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Structural, Optical and Dielectric Properties of (PS- In_2O_3/ $ZnCoFe_2O_4$) Nanocomposites

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The (PS-In_2O_3/ $ZnCoFe_2O_4$) nanocomposites have been prepared by using solution casting method. The structural, optical and dielectric properties of (PS-In_2O_3/ $ZnCoFe_2O_4$) nanocomposites have been studied to use it for different optoelectronics applications. The structural properties include FTIR, optical microscope and SEM. The results of optical properties for (PS-In_2O_3/ $ZnCoFe_2O_4$) nanocomposites showed that the absorbance, absorption coefficient, refractive index, extinction coefficient, dielectric constants and optical conductivity of (PS-In_2O_3) nanocomposites were increased with the increase in $ZnCoFe_2O_4$ nanoparticles concentrations while the transmittance and energy band gap were decreased with the increase of the $ZnCoFe_2O_4$ nanoparticles concentrations. The(PS-In_2O_3/ $ZnCoFe_2O_4$) nanocomposites have high absorbance in the UV-region. The results of dielectric properties showed that the dielectric constant, dielectric loss and A.C electrical conductivity of (PS-In_2O_3) nanocomposites increase with increase in $ZnCoFe_2O_4$ nanoparticles concentrations. The dielectric constant and dielectric loss decrease while the electrical conductivity increases with an increase in frequency.

Keywords: Polystyrene, Nanocomposites, Optical properties, Dielectric, $ZnCoFe_2O_4$.

Introduction

Nanotechnology has attracted a great deal of attention in the last few years as miniaturization and nanomaterials are often foreseen to be the key for a sustainable future. In this regard, an essential part of the scientific community is currently focused on a very challenging and relevant research's direction, which is the synthesis of novel nanostructured hybridmaterials capable of absorbing the photonic energy coming from the sunlight with the aim of turning it into electrical or chemical energy. Whereas, growing concerns regarding energy and environmental problems have stimulated extensive researches on solar energy utilizations. Among them, various strategies are explored for photocatalytic hydrogen production for fuel cells and/or degradation of organic dyes using semiconductor photocatalysts. From the point of view of the materials, photocatalysts require a series of characteristic properties depending on their applications, including particle size, specific surface area or space between the electronic levels, among others [1]. The applications of nanocomposites are quite promising in the fields of microelectronic packaging, optical integrated circuits, automobiles, drug delivery, sensors, injection molded products, membranes, packaging materials, aerospace, coatings, adhesives, fire-retardants, medicaldevices, consumer goods, etc[2]. By mixing organic molecules and inorganics at the nano level, robust materials, called\ organic–inorganic hybrids, are created, which have multiple functions originating from both components [3]. Because of their high durability, hybrids are regarded as a platform for realizing advanced optoelectronic materials containing conjugated molecules and polymers [4]. By mixing organic molecules and inorganics at the nano level, robust materials, called organic–inorganic hybrids, are created, which have multiple functions originating from both components. Because of their high durability, hybrids are regarded as a platform for realizing advanced optoelectronic materials

containing conjugated molecules and polymers. For example, electric-conductive hybrids are obtained by introducing conductive organic crystals into a polymer hybrid matrix based on silica .In particular, the resulting hybrids show a waterproof character and higher heat resistance than that of the pristine organic crystal . By loading a series of conjugated molecules onto hybrid matrices, multiple optical properties are readily expressed. Intense white-light luminescence is observed from dye-loaded robust hybrids . Thus, hybrid formation is currently recognized as a valid strategy for enhancing durability of organic products including conjugated polymers. However, hybrid formation is usually performed via the sol-gel reaction in polar solvents with acid or base catalysts Thereby, aggregation followed by generation of inhomogeneity and degradation of conjugated polymers is often induced during the sol–gel reactions. Furthermore,carrier-transport ability could decrease after hybrid formation compared to that of the pristine organic material due to intrinsic high electric resistance of silicate. Thus, our next challenge is not onlyto establish the facile manner for hybrid formation without critical losses of electric properties of conjugated polymers but also to systematically study the electric properties of the polymersinside hybrids [5]. Nanocomposite materials have been extensively used in electrical applications. The fact that they are oftenmade up of at least two constituents or phases enables us to tailor materials for special purposes. The electrical properties of a composite system are determined by the properties of the constituents, interaction between them, and geometrical configuration. In designing composite materials with specified properties for electrical applications, one should take these parameters into consideration [6]. Polystyrene (PS) is amorphous polymer with bulky side groups. General purposes PS are hard, rigid, and transparent at room temperature and glass like thermoplastic material which can be soften and distort under heat. It is soluble in aromatic hydrocarbon solvents, cyclohexane and chlorinated hydrocarbons [7]. In this paper, preparation of (PS-In_2O_3/ $ZnCoFe_2O_4$) nanocomposites and studying their structural, optical and dielectric properties.

Materials and Methods

The materials used in this paper are polystyrene (PS), indium oxide nanoparticles (In_2O_3 NPs), zinc cobalt oxides ($ZnCoFe_2O_4$). The (PS-In_2O_3) nanocomposites were prepared by concentration 98:2. The $ZnCoFe_2O_4$ nanoparticles

were added to (PS-In_2O_3) nanocomposites with weight percentages are (0,2,4,6 and 8) wt.%. The specimens were prepared using casting technique thickness ranged between (108-120) μm. The spectrophotometer's double beam (shimadzu, UV-18000 A) using to measure the optical properties of (PS-In_2O_3-$ZnCoFe_2O_4$) nanocomposites in wavelength (200–800) nm. The dielectric properties (dielectric constant, dielectric loss, A.C electrical conductivity of (PS-In_2O_3/$ZnCoFe_2O_4$) nanocomposites were measured by using (LC Meter) in the frequency (f) range (100 Hz -5 MHz) at room temperature.

Absorption coefficient (α) is defined by following equation [8]:

$$\alpha = 2.303A/t \quad \text{..........} \quad (1)$$

Where A: is the absorbance and t: is the sample thickness.

