Synthesis of (Polymer−SnO₂) Nanocomposites: Structural and Optical Properties for Flexible Optoelectronics Applications

Ahmed Hashim and Zinah Sattar Hamad

University of Babylon,
College of Education for Pure Sciences,
Department of Physics,
Babylon, Iraq

In this paper, fabrication of polyvinyl alcohol (PVA)/tin dioxide nanoparticles (SnO₂ NPs) nanocomposites for UV-shielding is investigated. The structural and optical properties of (PVA−SnO₂) nanocomposites are studied. The results of optical properties for (PVA−SnO₂) nanocomposites show that the absorbance (A), absorption coefficient (α), extinction coefficient (K), refractive index (n), real (ε_1) and imaginary (ε_2) parts of dielectric constant, and optical conductivity (σ_{op}) of PVA increase, while transmittance (T) and energy band gap (E_g) decrease with an increase in SnO₂ nanoparticles' concentration. The results show that (PVA−SnO₂) nanocomposites can be used for flexible electronics applications.

У цій роботі досліджено виготовлення нанокомпозитів з наночастинок діоксиду Стануму (SnO₂) та полівінілового спирту (PVA) для УФ-захисту. Вивчено структурно-оптичні властивості нанокомпозитів PVA−SnO₂. Результати щодо оптичних властивостей нанокомпозитів PVA−SnO₂ показують, що спектральна поглинальна здатність (A), коефіцієнт поглинання (α), коефіцієнт екстинкції (K), показник заломлення (n), реальна (ε_1) й уявна (ε_2) частини діелектричної константи та оптична провідність (σ_{op}) PVA збільшуються, тоді як коефіцієнт пропускання (T) та ширина енергетичної щілини (E_g) зменшуються із збільшенням концентрації наночастинок SnO₂. Результати показують, що PVA−SnO₂-нанокомпозити можна використовувати для застосувань у гнучкій електроніці.

1. INTRODUCTION

Protection against ultraviolet radiation is an important issue in modern technological era. The oxidation caused by the action of UV rays can form basis for acute mutilation to both living organisms and materials, *e.g.*, action of photonic energy may produce undesired breakage of chemical structures in non-UV protecting materials, which can be detrimental to living organism. Additionally, skin photoaging might take place under intense ultraviolet light. UV-rays can also cause degradation of the organic molecules including polymers, bleaches, tinctures and semiconductor photocatalysis. UVC range (100−290 nm) light rays having energy of about 4.43−12.4 eV can cause more serious harm than that of UVB (290−320 nm) and UVA (320−400 nm) light rays possessing energies of about 3.94−4.43 eV and 3.10−3.94 eV, respectively. Therefore, it is intensely desired to develop a material, which can block various ranges of ultraviolet rays particularly in the UVC range to minimize the possibility of damage. Such materials can be tailored by reinforcing inorganic fillers into a transparent polymer matrix, so that band gap in the desired region can be achieved which can further help in UV blocking. In order to make practical use of such materials, it is appropriate to use them in the form of either solutions or polymeric films of fine powder. The use of reinforced polymer matrix is advantageous over host material because such composites can be employed as UV protecting shields. The inorganic nanoparticles having capability of cutting the UV absorption can be incorporated in polymer leading to the enhancement in their properties so that their utility in day-to-day life is dramatically enhanced [1].

The production of novel polymeric nanocomposites have been widely studied by the current applications on nanosize inorganic fillers in the food packaging field, barrier applications, sensors, antimicrobial, conductive, coatings, antiballistic products and other materials. The characteristics and properties of the nanocomposites are influenced by the type of filler used as well as by the polymeric matrix. The applications encompass several areas such as electronic, medicine, military, aerospace, marine, and vehicles [2]. Polymer-matrix composites (denoted as PMCs) have consistently been of interest for decades, because they possess markedly improved mechanical properties (tensile modulus and strength), thermal stability, chemical resistance, flame retardation and barrier resistance as compared with pure polymers. It is well known that the interfacial effect between nanoparticles and the polymer matrix greatly affect the properties of nanocomposites. It is generally believed that the dispersion of fillers in the polymer matrix is an important issue for improving the properties of nanocomposites [3].

The optical properties of doped polymers have been attracted considerable attention because of the range of technological applications

that include solar cells, coatings, light emitting diodes, sensors and electrochemical cells. The attention of researchers has drawn to study effect of doping on the optical properties of solid polymer electrolytes be tailored to a specific requirement by the addition of suitable dopant substances.

