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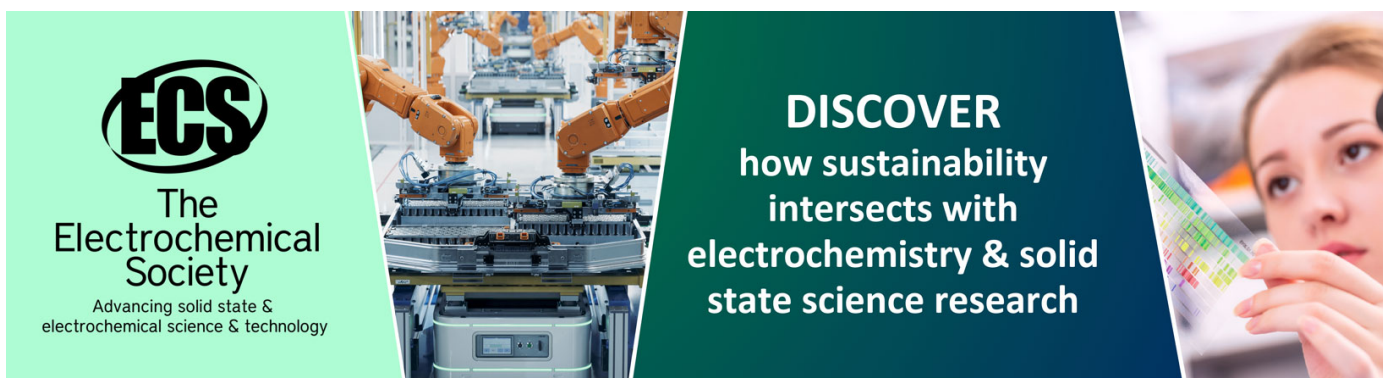
Structural, morphological and optical properties of spray pyrolysis TiO_2 :GO nano films

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Structural, morphological and optical properties of spray pyrolysis TiO₂:GO nano films

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Abstract

Thin films of pure and doped nano titanium dioxide (TiO₂) were prepared using a chemical pyrolysis technique (CPS), with different nanosize graphene oxide (GO) concentrations in the range (3-9)wt%. The structural, morphological and optical characteristics of these films were investigated. X-ray diffraction (XRD) technique measurements revealed that the structure properties of TiO₂ have polycrystalline structure with anatase phase. AFM analysis showed the grain size of TiO₂ films with different concentrations was decreased after doping with high concentration of GO ratio. Roughness of these films decreased too after adding of GO impurity for all films from (7.65-5.6)nm except 5wt% percentage where increased to 13.7nm. Optical properties of TiO₂ are affected by stimulants of GO, where the refractive index and the real part dielectric constant decrease, while the extinction coefficient and the imaginary dielectric constant increase after continuous addition of GO up to 7wt% and then increases with an increase in the further percentage of impurities. Energy gap values decreased after doping up to 7wt% with GO where the values lies in the range was 3.31 to 3.2eV while arrived to 3.49eV with more increasing of impurity percentage.

Keywords: TiO₂ metal oxide, GO graphene oxide, structure, morphological and Optical properties.

Introduction

Titanium dioxide, TiO₂, has gained much attention due to its applications as photocatalyst, solar cell electrodes and gas sensors. The structure and optical properties of TiO₂ depend to a large extent on deposition technique. A number of techniques have been used to deposit TiO₂ films: the direct current of reactive magnetron sputtering and thermal annealing method, pressing method and the dipping coating. Another way to influence the properties of TiO₂ films is stimulants with elements such as indium (In), chromium (Cr), cadmium (Cd), cesium (CE) and iron (Fe) on TiO₂ films obtained by spraying RF [1].

Nanocrystalline TiO₂ has many important applications, due to the stability of modern dyes, the traditional biological treatment methods of industrial wastewater are ineffective, often resulting in intensively colored discharge from treatment facilities [2].

The function of nanoparticles depends directly on the size of the particles, nanostructure and the morphological organization [3].