The indirect transition model for amorphous semiconductors is [9]:

$$\alpha h\upsilon = B(h\upsilon - E_g^{opt \cdot})^r \quad (2)$$

Where B is a constant, hυ is the photon energy , Egis the optical energy band gap,

r = 2 for allowed indirect transition and

r = 3 for forbidden indirect transition.

The Refractive index (n) is given by following equation [9]:

$$n = (1+R^{1/2})/(1-R^{1/2}) \quad \text{.........} \quad (3)$$

Where R is the reflectance.

The extinction coefficient (k) is calculated by using the following equation [9]:

$$K = \alpha\lambda/4\pi \quad \text{…..............} \quad (4)$$

The dielectric constant is divided into two parts real(ε_1), and imaginary (ε_2). The real and imaginary parts of dielectric constant (ε_1 and ε_2) are calculated by using equations [10]:

$$\varepsilon_1 = n^2 - k^2 \text{ (real part)} \quad \text{…..... } (5)$$

$$\varepsilon_2 = 2nk \text{ (imaginary part)} \text{…… } (6)$$

The measured capacitance, C(w) was used to calculate the dielectric constant ,έ(w) using the

following equation [11]:

$$\varepsilon' = \frac{C_p}{C_o} \qquad \dots\dots(7)$$
$$\varepsilon'' = \varepsilon' D \qquad \dots\dots(8)$$

The dissipated power in the insulator is represented by the existence of alternating potential as a function of the alternating conductivity, using:

$$\sigma_{A.C} = w\varepsilon''\varepsilon_o \qquad (9)$$

$\acute{O}_{AC}$ is a measurement for the generated temperature in the insulating material resulting from the rotation of the dipoles in their positions, (or the vibration of the charges) as a result of the alternating of the field [11].

Results and Discussion

Figure 1 shows the images of (PS-In₂O₃/ZnCoFe₂O₄) nanocomposites for samples with different concentrations of In₂O₃ nanocomposites and different concentrations of Ferrite ZnCoFe₂O₄ at magnification power (40X). The figure shows that the ZnCoFe₂O₄ nanoparticles are aggregated as clusters at lower concentrations. When increasing the concentrations of ZnCoFe₂O₄ nanoparticles, the nanoparticles form paths of network inside the (PS). Figure 2 shows the SEM images (PS-In₂O₃/ ZnCoFe₂O₄) nanocomposites. Scanning electron microscopy has been used to study the compatibility between various components of the polymers, In₂O₃ and ZnCoFe₂O₄ nanoparticles. The films exhibit uniform density of grain distribution at surface morphology and surfaces morphology of the (PS-In₂O₃/ ZnCoFe₂O₄) nanocomposites show many aggregates or chunks randomly distributed of nanoparticles on the films surface. The results show an increase in the number of aggregations on the surface in accordance with increasing [12]. Figure 3 shows the FTIR spectra of pure polystyrene take at room temperature in the range 4000–500 cm⁻¹. The polystyrene doped by In₂O₃ and ZnCoFe₂O₄ nanoparticles. The characteristic peaks around 3260 cm⁻¹ in the spectra are due to the presence of the stretching vibration of hydroxyl group OH of polystyrene, while the spectral bands between 3500 and 3900 cm⁻¹ are due to OH stretching vibration of polystyrene, respectively and the bands around 2921 cm⁻¹ correspond to the CH₂ asymmetric stretching. The C=O band at about 1705 cm⁻¹ is important for further discussions, the position of this band indicates that the carboxylic acid groups form dimmers. The sharp band 1085 cm⁻¹ corresponds to C-O stretching of acetyl groups present on the polystyrene backbone that remains the same for undoped but broads for doped samples and the peak observed at about 650 cm⁻¹ is due to the OH out of plane. The figure indicate the bonding nature between In₂O₃/ZnCoFe₂O₄ nanoparticles and polystyrene [13].

Figure 4 shows the variation of the optical absorbance spectra of (PS-In₂O₃/ ZnCoFe₂O₄) nanocomposites with the photon wavelength for different concentrations of ZnCoFe₂O₄ nanoparticles . Figure 5 shows that transmittance spectrum as a function of wavelength for (PS-In₂O₃/ ZnCoFe₂O₄) nanocomposite. From the figures that absorbance increases and transmittance decreases with the increase in the concentration of ZnCoFe₂O₄ nanoparticles which is related to the increase the number of charges carries[14-21]. The absorption coefficient of nanocomposites is shown in Fig. 6. The figure shows that the absorption coefficient of (PS-In₂O₃/ ZnCoFe₂O₄) nanocomposites increases with increase of ZnCoFe₂O₄ nanoparticles concentrations, this increase attributed to increase the number of carries charges which causes to increase the absorbance. Figures 7 and 8 show the energy band gap of nanocomposites. From the values of the absorption coefficient, it can be concluded that the nanocomposites have indirect energy band gap, it is decrease with increasing the ZnCoFe₂O₄ nanoparticles, this behavior is due to the creation of levels in the energy gap [22-25].

