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Synthesis and Optical Properties of Brookite phase TiO_2 thin Films Nanocomposites

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Abstract
Thin films of titania nonocoposites have been prepared by simple method using spin coating technique deposited on ITO glass substrates. The study used different thicknesses of thin films 37.73nm, 37.65 nm ,37.60 nm ,35.57 nm and 35.42 nm respectively. The refractive index and the energy bandgap were investigated by means of absorption, transmittance and reflectance spectra. The peaks of XRD patterns established all of as–prepared samples are brookite structure. The study revealed that the average value of refractive index for all samples is equal to 2.04. Also, the result confirmed the nanocomposite that growth with thickness of 37.73 nm has lowest energy bandgap of 3.83 eV and this may leed to highest coductivity comparing with other thin films.

Keywords: *ITO glass substrate, XRD technique, thin film, bandgap.*

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I. Introduction

Titanium dioxide (TiO_2)belong to the family of metal oxides and has a unique position among semiconducting oxides due to its own properties and wide range of applications. Titanium dioxide (TiO_2) is non-toxic naturally occurring transition metal oxide of titanium. The TiO2nanocrystals have significant properties because the quantum effect dominates on the regular physics of material. Generally TiO_2 is used as whitening agent as in paints, toothpaste, cosmetics and many more. TiO_2 was never considered as a material for technological device until 1967 when a scientist Akira Fujishima saw flakes on wall painted with TiO_2 and discovered photo catalytic splitting of water on TiO_2 electrodes without using electricity [1]. Apart from the bulk TiO_2 material, TiO_2 nanomaterial has high surface to volume ratio which causes more exposed surface area, means the confinement of the charges in it tend to have discrete energy states which is responsible for unique properties. Titanium dioxide is a well-known photocatalyst for water and air treatment, as it treats almost all organic contaminant and release in the form of H_2O and O_2. Pure TiO2 is either colorless or white, but it also tends to exist in other colors (yellow, red, brown, black, etc.) due to the presence of impurities (e.g. iron, niobium, chromium, tantalum, and vanadium).TiO_2 is thermally stable and very resistant to any chemical reactions. Heating causes blue color change from white, which shows there is oxygen deficiency. TiO_2 is inert to most acids and alkalis. It is slowly soluble in hydrofluoric acid and concentrated H_2SO_4 [2]

The TiO_2 exist in 3 types of crystal structures: tetragonal anatase and rutile and orthorhombic brookite with energy band gap of 3.2, 3.03 and 3.11 eV respectively.

Among the different TiO_2 structures, anatase is a metastable phase that contains four shared edges per octahedron and it shows photo catalytic behavior with response to ultraviolet photons. The rutile is the thermodynamically most stable phase at all temperatures and is formed by sharing two edges per octahedron with the largest index of refraction. Rutile is good for electronic components because of better conductivity than other phases. Brookite is the most distorted & unstable phase and shares three edges per octahedron, due to this, only anatase and rutile crystal can be utilized for technological point of view [2 , 3].

TiO_2 nanostructures can be synthesized by using various techniques. Some of them are hydrothermal [4-6], solvothermal method [7, 8], sol-gel synthesis [9], physical and chemical vapor deposition [10, 11] electrochemical methods [12, 13]. Among those methods, the researchers have good turned to use the low-temperature reaction (like hydrothermal and sol-gel methods) for synthesis nanostructures. Brookite structure is recognized as an active phase, in some cases showing enhanced performance with respect to anatase, rutile or their mixture. The peculiar structure of brookite determines its distinct electronic properties, such as band gap, charge–carrier lifetime and mobility, trapping sites, surface energetic, surface atom arrangement and adsorption sites.

In this study, a sol-gel method has been used to prepare a solution of TiO_2. Then TiO_2solution deposited on glass substrates by using spin coating technique to prepare TiO_2 /ITO nanocomposite using five films with different thickness. Moreover, the effects of the different thickness on the structural and optical properties were investigated. The samples were characterized by XRD, and UV-visible spectroscopy.

