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Improvement Optical Properties of PVA/ TiO_2 and PVA/ ZnO Nanocomposites

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Abstract

The optical properties of polyvinyl alcohol (PVA) doped TiO_2 and ZnO nanoparticles respectively, were studied. PVA/TiO_2 and PVA/ZnO nanoparticles were prepared by the pulsed laser ablation technique (PLA).The optical properties of PVA/ TiO_2 and PVA/ ZnO nanocomposite solution have been investigated by transmittance data and absorption spectra. The optical band gap (Eg) was determined and the optical absorption spectra showed that a direct transition. The energy gap of PVA/ ZnO nanoparticles have been observed the decreases its value and increasing in the optical conductivity as compared to PVA/ TiO_2.The refractive index (n), extinction coefficient (k) and dielectric constant have been also investigated; it was found that all the above parameters affects by doping.

Key Word: PVA, nanoparticles, composites.

الخلاصة

تم دراسة الخواص البصرية لمحلول بولي فينيل الكحول المشوب بجسيمات اوكسيد الخارصين و اوكسيد التيتانيوم النانوية على التوالي. حيث حضرت المحاليل المشوبة بطريقة الليزر النبضي. تم تشخيص الخواص البصرية بواسطة طيفي النفاذية و الامتصاصية. و حسبت فجوة الطاقة للانتقال المباشر حيث وجد نقصان في فجوة الطاقة لمحلول PVA/ ZnO و زيادة في التوصيلية البصرية بالمقارنة مع المحلول PVA/ TiO_2. تم التحقق من قيم معامل الانكسار و معامل الخمود و ثابت العزل الكهربائي ووجد بان كافة هذه المعلمات قد تأثرت بالتشويب.

Introduction

Organic-inorganic nanocomposite materials (hybrid materials) have been expansively studied in the past few years. Principally, polymer metal hybrid for instance polymer-ZnO -nanoparticles composites is hopeful efficient materials in numerous fields for example optical, electrical, thermal, mechanical, and antimicrobial characteristics. (PVA) could be measured as excellent host material for metal due to its first-rate thermostability, high mechanical strength, chemical resistance, water solubility [1], and doping dependent electrical conductivity along with its consideration amid the supreme polymers as host matrix for ZnO and TiO2 nanoparticles. Among the wide bandgap semiconductors, zinc oxide ZnO is one of the plurality studied direct bandgap (Eg) (extend from 3.3 to 3.4 eV at room temperature) n-type semiconductor material relating to II–VI semiconductor group with unique physical properties for situation comparatively lower growth temperature, great area native substrates, high radiation solidity and big exaction binding energy of 60 meV. The appropriate bandgap (Eg) of ZnO has made it a potential candidate in optoelectronics, photocatalysis and photodetector applications in the ultraviolet wavelength range [2]. Titanium dioxide TiO2 has band gap (Eg) of about 3.2 eV and using in solar energy alteration owing to its high photoactivity. With unique characteristics in-band locating and surface structure, nanosized TiO2 gives, in relating to photocatalysis, an extent of different possible applications, for instance, a smart matter with self-cleaning and super-hydrophilic characteristics [3].In the present work, ZnO and TiO_2 nanoparticles have been synthesized by the pulsed laser ablation technique (PLA). The samples were characterized by UV–

visible spectroscopy. Also, we had studied the optical characteristics of PVA/ZnO and PVA/TiO_2 nanocomposites based on ZnO and TiO_2 nanoparticles as inorganic filler material and (PVA) like the chief matrix

Materials and Methods

The essential experimental setup has been portrayed already and is appeared in Figure 1.

