RESEARCH ARTICLE

Preparation and Characterization of ZnO Nanorods and Analysis of the Effect of Photo Irradiation on the Physical Properties of Polymer Nano Composites

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ABSTRACT

This study investigatedthe photodegradation of polyvinyl alcohol (PVA) based nanocomposites with different weight ratios of Zinc oxide (ZnO) nanorods prepared hydrothermally.Scanning electron microscopy, atomic force microscopy,and X-ray diffraction analysis are utilized to study the morphological characteristics and size of ZnO nanorods were studied via, where, films were made by mixing with a polymer solution at different weight percentages of1%, 2%, 3%, 4%, and 5% and a thickness of 70±5 μm. The as-prepared samples were exposed to photoradiation at a wavelength of 356 nm at different time points. The photodegradation of the prepared films with and without additives were assessed with Fourier transforminfrared spectroscopy and ultraviolet-visible spectroscopy to monitor the changes in hydroxyl coefficient, carbonyl coefficient and dissociation constant (K_d), which was used to illustrate the effect of ZnO nanorod addition. The prepared ZnO nanorods showeda wide range of applications inPVAphotodegradation.In addition to the mean chain scission and degradation degree, the molecular weight and chain scission decreased in the presence of the ZnO nanorods, and this observation was consistent with that described in other studies.

Keywords: Zinc oxide, Polymer, Photodegradation, Polyvinyl alcohol.

INTRODUCTION

Nanotechnology involves the preparation of nanoscale materials [1].ZnO is one of the versatile and technologically important semiconducting materials that exhibit a direct and wide band gap (3.3eV). It has been extensively explored because of its electrical, and piezoelectric [2-6], chemical [7], optical [8], and magnetic [9] properties. ZnO has also

been recognized as an important material because of its wide applications, such as catalysts [10],semiconductors [11], gas sensors [12], ultraviolet (UV)-shielding materials [13], piezoelectric devices [14], photochemicals [15],polymer coatings [16],and antibacterial agents [17].ZnO is a multifunctional material,as such,studies on ZnOnanoparticleshave focused on their preparation through various methods, including solid-state reaction [9], microwave-assisted method [18],flame spray pyrolysis [19],sol-gel method [20],hydrothermal method [21],sonochemical route [22],and mechanochemical methods [23].ZnO films have been prepared via several techniques, such as electrochemical deposition [24], chemical vapor deposition (CVD) [25], hydrothermal or solvothermal methods [26],spay pyrolysis technique [27],electrodeposition [28], chemical bath deposition [29], sputtering [30], metal-organic CVD [31], evaporation[32], molecular beam epitaxy, atomic layer epitaxy [33, 34], and pulsedlaser deposition [35].According to the importance of polyvinyl alcohol (PVA) as water-soluble transparent polymer extensively, it has been used in industries ,as well as , it is considered as an excellent physical and chemical properties, good chemical resistance, non-toxicity, biodegradability, good film formation capacity, and high crystal modulus. The fact is that, PVA is utilized in as ahydrolyze form with 85% hydrolysis degree [36]. Indeed, it is a polymer which has various pharmaceutical, biomedical, and technological applications [37]. For example, it can be applied to coat ZnO [38], Ag [39], and titanium dioxide [40]. In this study, a new type of ZnO nanorods was prepared by using hydrothermal method and used as a UV photoinducer for PVA degradation.

MATERIALS AND METHODS

Chemicals

It is important to note that the deionized distilled water was involved to make all the solutions. In addition, the standard metal ion solution, Zinc nitrate hexahydrate [$Zn(NO_3)_2{\cdot}6H_2O$], was commercially obtained from Aldrich. Anyhow, the analytical grade of this study was based on all of the chemicals and reagents.

Growth Layer Preparation

In this process, 0.5 g of zinc nitrate, 5 g of hexamethylenetetramine, and 100 ml of deionized water were placed in a beaker and mixed using a magnetic stirrer for 1 hrs. At room temperature. The prepared growth layer solution was placed in another beaker where seed-coated substrates were immersed. The resulting mixture was kept in an oven at 90°C for 3 hrs. Slides were taken out from the beaker and rinsed with water to separate residuals. The substrates were subjected to annealing at 500°C for 1 hrs. The ZnO nanorods were prepared at pH values of 7.5.

Sample

The first step of preparing the specimens which represented by films was based on dissolving PVA with a constant concentration of 10% w/v of the polymer solution, where, this polymer dissolved in deionized waterat 40 ^{o}C.This stock solution was mixed with 1ml of the used ZnO nanorods as the stabilizer of weight ratios (1% , 2% , 3% , 4% , and 5%)and casted using glass flakes to form PVA films with a thickness of70 ±5µm.The films were then cut into parts of 1.5 cmx3cm for measurements.

The Samples Irradiation

An accelerated irradiator, assembled to the one in a laboratory, supplied with a power of 125 Watts and a light filter with a length of 356 nm for 16 hrs. was used to irradiate the specimens. Under many circumstances, the samples were located in vertical and parallel orientations subjected to the lamp to make sure that the light fell on vertically over the films tube. Therefore, the films positions periodically were changed to ensure the light coincidence. Polymeric films with and without PVA were irradiatedwith UV at different periods, ranging from4 hrs. to 16 hrs.(Table 2).

The Studies of Spectral

Variations of the polymeric films were examined through fouriertransformer infrared (FT-IR) spectroscopy, measurementof the growth level of the hydroxyl group (I_{OH}) and carbonyl group (I_{CO}) as means of PVA degradation behavior under light of fact, and UV measurements to determine the absorbed band intensities calculated before and after irradiation was administered [41].

Morphological analysis

Morphological analysis is mainly performed to describe the state of degradation. In this process, molecules become reflected on a polymer surface because of the effect of high-energy light (UV), thereby changing the color of the surface or the color of the whole polymer this phenomenon reflects the loss of the physical, andelectrical,mechanical properties, thereby causing softness and pitting on external surfaces [42].

Material Characterization

X-ray diffraction (XRD) with CuKα radiation (λ = 1.5418 Å) was conducted to investigate the phase composition and crystalline properties of the sample.The quality of surface morphology and the quantity of elemental composition were analyzed through scanning electron microscopy (SEM) and atomic force microscopy (AFM).The chemical functional groups of the sample that did not undergo annealing were characterized through FT-IR.

RESULTS AND DISCUSSION

Structural Characterization

Fig. 1 shows the XRD pattern of the sample powder compared with that of ICDD no 01-076-0704 as the standard reference of the ZnO phase. The diffraction peaks indexed to (100), (002), (101), (102), (110), (103), and (112) planes were observed, confirming the ZnO hexagonal wurtzite structure. The scanned 2θ axis of the XRD graph, showed that three strong peaks at 31.73º, 34.38º, and 36.20º were attributed to (100), (002), and (101) ZnO planes, respectively (Table 1).

SEM Measurements

We identified the morphological characteristic and structures of the particles and measured the grain size of the samples prepared hydrothermally.Fig.2shows the SEM micrograph of the ZnO nanorodssynthesized hydrothermally at different magnifications.