Figure 9 shows the variation of refractive index (n) with photon energy. The values of refractive index increase exponentially with increasing photon energy. This increase indicates that the electromagnetic radiation passing through the material is faster in the low photon energy. Figure 10 represents the variation of the extinction coefficient (k) with the incident photon energy. In this figure the variation is simple in the low energy region while the variation increased in the high photon energy region this behavior may be as a result to the variation of the absorption coefficient which leads to spectral deviation in the location of the charge polarization at the attenuation coefficient due to the loses in the energy of the electron transition between the energy bands [26].
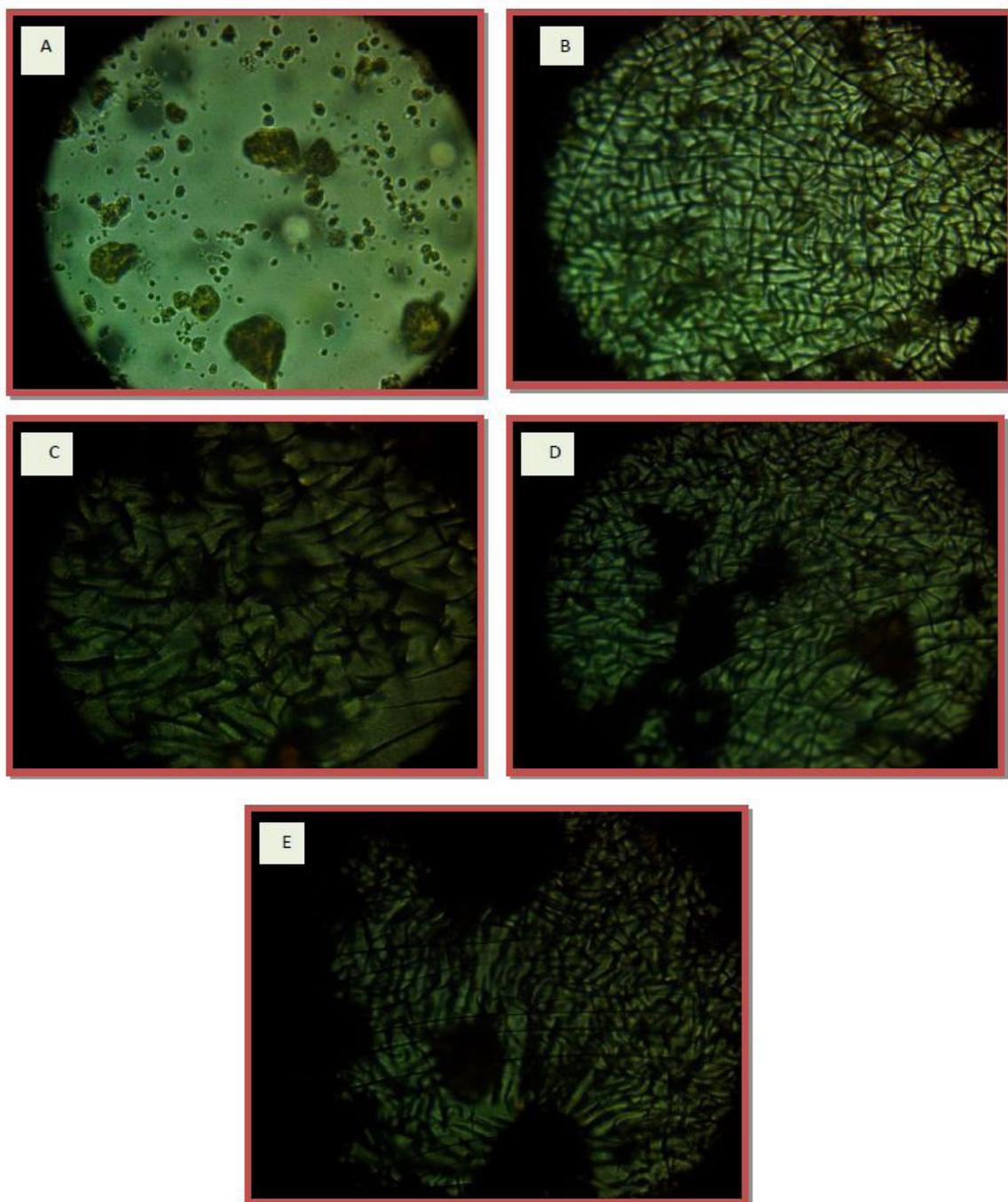
Fig. 1. Photomicrographs (40X) for (PS- In$_2$O$_3$/ ZnCoFe$_2$O$_4$) nanocomposites (A) for (PS- In$_2$O$_3$) (B) for 2wt.% ZnCoFe$_2$O$_4$ nanoparticles, (C) for 4wt.%ZnCoFe$_2$O$_4$ nanoparticles, (D) for 6wt.% ZnCoFe$_2$O$_4$ nanoparticles, (E) for 8wt.% ZnCoFe$_2$O$_4$ nanoparticles.
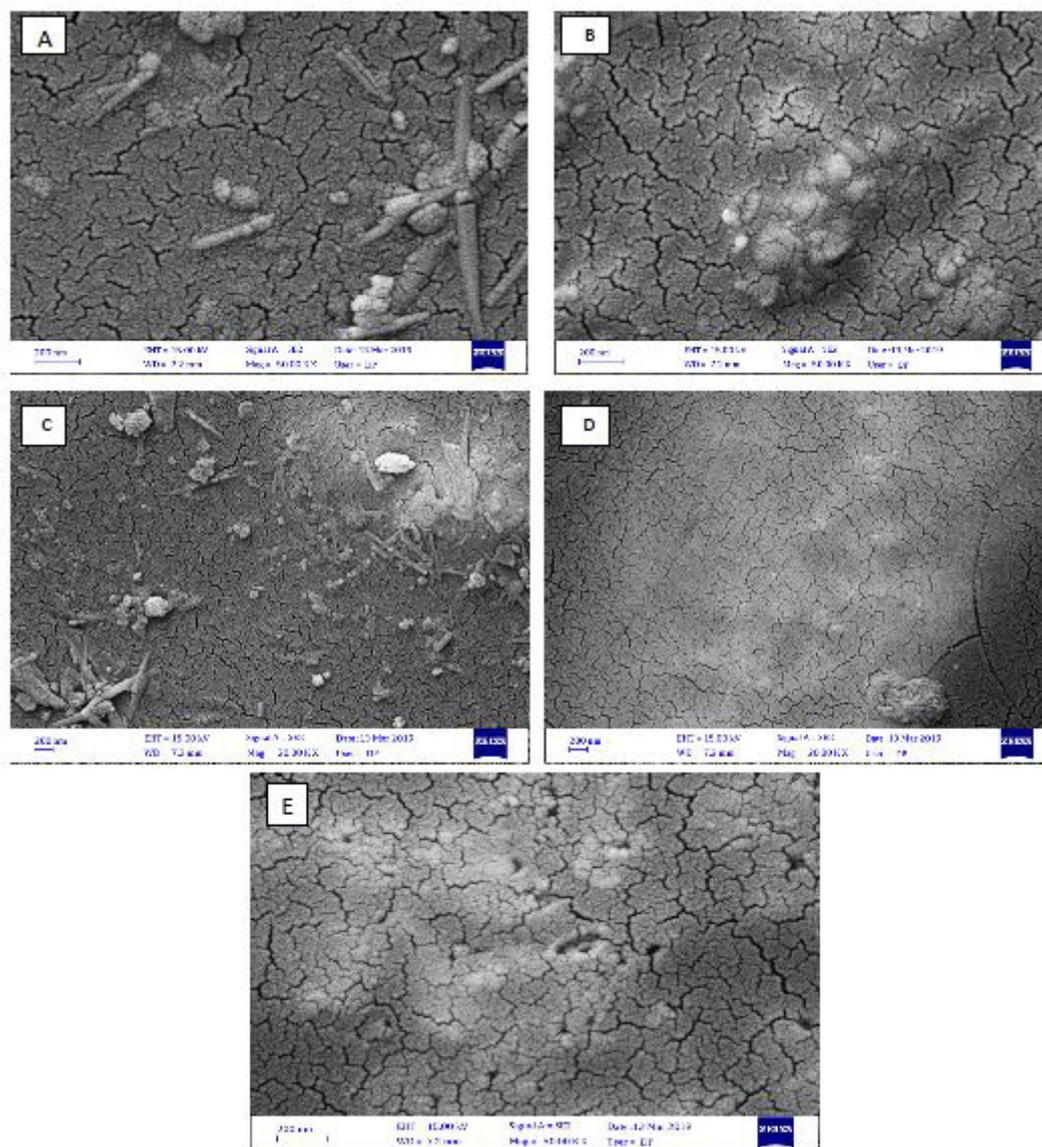