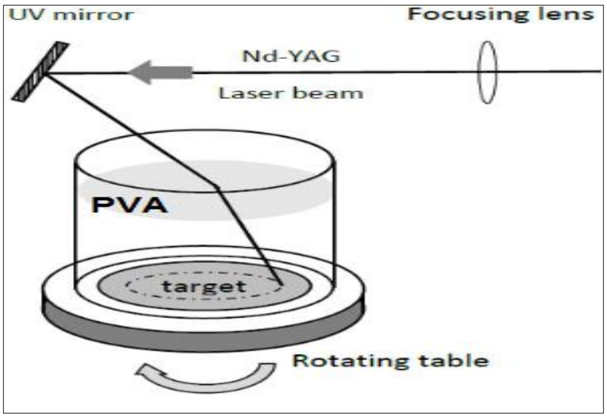

Figure 1: Experimental setup.

The compartment with the aqueous solution of (PVA) is a glass cylinder with a thin metallic target located at the underside. High purity (99%) thin discs of Zn and Ti with a diameter of 31 mm are used. The total system rotates gradually around its vertical axis throughout the ablation process in arrange to keep away from the growth of deep holes in the target, and thus preserve the same surface conditions for each laser pulse. The (PVA) solution was accomplished by solving the comparable amount of the polymer, acquired commercially, in the equal volume of deionized water. The source of radiation was a Nd: YAG polarized laser (Quantel, Brilliant B) working in its third harmonic (THG) ¸ (λ= 335 nm), emitting pulses of time of 8 ns at a frequency of 10 Hz. The beam spot on the target surface had a diameter of 0.5 mm and the laser fluence was 17 J/cm^2 per pulse. The laser energy was monitored with an energy detector (Gentec, Model ED-200) and could be varied by appropriately delaying the Q-Switch system of the laser's optical cavity. The extent of the ablation progression, ablation time (t), for together metallic targets was amid 20 min and 40min, depending on the possible concentration of metallic particles [4].

Results and Discussion

The optical transmission spectrum for (PVA) polymer and nano-oxide metals doped (PVA) polymer solutions versus of wavelength in the range of (200-900) nm are shown in Figure 2. The transmittance spectrum in the range of 210 to 248 nm is sharp decrease observed in due to the presence of the (PVA) polymer band gap [5]. That its intensity continuously decreasing with doping PVA/ TiO_2 and PVA / ZnO polymer solutions, respectively. This figure clearly indicates that after adding nano-oxide metals in (PVA) polymer shifted the spectrum towards low wave length [3].

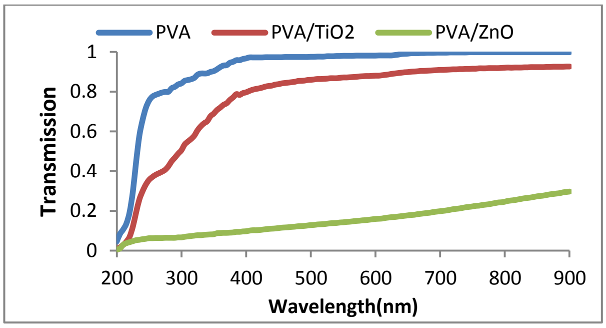

Figure 2: Optical Transmittance of (PVA) polymer, PVA/ TiO_2 and PVA/ ZnO polymer solutions.

The behavior of absorbance curves of all samples are shown in Figure 3, its performance is reverse to that of the transmission spectrum. Pure (PVA) is a colorless polymer without any obvious absorption in the visible range. The absorption spectrum of pure (PVA) solution has a broad absorption band around (264–294) nm. These bands are assigned to the electronic transitions $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$, respectively [1]. ZnO presents an absorption band around 363nm in the PVA/ ZnO [6]. And PVA/TiO furthermore absorbance band around 350 nm, conformable to TiO_2 [3]. The absorption edge for nano-oxide metals doped (PVA) polymer shifts towards lower energies (red shift) in comparing with the pure (PVA) at room temperature. The mechanism of UV absorption in such materials comprises the utilization of photon energy to excite electrons from the valence band to conduction band [3].