AFM Measurements

AFM is essential for studying the morphological characteristics of ZnO nanorods. Quantitative information from individual ZnO can be generated through the software-based image processing of AFM data. Individual particles determination was based on the size information (length, width, and height) and other physical properties (morphological characteristics and surface texture).AFM can be functioned in liquid or gas media, therefore, this capability is considered as highly advantageous for the characterization of ZnO. In our study, AFM was applied to analyze the morphological characteristics and size of the particles and the topography of the ZnO surface structure. As noticed in Fig. 3, the AFM images presenting the two - and three-dimensional views of the surface structure of the ZnO nanorods, which were grown hydrothermally. The images indicated that the ZnO nanorods had small particles size distribution with a diameter of 52.16 nm

FT-IR Spectroscopy

The FT-IR spectra of all of the samples, palletized with KBr were recorded from 400 $cm^{-1}$to 4000 cm^{-1}(Fig. 5). The spectra consisted of seven vibrational bands. The transmittance spectrum of the as-deposited ZnO film showed the main absorption bands centered at 1222.79 and 3431.13cm^{-1}, and several small features were located at 528.46, 867.91, 1504.37, 1635.52, 2329.85, 2887.24 and 3014.53 cm^{-1}. The absorption bands that centered at 484.10and 528.46 cm^{-1} could be associated with ZnO bond vibration, compared with that of the standard FT-IR of the ZnO powder. A strong peak at 3431.13 $cm^{-1}$was observed in the as-deposited ZnO film, which is sensitive to the stretching vibrations of –OH [28]. The other absorption bands at 2887.24, 1635.52, and 867.91 cm^{-1} can be related to N–H and, N–O bonds [30].

UV–vis Spectroscopy

The process of characterizing the optical absorption properties of the ZnO nanorods involved conducting UV–vis spectroscopy, where, the UV–vis absorption spectra of the samples was achieved at a room temperature [43] and were recorded in the wavelength range of 200 –800nm through a Shimadzu UV 3600 UV–vis–NIR spectrometer (Shimadzu Corporation, Kyoto, Japan).The photodegradation of the PVA films at different concentrations was studied through UV–vis spectroscopy, by exposing the PVA films to UV radiation for a given period to change the color of the filmsto yellowish. This change indicated the photolysis of the polymer (Table 2) . Through observing the absorption spectrum in terms of time irradiation, these films varied and reflected when calculating the rate of decomposition (K_d) via recording the absorption spectrum of UV and during the process at different times of irradiation. We observed that the absorption spectrum of these films varied in terms of the time of irradiation as shown in Fig.6.

The rate of change in the absorption spectrum with respect to the time of irradiation was .dependent on the ZnO nanorod additive concentration, which increasedas the ZnO nanorod concentration increased due to the increase in the active substance content (Figs.7–11). To calculate the rate constant ofthe photolysis of polymeric films in the presence of the ZnO nanorod additive, where,the relationship between the time of irradiation and the logarithm of absorption (A_∞-A_t) was drown as shown in (Figs. 12–16).The slope apparently shown as a straight line, indicating that the interaction light of this ZnO nanorod was of the first class, which was the constant determinant rate of photolysis (K_d) atvarious concentrations under the same conditions was previously determined as noticed in (Table 3).This result suggested that $K_d$was sensitive to additive concentrations,whose increase was consistent with those described in previous studies [44].This finding confirmed that the additive accelerated the interaction between the light and polymer

FT-IR Spectrum of PVA

The exposure of pure PVA to high-energy rays with a wavelength of 356 nm alteredthe FT-IR spectrum [45] and yielded two broad bands.The first band of the carbonyl group (C=O) appeared at 1600–1700 cm^{-1}, which increased with irradiation time [46]. This band was present with few values before the films were irradiated because of the stress induced by thermal oxidationduring manufacturing (Fig.17). The second band of the hydroxyl and hydro peroxide polymer appeared at 3200-3600 cm^{-1}, where the absorbance increasedas the ZnO concentration increased (Fig.19).Therefore, the coefficients of the increase in the absorption of I_{OH} and I_{CO} were high at high additive concentrations (Tables 4, and 5and Figs. 20 and 21) as calculated using the base-line method [47].These results showed correspondence of the values calculated from the decomposition constant values (highest K_d). The calculations via the viscometer method showed the average molecular weight of the polymeric film before and after addition, suggesting that the average molecular weight decreasedas the irradiation time was extended. The additive concentration of the ZnO nanorodwas comparable with that of the reference becauseof the fragmentation of the polymeric chains (Tables 6, and 7), and the viscous molecular weight rapidly decreased at the beginning of

irradiation [48].Consequently, the most apparent results revealed that the bonds between the polymer chains were formed randomly along the polymeric chain, where, this observation was firmly established by the linear relationship of the average chain scission (S) and the degree of degradation(α) through time [44], revealing that Sand α of the chips of pure PVA were less than those supported by the ZnO nanorod additive. This study provided a basis for using ZnO nanorods as a good catalyst to photodegrade plastic materials, reduce environmental pollution, and accelerate their decomposition.

CONCLUSION

Rod-like ZnO nanorods were successfully synthesized hydrothermally in a nanosize range with a diameter of approximately 52.16 nm. The synthesized ZnO nanopowder obtained exhibited good crystallinity.The addition of ZnO nanorods increased the photodegradation rate because of the absorption of UV light. The degradation rate increased when the nanorodswere exposed to irradiation for16hrs.By studying the impact of different concentrations of ZnO nanorodson polymer degradation, we found that the rate of polymer degradation increased asthe concentration of each ZnO nanorod increased. These results and the calculated average viscous molecular weight, average numerical S, andαconfirmedthe increasein the photodegradation rate.

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Table 1. The structural parameters of ZnO nanorods as obtained from XRD analysis.

2θ(degree)		
hk1	**Observed**	**JCPDS**
100	31.73°	31.76°
002	34.38°	34.42°
101	36.20°	36.25°
102	47.54°	47.53°
110	56.56°	56.60°
103	62.80°	62.86°
112	67.80°	67.96°

Table 2.Absorbance values of the PVA with thickness 70±5 μm containing different concentrations of the ZnOnanorods and calculated at 283.5 nm spectrum measurements of UV–Vis with time

Irradiation Time (hrs.)	Absorbance				
Concentration %	0.0	4	8	12	16
PVA	0.108	0.137	0.160	0.200	0.273
PVA + 1 % ZnO	0.111	0.243	0.310	0.412	0.486
PVA + 2% ZnO	0.112	0.364	0.607	0.685	0.850
PVA + 3 % ZnO	0.113	0.466	0.723	0.802	0.916
PVA + 4 % ZnO	0.114	0.543	0.825	0.932	1.100
PVA + 5% ZnO	0.117	0.573	0.884	0.994	1.215

Table 3. Values constants of rate decomposition K_d of the ZnO nanorods in PVA films

Concentrations %	K_d(Sec) $^{-1}X10^{-4}$
1	5.361
2	6.245
3	6.541
4	6.7417
5	6.789

Table 4. Coefficient growth values carbonyl (I_{CO}) with irradiation time for PVA containing concentrations different of the ZnO nanorods