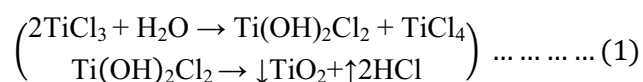


Adding impurities to the metal oxide semiconductors is the most common method of obtaining selective devices [4]. More papers for TiO₂ material pure and doped are studies by Oja et al., they prepared TiO₂ films by the spray pyrolysis method at substrate temperatures of 315 to 500 °C [5]. Yingqiang et al.,

Pure TiO₂ molecules and fluorine (F-TiO₂) were prepared by one-pot hydrothermal synthesis, quartz crystal microbalance (QCM) resonators were used to detect trace levels of nerve agent catalyst effect. From dimethyl methylphosphonate (DMMP) sensing measurements [6]. Znad et al., Mixed oxide photocatalysts of Ta/TiO₂ and Nb/TiO₂ were prepared with a simple impregnation method [7]. The aim in this work deals with the preparation thin and pure TiO₂ films of different concentrations with GO, studying the structure, morphological and optical properties.

Experimental

Semiconductor metal oxide TiO₂ pure and doped of organic material GO at different concentrations (3, 5, 7 and 9)wt% were prepared in this work. All TiO₂ thin films prepared with aqueous solution of titanium (III) chloride (TiCl₃) from (Merck KGaA, Germany) using chemical spray pyrolysis (CPS) technique. These films were manufactured with molarity (0.1M) of all experiments. TiO₂ thin film chemical equation were formed according to [8]:



To prepare thin films nanostructured by chemical spray pyrolysis more parameters like nozzle to substrate distance, flow rate and deposition time of solution, concentration and deposition temperature were used of films for good. The nozzle were used to spray on the heated glass substrate at 300°C. These thin films were annealing at 600°C for one hour.

The structure, morphological and optical characteristics of these films were studied. XRD diffraction was performed using (Shimadzu X-Ray diffractometer) type (XRD 6000). Absorbance and transmittance spectra were measured in the wavelength range (200-800)nm using the computerized UV-visible spectrophotometer (Shimadzu UV-1601 PC). Light sources are halogen lamp and deuterium socket lamp.

Results and discussion

The structure properties of the nano TiO₂ and TiO₂:GO can be identified during the XRD study phase using X-ray diffraction analysis (XRD). Figure (1) illustrate the XRD of pure TiO₂ material were found possess many diffraction peaks at (101), (103), (200), (105) and (211) directions with 2θ are (25.2119), (37.8121), (48.0069), (53.8488) and (54.937) degree respectively. These many peaks which refer to the formation of polycrystalline TiO₂. This result is in agreement with [9, 12]. The appearance of many peaks affirm the formation of polycrystalline TiO₂.

The crystal structure phase is found anatase phase which agree with (ASTM) card no. [96-900-9087]. The orientation along the plane (101) was the angle of diffraction $2\theta = 25.2119^\circ$, $d = 3.5169\text{\AA}$ according to Card No. [96-900-9087].

After doping with GO in different concentrations (3, 5, 7, and 9)wt.% , the peaks show a variation in the intensity of the peaks with a difference in the addition of impurities percentage. The peaks intensity increased after doping until up to 7% and hence the intensity of peaks returned decreased again at 9wt% percentage. Full width of half maximum FWHM decreases but crystallite size increased with percentage up to 7wt% where the behavior of recorded values appeared (0.5728, 0.5160, 0.5483, 0.4516, 0.5484)Deg and (14.21181, 15.77863, 14.84538, 18.02645, 14.84174)nm for FWHM and crystallite size respectively.