II. Samples Preparation

The sol- gel method was used to synthesize the as-prepared samples of titanium oxide nano copmposites. Dimethylformamide(C_3H_7NO) and titanium oxide powder were used as starting materials. Ten ml of C_3H_7NO was added to 5.03 gm of titanium oxide powder. The mixture solution was rabidly stirring at room temperature with the help of a magnetic stirrer to maintain the homogeneous mixture. The white solution has been used to prepare the films by spinner (spin coating). The films were prepared in ITO glass slides. The ITO glasses were cleaned with ethanol before, washing with deionizer water and acetone. The coating of the films on ITO glass was performed at room temperature and the rotation speed was changed in each sample to obtain different thicknesses of thin films according to the different number of rotations.

III. Results and Discussion

Figures 1,2 and 3 represent the XRD patterns of as- synthesized TiO_2 thin films nanocomposites labeled as shaza1, shaza 2, shaza 3, shaza 4 and shaza 5. The characteristic diffraction peaks of all TiO_2 samples nanocrystals are appeared at 2-theta values of 21.815°, 24.637°, 30.627°, 32.314°, 38.778° and 50.291° , corresponding to crystalline diffraction planes of (110), (120) or (111), (121), (112), (221) and (231) respectively. The XRD patterns for all samples showed that there is a sharp peak at $2\Theta = 24.637^\circ$ corresponding to (111) plane. Interestingly, among the all samples, the highest intensity is found to be about 600 (a.u) for sample 5 that growth on the substrate of thickness 35.42 nm which indicated that the crystalline of the particles of the as-synthesized TiO_2 films samples improve with decreasing the thickness of the glass substrates . Moreover, there are unknown peaks can be detected in the XRD patterns, which imply the as-synthesized TiO_2 nanostructures obtained in this study are not enough pure. Interestingly, the crystal structure of as –synthesized TiO_2 in this study produced orthorhombic structure with lattice constant of a = 4.531, b = 9.21 and c = 4.9 nm and the Space Group is Pbcn (60). The density is found to be 4.3469 g/cm^3 for all samples in a agreement with the standard value 4.6g/cm^3. These results are mostly correspond to the reference line patterns of JCPDS : No 29-1360 [13] of TiO_2 brookite structure. Also the XRD data established that, the d-spacing for all samples of as-synthesized TiO_2 films nanostructures decreases with increasing the value of 2 theta (2Θ) be in agreement with Bragg's law. Table (1) shows the crystal size of as-synthesized TiO_2 films, obtained by using the Debye Scherrer formula [14].

$$D = \frac{0.9\,\lambda}{\beta cos\theta} \qquad (1)$$

D is the grain size, λ is the wavelength of x-ray radiation equal to 0.154 nm , β is the full width at half maximum (FWHM) of the diffraction peak and θ is the reflection angle [15]. The results in table 1 shows that the average crystallite size of as-synthesized nanocomposites of TiO_2 are 37.73 nm, 36.65 nm , 36.60 nm, 35.57 nm and 35.42 nm for samples 1, 2,3,4 and 5 respectively. Moreover, these results confirmed the average crystalline size decreased when decreasing the thickness of the glass substrate [16].

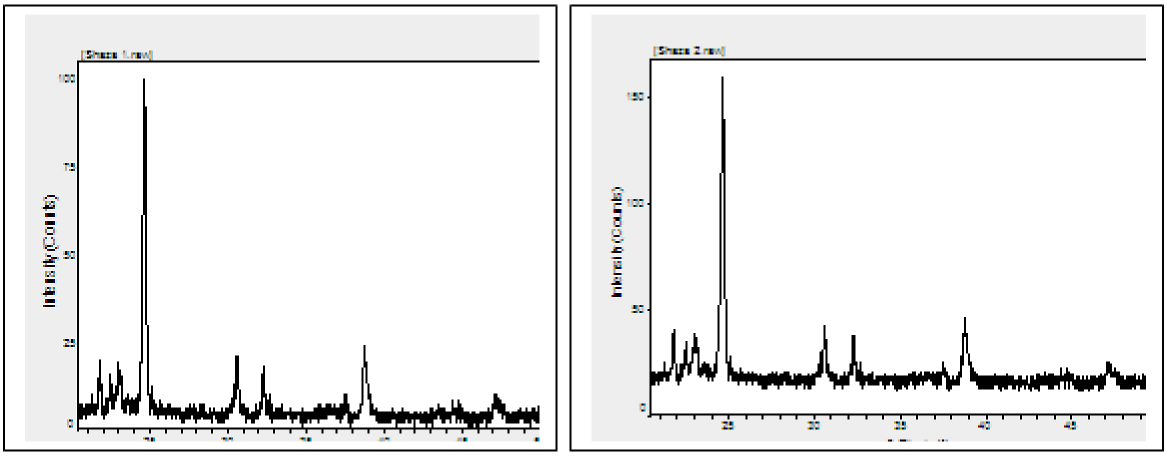

Figure (**1**): The XRD patterns of the as- synthesised TiO_2 nanocomposites for sample 1 and sample 2.