Irradiation time (hrs.) / Wt. % of Addition	Carbonyl Index (I_{CO})				
	0.0	4	8	12	16
PVA	0.378	0.551	0.649	0.800	0.902
PVA + 1 ZnO	0.396	0.632	0.683	0.839	1.173
PVA + 2 ZnO	0.401	0.666	0.831	1.008	1.400
PVA + 3 ZnO	0.439	0.965	1.045	1.183	1.608
PVA + 4 ZnO	0.469	0.993	1.293	1.373	1.930
PVA + 5 ZnO	0.496	1.066	1.379	1.632	2.121

Table 5. Coefficient growth values hydroxyl (I_{OH}) with irradiation time for PVA containingconcentrationsdifferent of the ZnO nanorods

Irradiation time (hrs.) / Wt. % of Addition	Carbonyl Index (I_{OH})				
	0.0	4	8	12	16
PVA	0.272	0.505	0.563	0.733	0.810
PVA + 1 ZnO	0.282	0.586	0.625	0.793	1.113
PVA + 2 ZnO	0.303	0.655	0.706	0.982	1.252
PVA + 3 ZnO	0.340	0.839	0.954	1.086	1.582
PVA + 4 ZnO	0.393	0.860	1.195	1.287	1.747
PVA + 5 ZnO	0.408	0.933	1.270	1.551	2.069

Table 6. Values calculated from measuring of the viscous molecular weight for pure PVAchips

Time Irradiation (hrs.)	$\overline{(M_v)}x10^3$	$(M_v)^2x10^9$	$\frac{dM_v}{dt} = \frac{M_{v0} - M_{vt}}{t}$	Degree of Polymerization P	$\frac{1}{P}x10^{-4}$	Deg. Degree *a x10*$^{-3}$	Ava. Chain Scission (S)
0	51.404	2.642	∞	1168.272	8.559	0.0	0.0
4	41.591	1.729	0.681	945.250	10.579	0.202	0.235
8	35.809	1.282	0.541	813.840	12.278	0.371	0.433
12	31.405	0.986	0.462	713.750	14.010	0.545	0.636
16	28.379	0.805	0.399	644.977	15.504	0.694	0.810

Table 7.Values calculated from measuring of the viscous molecular weight for PVA with concentration 4 %ZnO nanorods

Time Irradiation (hrs.)	$\overline{(M_v)}x10^3$	$(M_v)^2x10^9$	$\frac{dM_v}{dt} = \frac{M_{v0} - M_{vt}}{t}$	Degree of Polymerization P	$\frac{1}{P}x10^{-4}$	Deg. Degree *a x 10*$^{-3}$	Ava. Chain Scission (S)
0	51.404	2.642	∞	1168.272	8.559	0.0	0.0
4	38.282	1.465	0.911	870.045	11.493	0.293	0.342
8	31.988	1.023	0.674	727.000	13.755	0.519	0.606
12	27.925	0.779	0.543	634.659	15.756	0.719	0.839
16	24.603	0.605	0.465	559.159	17.884	0.932	1.088

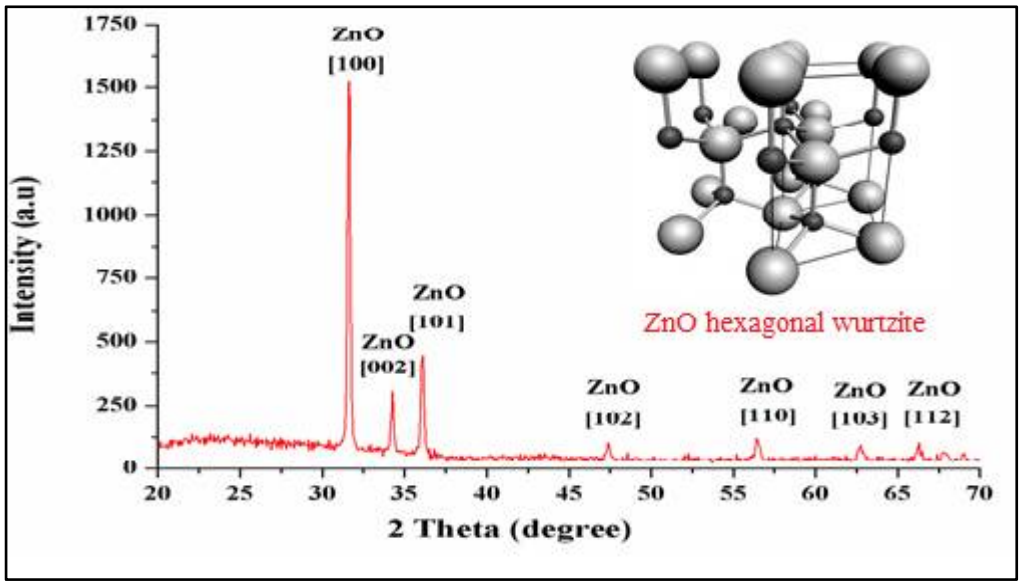

Fig.1. X-ray diffraction pattern of ZnO nanorods compared to standard ZnO phase (ICDD no 01-076-0704).