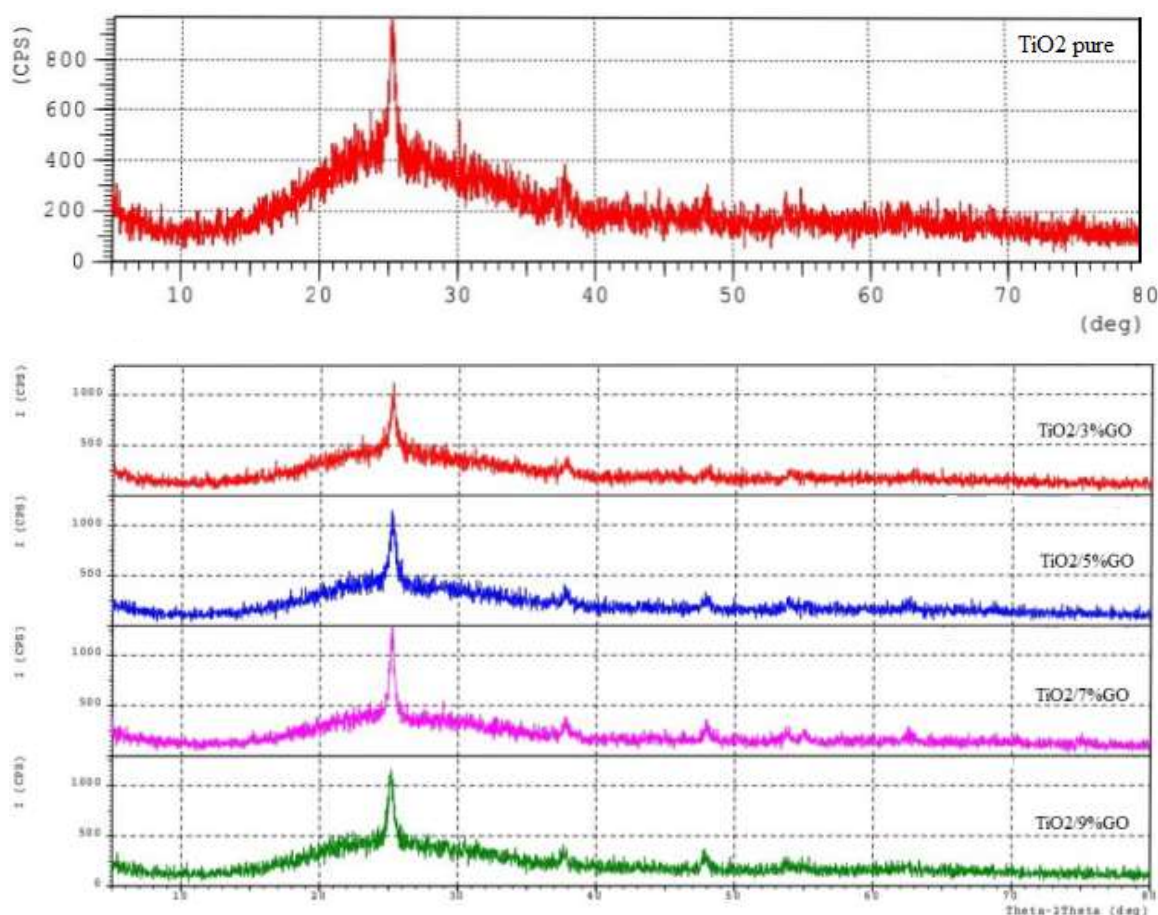


Figure (1): XRD of TiO₂ doped and undoped thin films.

Surface morphology of TiO₂ thin films was determined by Atomic Force Microscopy (AFM). The chart of surface morphology at three dimensional for TiO₂ pure and with doped GO for different concentrations (3, 5, 7 and 9)wt.% are shown in AFM images as cleared in figure (2). From

AFM images average roughness, average diameter and root mean square roughness (r.m.s) are calculated as mentioned in table (1). This subtle morphology and film roughness can be clearly seen. The results grain size is uniform. AFM images of all samples appear to have granular structure. AFM of pure TiO_2 shows that there is an much bigger quasi barshape grain formed in the film. It has good homogeneity that reveals uniform growth of films. Grain size of TiO_2 films with different concentrations decreased after doped at 3wt% percentage after that, increasing was happened at 5wt% then it went down again with an increase in the rate of GO doping.

Roughness of these films decreased too after adding of GO impurity for all films from (7.65-5.6)nm except 5% percentage where increased to 13.7nm. This increase is due to the presence of many hillocks, which are faceted and distributed randomly on the relatively smooth surface, so the increase in roughness can be clarify by granular growth and some condensation of the structure of the deposition processes.

