Optical properties for prepared polyvinyl alcohol/ polyaniline/ ZnO nanocomposites

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Abstract
The optical energy gap and optical constants such as the reflective index, dielectric constant have been evaluated due to The optical transmission and UV-VIS absorption spectra have been recorded in the wavelength (200 - 1100 nm) for PVA/PANI polymer blends and PVA/PANI/ZnO nanocomposites with different concentrations of ZnO (0.02, 0.05, 0.07, 0.1 and 0.2) wt %. The results indicate that the materials have allowed direct transition. The reflection index and dielectric constant are increase with wavelength.

Key words
Polyvinyl alcohol, polyaniline, ZnO, nano composite, optical properties.

Introduction
The conducting polymer has emerged as a new class of materials because of their unique electrical, optical and chemical properties. By proper doping the conductivity of these materials can be varied from semiconducting to metallic regime. Polyaniline has been studied extensively due to its ease of synthesis in aqueous media. Due to its environmental stability, and special electrical and optical properties [1, 2]. During the last decade there has widespread in conducting polymer. Polyaniline (PANI) is one of the most useful conducting polymers due to their simple synthesis, good environmental stability. It also has wide range of electrical properties which can be easily controlled by changing its oxidation and protonation states [3, 4]. However, major problems relating to successful utilization of the PANI are poor mechanical property and low solubility in aqueous and organic solvent. Improvement of polyaniline properties can be achieved either by forming composites and nano composites of aniline, or blending with...
commercially available polymers or inorganic material which offer better mechanical and optical properties, stability and process ability of the PANI [1, 5]. With the advent of advancement in the field of nano science and nanotechnology in the recent years, nanocomposites of different metals and conducting polymers or metal oxide-polymer have become an important class of materials. These materials find potential application as sensors, UV detectors, catalysts, biosensors, and piezoelectric materials [6, 7]. The nanocomposites differ from pure polymers and inorganic metal oxide nanoparticles in some physical and chemical properties. Among various metal oxide nanoparticles, ZnO is a key technological and multifunctional inorganic material with unaccountable application such as sensors, optical, electronic magnetic, catalytic and detection of biological molecules [8, 9]. These unique nanostructures unambiguously demonstrate that ZnO has the richest family of nanostructure among all materials both in structure and in properties. It has a direct band gap of 3.37 ev and high exaction binding energy of 60mev at room temperature [10, 11]. Polyvinyl alcohol is an important water-soluble transparent polymer, and is extensively used in industries due to the excellent chemical and physical properties, non-toxicity, good chemical resistance, good film formation capacity; biodegradability and high crystal modulus [12]. Several reports are dealing with the preparation of nanocomposites materials such as PVA/PANI/Ag [13], PVA/PANI [14], and ZnO/PANI [15].

The aim of this work
Nanocomposites are of great interest in recent years because they are considered to be novel functional materials with a wide range of potential application in bio and chemical sensors, electronics, catalysis and optics. The goal of this project was prepared PVA/PANI/ZnO nano composite and then calculation the optical energy gap of different concentration of ZnO nano particle and finally determined optical constants such as the reflective index, dielectric constant.

Basic relations
The complex refractive index N is given by:
\[ N = n - ik \]  
(1)
where, \( n \) is the real refractive index, and extinction \( k \) which is the imaginary part of \( N \) and can be obtained from the relation
\[ k = \alpha \lambda / 4\pi \]  
(2)
where, \( \alpha \) is the absorption coefficient which is the decrement ratio of incident radiation relative to unit length in the direction of wave propagation inside the medium. \( \lambda \) is wavelength. The reflectance part \( R \) of incident electromagnetic plane wave can be obtained when the transmittance \( T \) and the absorbance \( A \) part are known since
\[ R = 1 - (A + T) \]  
(3)
For normal incident of plane electromagnetic wave the reflectance is given by the Eq. (4)
\[ R = \frac{(1 + n)^2 + k^2}{(1 - n)^2 + k^2} \]  
(4)
which leads to
\[ n = \frac{(4R/(1-R)^2)^{1/2} - k}{2R(1-R)^{1/2}} - (R+1/R-1) \]  
(5)
Thus n can be calculated when the reflectance \( R \) and \( k \) values are known. The transmittance part of incident light is depending on \( \alpha \) through the following equation [16].
\[ I = I_0 \exp^{-\alpha t} \]  
(6)
The dielectric constant $\varepsilon$ which represent the responsively of electron in matter to be the incident electromagnetic field, depends on frequency. Its real part $\varepsilon_1$ which represent polarization term and its imaginary part $\varepsilon_2$ can be calculated from Eqs. (7) and (8) respectively [17].

$$\varepsilon_1 = n^2 - k^2$$

(7)

$$\varepsilon_2 = 2nk$$

(8)

Put the empirical equation between the optical energy gap and energy of incident photon which is

$$(\alpha h\nu) = B (h\nu - E_{opt})^r$$

where $A$ is a constant, $h\nu$ is the energy of incident photon, which can be calculated using the following equation

$$h\nu = \frac{1240}{\lambda_{nm}}$$

(10)

and $r$ is the order of the optical transition depending on the nature of electronic transition.

**Experimental work**

1. **Raw material**
   The raw material used to prepare the samples were: Aniline hydrochloric ($C_6H_5 NH_2.HCl$) supplied by Hopkin and Williams company and purity 99.99 %, Ammonium persulphate ($NH_4)_2S_2O_5$ supplied by BDH company and purity 99.5%, Hydrochloric Acid (HCl) supplied by BDH-England company and purity 37 %, Zinc oxide (ZnO) supplied by Hopkin and Williams company and purity 99.99%, Acetic acid ($CH_3.COOH$) supplied by BDH company and purity 99.8%, Sodium hydrochside (NaOH)supplied by Fluka-Garantie company and purity 97%, polyvinyl alcohol (PVA) supplied by BDH company and purity 99.9 %.