Fig. 2. SEM images of (PS- In$_2$O$_3$/ ZnCoFe$_2$O$_4$) nanocomposites, (A) for (PS- In$_2$O$_3$), (B) 2 wt.% ZnCoFe$_2$O$_4$ nanoparticles, (C) 4 wt.% ZnCoFe$_2$O$_4$ nanoparticles, (D) 6 wt.% ZnCoFe$_2$O$_4$ nanoparticles, (E) 8 wt.% ZnCoFe$_2$O$_4$ nanoparticles.
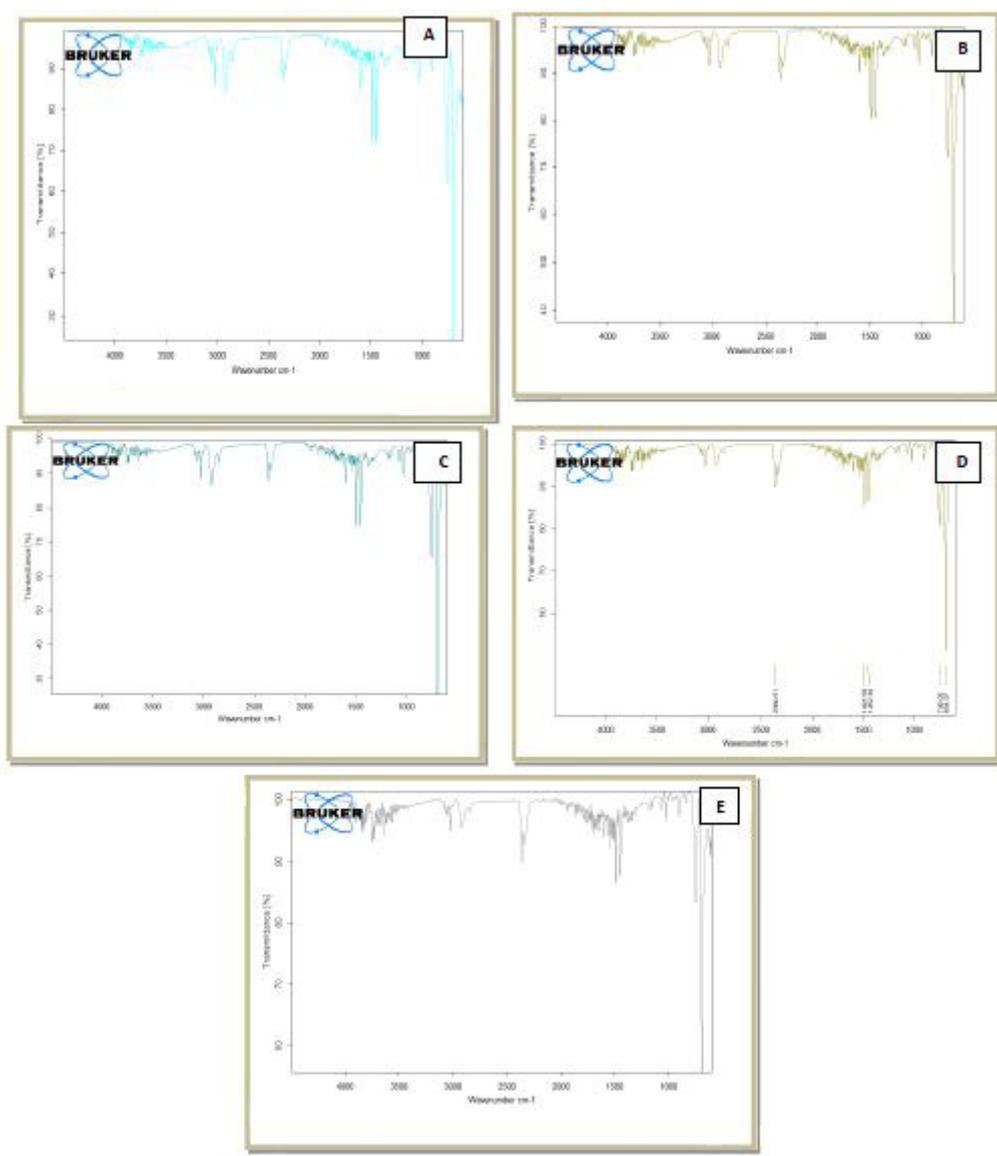
Fig. 3. FTIR spectra for (PS- In$_2$O$_3$/ ZnCoFe$_2$O$_4$) nanocomposites: (A) for (PS- In$_2$O$_3$), (B) 2 wt.% ZnCoFe2O4 , (C) 4 wt.% ZnCoFe2w,(D) 6 wt.%ZnCoFe$_2$O$_4$, (E) 8 wt.% ZnCoFe$_2$O$_4$
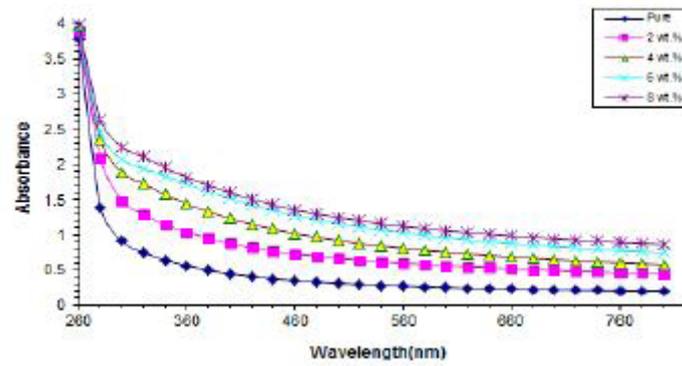
Fig. 4. Variation of absorbance for (PS-In$_2$O$_3$/ ZnCoFe$_2$O$_4$)nanocomposites with wavelength.
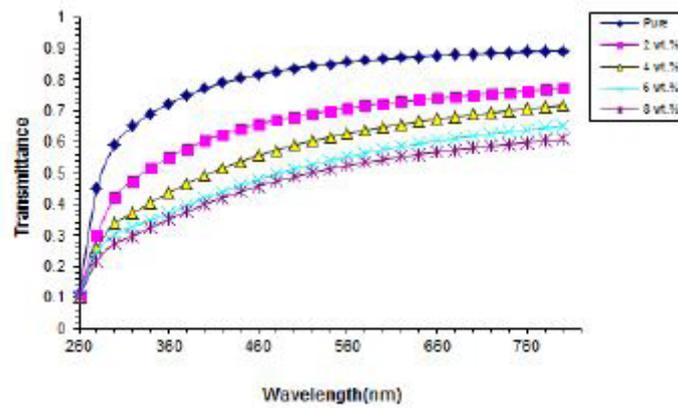
Fig. 5. Variation of transmittance for (PS-In$_2$O$_3$/ ZnCoFe$_2$O$_4$) nanocomposites with wavelength.
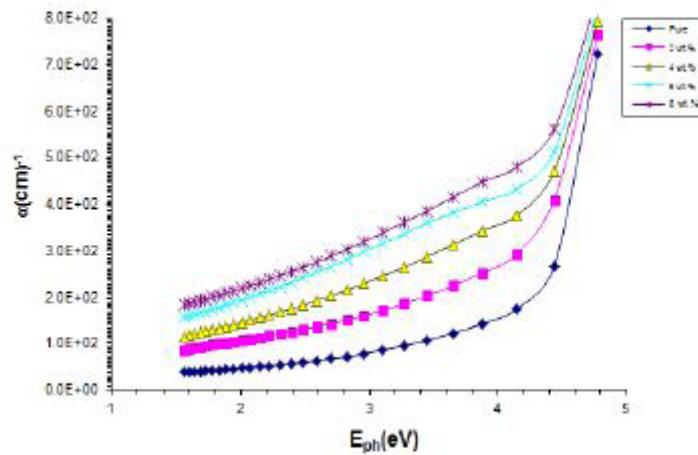
Fig. 6. Variation of absorption coefficient (α) for (PS-In$_2$O$_3$/ ZnCoFe$_2$O$_4$) nanocomposites with photon energy.
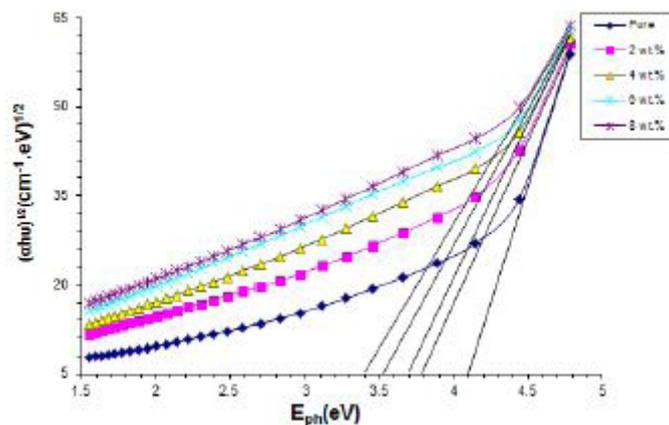
Fig. 7. Variation of $(\alpha h\upsilon)^{1/2}$ for (PS-In$_2$O$_3$/ ZnCoFe$_2$O$_4$) nanocomposites with photon energy.
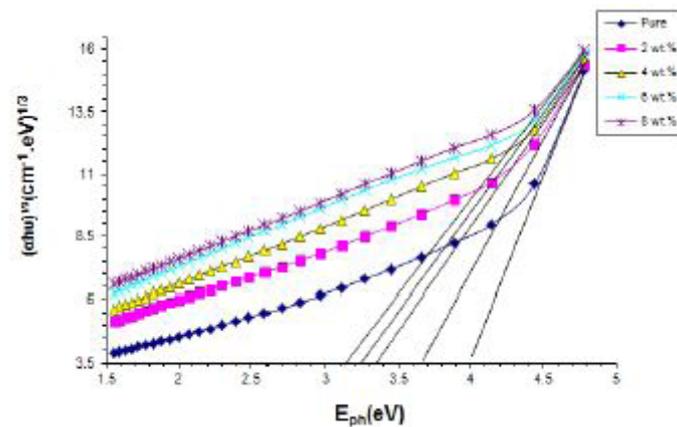
Fig. 8. Variation of $(\alpha h\upsilon)^{1/3}$ for (PS-In$_2$O$_3$/ZnCoFe2O4) nanocomposites with photon energy.
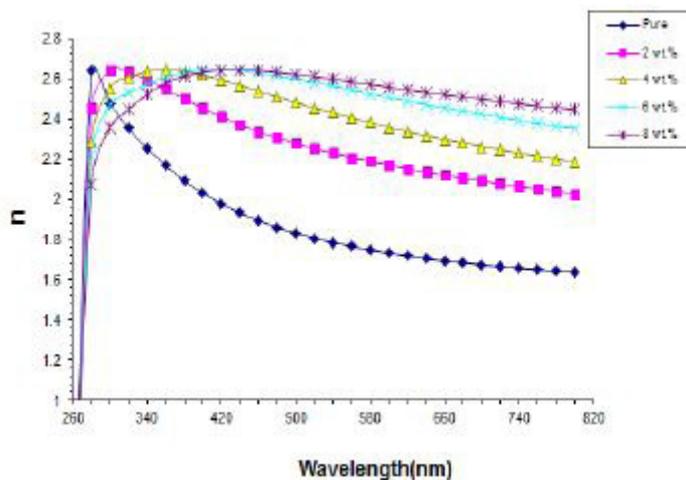
Fig. 9. Variation of refractive index for (PS-In$_2$O$_3$/ ZnCoFe$_2$O$_4$) nanocomposites with wavelength.