Measurements and determination the optical absorption and especially the absorption edge present a useful method for the investigation of optically induced transition and for getting information about the band structure [4]. Polyvinyl alcohol (PVA) is a polymer with carbon chain backbone attached with hydroxyl groups. These OH groups can be a source of hydrogen bonding and hence assist in the formation of polymer blends. PVA is non-toxic, water-soluble synthetic polymer, which is widely used in the polymer blends due to its good physical and chemical properties, excellent film forming characteristics, emulsifying capability, non-carcinogenic, biodegradable and biocompatible qualities. These unique characteristics enable it for its applicability in pharmaceutical fields, drug-coating agents, material for surgical structures and cosmetic industries [5].

The new production of composites contain carbides [6−12], metal and oxides [13−25], ionic materials, and biomaterials [26−28]. The nanocomposites have different modern applications such as piezoelectric and pressure sensors [29], antibacterial, *etc.* [30]. Tin oxide is widely used and studied *n*-type semiconductor with wide band gap and crystalline structure. Studies have been carried out on tin oxide based gas sensors, dye sensitized solar cells optical devices, optoelectronic devices and hybrid microelectronic devices. The compound has lately also been identified as possible electrode material for lithium cells and photo catalysis. With properties such as transparency in semiconductivity, it is an oxide of great interest from the technological point of view for white pigment for conducting coatings. Tin oxide nanoparticles are synthesized through different chemical roots such as co-precipitation, hydrothermal, sol−gel, sonochemical polymer, precursor method among others [31]. Tin dioxide is an *n*-type semiconductor oxide with a wide energy gap.

Tin dioxide (SnO$_2$) has attracted much attention for its various applications, such as catalyst, catalytic support, biomedical, pharmaceutical, gas sensor, rechargeable Li battery and optical electronic device. However, the catalytic activity of gold supported on tin dioxide is gearing up attention in recent years. It is observed that these nanocomposites showed excellent catalytic property of CO oxidation at low temperatures [32].

2. MATERIALS AND METHODS

The (polyvinyl alcohol and tin dioxide) nanocomposites were fabricated

by using casting technique. The PVA/SnO$_2$ nanocomposites were prepared with different concentrations of PVA and SnO$_2$ nanoparticles where dissolve 1 gm of PVA in 20 ml of distilled water by using magnetic stirrer to mix the polymers for 1 hour to obtain more homogeneous solution. The SnO$_2$ nanoparticles were added to the PVA solution with concentrations of 2, 4 and 6 wt.%. The optical properties of PVA/SnO$_2$ nanocomposites are measured by using the double beam spectrophotometer (Shimadzu, UV-1800°A) in wavelength 200–800 nm.

The absorption coefficient (α) of nanocomposites is given by the equation [33]:

$$\alpha = 2.303A/t, \tag{1}$$

where A is the absorbance of sample, and t—the sample thickness in cm. The non-direct transition model for amorphous semiconductors was determined by following equation [34, 35]:

$$\alpha h\upsilon = B(h\upsilon - E_g)^r, \tag{2}$$

where B is a constant, $h\upsilon$ is the photon energy; E_g is the optical energy band gap; $r = 2$ or 3 for allowed and forbidden indirect transitions.

The extinction coefficient (k) of PVA/SnO$_2$ nanocomposites is given by using the following equation [36, 37]:

$$K = \alpha\lambda/(4\pi). \tag{3}$$

The refractive index (n) of PVA/SnO$_2$ nanocomposites can be calculated by using the following equation [38, 39]:

$$n = (1 + R^{1/2}) / (1 - R^{1/2}). \tag{4}$$

The real and imaginary parts of dielectric constant (ε_1 and ε_2) were calculated by using equations [40, 41]:

$$\varepsilon_1 = n^2 - k^2, \tag{5}$$

$$\varepsilon_2 = 2nk. \tag{6}$$

The optical conductivity was calculated by using the equation [42]:

$$\sigma = \alpha nc/(4\pi). \tag{7}$$

3. RESULTS AND DISCUSSION

The optical absorbance of pure PVA and SnO$_2$–PVA nanocomposites is

presented in Fig. 1. The pure PVA film is highly transparent in nature because its spectrum does not display any peak in the visible region but it displays a peak in ultraviolet region of electromagnetic spectrum, so it can be used as a polarizer [43], flexible electronic applications and UV-shielding.

