocomposites by FE-SEM. Surface morphology was analysed with SEM which is shown in Fig. 2. It was observed that white particles were randomly spread over the surface of SiO_2/PVA-PEG nanocomposites. Due to the high surface energy of SiO_2 fillers, non-uniform dispersion occurs in the prepared matrix[18-19]. SiO_2 aggregates were formed in PVA-PEG polymer matrix with the size of 85 nm. This aggregation arises due to the hydrophilic nature of SiO_2 which in turn creates disturbance on the dispersion of SiO_2 NPs over the

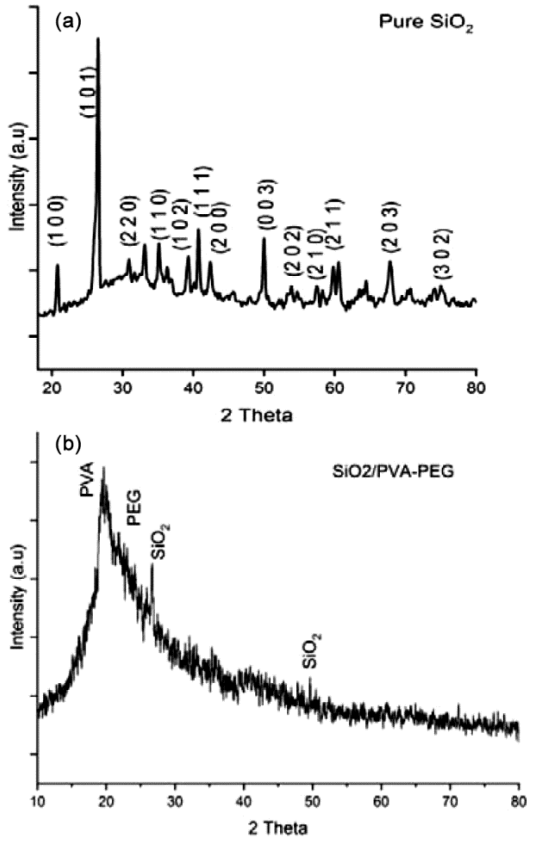

Fig. 1 — XRD pattern of (a) Pure SiO_2 (b) SiO_2/PVA-PEG

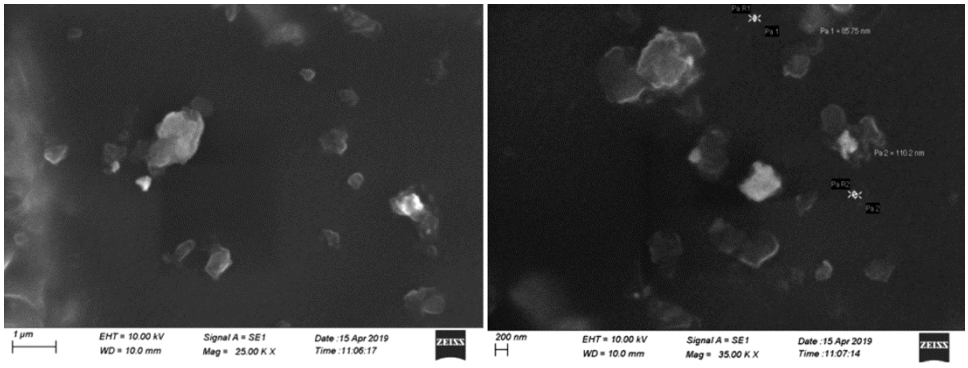

Fig. 2 — SEM picture of Si/PVA-PEG

polymer matrix[7]. It reveals that the SiO_2 nanoparticles are non-uniformly dispersed and exhibits strong interaction with PVA-PEG via hydroxyl group present in the polymer matrix.