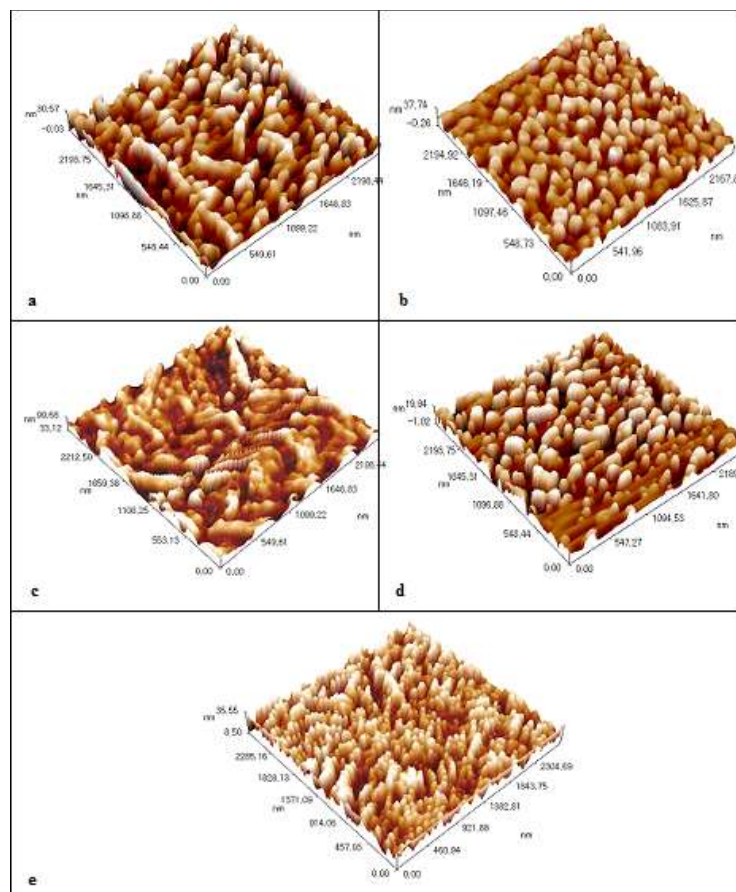


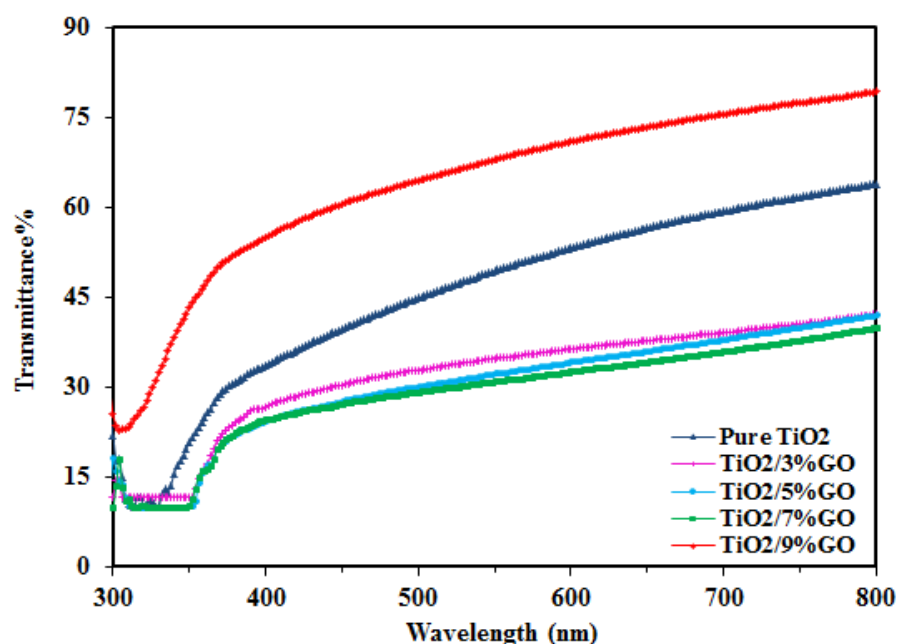
Figure (2): AFM images for TiO_2 films where represents: (a) TiO_2 pure, (b) $\text{TiO}_2/3\% \text{GO}$, (c) $\text{TiO}_2/5\% \text{GO}$, (d) $\text{TiO}_2/7\% \text{GO}$, (e) $\text{TiO}_2/9\% \text{GO}$.

Table (1): AFM parameters of TiO₂ films pure and doped with organic material GO.

GO%	Roughness average (nm)	Average Diameter (nm)
0	7.65	113.97
3	6.26	86.73
5	13.7	113.31
7	5.24	83.64
9	5.60	77.50

Optical properties was obtained by UV -VIS spectroscopy of TiO₂ thin films. Figure (3) shows the UV -VIS transmission spectrum in the region (300-800) nm for TiO₂ pure and doped GO films. This figure illustrate that the transmittance intensity increases with increasing wavelength but the transmittance decreased as the concentration of doped material GO increase for more samples. Transmittance decreased as the doping rate increased for law doping ratio arrival to 7wt% percentage but at 9wt% it increased again. This decreased is due to the increased absorption within the visible area of the spectrum.