By increasing the loadings of SnO$_2$ nanoparticles, the transparency of PVA was further decreased as shown in Fig. 2. The pure PVA spec-
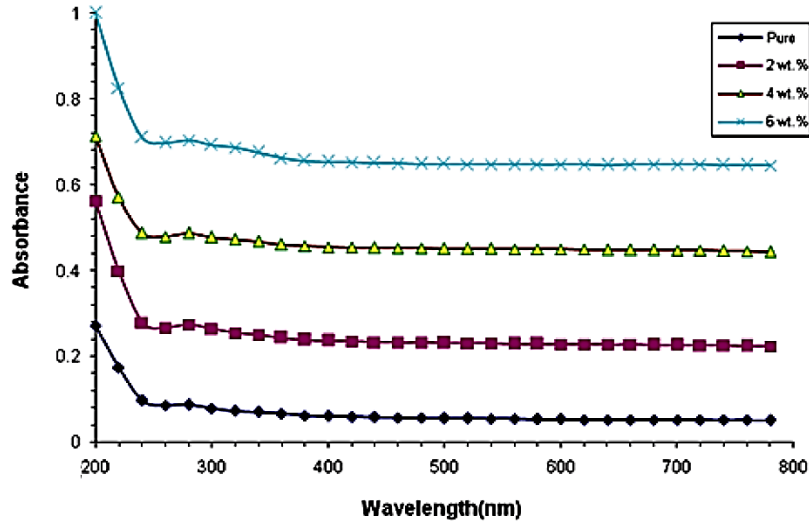

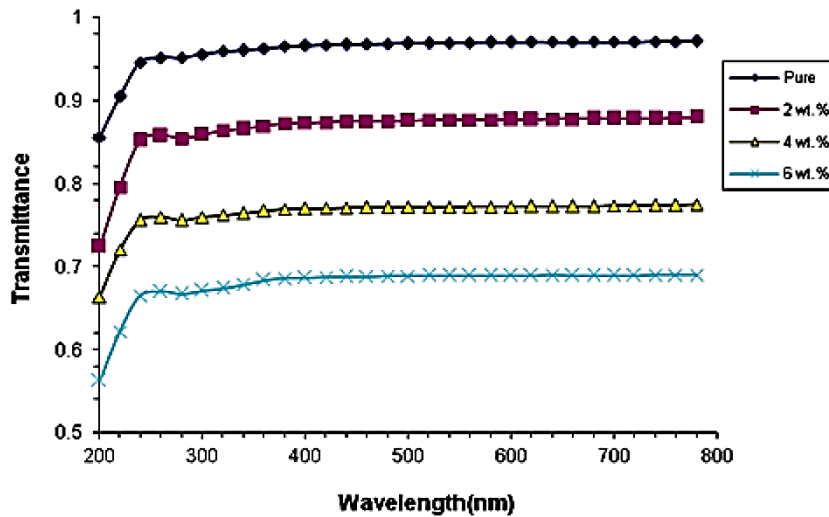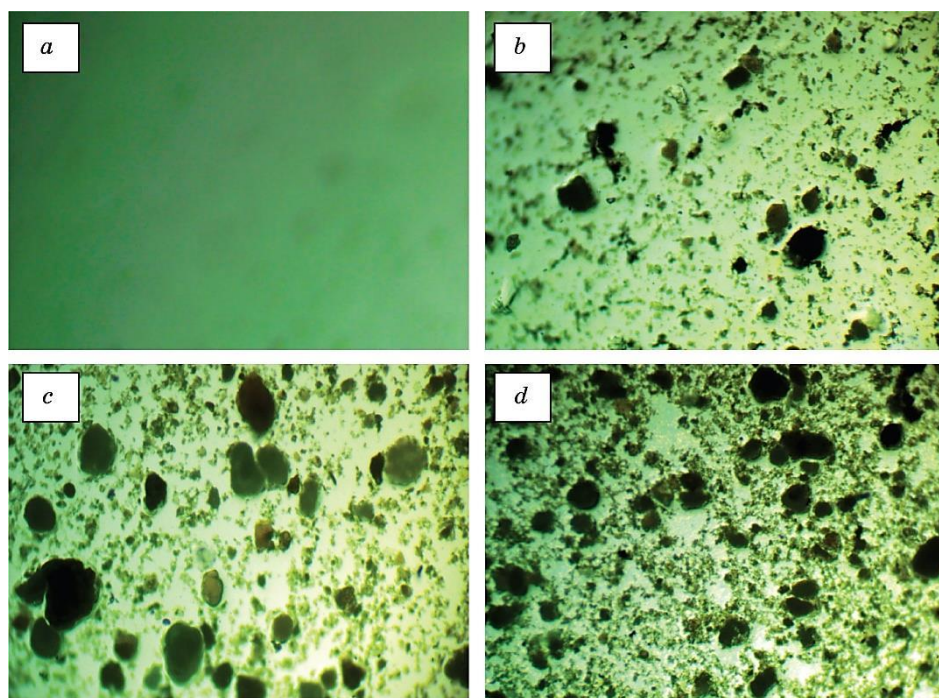**Fig. 1.** Optical absorbance of pure PVA and SnO$_2$−PVA nanocomposites.