Vibrational analysis

Vibrational studies of SiO_2/PEG-PVA polymer nanocomposites was analysed using Spectrum TWO PERKIN ELMER spectrophotometer. FTIR spectrum of pure SiO_2 and SiO_2/PVA-PEG are shown in the Fig. 3. Forpure SiO_2 nanoparticles, the weak IR bands at 794 cm^{-1} is concomitant with Si−O stretching vibration. Similarly Si−O−Si out of plane bending vibration and Si−O−Si stretching vibrations are identified at 459 cm^{-1} with low frequency and 555 $cm^{-1}$with moderate frequency respectively. Si−C stretching vibration is observed at 2322-2355 cm^{-1} [20]. Si−OH stretching vibrations is spotted at 910 cm^{-1}due to the nature of SiO_2.

In IR spectra of SiO_2/PVA-PEG nanocomposites, IR peaks corresponding to the SiO_2 are observed only at limited range like 945, 555 & 459 cm^{-1}. The shift in the IR peak is observed at 945 cm^{-1} from 1090 cm^{-1} due to the emergence of strong hydrogen bonding between SiO_2 and polymer matrix[21]. The strong and broad band observed at 1093 cm^{-1} is attributed to the C−O stretching vibration of PVA-PEG[22]. In general the OH stretching vibrations of absorbed water is ascribed in the range of 3200-3400 cm^{-1} with strong intensity. The bands at 2874 cm^{-1} and 1454 cm^{-1} with moderate intensity are attributed to the -CH symmetric stretching and bending vibrations of PEG respectively. The weak bands observed at 842-886 cm^{-1} and 1348 cm^{-1} corresponds to the CH_2 rocking and CH_2 wagging mode[23-26].

UV-Vis Studies

The transmission spectrum of the thin films was obtained using Lambda 35, PERKIN ELMER Spectrophotometer version measuring in the spectral range from 200 nm-1100 nm. The transmittance spectrum of SiO2/PVA-PEG nanocomposites is shown in the Figs. 4(a-b). The spectral results clearly indicate that the polymer nanocomposites have poor transparency in ultraviolet and visible region due to the scattering loss caused by SiO_2 with large diameter. It leads to poor transparency in the polymer matrix[15].

The optical band gap value of polymer matrix was calculated using Tauc's[27] relation given as follows.