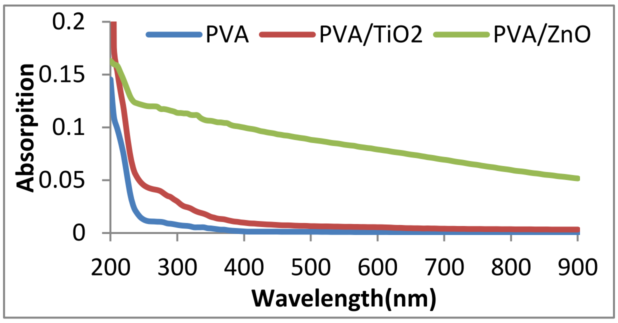

Figure 3: Optical Absorption spectra of (PVA) polymer, PVA/ TiO_2 and PVA/ ZnO polymer solutions.

The intensity of energy propagation throughout an absorbing identical midst is represented by lamberts law, which states that the intensity falls off exponentially with distance [7]:

$$I= I_o e^{-\alpha x} \quad (1)$$

(α): indicate to the absorption coefficient (cm^{-1}) and (x) indicate to the thickness of sample (cm).

$$\alpha x = 2.303 \log \frac{I}{I_0} \quad (2)$$

The expression (log I / I_O) has been placed equalize to the quantity absorbance (A):

$$\alpha = 2.303 \log \frac{A}{x} \quad (3)$$

In Figure 4: demonstrate an increase in the absorption coefficient with increasing wavelength was observed for sample. This possibly ascribed to the electronic transition from the bonding molecular orbit to nonbonding molecular orbit [8].

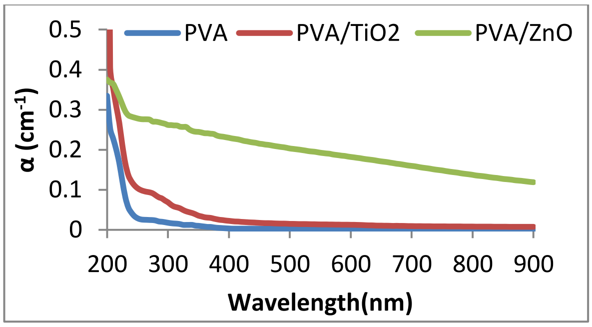

Figure 4: Optical absorption coefficient α as wavelength of (PVA) polymer, PVA/ TiO_2 and PVA/ ZnO polymer solutions.

The energy gap is indispensable to expand the electronic band structure of film material. It can be resolute from a straight line, obtained by plotting (αhν)1/r as a function of photon energy (hν) given away in Figure 5.This fellow of Equation Tacue where:

$$\alpha h\nu = B(h\nu - E_g)^P \quad (4)$$

In this Equation, (B) is constantly conditioned onto the material and the type of optical transition (direct or indirect), and the index (P) is concerning to the distribution of the density of states is an index which be assuming the qualities 1/2, 3/2, 2 and 3 count on the nature of electronic transition. The optical energy gap of pure (PVA) sample is equivalent to 5.4 eV [10].The extracted energy gap of sample are 5.2 eV and 4.8 eV for nano-oxide metals TiO_2 and ZnO respectively.

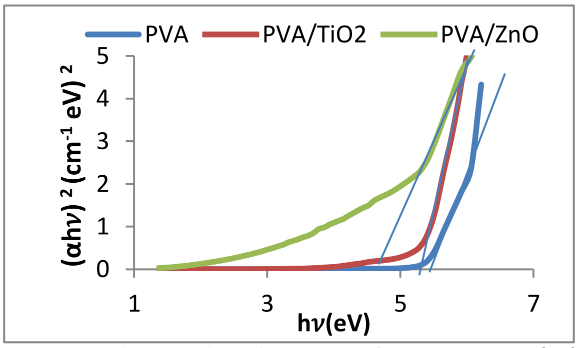

Figure 5: Plot of (αhν)1/p against photon energy of of (PVA) polymer, PVA/ TiO_2 and PVA/ ZnO polymer solutions.