Figure 11 shows the real dielectric constant of (PS-In$_2$O$_3$/ ZnCoFe$_2$O$_4$) nanocomposites as a function of the photon energy, while Figure 12 displays the imaginary dielectric constant as a function of the photon energy. Figures 11 and 12 show that the real and imaginary parts of the dielectric constant decrease with an increase in the photon energy. The data on the real and imaginary parts of the dielectric constant provide knowledge concerning the loss factor, which is the ratio between the imaginary and real parts of the dielectric constant. These results indicate that, in the synthesized material, the loss factor increases with a decrease in the photon energy. The real part of the dielectric constant decreases a little-bit rapidly with an increase in the photon energy in the higher energy region but it decreases gradually in the lower one. However, the imaginary part of the dielectric constant decreases gradually with an increase in the photon energy [26]. The optical conductivity is one of the powerful tools for studying the electronic states in materials. The plot of the optical conductivity of (PS-In$_2$O$_3$/ ZnCoFe$_2$O$_4$) nanocomposites versus the photon energy is depicted in Fig. 13. The spectrum indicates that the optical conductivity increases with the photon energy which is due to a decrease in the direct band gap due to the addition of the dopant, the optical conductivity increases. It is very clear from the graph that the optical conductivity increases with the doping of material [27].

Figure 14 shows the variation of dielectric constant with concentrations of nanoparticles for (PS-In$_2$O$_3$/ZnCoFe$_2$O$_4$). nanocomposites, at 100Hz. The dielectric constant of nanocomposites is calculated by using Equation (7). As shown in the figure, the dielectric constant of nanocomposites increases with the increasing of the concentration of ZnCoFe$_2$O$_4$ nanoparticles. This behavior could be interpreted from interfacial polarization inside the nanocomposites in applied alternating electric field and the increasing of the charge carriers [28].

