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Structural and Optical Properties of Annealed TiO_2 Powder Synthesized by Hydrothermal Method

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Abstract

Titanium dioxide (TiO_2) Nano powder has been synthesized by hydrothermal method. The reaction took place between titanium tetrachloride ($TiCI_4$) and mixture solution consisted of deionized water and ethanol, in the ratio (3:7) respectively. Structure and surface morphology of TiO_2 Nano powder at different annealing temperatures in the range 200-800°C for 120 min were characterized by X-ray diffraction (XRD), Atomic Force Microscope (AFM), Scanning Electron Microscopy (SEM), FT-IR and UV/visible spectroscopy measurements. The results show that with an increase in annealing temperature, the value of the intensity of (110) peak for rutile phase increases while the value of the full-width at half maximum (FWHM) decreases, and the band gap decreases with increasing temperature.

Keywords: Titanium dioxide (TiO_2), hydrothermal.

الخصائص الهيكلية والبصرية من مسحوق ثاني أكسيد التيتانيوم النانوي توليفها بواسطة طريقة الحرارية المائية

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الخلاصة

حضر اوكسيد التيتانيوم بتقنية الحراره المائيه في الأوتكليف، حصل التفاعل بين رباعي كلوريد التيتانيوم ومزيج متكون من ماء لاايوني وايثانول بنسبة (7:3) بالتتابع. تركيب وطبغرافية السطح لاوكسيد التيتانيوم النانوي الملدن بدرجات حرارية مختلفة (200-800) °م لمدة 120 دقيقة تم تشخيصها بواسطة قياسات حيود الاشعة السينية (XRD)، مجهر القوة الذرية (AFM)، المجهر الألكتروني الماسح (SEM) ومطيافية الأشعة تحت الحمراء (FT-IR) والأشعة فوق البنفسجية/المرئية (UV/Visible). اظهرت النتائج ان شدة القمة (110) لطور روتايل تزداد بزيادة درجة حرارة التلدين بينما العرض عند منتصف الارتفاع (FWHM) يقل وان فجوة الطاقة تقل مع زيادة درجة حرارة التلدين.

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1. Introduction

Titanium dioxide (TiO_2) or titania is a very well-known and well-researched material due to the stability of its chemical structure, biocompatibility, physical, optical and electrical properties. It is n-type semiconductor material with wide band gap (Eg= 3-3.3eV) [1]. TiO_2 has high absorption to be like high transparent stability in the visible area and low conductivity, have high refractive index, low cost, nontoxicity, mechanical hardness, novel optoelectronic properties and easy availability [2-4]. These properties make TiO_2 the in solar cells, fuel cell, chemical sensors for hydrogen gas evolution, a pigment, self-cleaning surfaces, resistance to photochemical, chemical erosion and environmental purification applications [5, 6].

TiO_2 exists in three different crystalline phase which are anatase, rutile, and brookite [7]. Anatase and rutile have a crystalline structure that corresponds to the tetragonal system while brookite has an orthorhombic crystalline structure [8]. As a bulk material, rutile is the stable

phase. However, anatase is the generaly favor for solution phase preparation [9]. Anatase and brookite are a metastable phase and readily transform to rutile when heated [10].

Several methods have been reported in the literature to prepare TiO_2, including the hydrolysis of acidic solutions of Ti (IV) salts, oxidations of $TiCl_4$ on gaseous phase [11], hydrolysis of titanium alkoxides, sputtering, chemical vapor deposition and sol-gel process [12]. Among these technique, hydrothermal method. The hydrothermal technique has emerged as one of the most promising technique as this method produces samples with a good homogeneity at low cost [13] were usually found that different routes often produced different results. Even for the same route, using a different amount of the starting materials, the obtained prtical size is different [14]. In the present work, we have prepared TiO_2 nanostructures using $TiCl_4$ as a precursor.

2. Experimental

All reagents were of analytical grade purity and no further purification was done before use. Titanium tetrachloride ($TiCl_4$), purity 99.9%; ethanol (EtOH) grade, purity 97%.

2.1 Synthesis of TiO_2 nanostructures.

TiO_2 nanostructures were prepared via solvothermal method using titanium chloride ($TiCl_4$), ethanol (EtOH) and deionized water as the starting materials. Five milliliters of $TiCl_4$ was added slowly under stirring into a round bottom flask putting in an ice bath. The round bottom flask has a mixture solution consisted of deionized water and ethanol, in the ratio (3:7) respectively. The process was done under the fume hood. After 30 minutes with vigorous stirring on the magnetic stirrer, the colorless solution poured into a 50 ml Teflon-lined stainless-steel autoclave. The autoclave was sealed and placed in an oven at 200 °C for 6 h. Then, the autoclave was allowed to cool to room temperature naturally. The white precipitate ($Ti(OH)_4$) was washed with distilled water (about 3 times), and collected by centrifugation, washed with ethanol (2 times) and annealed at specify temperature (200-800°C). The reaction took place according to following steps:

$$TiCl_4 + 3CH_3CH_2OH + H_2O \xrightarrow{\text{ice bath/stirring}} Ti(OCH_2CH_3)_3(OH) + 4HCl$$

$$Ti(OCH_2CH_3)_3(OH) \xrightarrow{\text{autoclave}} Ti(OH)_4 + 3CH_2CH_2$$

$$Ti(OH)_4 \xrightarrow{\text{annealing}} TiO_2 + 2H_2O$$

The overall :

$$TiCl_4 + 3CH_3CH_2OH + H_2O \xrightarrow[\text{2.autoclave 3. Annealing}]{\text{1. ice bath/stirring}} TiO_2 + 4HCl + 3CH_2CH_2 + 2H_2O$$

3. Results and Discussion

Titanium dioxide Crystalline has been prepared by thermal process using titanium tetrachloride in aqueous solution and subsequently annealed at 200, 400, 600 ,800°C. In a general the hydrothermal process for preparing TiO_2, the primarily formed structure phase observed at low temperature is brookite , which transforms to rutile phase only upon annealing [15]. Note that the rutile XRD peaks became sharper as annealing treatment prolonged indicating the formation of r-TiO_2.

Characterization of TiO_2

The XRD was employed for identification and understanding the crystalline growth nature of titanium dioxide structures prepared by the solvothermal method. Annealing are common treatment used to improve the crystalline of TiO_2 powders [16].

The annealing temperature It is important to influence on the structure of titanium dioxide powders. The XRD pattern can be well indexed the phase structure of the prepared products. The XRD patterns of the powders annealed at different temperatures are shown in Figure-1. Figure-1(a) shows the diffraction patterns of $Ti(OH)_4$ at annealing temperature 200°C. the diffraction peak for the plane (110) at 2θ= 27.60 refer to the tetragonal structure belonged to rutile phase, and diffraction peak for the plane (002) at 2θ= 28.53° refer to the orthorhombic structure belonged to brookite phase. All the XRD patterns correspond well to the structure of $Ti(OH)_4$ according to the (JCPDS Card No.21-1276 and JCPDS Card No.29-1360).

At the annealing temperature of 800°C, brookite was totally transformed into rutile Figure-1(d). And based on that the grain size for that peak alone calculated, using the Debye- Scherer formula:

$D = k\lambda / \beta\cos\theta$ ……………………………………………………………………………….(1)

Where k is the constant (0.9), λ is the wave length of X-ray (1.54nm), β is the full width half maximum (FWHM) of the peak and Θ is the reflection angle

Table -1 shows the obtained details resulted from XRD for the prepared product ($Ti(OH)_4$) at different annealing temperature (200, 400, 600 and 800°C) for 120 min.

The increase of annealing temperatures from 400 to 800°C increased the intensity of diffraction peaks and increase the lattice constant is in agreement with the reference [17].