2. **Preparation of ZnO nanoparticles**
   The micro particles ZnO powder 1 g was dissolved in 100 ml of 0.17 ml acetic acid and the solution was sonicated for 30 minutes in other to obtain zn$^{+2}$ cations. Measurements in the water $pH=7.1$. Then, 50 ml of 1 M Sodium hydrochside NaOH was added dropwise with magnetic stirring until the attained $pH=10$. The solution was heated in water bath at (45-80 °C) for about 4 hours. It was filtered nano paper and washed with distilled water two times and then dried in an oven 55 °C for 3hour. The ZnO powder was examined by atomic force microscopy.

3. **Preparation of PVA/PANI/ZnO nanocomposites**
   The 6.5 g of PVA was dissolvedin100ml 0.1 M of HCl. The mixture was heated in water bath at 70 °C for about 1 hour. To allow polymer to dissolve completely to yield clear solution and then cooled at room temperature for half an hour. The 1.3 g aniline hydrochloride added to mixture at 0 °C. 10ml of ammonium persulphate was added to the mixture. The mixture allowed to complete the reaction for 8 hour under constant stirring. The blue green mixture was prepared. A glass plate of 10cm in diameter was washed with hot water and then cleaned with acetone and draw 30ml of the mixture to casting onto a glass, then dried at room temperature for 72 hour. In the same way, different amount of ZnO Nano (0.02, 0.05, 0.07, 0.1 and 0.2 wt %) g were added to the mixture as shown in Fig. 1.
A UV-vis spectrometer was used to study the transmission and absorption spectra of the samples at wavelength range 200-1100 nm. The absorption was used to determine the optical energy gap and optical constant.

**Results and discussion**

1. **AFM analysis of ZnO**
   Atomic Force Microscopy (AFM) or surface morphology analysis has been used to characterize the external surface roughness which has been regarded as one of the most important surface properties, and particle size of the ZnO nanoparticle. The results of the surface morphology analysis of the ZnO nano are shown in 3D view in Fig. 2. AFM images for all applied layer were estimated in addition to the statically determining the particles size distribution.

**Fig. 2:** (a) and (b) AFM image of synthesized ZnO Nanoparticle in 2D and 3D view.

**Fig. 3:** The granularity cumulating distribution for ZnO nanoparticle.
2. The optical energy gap

The optical energy gaps (Eg) for PVA/PANI blends and PVA/PANI/ZnO nano composites have been determined. Table 1 states the optical energy gap for PVA/PANI blends and PVA/PANI/ZnO nanocomposites. Fig. 4(a, b, c, d, e, f) shows the plot of (αhν)² versus hν with different ZnO concentration. The plot is linear indicating the direct band gap nature of the polymer composites. Extrapolation of the line to the hν axis gives the band gap. The reduction in the optical band is probably due to the modification of the polymer structure. The optical energy gap increases with increasing of ZnO concentration this is due the increase of the density of localized state in Eg.

3. Index of refraction

The variation of the index of refraction as a function of the wavelength for PVA/PANI/ZnO nano composites has been determined. Fig. 5 shows the variation of index refraction as function of wavelength. It was found that (n) change with (λ) in the range (350-950) nm. It is shown that the index of refraction is increased in the PVA/PANI/ZnO nano composites. The increasing in index of refraction can be attributed to the affect ZnO nanoparticles which may increase the cross linking degree between polymer chains, and hence increasing the density in the Nano composite [18].

4. Real dielectric constant

The real dielectric constant (ε_r) which depend on the frequency of the electromagnetic wave. The variation of ε_r versus wavelength in the range (200-1000) nm for PVA/PANI/ZnO hybrid nanocomposites has been determined. Fig. 6 shows the variation of ε_r with the increase of the wavelength of the incident radiation is due to the change of reflectance and absorbance [19]. The behavior of ε_r is similar to that of the refractive index because of the smaller value of k² compared with n².

<table>
<thead>
<tr>
<th>Specimen</th>
<th>E_g (eV)</th>
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<tbody>
<tr>
<td>PVA/PANI</td>
<td>2.5</td>
</tr>
<tr>
<td>0.02</td>
<td>2.49</td>
</tr>
<tr>
<td>0.05</td>
<td>2.51</td>
</tr>
<tr>
<td>0.07</td>
<td>2.46</td>
</tr>
<tr>
<td>0.1</td>
<td>2.53</td>
</tr>
<tr>
<td>0.2</td>
<td>2.52</td>
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Table 1: The types of specimens and its optical energy gap.
Fig. 4 (a, b, c, d): Determination the optical energy gap for PVA/PANI and PVA/PANI/ZnO nanocomposites.
Fig. 4 (e and f): Determination the optical energy gap for PVA/PANI and PVA/PANI/ZnO nanocomposites.

Fig. 5: Variation of the index of refraction with the wavelength for PVA/PANI/ZnO nanocomposites.
Fig. 6: The real dielectric constant with the wavelength for PVA/PANI/ZnO nanocomposites.

Conclusions

PVA/PANI/ZnO hybrid nanocomposites were prepared in different concentration of ZnO nano. Measurement of optical energy gap and optical parameters such as refractive index and dielectric constants are strongly depending on the light wavelength. Was notice that all samples have allowed direct optical energy gap.

References