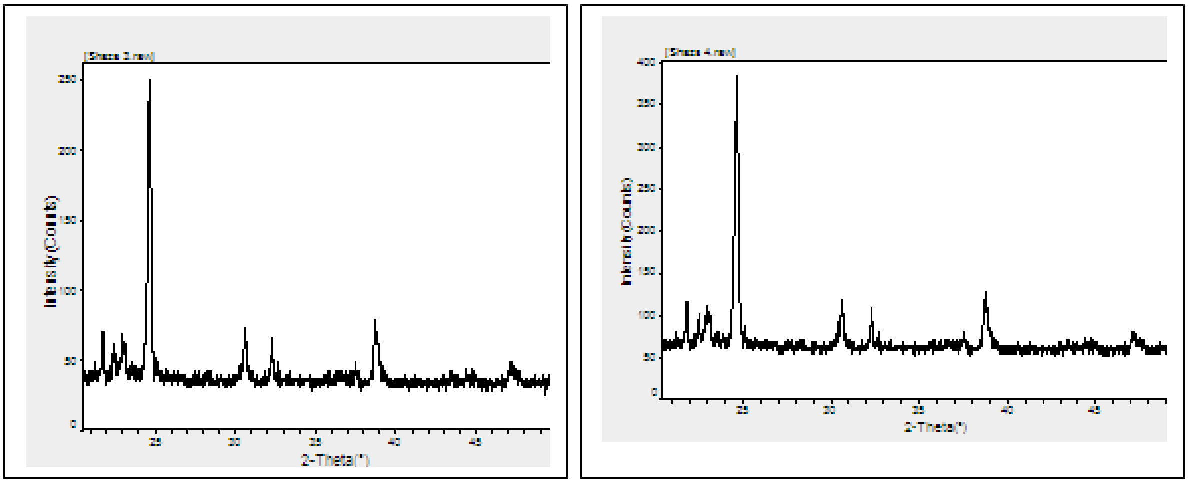

Figure **(2)**: The XRD patterns of the as- synthesised TiO_2 nanocomposites for samples 3 and 4.

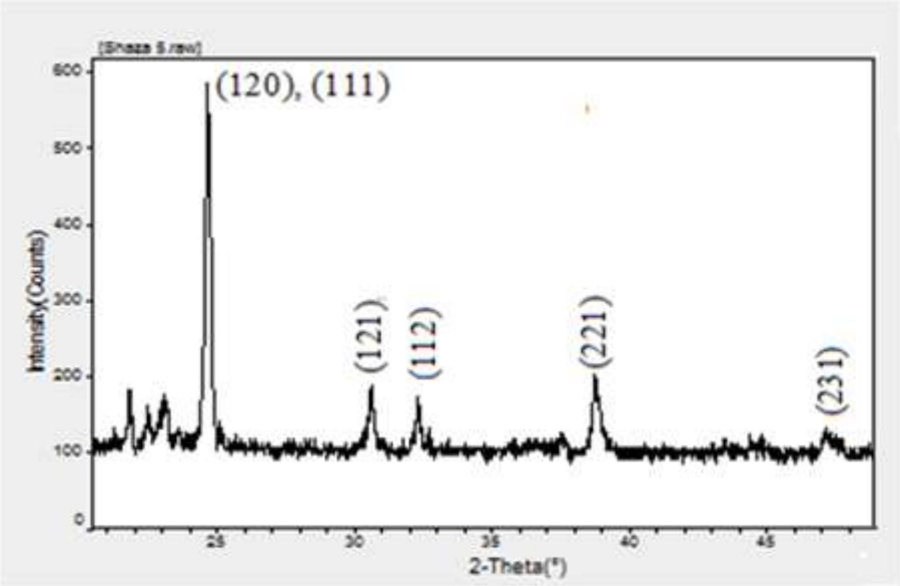

Figure **(3)**: The XRD patterns of the as- synthesised TiO_2 nanocomposites for sample 5.