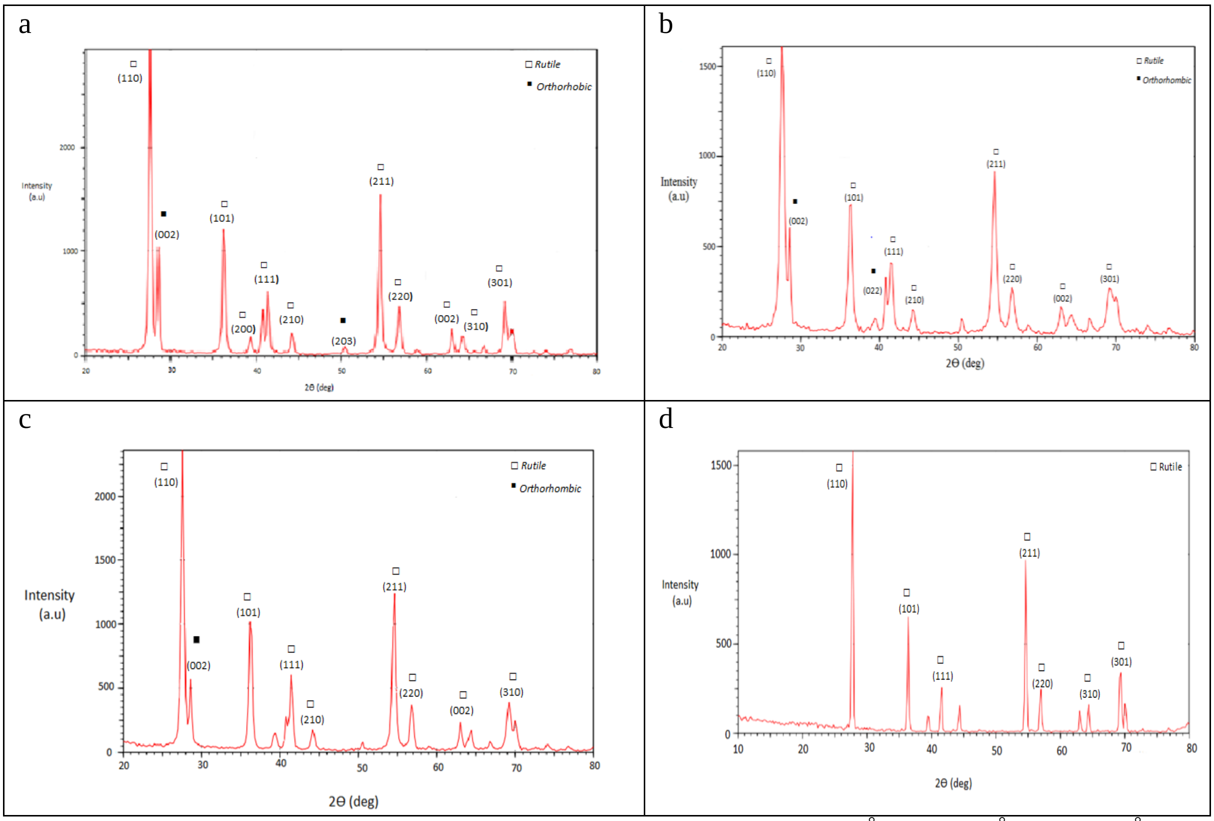


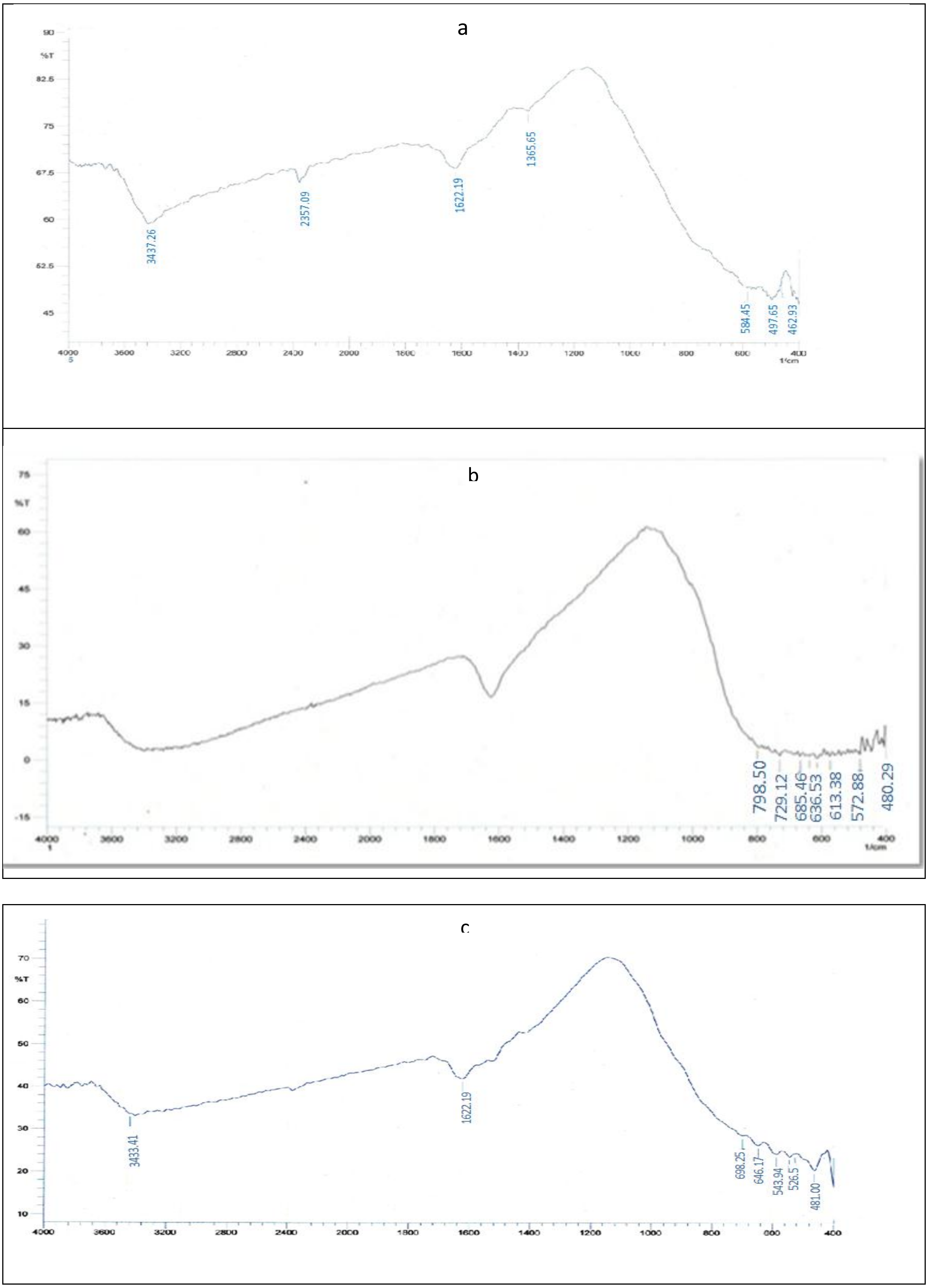
Figure 1- XRD patterns of TiO_2 with annealing temperatures at: (a) 200°C, (b) 400°C, (C) 600°C and (d) 800°C for 120 min.