Fig. 2. Transmittance spectra of pure PVA and SnO$_2$−PVA nanocomposites.

Fig. 3. Microscopy images ($\times 10$) for (PVA–SnO$_2$) nanocomposites: (*a*) for PVA; (*b*) for 2 wt.% SnO$_2$; (*c*) for 4 wt.% SnO$_2$; (*d*) for 6 wt.% SnO$_2$.

trum shows an absorbance peak at 200 nm due to $(CH=CH)_4-CO-$ structure. It also displays two other absorbance peaks at 280 and 330 nm due to $\pi-\pi^*$ and $\nu-\pi^*$ transitions, respectively [43]. The absorbance of (SnO$_2$–PVA) nanocomposites is increased as well as the transmittance with an increase in SnO$_2$ nanoparticles' concentration. This is due to increase the number of free electrons, which absorb the incident light [44], as shown in Fig. 3.

The variation of absorption coefficient of SnO$_2$–PVA nanocomposites with the photon energy for different concentrations of tin dioxide nanoparticles is shown in Fig. 4. The absorption coefficient of SnO$_2$–PVA nanocomposites is increased with the increase in SnO$_2$ nanoparticles' concentration that is attributed to increase the number of carries charges in nanocomposites. The absorption coefficient values are less than 10^4 cm^{-1}; this means that the SnO$_2$–PVA nanocomposites have indirect energy gap, which is shown in Figs. 5, 6 for allowed indirect and forbidden indirect transition of nanocomposites, respectively. The energy band gap of PVA is decreased with the increase in tin dioxide nanoparticles' concentration; this is due to increase of the localized level in energy band gap [45].

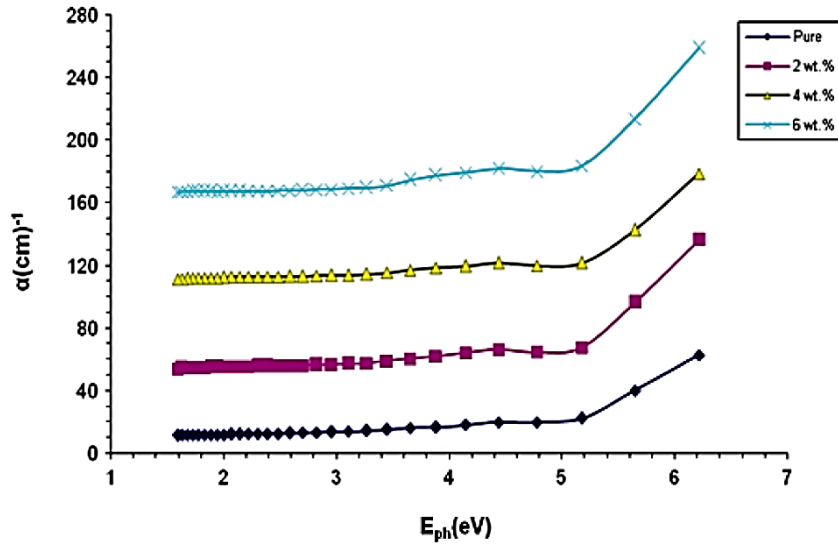The refractive index and extinction coefficient of SnO$_2$–PVA nanocomposites are shown in Figs. 7, 8.

