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The effect of ZnO and TiO_2 nanoparticles on linear and nonlinear optical properties of PVA polymer thin film

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Abstract

In this work, titanium oxide nanoparticles and zinc oxide nanoparticles were synthesized and employed to form PVA nanocomposite. Spectral absorbance was measured experimentally (UV-Visible-NIR). Linear and nonlinear refractive index were calculated. ZnO-PVA nanocomposite presented larger values of nonlinear refractive index than that of TiO_2- PVA nanocomposite.

Keywords: PVA nanocomposite, ZnO, TiO_2, linear and nonlinear optical properties, polymer thin film

Introduction

Easy fabrication and manipulation of the polymers are attractive characteristics that make polymers as a suitable candidate for using in different nonlinear optical applications such as ultrashort laser pulses compression, real time holography, phase conjugators and optical correlators [1-4]. Enhancing linear and nonlinear optical properties of polymers takes place via the changing of the filler nature, size and its distribution in a polymer matrix [5-7] and the incorporating of nanoparticles in polymer matrix [7-9]. TiO_2 was incorporated in PEO/PVP polymer and enhance its optical properties [10].TiO_2 NPs are put into thin films , the optical band gap values (Eg) of the fabricated nanocomposite films decreased [11-14].The nanocomposite PVA/ZnO and PVA/TiO2 have the highest absorption, lowest energy gap, and the highest optical conductivity for PVA solution [12-27]. In this work, we investigate the linear and nonlinear optical properties for nanocomposite thin film of PVA that doped with TiO_2 and ZnO in order to compare between the effect of these nanoparticles in PVA optical properties in order to produce polymeric thin film that enhance the efficiency of ultrashort laser pulse compression

Material and method

Synthesis of titanium oxide nanoparticles

The first step is to mix 5.765 ml of titanium tetraisopropoxide in 20 ml of ethanol solution while stirring continuously for 30 minutes. 11.53 g of citric acid was dissolved in 10 ml H_2O under heating at 60ºC after that, add titanium tetraisopropoxide solution with a few drops. The item spent 20 minutes in the ultrasonic bath. The filtered sample was dried in a 110 °C oven for five hours before being further annealed for two hours at 550 °C. The produced TiO_2 NPs were collected and further processed with characterization.

Synthesis of zinc oxide nanoparticles

The precursor zinc acetate dihydrate (0.01 M)/0.5 ml was mixed with (0.01 M)/10 ml CTAB complete the mixture with H_2O till 100 ml, heat in the water bath at 80ºC for 2 hr. modify the medium with the ammonia solution (25%) till pH=10 and the color change from colorless to give white precipitate, washed with distilled water and ethanol for three times, respectively. The filtered sample was dried in a 120 °C oven for 2 hours before calcined at 550 °C for two hours to produce ZnO nanoparticles.

Fabrication of TiO_2-PVA nanocomposite sheet

In a typical procedure for synthesizing TiO_2-PVA nanocomposite sheet, 0.5 g of PVA was dissolved in 5 ml H_2O with stirring for 10 min while adding various amounts of titanium oxides concentration (ranging between0.025 and 0.05g). The mixture was sonicated for 10 min, then stirred for another 30 min until the homogenous suspension was obtained. The prepared solution expanded onto the glass surface, after drying for 24 hr under a vacuum. it is inserted in cool water to isolate the sheet from the glass surface.

Fabrication of ZnO-PVA nanocomposite sheet

In a typical procedure for synthesizing ZnO-PVA nanocomposite sheet, 0.5 g of PVA was dissolved in 5 ml H_2O with stirring for 10 min while adding various amounts of Zinc oxides concentration (ranging between0.025 and 0.05g). The mixture was sonicated for 10 min, then stirred for another 30 min until the homogenous suspension was obtained. The prepared solution expanded onto the glass surface, after drying for 24 h under a vacuum. it is inserted in cool water to isolate the sheet from the glass surface.