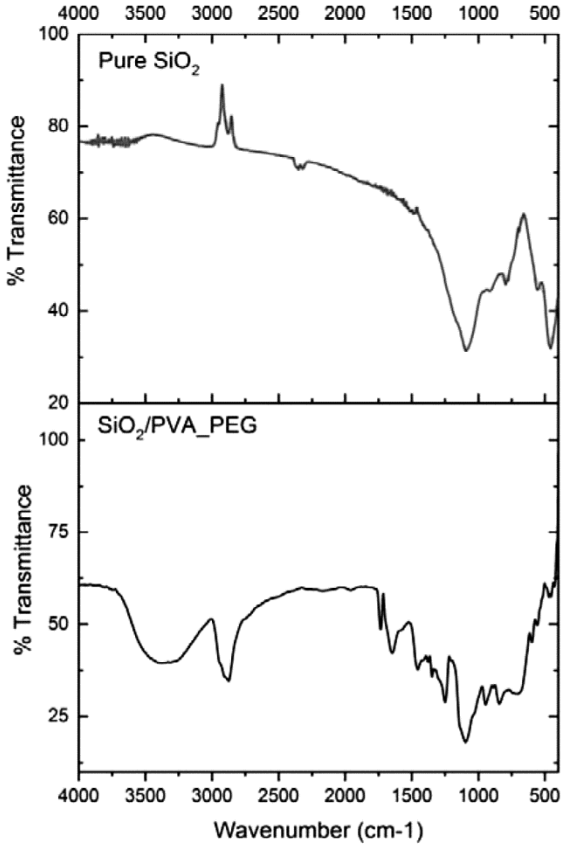

Fig. 3 — FTIR spectrum of SiO_2/PVA-PEG

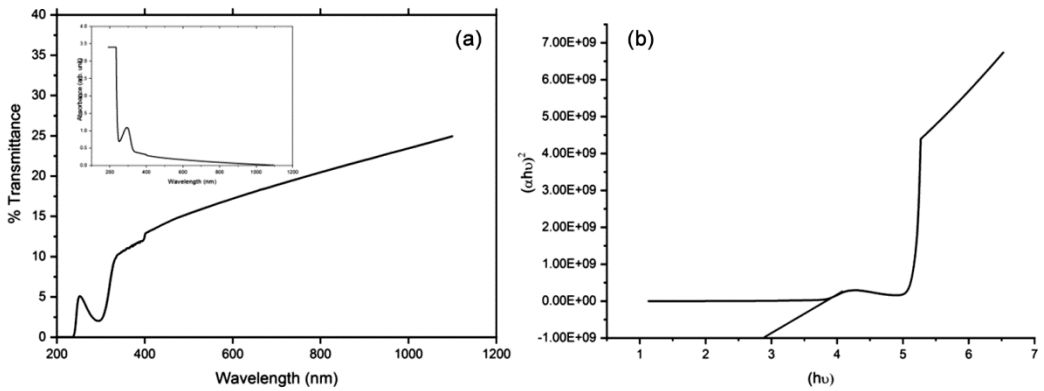

Fig. 4 — (a) Optical transmission and absorption spectrum of SiO_2/PVA-PEG and (b) Plot between hυ vs. $(\alpha h\upsilon)^2$.

$$(\alpha h\upsilon)^2 = A(h\upsilon - E_g)$$

A plot between $(\alpha h\upsilon)^2$ and $h\upsilon$ is drawn which is shown in Fig. 4b. It is reported that the band gap value of pure SiO_2 is 3.5 eV. The band gap value was reduced to 2.88eV for SiO2/PVA-PEG polymer nanocomposites as shown in the Fig. 4b. It was attributed to the formation of localized defects in polymer matrix[28]. The reduction in band gap is observed due to the presence of disorderliness in the polymer nanocomposites.

Z Scan analysis

Figure 5 (a-b) show the z scan of open aperture and closed aperture curve of SiO_2/PVA-PEG nanocomposites irradiated with semiconductor-continuous wave laser of wavelength 532 nm and focal length 103 mm. The open aperture represents the normalised transmittance valley, displaying the presence of incited assimilation in the polymer nanocomposites. Intensity of incident beam 3.47 kW/cm^2 was applied to the composites and output was traced with photo detector. The presence of nonlinearity was observed from nonlinear absorption coefficient $\beta = 2\sqrt{2}\Delta T / I_0 L_{eff}$, Here L_{eff} is a effective thickness and it was calculated from linear absorption coefficient, $L_{eff} = (1 + e^{-\alpha L})/\alpha$. Linear absorption coefficient was calculated by using the relation $\alpha = 2.303 \log\left(\frac{1}{T}\right)/t$.

The value of distance between normalised peak and normalised valley was estimated from the relation $\Delta T_{P-V} = 0406(1-S)^{0.25}\left|\Delta\Phi_0\right|$ which was substituted to the equation of nonlinear absorption coefficient. In which $\beta>0$ indicates the two photon absorption effect of the material and the value was calculated in the order of $10x^{-5}$ cm/W[29].

The phase shift happens by optical wave travelling a separation L in the sample estimated with following relation

$$\Delta\phi_0 = \frac{2\pi}{\lambda} n_2 L_{eff} I_0$$

Where n_2 is a non linear refractive index which was found to be 9.92×10^{-10} cm^2/W and the positive indicates the self focusing effect in the prepared polymer nanocomposites.

Imaginary part of third order susceptibility was contingent on two photo absorption process only which means that it depends on non linear absorption and it was calculated using the relation, $\mathrm{Im}\,\chi^{(3)}(esu) = \frac{10^{-2}\varepsilon_0 C^2 n_0^2 \lambda\beta}{4\pi}(cm/W)$ and found to be 3.79×10^{-08}esu.

The real part of of third order susceptibility has been attributed to the nonlinear refractive index and it was computed using the relation $\mathrm{Re}\,\chi^{(3)}(esu) = \frac{10^{-4}\varepsilon_0 C^2 n_0^2 n_2}{\pi}(cm^2/W)$ and found to be 5.57×10^{-08}.