Fig. 4. Variation of absorption coefficient of SnO$_2$–PVA nanocomposites with the photon energy for different concentrations of tin dioxide nanoparticles.
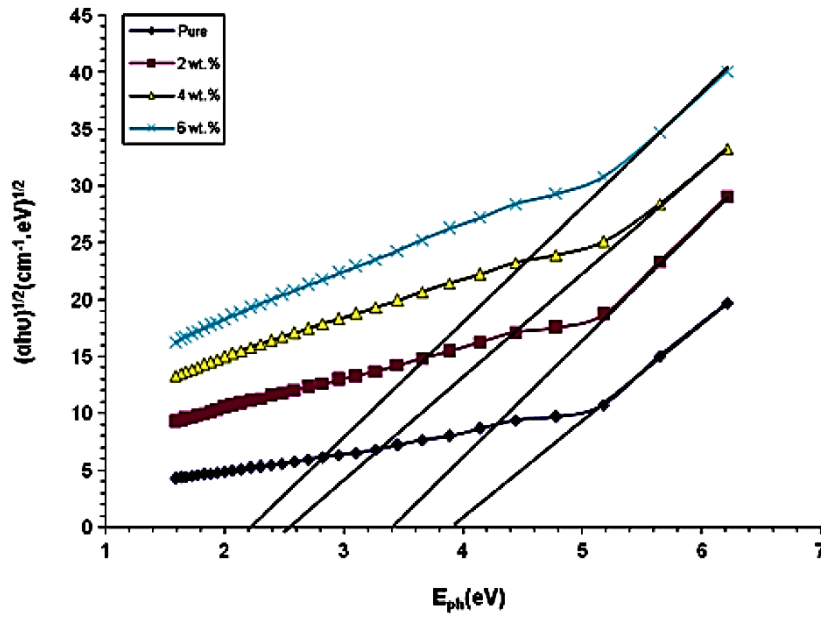

Fig. 5. Energy band gap for allowed indirect transition of nanocomposites.
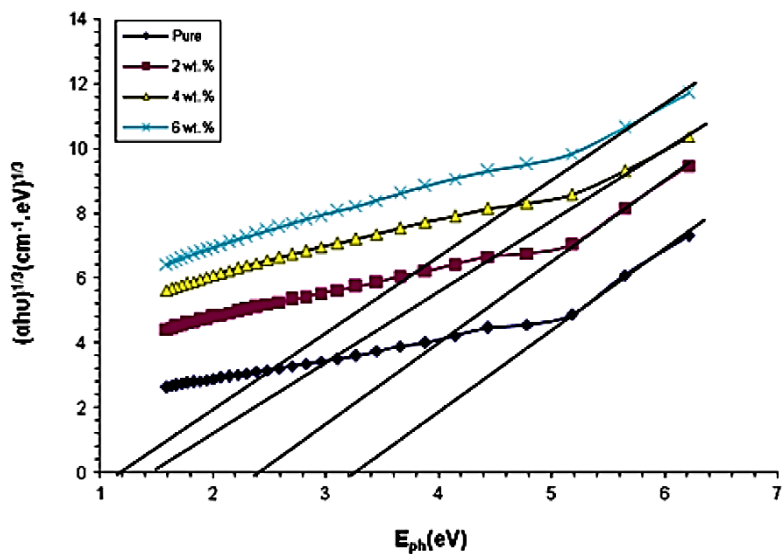
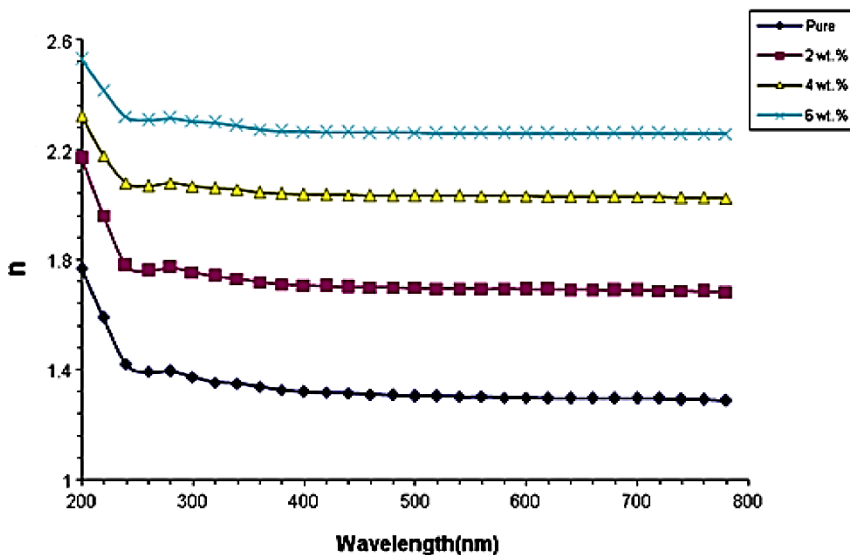**Fig. 6.** Energy band gap for forbidden indirect transition of nanocomposites.