Transmittance curve for doped and undoped films showed rapid increase within the range (310-380)nm and gradual increased within the range (386-800)nm, this because the occurrence of electron transitions in energy levels within the bands (interband transition). Table (3) appeared transmittance values at wavelength 500nm.

**Figure (3): Transmission spectra of TiO₂:GO thin films.**

The optical band gap data (E_g) is calculated by Tauc's formula as an eq. (2) to calculate the band gap energies for pure TiO_2 doped with GO thin films. Figure (4) shows a scheme $(\alpha h\nu)^2$ as a function of incident radiation energy. A typical optical energy gap is identified at the top of the absorption region where $\alpha > 10^4 \text{ cm}^{-1}$ by plotting $(\alpha h\nu)^{1/r} = 0$ where $r = 1/2$ of the direct allowed transmission [13].

$$\alpha h\nu = B' (h\nu - E_g)^{1/2} \dots\dots\dots (2)$$

Where B' represent inversely proportional to the amorphousity, ν is optical frequency.

It is clear from figure (4) that direct energy gap for TiO_2 film is 3.31 eV, this result agrees with [14-17]. Decreasing energy gap was event with increasing the doping ratio of GO, indeed the is gap decreased from 3.31-3.2 eV until increasing of impurity up to 7wt% after that increasing was happened again in the energy gap to 3.49 eV at 9wt% as shown in Table (3). This shift towards low energy side for optical energy gap related with increase of crystallite size which responsible for the increase of absorption coefficient [18,19]. The blue shift of energy gap at high doping ratio may be related with quantum confinement effect. Energy gap for the quantum dots (qd) is the band gap for the bulk ($bulk$) and the confinement energy for the hole and the excited electron EC as mentioned below [20]:

$$E_{g(qd)} = E_{g(bulk)} + \frac{h^2}{8R^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \dots\dots\dots (3)$$

Where, h is the Planck constant, R is the radius of the quantum dot, m_e^* the effective mass of the electron mass and the m_h^* is effective mass of the hole.

Table (3): The optical properties of TiO_2 samples.

GO%	T%	$E_g(\text{eV})$	n	k	ϵ_r	ϵ_i
0	44.86	3.31	2.59	0.340	6.592	1.762
3	32.83	3.27	2.42	0.472	5.638	2.289
5	30.11	3.23	2.32	0.510	5.132	2.367
7	29.18	3.2	2.28	0.522	4.929	2.385
9	64.46	3.49	2.34	0.186	5.478	0.875

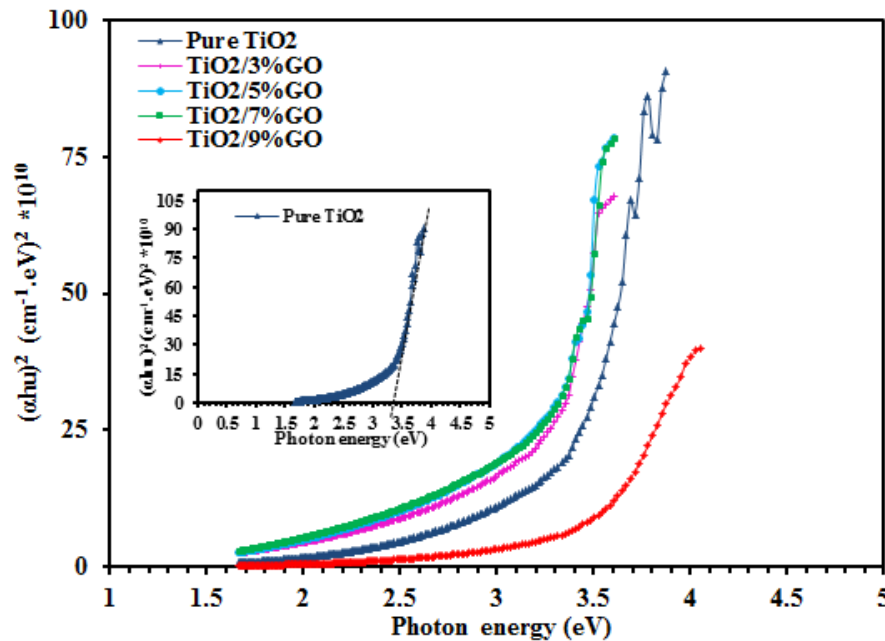


Figure (4): $(\alpha h\nu)^{1/2}$ as a function of photon energy for TiO_2 pure and doped thin films.