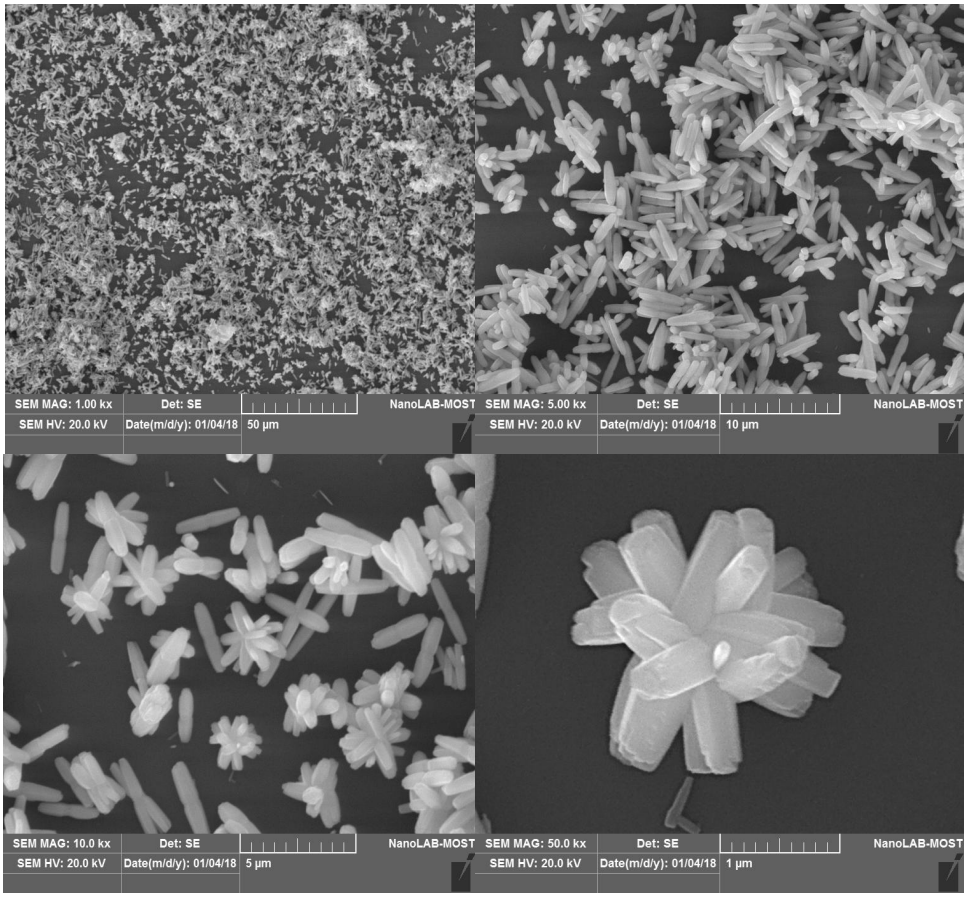

Fig. 2. SEM micrograph of ZnO nanorods synthesized in different magnification

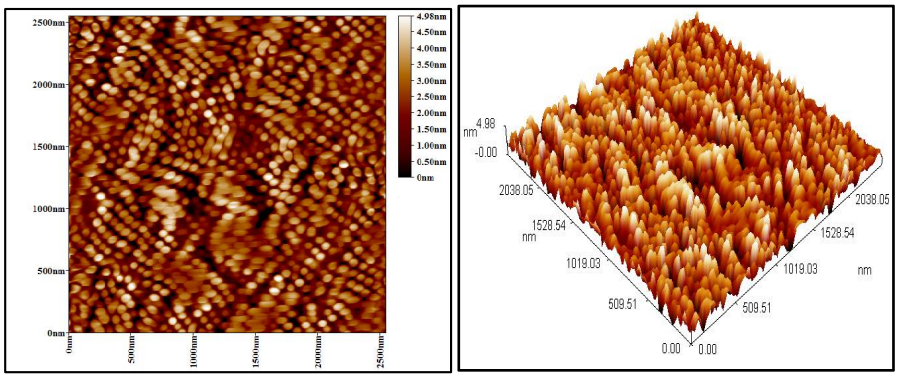

Fig. 3. AFM image of 2-dimensional and 3-dimensional of ZnO nanorods

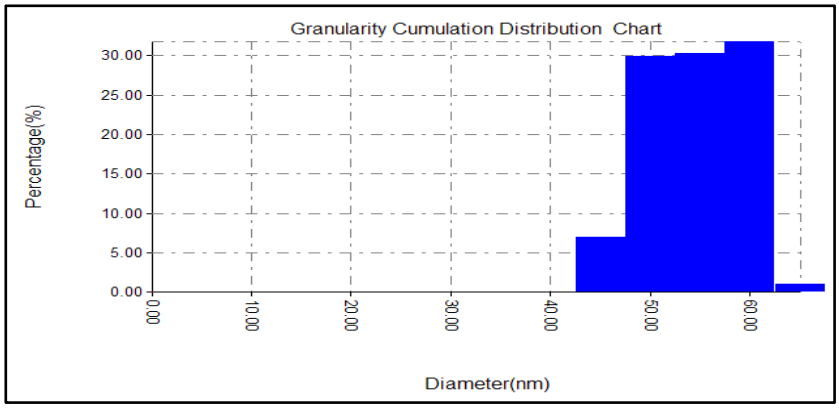

Fig.4. The average distribution for ZnO nanorods of diameter 52.16 nm

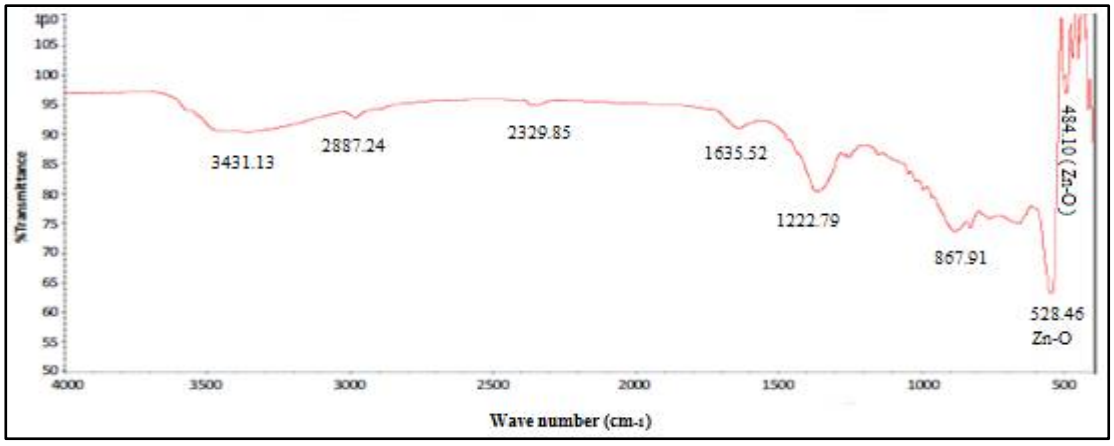

Fig. 5. FT-IR spectrum of ZnO nanorods

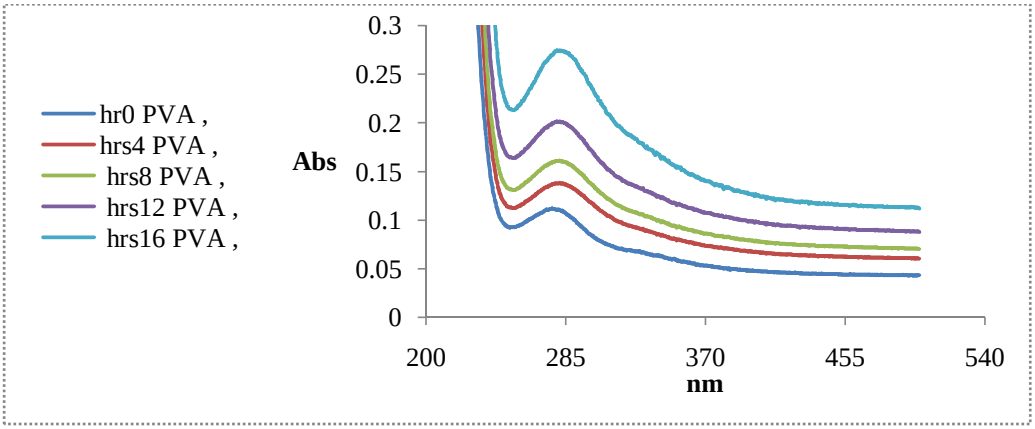

Fig.6. Change in the spectrum of UV–Vis for pure PVA with thickness70±5 μm at different times of irradiation