Fig. 7. Refractive index of SnO_2–PVA nanocomposites.

The figures show that the refractive index and extinction coefficient increase with the concentration of SnO_2 nanoparticles, which are related to the increase in the density of nanocomposite that lead to the scattering and the number of charge carriers as a result of the increase

in the reflectance and absorption coefficient [46].

The real and imaginary parts of the dielectric constant of the SnO$_2$–PVA nanocomposites shown in Figs. 9 and 10.

The dielectric constant of compound (ε) is divided into two parts: real (ε_1) and imaginary (ε_2) ones. The real parts of dielectric constant is
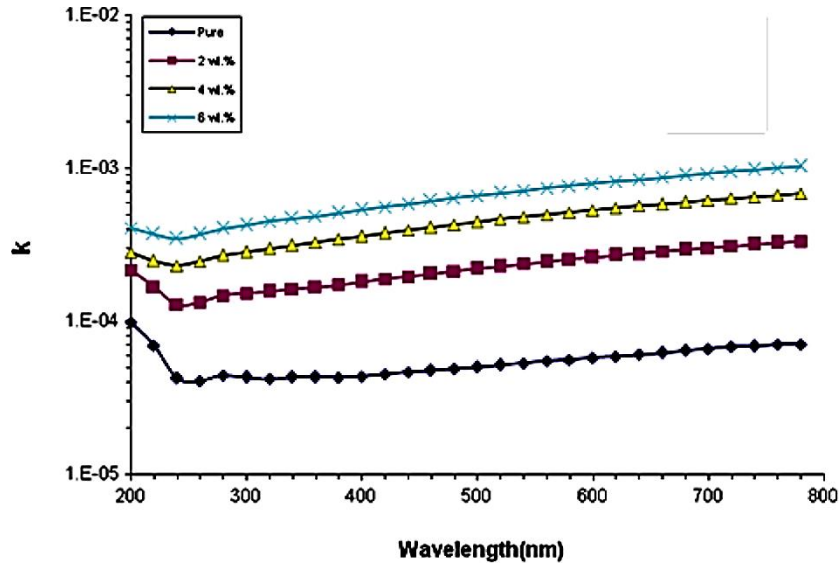

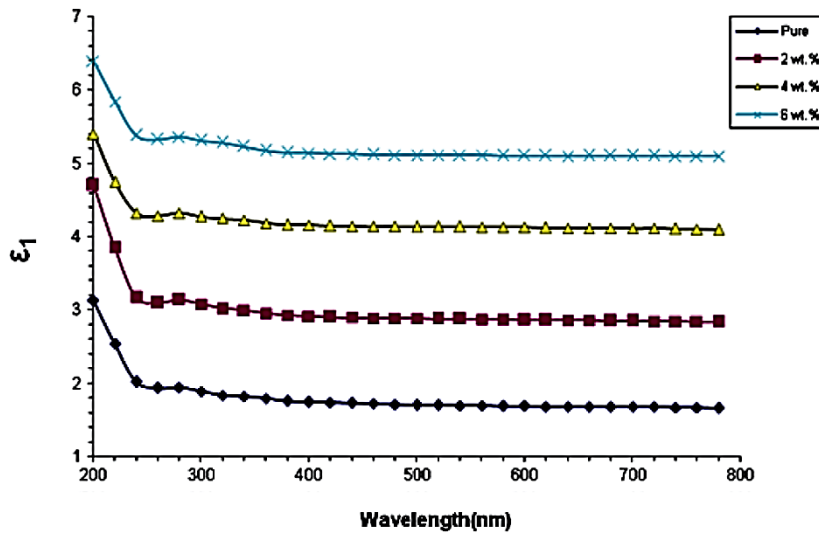**Fig. 8.** Extinction coefficient of SnO$_2$–PVA nanocomposites.