Table 1: shows the crystallite size of five samples of as-synthesized TiO_2 nanocomposites.

2Θ (^{0})	Crystal size D (nm)				
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
21.815	62.60	59.90	58.98	54.60	54.81
24.637	40.61	41.80	41.73	38.30	39.21
30.627	31.18	31.90	31.56	31.20	31.20
32.314	42.34	42.20	42.24	40.8	40.90
38.778	22.88	23.30	24.05	23.6	22.91
50.291	26.80	26.84	26.87	24.9	23.51
Average size	37.73	37.65	37.57	35.57	35.42

The refractive index (n) plays an important role in optical communication and the most desirable optical constants of photonic materials for the fabrication of quantum photonic devices. The refraction index (n) can be calculated by the following formula:

$$n = \left(\left(\frac{1+R}{1-R}\right)^2 - (k^2+1)\right)^{\frac{1}{2}} + \frac{(1+R)}{(1-R)} \qquad (2\,)$$

Where (R) is the reflectivity and k is the extinction coefficient where $k = \frac{\boldsymbol{\alpha\lambda}}{\boldsymbol{4\pi}}$. The refractive index is due to interactions that takes place between photons and electrons. Figure 4 shows the relationship between refractive index (n) and wavelength of as-synthesised TiO_2 thin films nanostructures. Figure 4, established that the average refractive index for all samples of as-synthesized TiO_2 thin films nanostructures has maximum value of 2.024. Also the pattern in Fig (4) demonstrated that longer wavelengths can be obtained when increasing the thickness of the films. As a result, decreasing the thickness of the films lead to shift the high peak to the region of shorter wavelengths and this behavior may due to the decreasing in the crystal size. In addition, the result established that the peaks for sample 1 and sample 2 of the refractive index patterns are almost showing blue- shift at the region of longer wavelengths. Therefore, the refractive index of as-synthesized TiO_2 thin films is confined between the wavelengths 284 and 310 nm. Take into a count the absorption and the scattering of incident light, can decrease the amplitudes of the transmission intensity of the oscillations at shorter wavelength and can shift the refractive index which corresponding to the crystallite of TiO_2 [17].

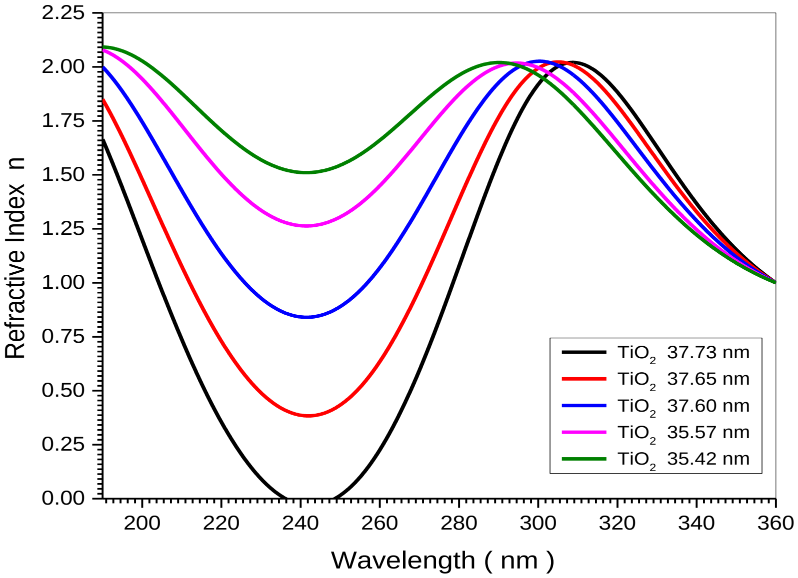

Figure (4): shows the pattern of the refractive index of as-synthesised TiO_2 nanocomposites as function of wavelength.