Table 1- The obtained result of the XRD for TiO_2 at different annealing temperature (200, 400, 600 and 800˚C) for 120 min.

Annealing Temperature for 90 min.	2θ(deg)	hkl	FWHM (β)	Grain Size (nm)	d XRD (nm)	Lattice parameter	
						a XRD (nm)	c XRD (nm)
200 ˚C	27.554	110	1.947	4.2001	0.3222	0.4557	0.3901
	54.342	211	1.569	5.6889	0.1486		
	36.143	101	1.166	7.1688	0.2483		
400 ˚C	27.600	110	0.340	19.1438	0.3228	0.4909	0.2967
	54.507	211	0.548	16.3608	0.1482		
	54.200	101	0.535	19.6072	0.2475		
600 ˚C	27.634	110	0.674	12.1218	0.32225	0.4561	0.4495
	54.535	211	0.697	12.8099	0.1481		
	36.279	101	0.658	12.7028	0.2474		
800 ˚C	27.763	110	0.473	17.2752	0.321	0.454	0.2984
	54.618	211	0.454	19.6717	0.1678		
	36.390	101	0.451	18.5132	0.2466		

Figure- 2(a)represent the FT-IR spectra of $Ti(OH)_4$ as-prepared and annealing at (200-800 ˚C) Figures-1(b) to 1(e). The spectra show there are broad peaks around to 3380 and 1620 cm^{-1} peaks are characteristic of surface-adsorbed water and hydroxyl groups (stretching and bending vibration of the O–H group respectively) [18]. These peaks are decreased and become smaller with increasing annealing temperature (200 to 800˚C), corresponding to decease amount of water in samples with increasing annealing temperature and the Ti-O stretching become broad and more significant.