The variation of dielectric constant of nanocomposites with frequency is shown in Fig. 15. The figure shows that dielectric constant decreases with the increasing of frequency of applied field, this may be attributed to the tendencies of dipole in nanocomposites samples for orienting themselves in the directions of the applied electrical fields and decreasing of space charge polarization to the total polarization. These are similar to the results of researchers [29].

Figure 16 shows the variation of the A.C electrical conductivity of (PS-In$_2$O$_3$/ZnCoFe$_2$O$_4$) nanocomposite with frequency. The figure shows that the electrical conductivity increases when increasing the frequency this can be attributed to the interfacial polarization [30].

The variation of electrical conductivity as function of the ZnCoFe$_2$O$_4$ concentration of (PS-In$_2$O$_3$/ZnCoFe$_2$O$_4$) nnocomposites at100Hz is shown in Fig (17). The A.C electrical conductivity increases with an increase in ZnCoFe$_2$O$_4$ nanoparticles which is due to increase of the charge carrier density in polymer matrix [31-36].

Figure 18 shows the variation of the dielectric loss of (PS-In$_2$O$_3$/ZnCoFe$_2$O$_4$) nanocomposites with frequency of applied electric field. The figure shows that the dielectric loss of nanocomposites decreases with increase of frequency of applied electric field, this behavior is attributed to a decrease of the space charge polarization contribution. In addition, the dielectric loss has high value for (PS-In$_2$O$_3$/ZnCoFe$_2$O$_4$) nanocomposites at low frequency and decreases with the increasing of the frequency [37].

The dielectric loss of (PS-In$_2$O$_3$/ZnCoFe$_2$O$_4$) nanocomposites increases with increasing of the concentration of nanoparticles, as shown in Fig. 19. This related to the increases of the charge carriers number. At low concentrations of nanoparticles, it forms clusters shape, when the concentration of nanoparticles reaches to 8 wt.%, the nanoparticles form a continuous network in the nanocomposites.The results are similar to the results of the previous researcher [38].