Refractive index (n) for optical materials and applications is parameter very important, from this determine the optical constants of the films. The refractive index of films is conclude from the following relation [21]:

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

Where R represent the reflectance, k is the extinction coefficient. The refractive index of films has been determined. Refractive index of all samples TiO_2 and $\text{TiO}_2\text{:GO}$ for different doping percentage with wavelength is drawn in figure (5). From this figure low values of refractive index was observed in the short wavelengths (300-360)nm and meanwhile increasing occurs in the higher wavelengths for all samples pure to 7wt% except 9wt% percentage where appeared high refractive index in the low wavelengths and hence decreasing occurs in the higher wavelengths.

The refractive index of TiO_2 films was found to decrease after the continuous addition of GO up to 7wt% and then get to increase with further addition of impurity percentage. The calculated experimental value was (2.59, 2.42, 2.32, 2.28 and 2.34) for samples (pure, 3, 5, 7 and 9)wt% respectively at 500nm. The material with a high refractive index is very useful in optics and photonics in which I used to reduce reflection losses in the interfaces that cause increased light output [22].

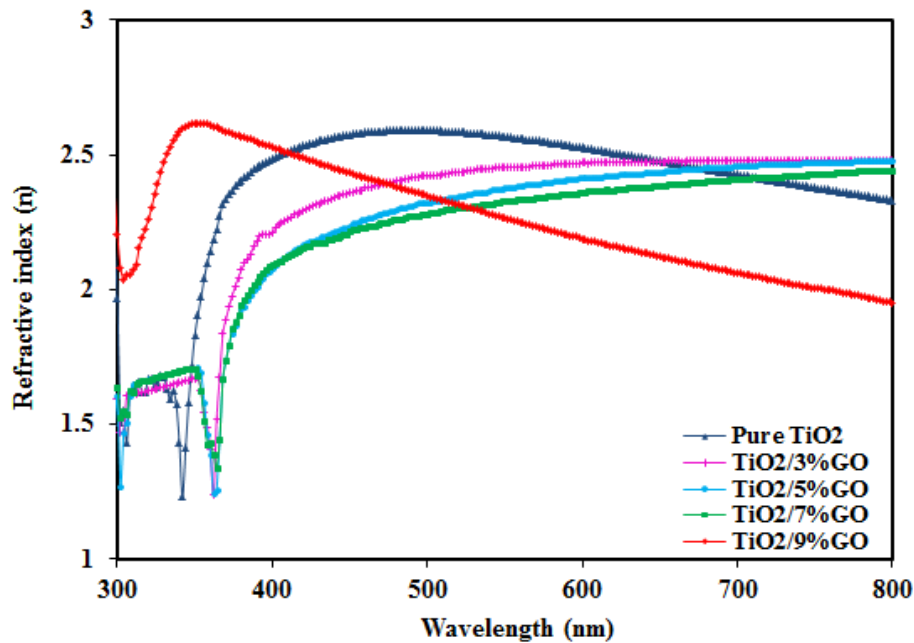


Figure (5): the refractive index versus wavelength for TiO₂ pure and doped thin films.

Figure (6) shows the extinction coefficient (k) of pure and doped thin films in wavelength in the range (300-800) nm. It was observed that the extinction coefficient is pure TiO₂ and 9wt% impurity percentage have the same behavior where (k) showed progressive reduction with wavelengths, but doped samples (3, 5 and 7)wt.% appears reduction of (k) in the short wavelengths and growing in long wavelengths. The extinction coefficient showed continuous increase for doping concentrations (3, 5 and 7)wt% and after that decreased again for 9wt%, see table (1). The decrease and increase of the associated extinction coefficient are related with decrease and increase of the absorption coefficient accompanied with the addition of dopant atoms. Equation of extinction coefficient is given by the following [23].

$$k = \frac{\alpha \lambda}{4\pi} \dots \dots \dots (5)$$

Where α is the absorption coefficient.