There is no peak at 2900 cm^{-1} for all spectra of titanium dioxide Nano powders regarding C-H stretching band, which means all organic compounds were removed from the samples after wishing and annealing. The broad intense band saw below 1200 cm^{-1} and around 560-460 cm^{-1} is due to vibration, stretching and bending of Ti-O-Ti group respectively [19]. Rutile phases of TiO_2 exhibit certain strong FT-IR absorption bands in the regions of 800−650 cm^{-1} [20, 21].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1622.19
1365.65
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b
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636.53
613.38
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c
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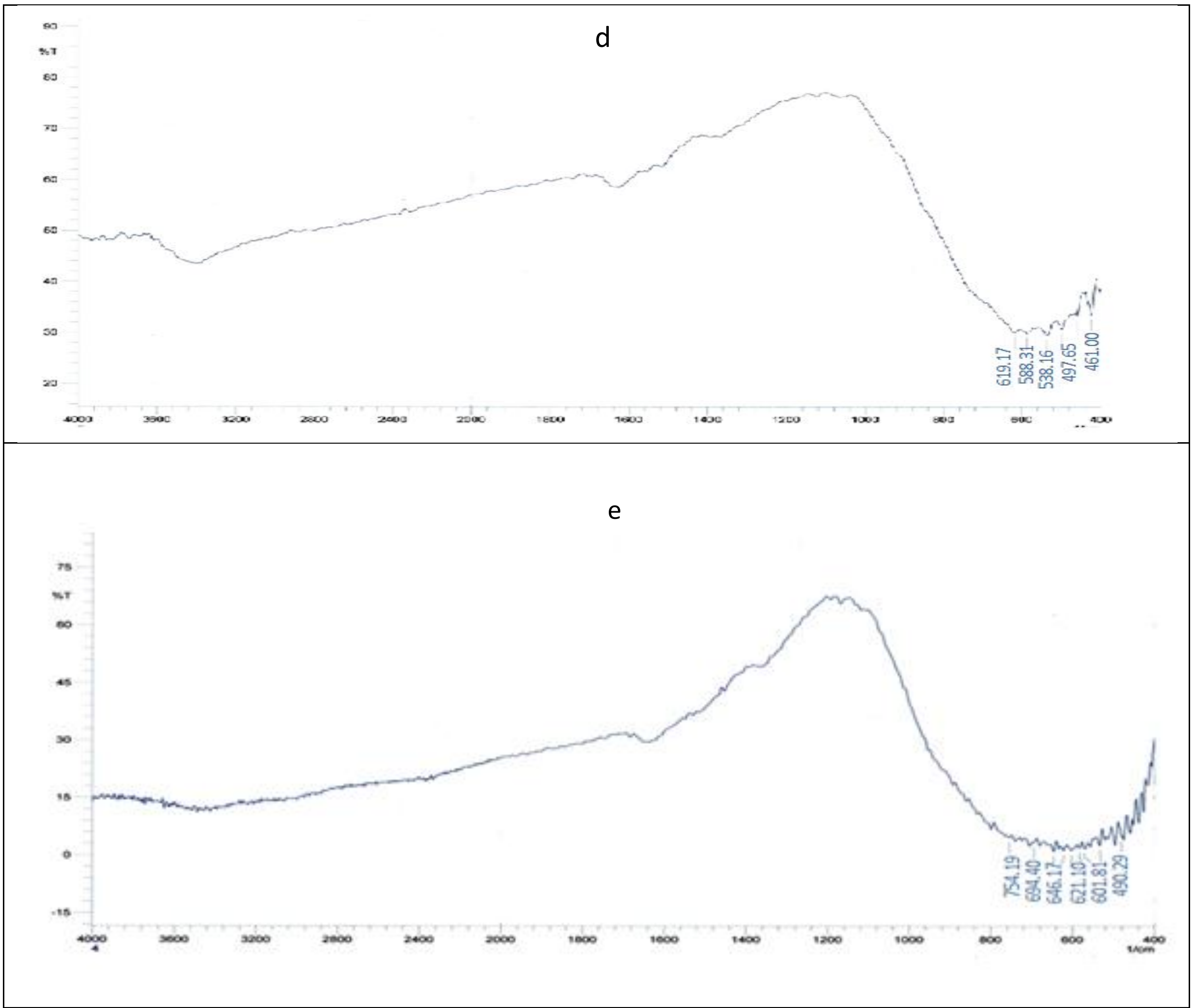
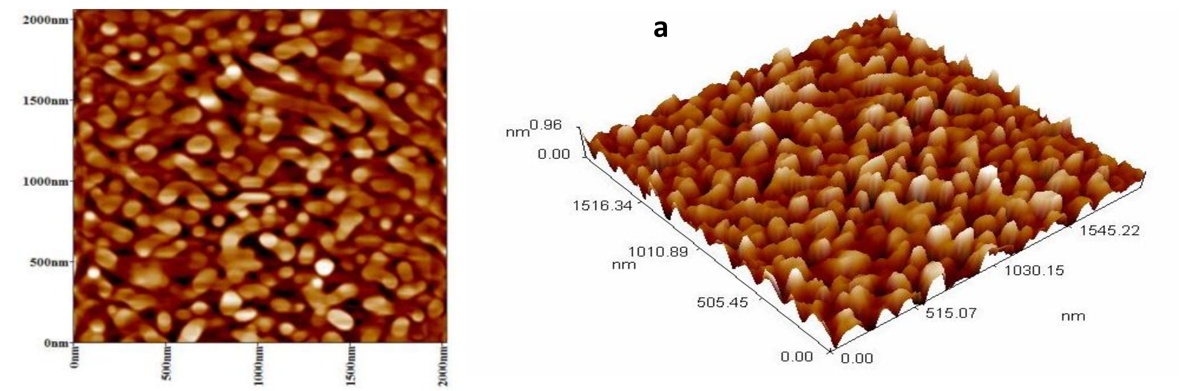
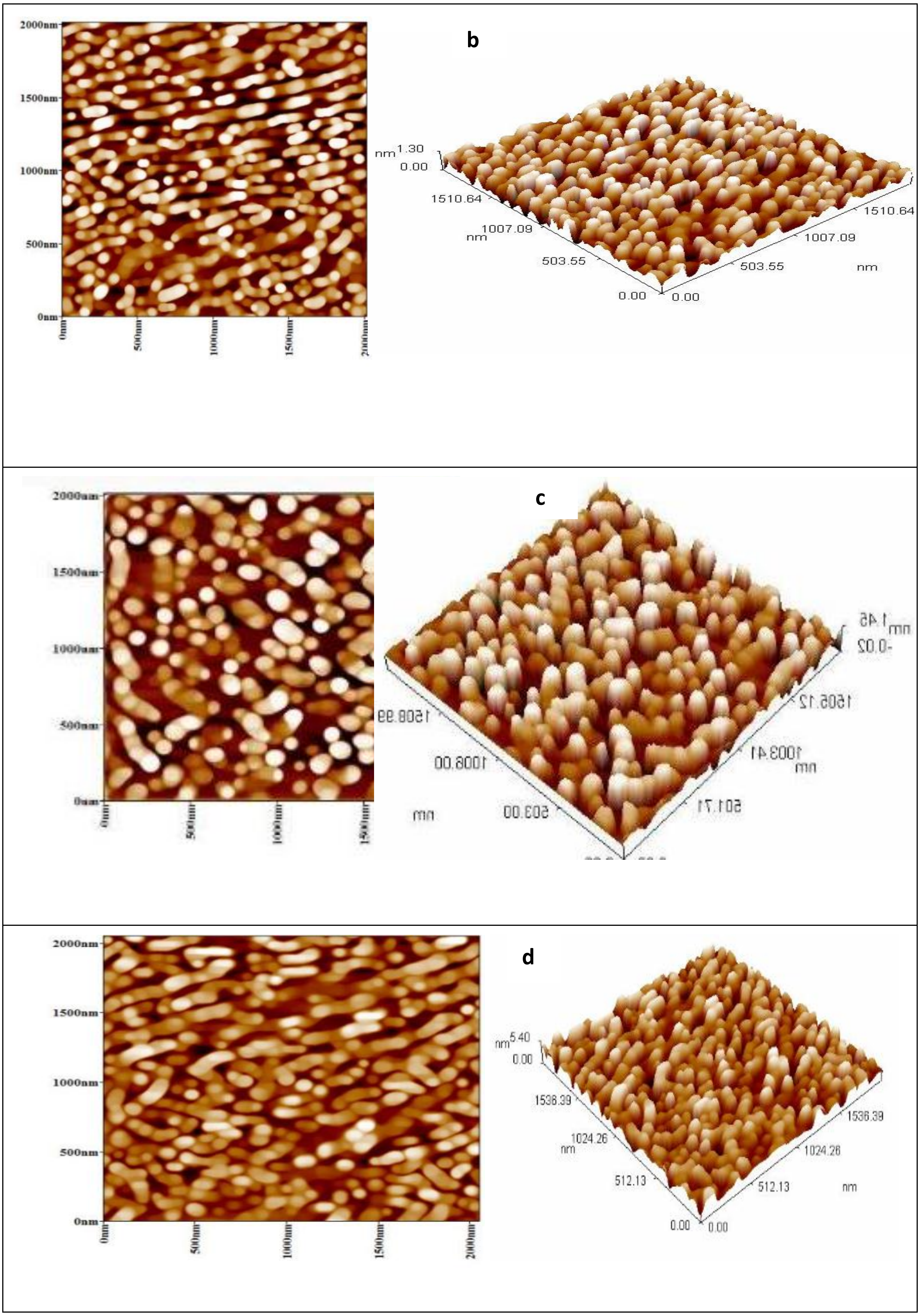