Conclusions

The absorbance of (polystyrene-indium oxide) increases with increase of the ZnCoFe$_2$O$_4$ nanoparticles concentrations. The (PS-In$_2$O$_3$/ZnCoFe$_2$O$_4$) have higher absorbance at UV region. The energy band gap of (PS-In$_2$O$_3$) nanocomposites decreases with increase in ZnCoFe$_2$O$_4$ nanoparticles concentrations. The absorption coefficient (α), extinction coefficient (k), refractive index (n) and real and imaginary dielectric constants are increasing with increase of the weight percentages of the ZnCoFe$_2$O$_4$ nanoparticles concentrations. The dielectric constant and dielectric loss decreases while the A.C electrical conductivity increases with increase in frequency. The dielectric constant, dielectric loss and A.C electrical conductivity are increased with increasing of the ZnCoFe$_2$O$_4$ wt.% content. From the results, the (PS-In$_2$O$_3$/ZnCoFe$_2$O$_4$) nanocomposites may be used for different optoelectronics applications.
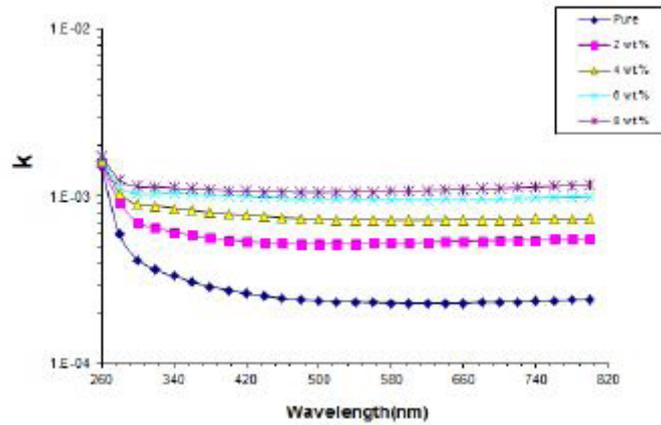
Fig. 10. Variation of extinction coefficient for (PS-In$_2$O$_3$/ ZnCoFe$_2$O$_4$) nanocomposites with wavelength.
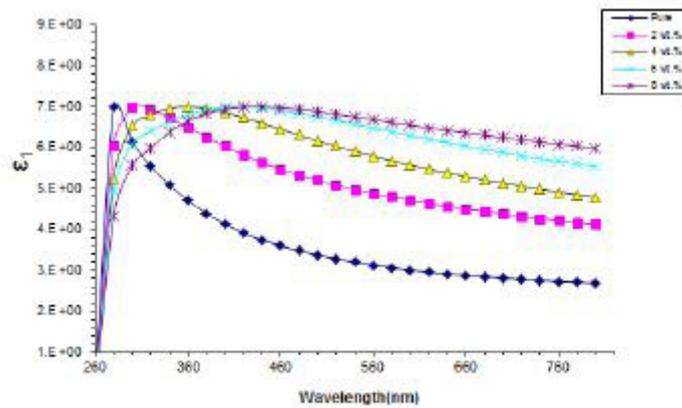
Fig. 11. Variation of real part of dielectric constant for (PS-In$_2$O$_3$/ ZnCoFe$_2$O$_4$) nanocomposites with wavelength
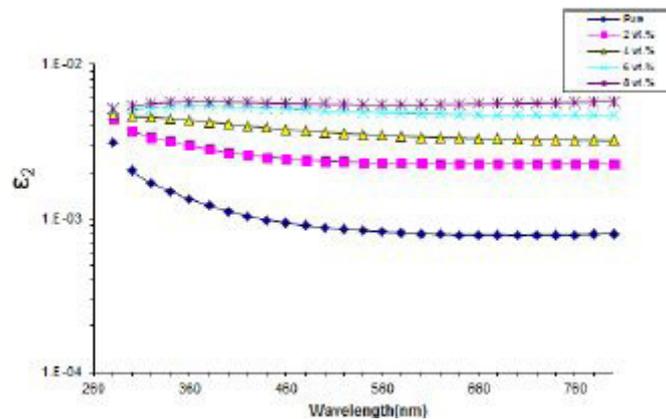
Fig. 12. Variation of imaginary part of dielectric constant for(PS-In$_2$O$_3$/ ZnCoFe$_2$O$_4$) nanocomposites with wavelength .
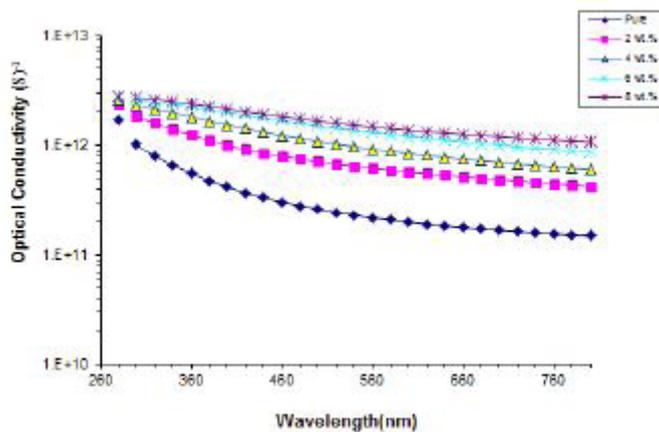
Fig. 13. Variation of optical conductivity for (PS-In$_2$O$_3$/ ZnCoFe$_2$O$_4$)nanocomposites with wavelength
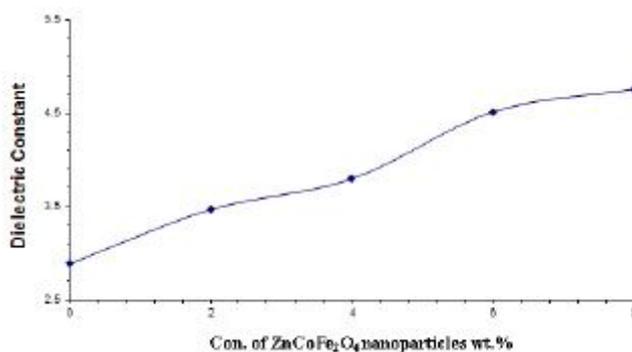
Fig. 14. The variation of dielectric constant with the concentration of filler at 100Hz
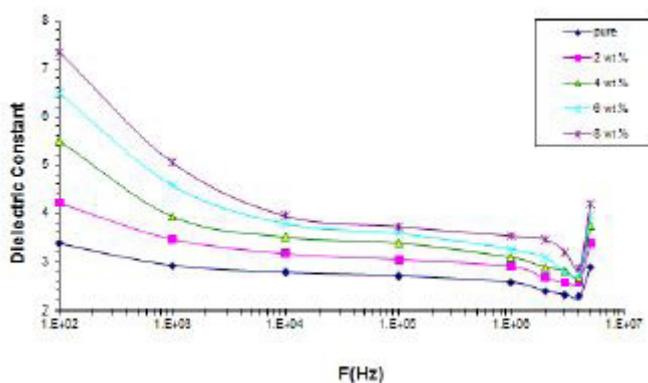
Fig. 15. The variation of dielectric constant with the frequency at room temperature.
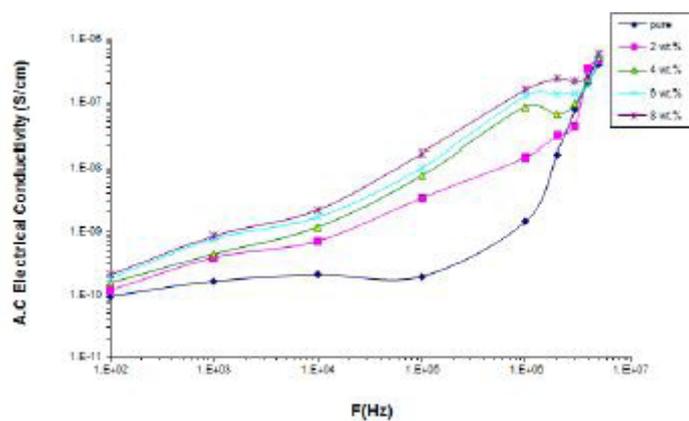
Fig. 16. The variation of electrical conductivity with the frequency at room temperature
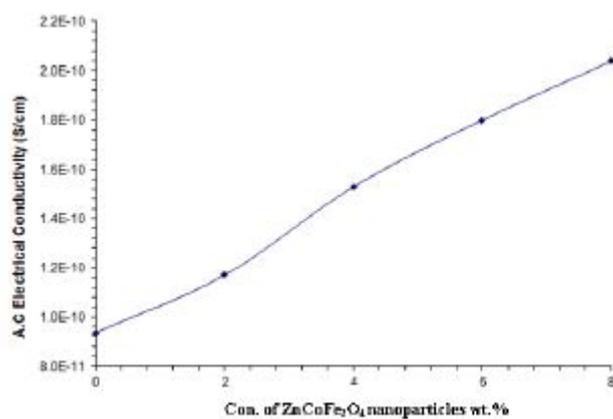
Fig. 17. The variation of A.C electrical conductivity with the concentration of filler at 100Hz.
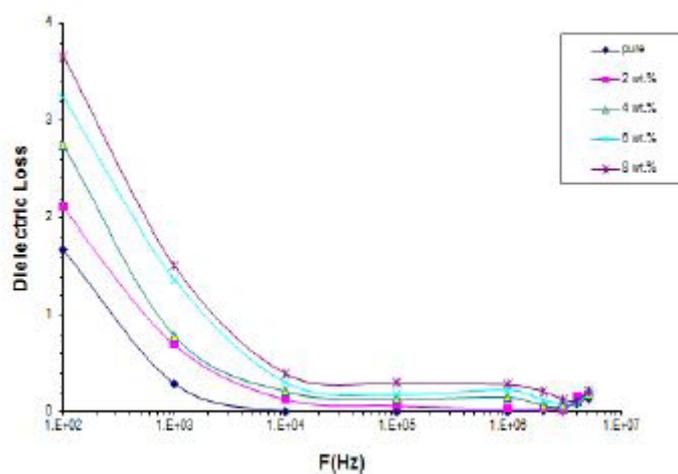
Fig. 18. The variation of dielectric loss with the frequency at room temperature.
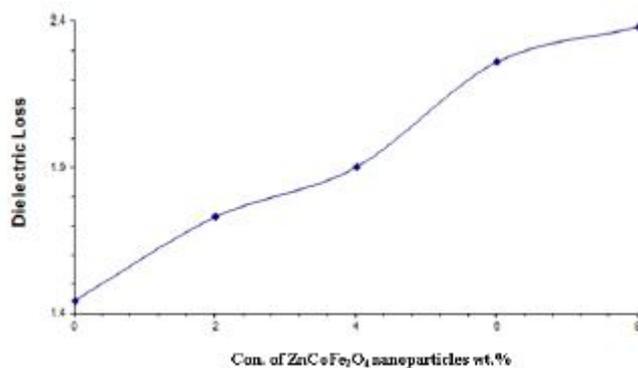
Fig. 19. The variation of dielectric loss with the concentration of filler at 100Hz.