The doping of the nano-oxide metals, affects the band gap of the involved polymer structure. This additionally affirms the presence of the inorganic fillers inside the host. The distinction of the computed values of optical band gap reflects the role of configuration of nano-oxide metals in altering the electronic structure of the (PVA) matrix. This diminution due to the induction of new levels in the band gap, lead up to simplify the transit of electrons from the valence band into these topical levels to the conduction band, consequently the conductivity increment and the band gap diminution [1]. Reflectance (R) of the films could be calculated using the subsequent relation [9]:

$$R + A + T = 1 \quad (5)$$

Where: T represent is the transmittance. Plot of reflectance (R) against wavelength are displayed in Fig. (6). It is clear that the reflectance (R) of the (PVA) solution increases slowly with increasing of wavelength within the range (200-900) nm. After doping by nano-oxide metals the reflectance for all samples is increment [10].

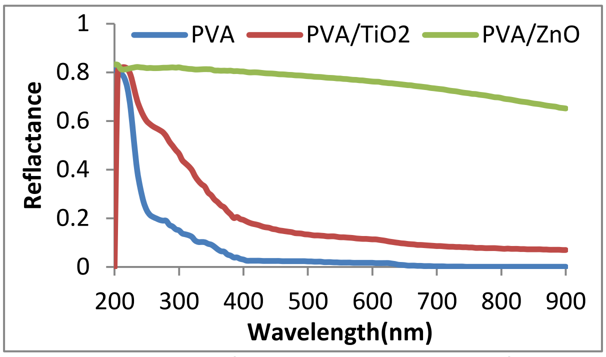

Figure 6: Optical Reflectance as wavelength of (PVA) polymer, PVA/ TiO_2 and PVA/ ZnO polymer solutions.

Refractive index (n) is one of the essential characteristics for an optical material for the cause that it is widely concerning to the electronic polarization of ions and the topical field inside materials. The complex constant refractive index (n) of the intended samples has been considered from the (R) using the next Equation [11]:

$$n = \sqrt{\frac{4R}{(R-1)^2} - R^2} - \frac{(R+1)}{(R-1)} \quad (6)$$

Figure 7: represent variation of the refractive index (n) with wavelength for the sample. That the refractive index of PVA/TiO_2 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 [2].

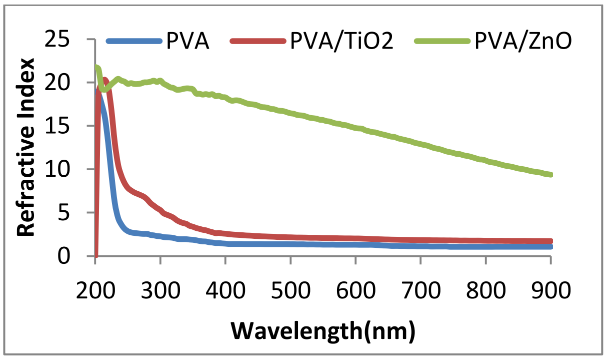

Figure 7: Dispersion of refractive index (*n*) of (PVA) polymer, PVA/ TiO_2 and PVA/ ZnO polymer solutions.

The extinction coefficient (k) describes differentiate of the material with respect to the light of a given wavelength and shows the absorption differences while the electromagnetic wave propagates through the material. The extinction coefficient (k) is absorption coefficient related according to the subsequent Equation:-

$$K = \frac{\alpha\lambda}{4\pi} \quad (7)$$

(λ): indicate to the wavelength. Figure 8: display the relationship between the extinction coefficients (k) as a function of wavelength for whole samples. The extinction coefficient of the doped PVA/ TiO_2 and PVA/ ZnO samples have a peak at λ= 270 nm, which decreases with increasing wavelength. The extinction coefficient (k) increases caused by surface plasmon absorption in doped samples.