Figure 2- FTIR transmittance spectrum of TiO_2 annealing at: (a) as-prepared, (b) 200°C, (C) 400°C (d) 600°C and (e) 800°C for 120 min.

Figure 3- shows a typical two, three-dimensional AFM images and the granularity accumulation distribution chart of TiO_2 powders with annealing at (a-200, b-400, c-600, and d-800) °C. The average grain size found to be (69.40-92.87nm). AFM results show that the grain size increase by increasing temperature this is due to improving the crystalline of the powders [22].

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nm

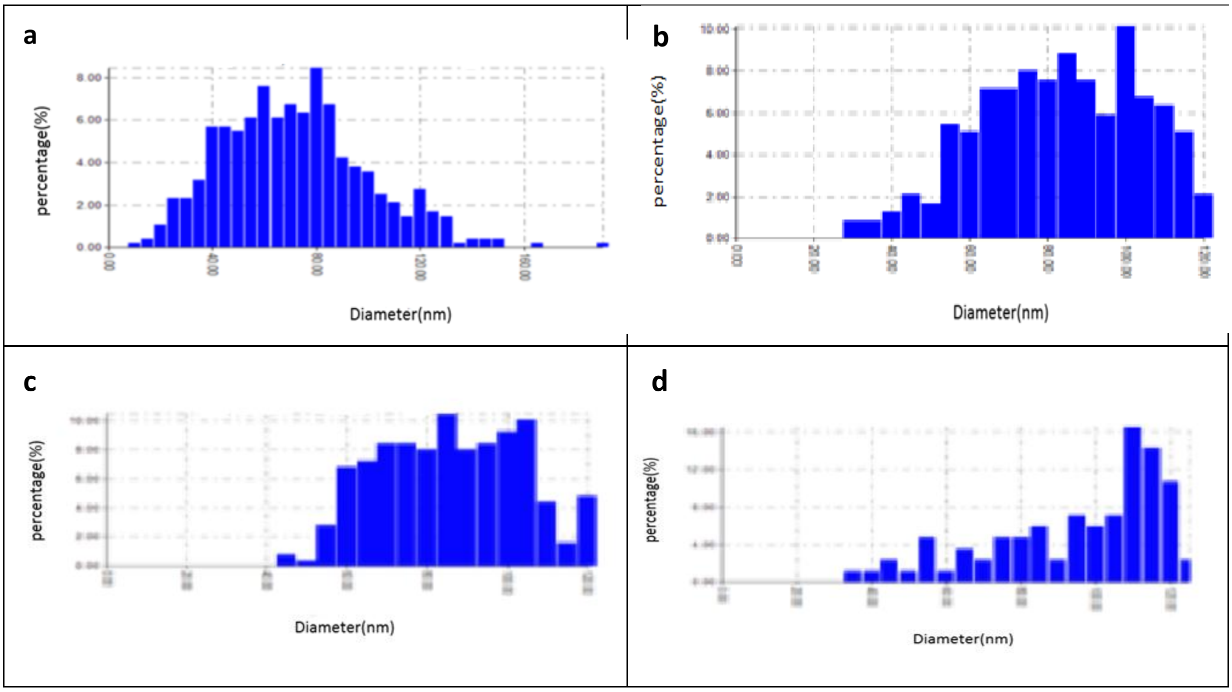

Figure 3- 2-D, 3-D dimensional AFM images and the granularity accumulation distributions chart of TiO_2 powders with annealing temperature at : (a) 200˚C, (b) 400˚C, (C) 600˚C and (d) 800˚C for 120 min.

Figure 4- shown the SEM images of TiO_2 that prepared by hydrothermal method at different annealing temperature (200-800)˚C according to the morphology of TiO_2 there are spherical shapes and change to the microsphere when annealing temperature at 600˚C. The SEM result revealed that the TiO_2 microspheres had a rough surface and were composed of many TiO_2 nanoparticle agglomerates.