Results and Discussion

Figure 1 illustrates the absorbance of pure PVA thin film in comparison with PVA that dopes with different concentrations of ZnO and TiO_2

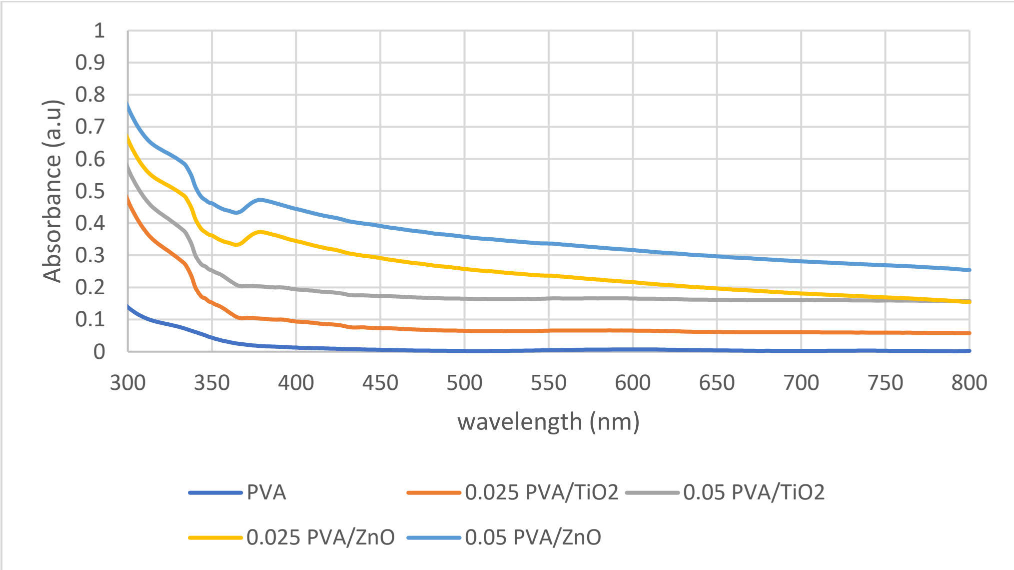

Fig. 1 Absorbance of pure PVA and TiO_2-PVA and ZnO-PVA nanocompsite

It is noticed from fig. 1 that the TiO_2-PVA and ZnO-PVA nanocomposite thin films have higher absorbance than the pure one. On other hand the absorbance of TiO_2-PVA nanocomposite is lower than that of ZnO-PVA nanocomposite. PVA and its nanocomposite have a wide absorption band around 300 nm. ZnO-PVA presents an absorption band around 363nm. The absorbance increases with increasing the concentration of nanoparticles in the nanocomposites