Eventually, using $\mathrm{Im}\,\chi^{(3)}$ and $\mathrm{Re}\,\chi^{(3)}$, the magnitude of $\chi^{(3)}$ was estimated using mathematical expression $\left|\chi^{(3)}\right| = \left[\left(\mathrm{Re}(\chi^{(3)})\right)^2 + \left(\mathrm{Im}(\chi^{(3)})\right)^2\right]^{0.5}$. The absolute value of third order nonlinear susceptibility was found to be 6.74×10^{-08}esu.

The obtained value of third order nonlinear susceptibility of SiO_2/PVA-PEG could be compared with other reported value of SiO_2 nanocomposites

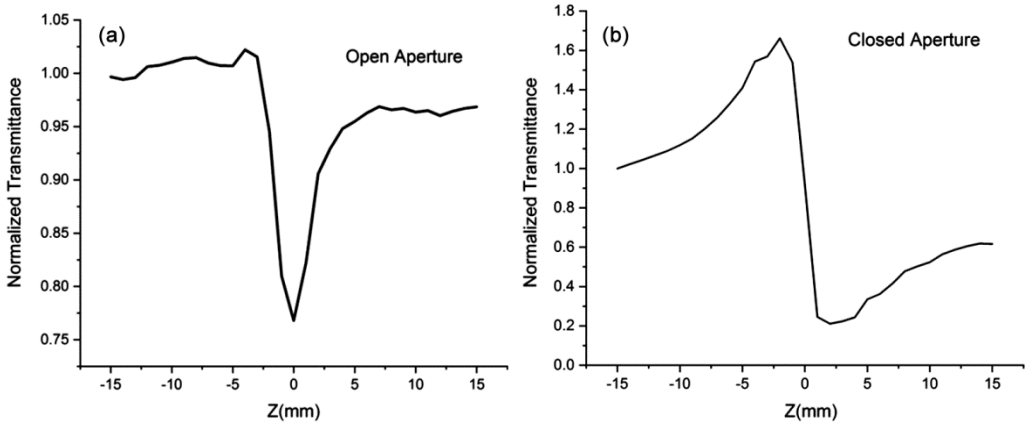

Fig. 5 — (a) Open aperture and (b) closed aperture Z-scan data of SiO_2/PVA-PEG

subordinate to different laser. The reported $\chi^{(3)}$ value of PUSOC/SiO_2 nanocomposites operated with Nd-YAG laser of second order frequency with wavelength of 532 nm was on the order of 10^{-7}esu[30]. The $\chi^{(3)}$ value of silica aerogels was found to be on the range of 6.9 $\times10^{-11}$ esu using laser of wavelength 532 nm[31]. The $\chi^{(3)}$ of Au/TiO_2/SiO_2 was found to be in the order of 1×10^{-6}esu by Nd:YAG laser operated at central wavelength of 532 nm[32]. From this observation it is concluded that SiO_2/PVA-PEG nanocomposites is a potential element for optical device application.

Conclusion

SiO_2/PVA-PEG polymer nancomposites was prepared by solvo casting method. Size and morphological studies was analysed using XRD and SEM. The phase changes from crystalline nature of SiO_2 nanoparticle to amorphous in polymer nanocomomposite was revealed using XRD. SEM analysis revealed the non-uniform distribution of SiO_2 leads to the aggregation of nanoparticle in thick film. The presence of hydrogen bond between SiO_2 and polymer matrix was confirmed at 945 cm^{-1} by vibrational studies. UV studies helped to find linear refractive index 1.4884 from the transmittance data and optical band gap which was found to be 2.88 eV from Tauc-plot. The third order nonlinear property was analysed using Z-scan data and third order nonlinear susceptibility was calculated as 6.74×10^{-08} esu with semiconductor continuous wave laser. The result was compared with other SiO_2nanocomposites and it was concluded that SiO_2/PVA-PEG polymer nanocomposites will be used as active components of opto-electronic devices.

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