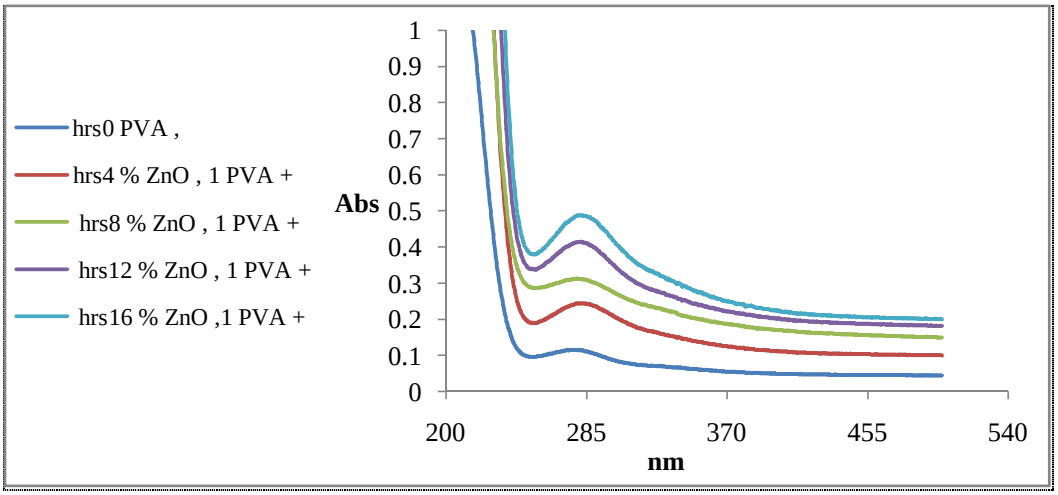

Fig.7.Change in the spectrum of UV–Vis for PVAcontaining concentration (1%) of the ZnO nanorods with thickness 70±5 μm at different times of irradiation

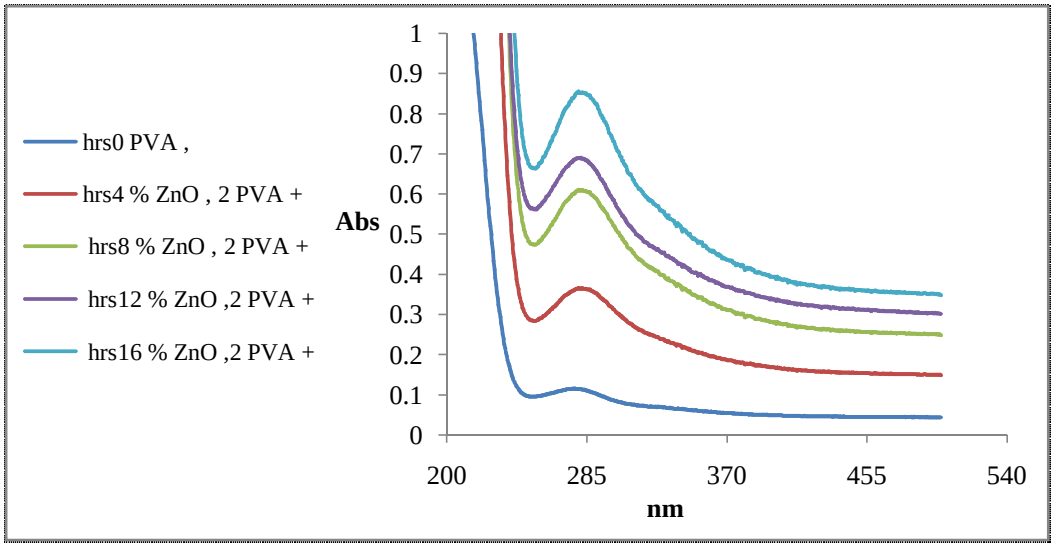

Fig. 8.Change in the spectrum of UV–Vis for PVAcontaining concentration (2%) of the ZnO nanorods with thickness 70±5 μm at different times of irradiation

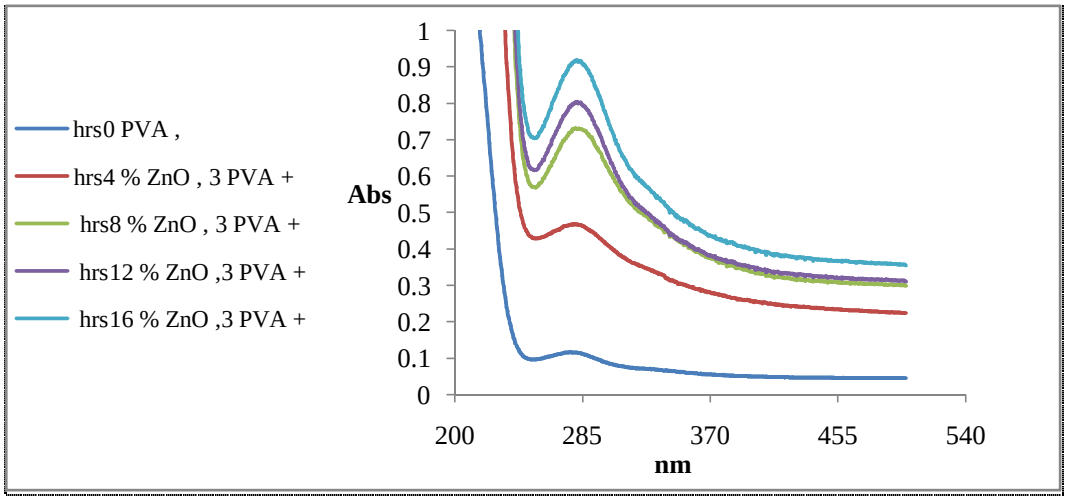

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Fig. 9.Change in the spectrum of UV–Vis for PVAcontaining concentration (3%) of the ZnO nanorods with thickness 70±5 μm at different times of irradiation

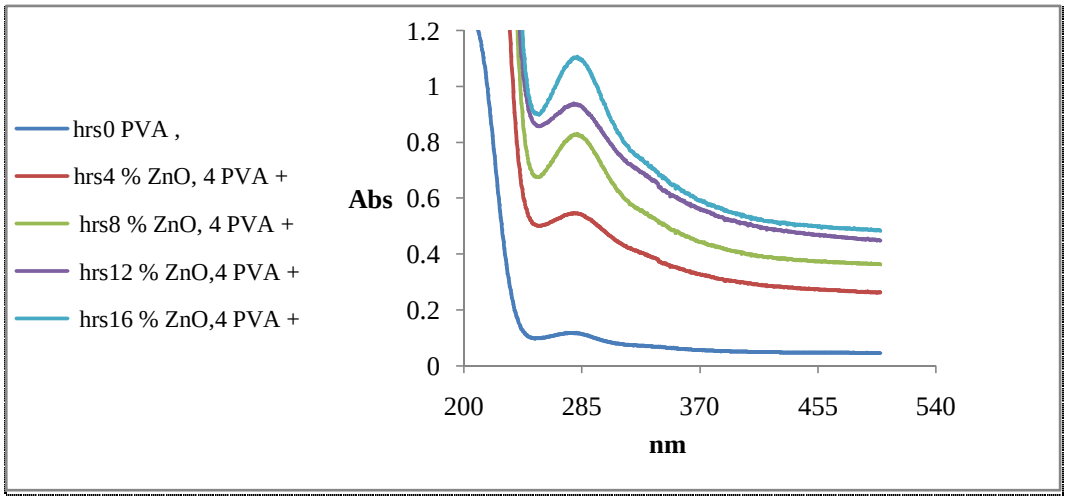

Fig. 10.Change in the spectrum of UV–Vis for PVAcontaining concentration (4%) of theZnO nanorods with thickness 70±5 μm at different times of irradiation