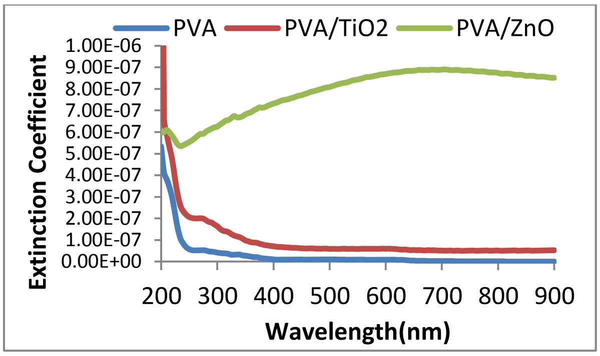

Figure 8: Dispersion of extinction coefficient (*k*) with wavelength of (PVA) polymer, PVA/ TiO_2 and PVA/ ZnO polymer solutions.

The Dielectric Constants is concluded that the variation of the real (ε_r) and imaginary ($\boldsymbol{\varepsilon_i}$) parts. Figure 9: demonstrate the Dielectric real part is depending on the refractive index for the reason that the extinction coefficient result is very small and could be deserted consistent with Equation:

$$\varepsilon_r = n^2 - K^2 \qquad (8)$$

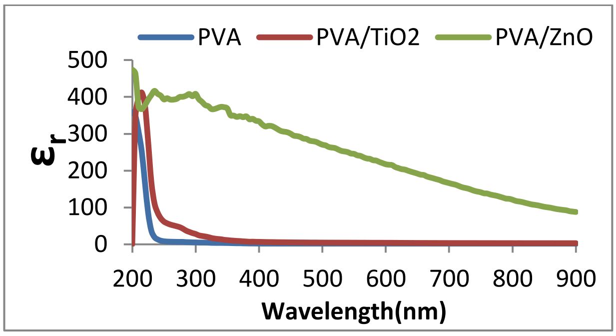

Figure 9: Real part of dielectric constant with wavelength of (PVA) polymer, PVA/ TiO_2 and PVA/ ZnO polymer solutions.

After doping the real part of dielectric constant ($\boldsymbol{\varepsilon_r}$) was increased in PVA/ ZnO more than PVA/ TiO_2, these results may be accredited to regarding real part of dielectric constant with refractive index. As the dielectric imaginary part ($\boldsymbol{\varepsilon_i}$) computed from Equation:-

$$\boldsymbol{\varepsilon_i} = 2\,nK \qquad (9)$$

Figure 10: illustrate the imaginary part of dielectric constant ($\boldsymbol{\varepsilon_i}$) was increased in PVA/ ZnO more than PVA/ TiO_2 which indicates that the samples have the no same structure. So, modify in the doping gave vary in the chemical composition of the polymer.

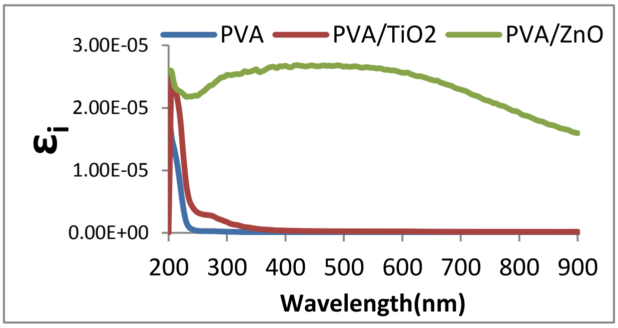

Fig. 10: imaginary part of dielectric constant with wavelength of (PVA) polymer, PVA/ TiO_2 and PVA/ ZnO polymer solutions.

Conclusion

Preparation of ZnO and TiO2 nanoparticles by laser ablation technique at fluencies of laser pulse in deionizer water is investigated. The nanocomposite PVA/ZnO and PVA/TiO_2 have the highest absorption, lowest energy gap, and the highest optical conductivity. The direct band gap of PVA/ZnO was found to be 4.8 eV though; the direct band gap energy of PVA/TiO_2 nanocomposite was 5.2 eV. Refractive index (n) and dielectric constant are increase with the dopant ZnO and TiO_2 nanoparticles.

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