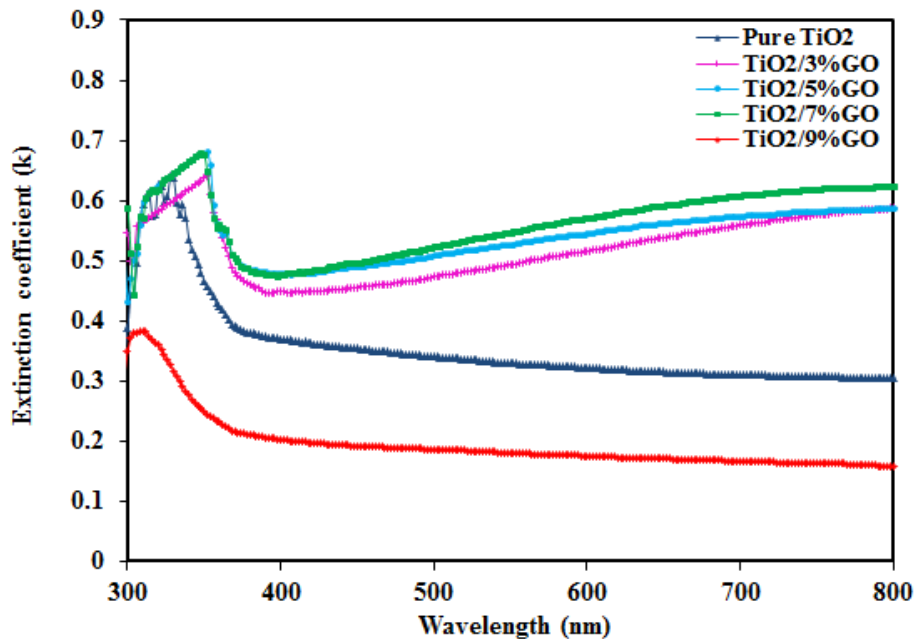


Figure (6): Extinction coefficient as a function of wavelength for TiO_2 pure and doped thin films.

The dielectric constant real ϵ_r and imaginary ϵ_i parts are associated by (n) and (k) . Real and imaginary values were calculated using equations [24].

$$\epsilon_r = n^2 - k^2 \quad \dots\dots\dots (6)$$

$$\epsilon_i = 2nk \quad \dots\dots\dots (7)$$

Real part values with the wavelengths range (300-800) is show in figure (7) for pure and with impurity thin films. It can be seen from this figure that the real part depends on the refractive index by equation (6) because the effect of the extinction coefficient is too small to be canceled [25]. Real part values show suggestion increase in the short wavelengths at (310-400)nm depending on the doping ratio of all films and then slightly increased was happened in the wavelength range (400-800)nm except 9wt% impurity where appeared different behavior.

The real part relation with concentration was increased after doped at short wavelengths up to for all samples percentage, after that at higher wavelengths get to decrease with addition of more impurity. The measured values were (6.592, 5.638, 5.132, 4.929 and 5.478) for samples (pure, 3, 5, 7 and 9)wt% at wavelength 500nm as show in table (2). Moving the curves heads to high or low wavelengths is by to an increased ratio of impurities to the relevant real part of the dielectric constant with the refractive index by equation (6) [25].

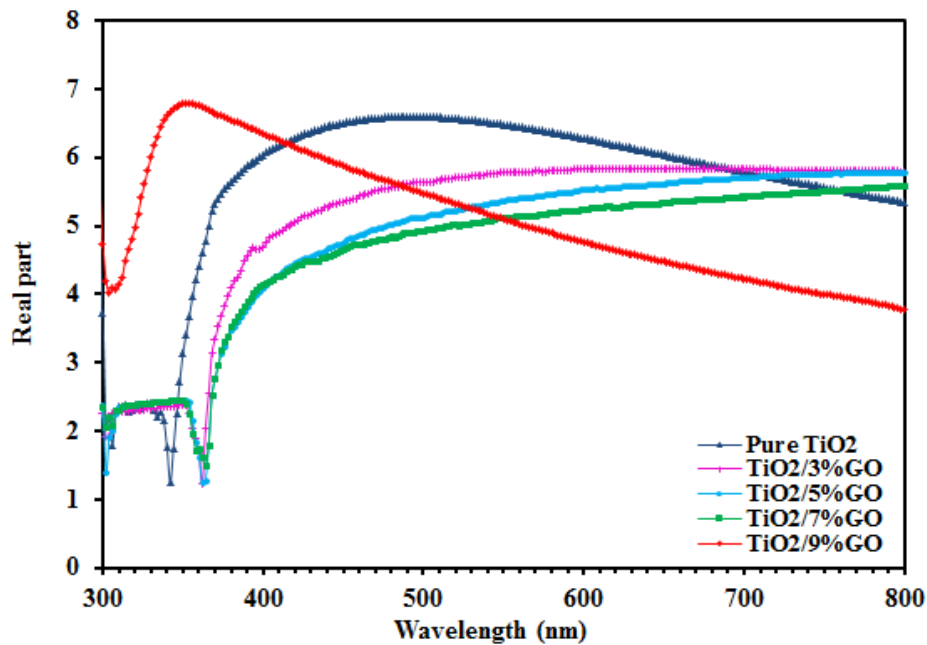


Figure (7): Variation the real part of dielectric constant as a function of wavelength for TiO_2 pure and doped thin films.