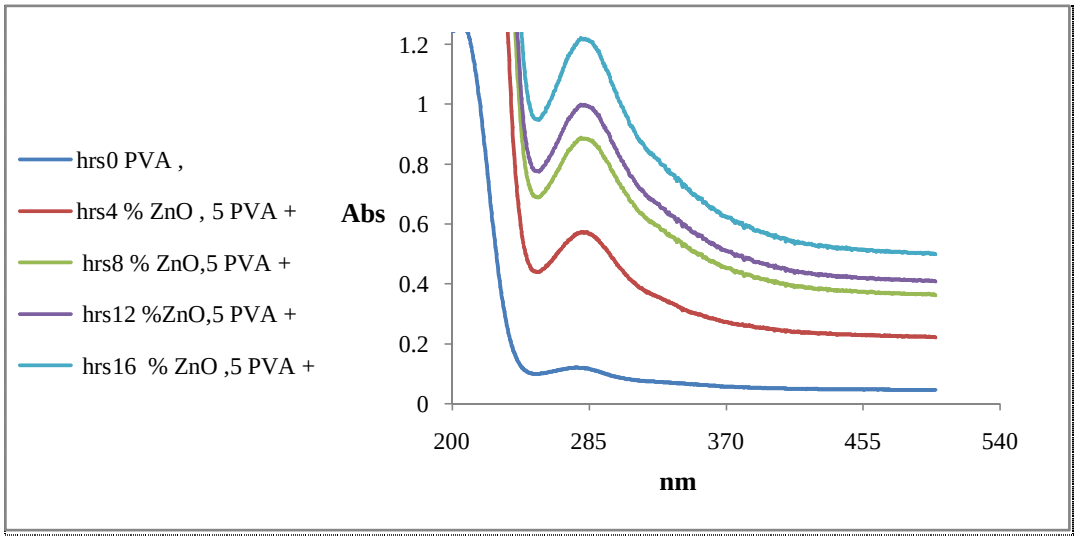

Fig. 11.Change in the spectrum of UV–Vis for PVAcontaining concentration (5%) of the ZnO nanorods with thickness 70±5 μm at different times of irradiation

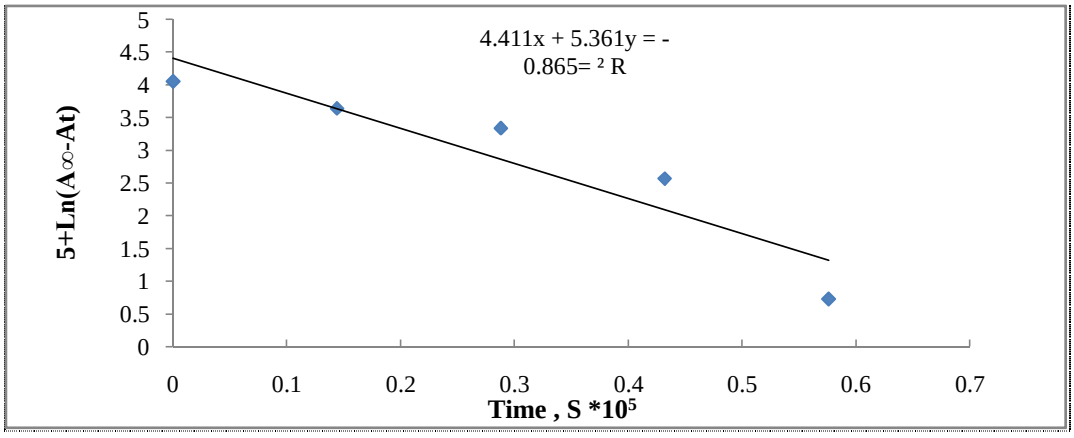

Fig. 12. The relationship between the logarithm of PVA films containing of ZnO nanorods with thickness70±5 μm and concentration (1%) with irradiation time

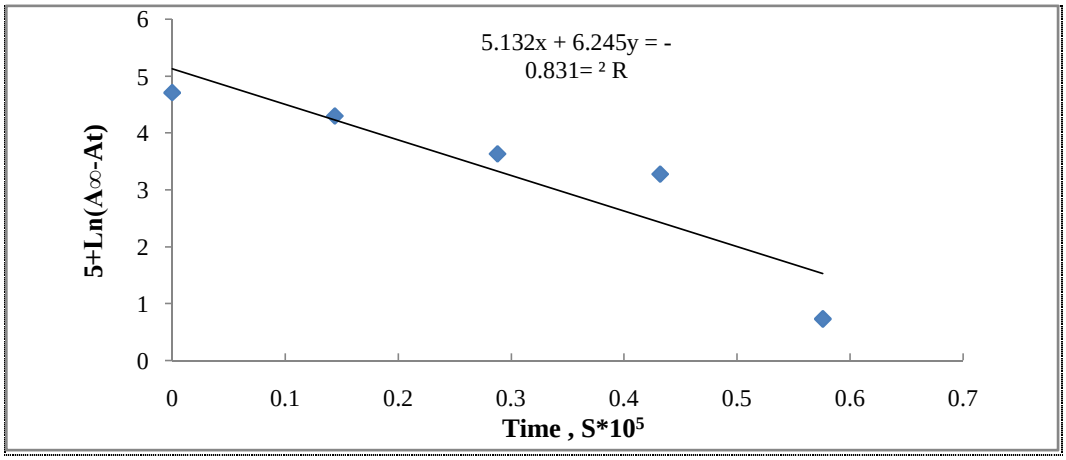

Fig. 13. The relationship between the logarithm of PVA films containing of ZnO nanorods with thickness70±5 μm and concentration (2%) with irradiation time

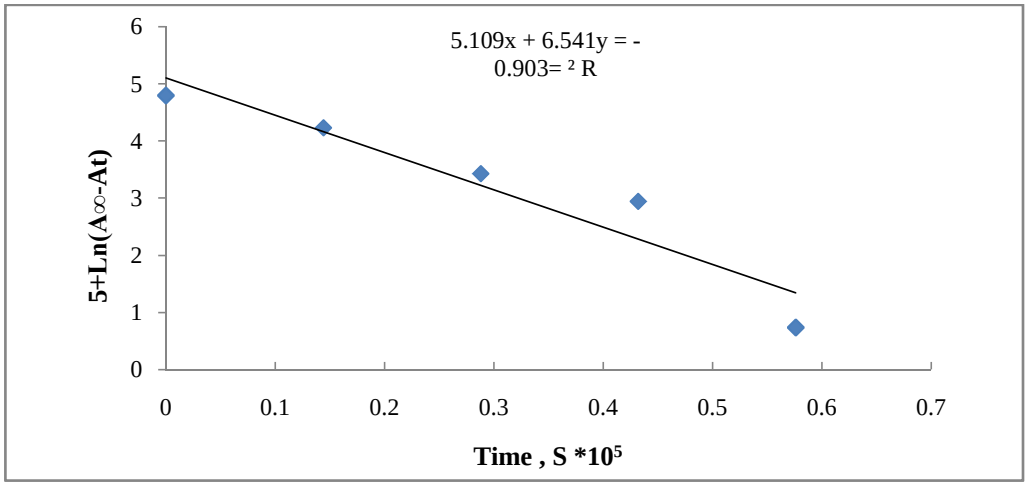

Fig. 14. The relationship between the logarithm of PVA films containing of ZnO nanorods with thickness70±5 μm and concentration (3%) with irradiation time