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الخصائص التركيبية، والبصرية، العزلية للمتراكبات (PS- In$_2$O$_3$/ ZnCoFe$_2$O$_4$) النانوية

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تم تحضير المتراكبات (PS-In$_2$O$_3$/ ZnCoFe$_2$O$_4$) النانوية بطريقة صب المحلول. درست الخصائص التركيبية. البصرية. العزلية للمتراكبات (PS-In$_2$O$_3$/ ZnCoFe$_2$O$_4$) النانوية لاستعمالها في التطبيقات البصرية والالكترونية المختلفة. تضمنت الخصائص التركيبية FTIR . و المجهر الضوئي. و SEM . بينت نتائج الخصائص البصرية للمتراكبات (PS-In$_2$O$_3$/ ZnCoFe$_2$O$_4$) النانوية ان الامتصاصية. ومعامل الامتصاص. ومعامل الانكسار. ومعامل الخمود. وثوابت العزل والتوصيلية البصرية للمتراكبات (PS-In$_2$O$_3$) النانوية تزداد مع زيادة تراكيز جسيمات ZnCoFe$_2$O$_4$ النانوية بينما النفاذية وفجوة الطاقة يقلان مع زيادة تراكيز جسيمات ZnCoFe$_2$O$_4$ النانوية. كما ان المتراكبات (PS-In$_2$O$_3$/ ZnCoFe$_2$O$_4$) النانوية تمتلك امتصاصية عالية في المنطقة فوق البنفسجية. اوضحت نتائج الخصائص العزلية ان ثابت العزل. والفقدان العزلي والتوصيلة الكهربائية المتناوبة للمتراكبات (PS-In$_2$O$_3$) النانوية تزداد مع زيادة تراكيز جسيمات ZnCoFe$_2$O$_4$ النانوية. ان ثابت العزل والفقدان العزلي يقلان بينما التوصيلية الكهربائية تزداد مع زيادة التردد.