Fig. 9. Real part of the dielectric constant of the SnO$_2$–PVA nanocomposites.

associated with the term that shows how much will slow down the speed of light in the material and the imaginary parts shows how a dielectric absorbs energy from an electric field due to dipole motion [47].

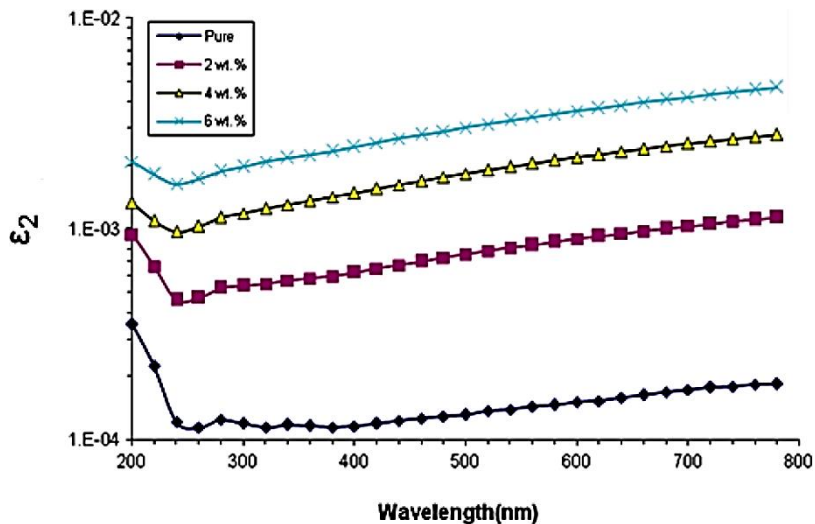The optical conductivity of the SnO_2–PVA nanocomposites with

Fig. 10. Imaginary part of the dielectric constant of the SnO_2–PVA nanocomposites.
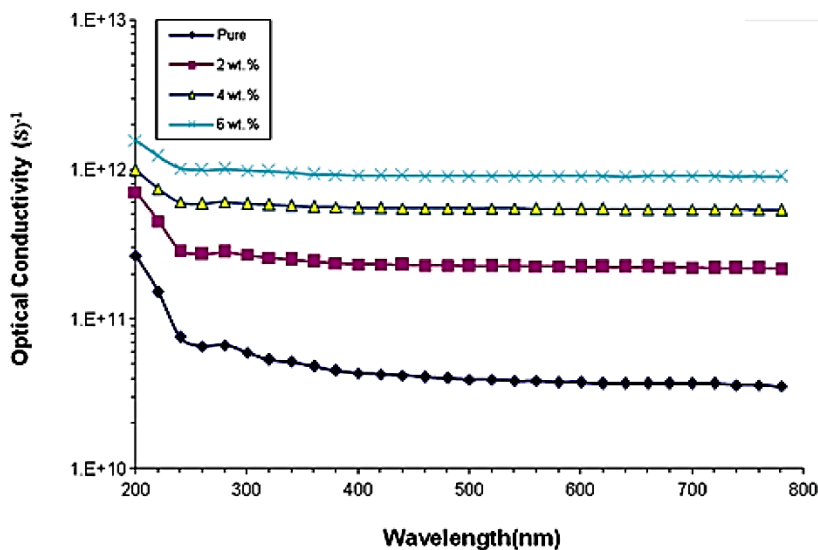

Fig. 11. Optical conductivity of the SnO_2–PVA nanocomposites with wavelength.

wavelength is shown in Fig. 11.

The term 'optical conductivity' means the electrical conductivity, which is resulted from the movement of the charge carriers due to alternating electric field of the incident electromagnetic waves. From this figure, it is noticed that the optical conductivity of PVA increases with increasing SnO_2 nanoparticles. This increase due to creation of new levels in the band gap leads to facilitate the crossing of electrons from the valence band to these local levels to the conduction band; consequently, the band gap decreases and the conductivity increase [48–52].

4. CONCLUSION

The optical absorbance of pure PVA increases, while the transmittance decreases with increase of SnO_2 nanoparticles' concentration. The absorbance of SnO_2−PVA nanocomposites have higher values at UV region, which can be used for flexible electronics applications and flexible UV-shielding. The optical energy band gap of polyvinyl alcohol decreases with increase in SnO_2 nanoparticles' concentration. The absorption coefficient, extinction coefficient, refractive index, real and imaginary parts of dielectric constant and optical conductivity of PVA increase with increase in SnO_2 nanoparticles' concentration.

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