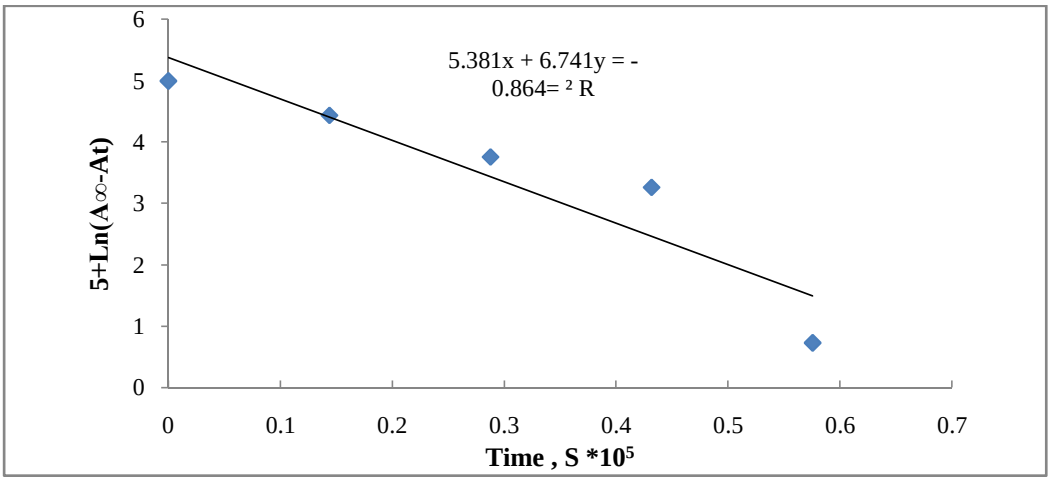

Fig. 15. The relationship between the logarithm of PVA films containing of ZnO nanorods with thickness70±5 μmand concentration (4%) with irradiation time

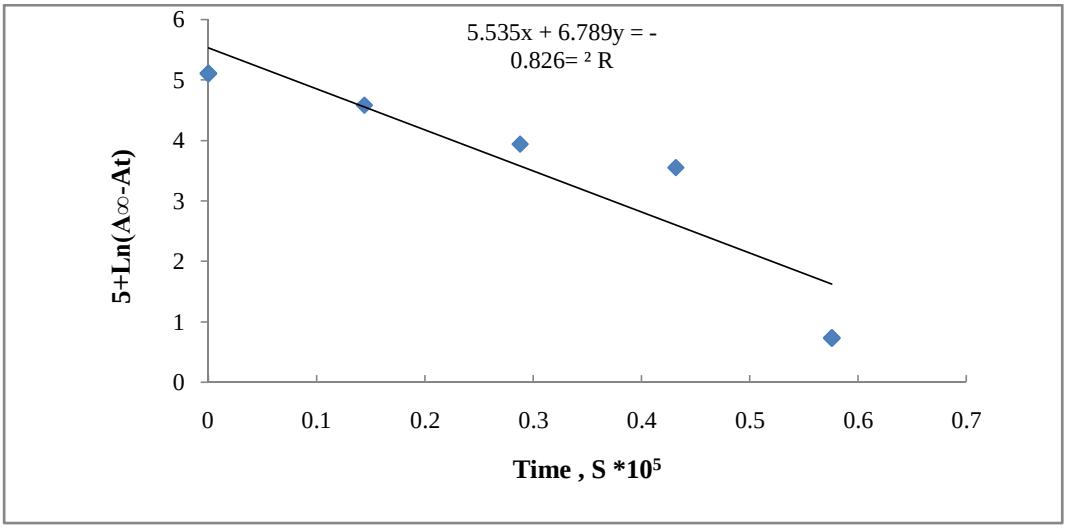

Fig. 16. The relationship between the logarithm of PVA films containing of ZnO nanorods with thickness70±5 μm and concentration (5%) with irradiation time

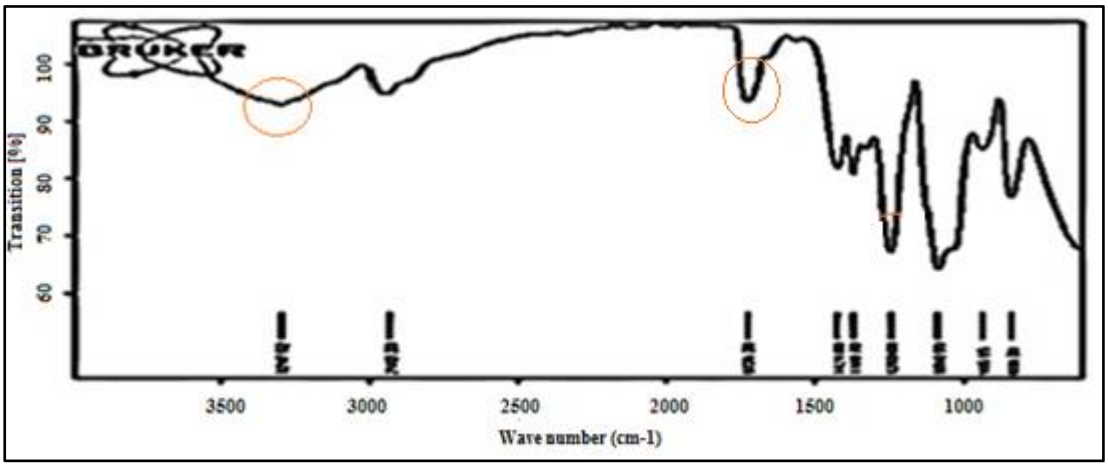

Fig. 17. FT-IR spectrum of pure PVA film with thickness 70±5 μm before irradiation

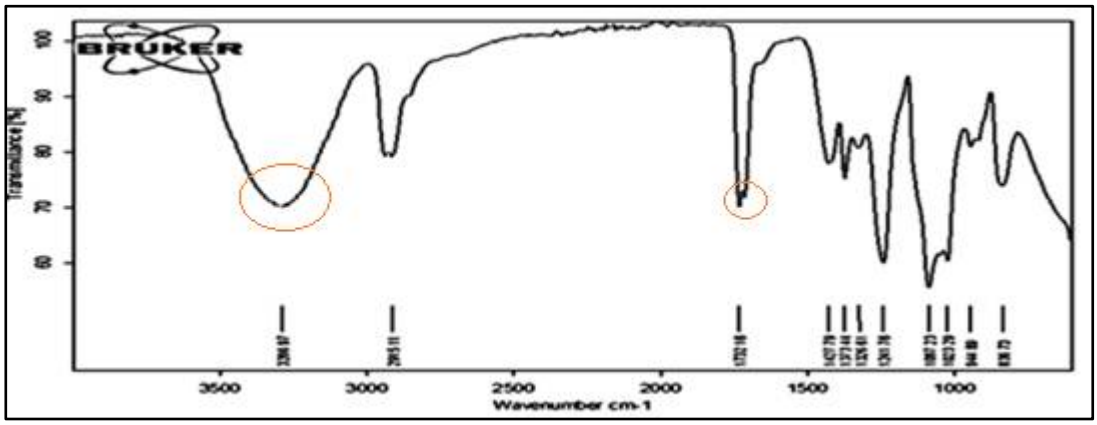

Fig. 18. FT-IR spectrum of pure PVA film with thickness 70±5 μmand the time of irradiation16 hrs.