The optical transitions in nanocomposite films can be easily understood by determining the optical band gap (Eg) by Tauc's plot [18]. The frequency dependent absorption coefficient is given by:

$$(\alpha h\upsilon)^2 = C(h\upsilon - E_g) \qquad (3)$$

Where **α** is the absorption coefficient equal to 2.03 A/t ; A and t are the absobance and the thickness of the film. C is constant depends on the inter band transition probability, hυ is the incident photon energy and E_g is the optical bandgap energy. Figure (3) shows the relation between absorbtion edge $(\alpha h\upsilon)^2$ for TiO_2 thin films nanocomposite as a function of photon energy (hυ). The optical bandgap energy are determined for different thickness of thin films of as-synthesised TiO_2 nanostructures. The optical bandgap values are obtained by extrapolating the straight portion of the curve to the value $(\alpha h\upsilon)^2= 0$ (Fig.5). The results in Fig. 5 indicated that the as-synthesized of TiO_2 nanocomposites that growth on the thin film with thickness of 37.73 nm has bandgap of 3.915 eV while for TiO_2 growth on the film with thickness of 35.42 nm has the highest value of bandgap 4.018 eV, which believed to possess a better coductivty [19]. This results are near to reported papers [19,20].
In general, increasing the thickness of the thin films will lead to decreasing in the energy band gap. The decreasing in the bandgap could be due to stress relaxation in the film of as-obtained nanoscomposite [21]. Also the decrease of the bandgap value may attributed to creation of new levels in the band gap which lead to facilitate the crossing of electrons from the valence band to the conduction band, consequently the band gap decrease[22, 23]. Moreover, it was observed that the slight different in the structures of as-synthesized samples TiO_2 confirmed the reason for the blue-shift of band gap.

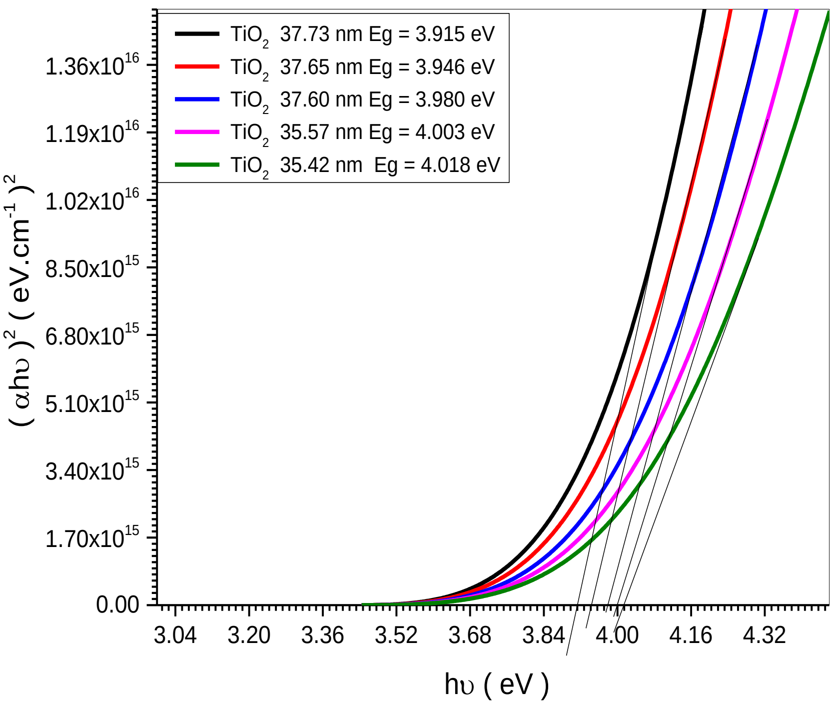

Figure (5): shows the band gap of as-synthesised TiO_2 nanocomposite as function of wavelength

IV. Conclusion

In this study, TiO_2 thin film was deposited on glass substrate using spin coatingprocess. The structural and morphological properties of TiO_2 thin films were investigated by XRD. The band gap andthe refractive index were calculated to analyze the optical property. XRD data confirmed the as-synthesized TiO_2 films are brookite structure and the crystal size of the nanocomposite ranged between 37.73 nm to 35.0 nm. The study shows that the average refractive index for all samples of as-synthesized TiO_2 films nanocomposites has maximum value of 2.024 and the energy band gap decreases with increasing the thickness of the thin films. These resultshave possibilities of applications in which material nanostructures can be used to produce optical and electronic properties.

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