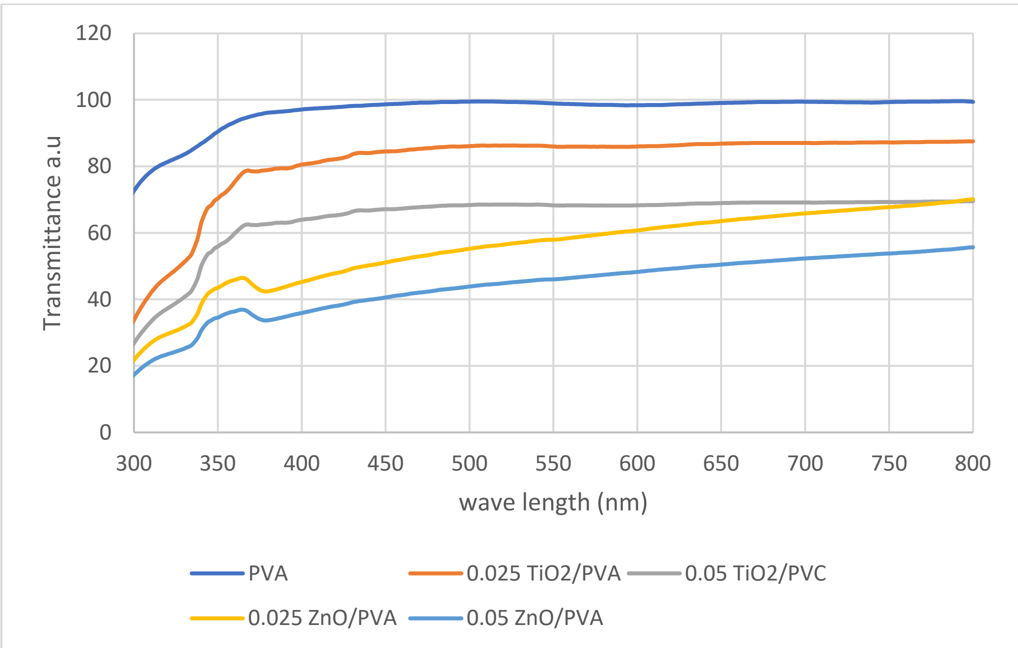

Fig. 2 Transmittance of PVA and nanocomposites

Figure 2 shows the spectral transmittance of PVA and nanocomposite in the opposite of the absorbance curve. PVA shows high transparency about 98%, while the ZnO nanoparticles leads to lowest transparency about 50%and the transparency decreased with increasing the concentration of nanoparticles in the nanocomposites. Reflectance of the sample were calculated via equation

$$R = 1 - \sqrt{\left(\frac{T}{100}\right)\exp(Abs\,)} \qquad (1)$$

where (Abs) is the absorbance as a function of the incident wavelength, T is transmittance and R is the reflectance. Also, the absorption index was calculated from the relation $k(\lambda) = \frac{\alpha\lambda}{4\pi}$, where α is the absorption coefficient and was determined via relation $\alpha = 2.303 * Abs/t$, where t is the thickness of a polymer sample.

According to Fresnel's equations, the normal reflectance as a function of both reflectance and absorption indices can be expressed as:

$$R = \left(\frac{(n(\lambda)-1)^2 + k^2(\lambda)}{(n(\lambda)+1)^2 + k^2(\lambda)}\right) \qquad (2)$$

The refractive index as a function of the wavelength can be determined by the algebraic solution of equation 2 to have:

$$n(\lambda) = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} + k^2} \qquad (3)$$

The dispersion of the refractive index n as functions of wavelengths for the PVA is plotted in figures (3)

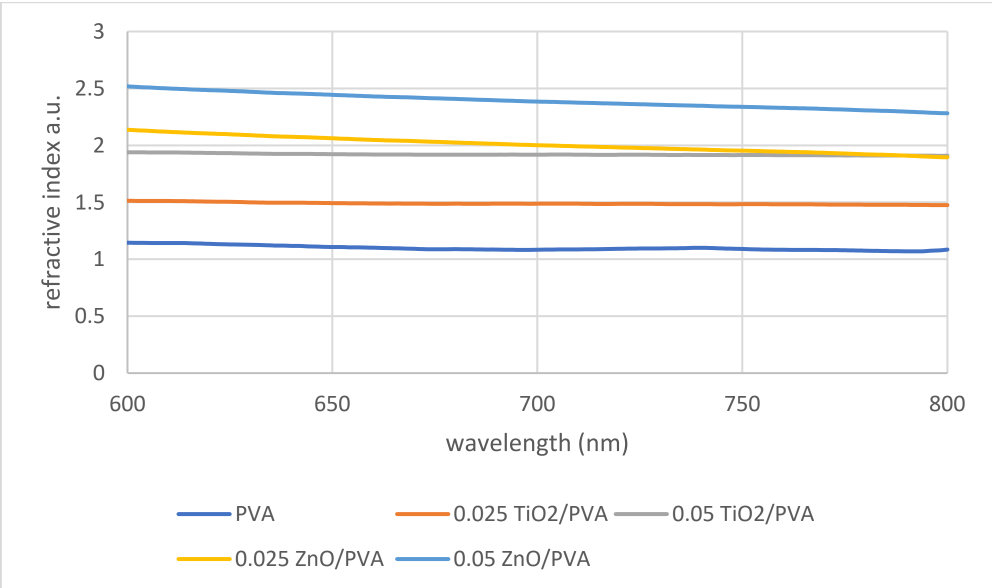

Fig 3 Linear refractive index of PVA and its nanocomposite

Figure 3 represent variation of the refractive index (n) with wavelength for the sample. That the refractive index of PVA/TiO2 and PVA / ZnO polymer solution is higher than the refractive index of pure PVA. This characteristic is essential in all conductors and due to the centralized change of charged particles in the medium [13].