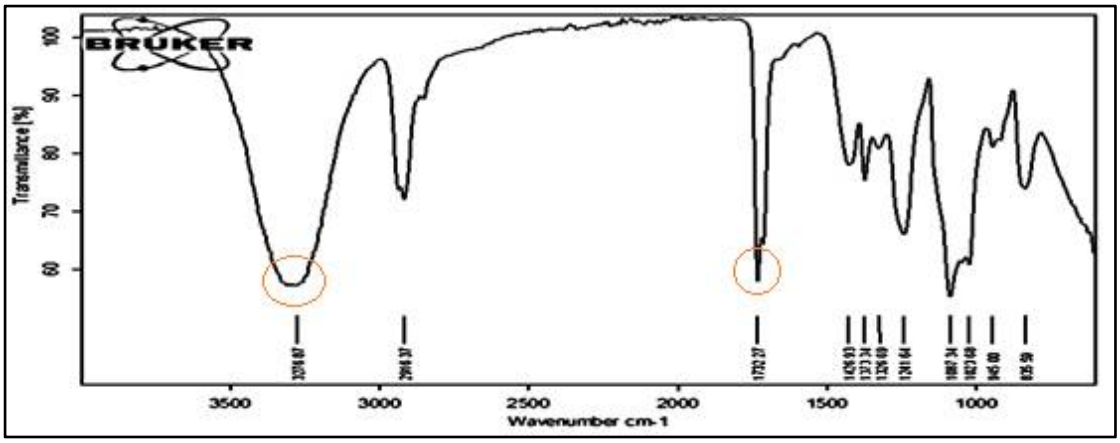

Fig. 19. FT-IR spectrum of PVA film with thickness 70±5 μm containingconcentration (5 %) of the ZnO nanorods and the time of irradiation 16 hrs.

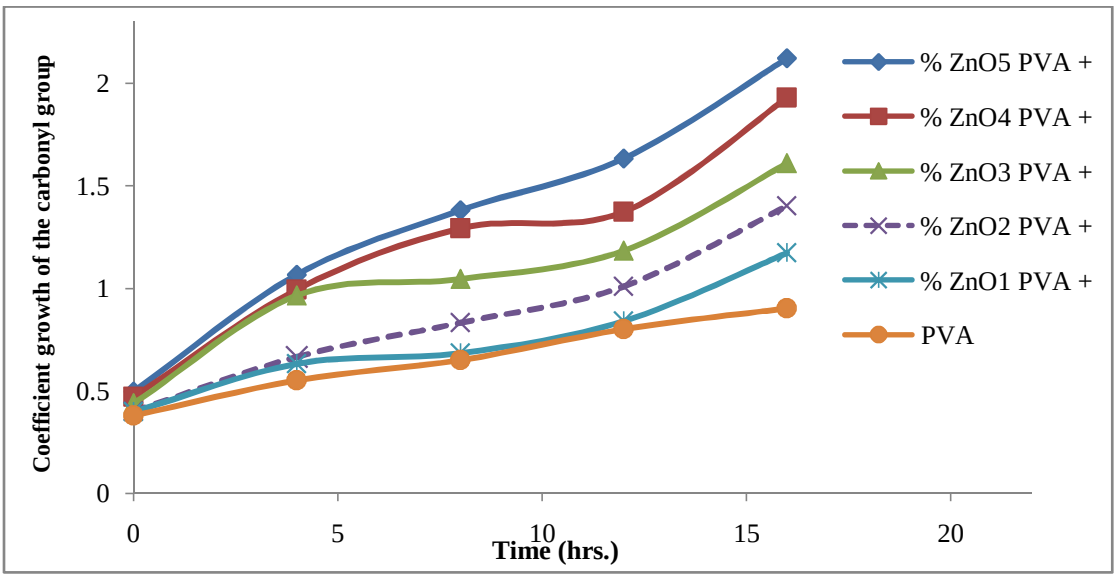

Fig. 20. The relationship between the absorption coefficient of the carbonyl and irradiation time of the results listed in the (Table 4)

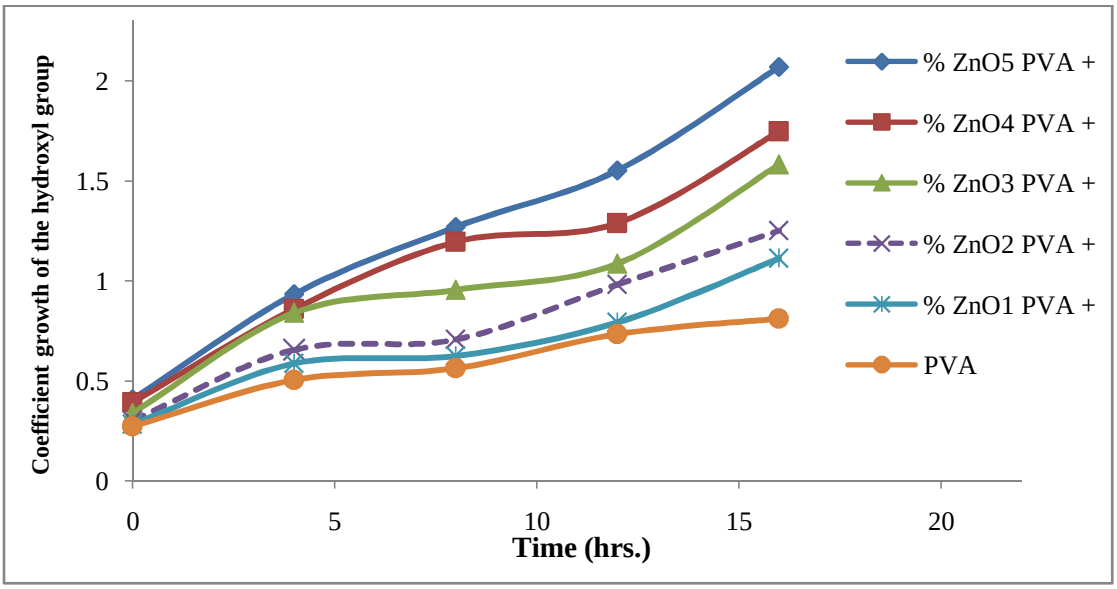

Fig. 21. The relationship between the absorption coefficient of the hydroxyl and irradiation time of the results listed in the (Table 5)