Figure (8) illustrate the imaginary part of dielectric constant dependence on wavelength in range (300-800)nm. This figure clearly represents the imaginary part's dependence on the extinction coefficient of equation (7) because the refractive index is very small [25, 26].

After addition of GO to the host material the imaginary part of ϵ_i get to increase, become higher up to 7% and then reduced with more addition of GO. The measured values were (1.762, 2.289, 2.367, 2.385 and 0.875) for samples (pure, 3, 5, 7 and 9)wt% at wavelength 500nm as show in table (2). The same reason previously mentioned to k can be given here to explain the behavior of ϵ_i .

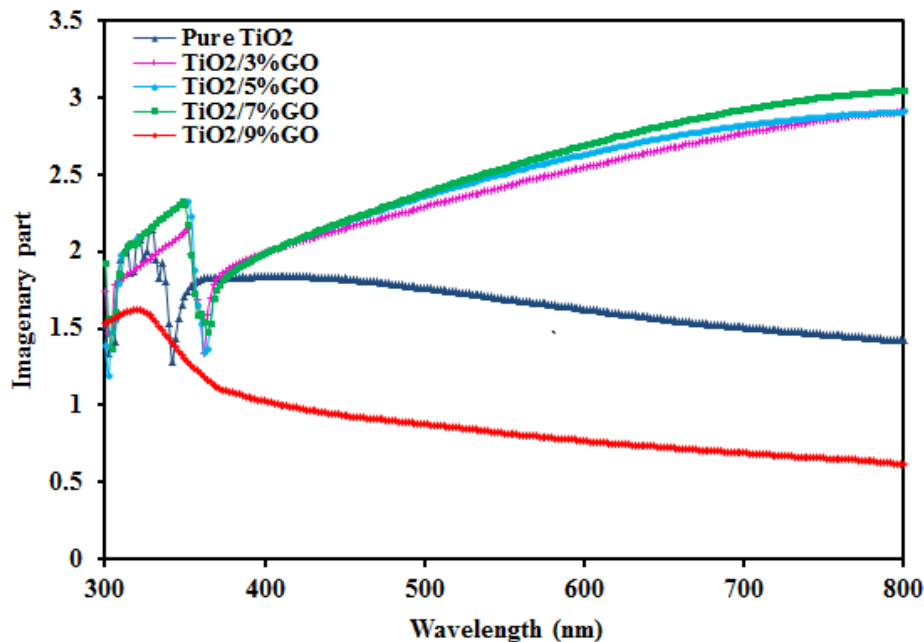


Figure (8): Variation the imaginary part of dielectric constant as a function of wavelength for TiO_2 pure and doped thin films.

Conclusions

TiO_2 pure and doped with graphene oxide GO at nanosize was investigated in this work. Results of structural, morphological and optical properties were achieved. XRD analysis showed all the prepared thin films pure TiO_2 and doped with graphene oxide have polycrystalline structure with anatase phase. The peaks intensity increased after doping up 7% and then after the intensity of peaks decreased. Full width of half maximum FWHM of the most pronounced peak increased while the crystallite size increased with increased of doping percentage and then the inverse to that take place at high doping ratio. The analysis AFM data showed the doping ratio has strong effect on the Grain size and. Optical constants grretly effected by the addition of GO . The optical energy gap showed red shift with the addition of GO to TiO_2 followed by blue shift with continuous addition of GO.

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Sartain, Photocatalytic Activity of Doped and Undoped Titanium Dioxide Nanoparticles Synthesised by Flame Spray Pyrolysis, Photocatalytic Activity of Doped and Undoped Titanium Dioxide Nanoparticles Synthesised by Flame Spray Pyrolysis. •*Platinum Metals Rev.*, 2013, 57, (1), 32–43.

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