By using the single oscillator formula of Wemple and Di-Domenico [14], the relation between $(n^2-1)^{-1}$ and $(h\omega)^2$ can be described as a linear relation.

$$n^2{}_{(w)} - 1 = \frac{E_o E_d}{(E_o^2 - (h\omega)^2)} \qquad (4)$$

Where E_o is the single oscillator energy and E_d is the dispersion energy.

The linear optical susceptibility of isotropic medium is given by the relation [14]

$$\chi^{(1)} = \frac{n^2-1}{4\pi} \qquad (5)$$

For a region far from the resonance, third order susceptibility can be expressed as function of The linear optical susceptibility by the relation

$$\chi^{(3)} = A(\chi^{(1)})^4 \qquad (6)$$

The mean value of constant, A, as evaluated from 97 experimentally found values is, $A = 1.7 \times 10^{-10}$ for $\chi^{(3)}$ in (esu) [14].

The nonlinear refractive index can be determined by the following equation and l showed as a function of wavelength in figure 4

$$n_2 = \frac{12\pi\chi^{(3)}}{n_o} \qquad (7)$$

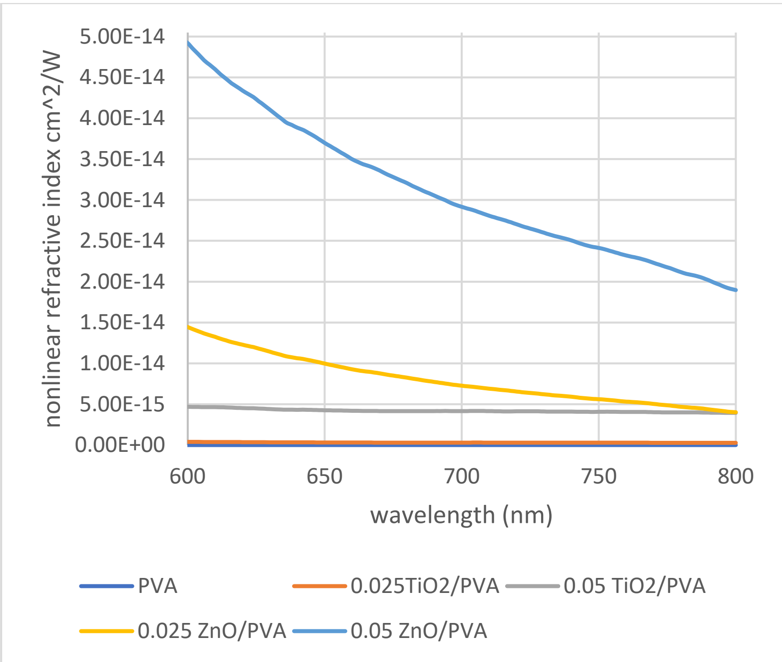

Figure 4 Nonlinear refractive index of PVA and PVA nanocomposites

Nonlinear refractive index is as important factor in a nonlinear process such as ultrashort laser pulse compression real time holography, phase conjugators and optical correlators. PVA nanocomposites present a higher value of nonlinear refractive index than the pure PVA. On other side these values of refractive index increased by increasing the concentration //of nanoparticles in PVA nanocomposite. ZnO/PVA nanocomposite exhibits larger values of nonlinear refractive index than that of TiO2/PVA nanocomposite.

Conclusion

ZnO/PVA nanocomposite exhibits larger linear and nonlinear refractive index values than that of TIO_2/PVA. Controlling the concentration of the ZnO and TiO_2 nanoparticles in PVA-nanocomposites introduces suitable values of nonlinear refractive index that enhance the efficient of nonlinear processes. ZnO and TiO_2/ PVA-nanocomposite present a god candidate for nonlinear process such as ultrashort laser pulse compression, real time holography, phase conjugators and optical correlators.

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