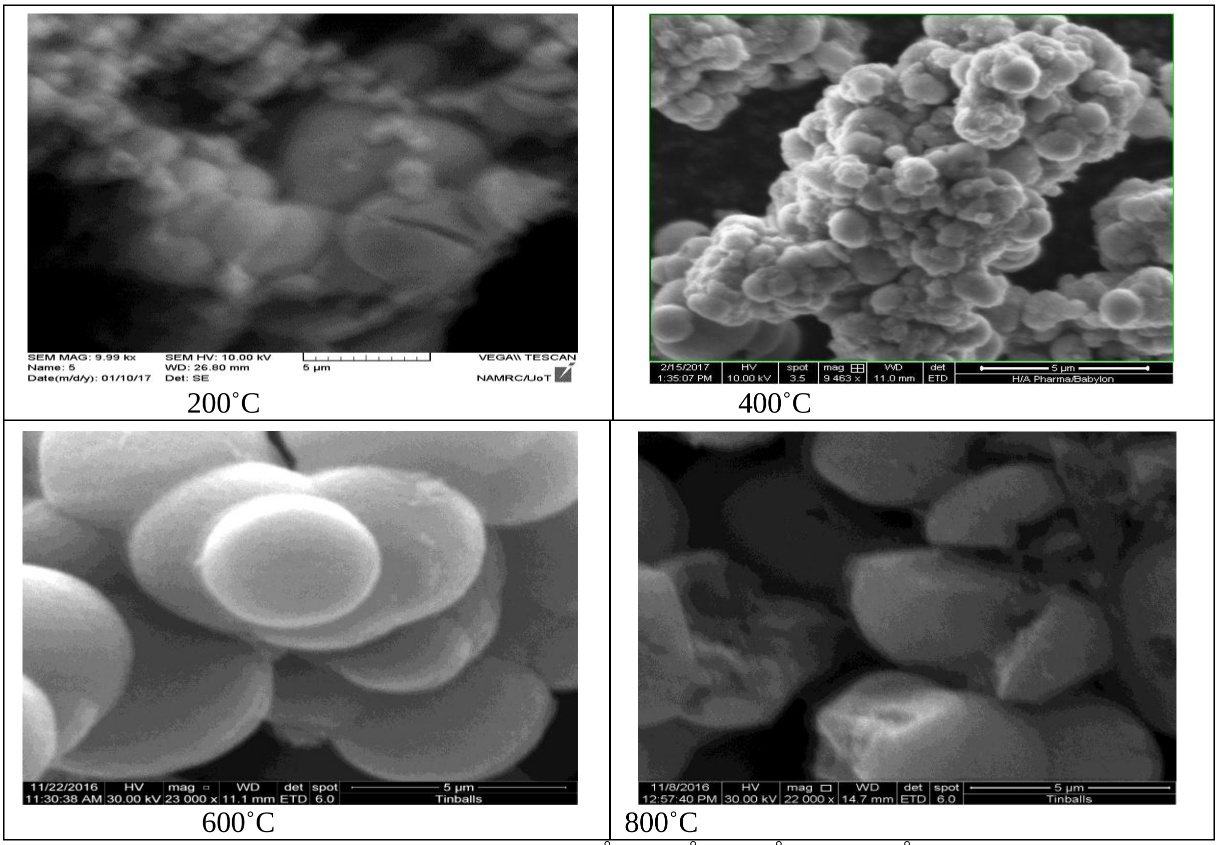

Figure 4- SEM image for TiO_2 nanoparticle at 200˚C, 400˚C, 600˚C and 800˚C for 120 min.

Figure 5- shows the UV-Visible of the optical transmittance curves as a function of the wavelength for the TiO_2 Nano powder at various annealing temperatures (200, 400, 600, and 800°C) for (120 min).Transmittance spectra were measured in the wavelength range of 350 - 850 nm. As can be seen, an increase in the annealing temperature which improves the optical transmission. Obviously, the Nano powders are fully transparent in the visible region and a sharp fall in the UV region 300-400 nm. The TiO_2 Nano powder spectra exhibit high visible transmittance, up to 99 % in the UV-Visible region for the TiO_2 Nano powders at 200˚C [23].

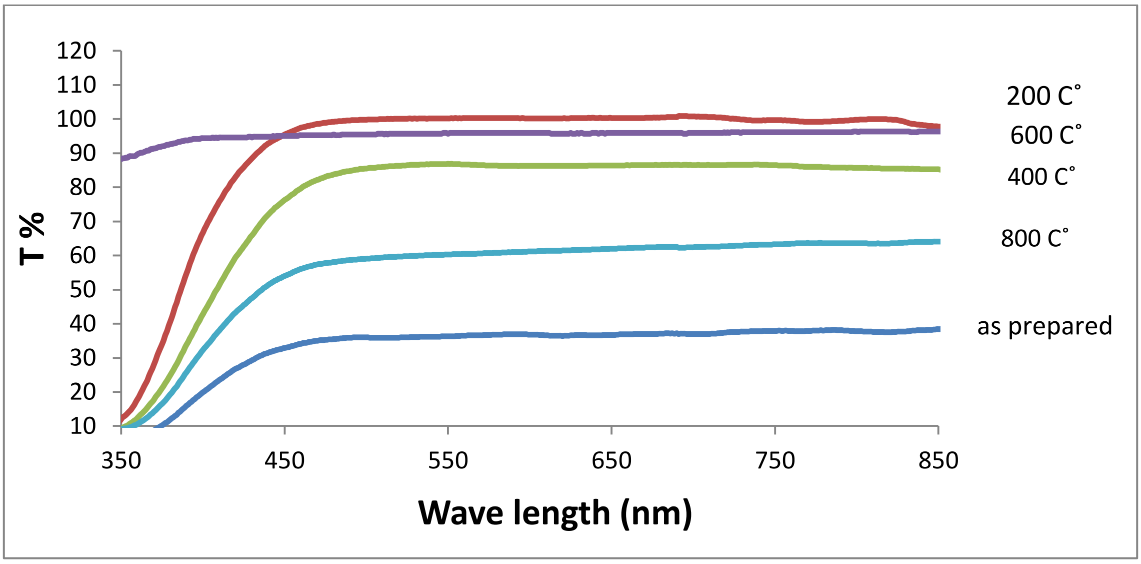

Figure 5- The optical transmittance spectra for titanium oxide (TiO_2) at different annealing temperature (200, 400, 600 and 800°C) for 120 min.

The optical band gap of the TiO_2 powder decreased with increasing annealing temperature at (400, 600, 800)°C, in the range of 3.5 to 3.15eV. It can be seen that the band gap energy decreased with the increasing grain sizes due to the increases annealing temperatures, the absorption edge red shifts towards lower energy side, indicating the decrease in the band gap. Indeed, the absorption edge shifts (showed in Figure-6) leads to a very good agreement with those of the band gap energies. The relationship between the absorption coeffcient (α) and the incident photon energy (hν) can be expressed by the following equation:

$\alpha = A(h\nu - Eg)\ n/h\nu$ ……………………………………………………………………..…(2)

Where α is the absorption coefficient, Eg is the absorption band gap, A is constant, n depends on the nature of the transitions [13].

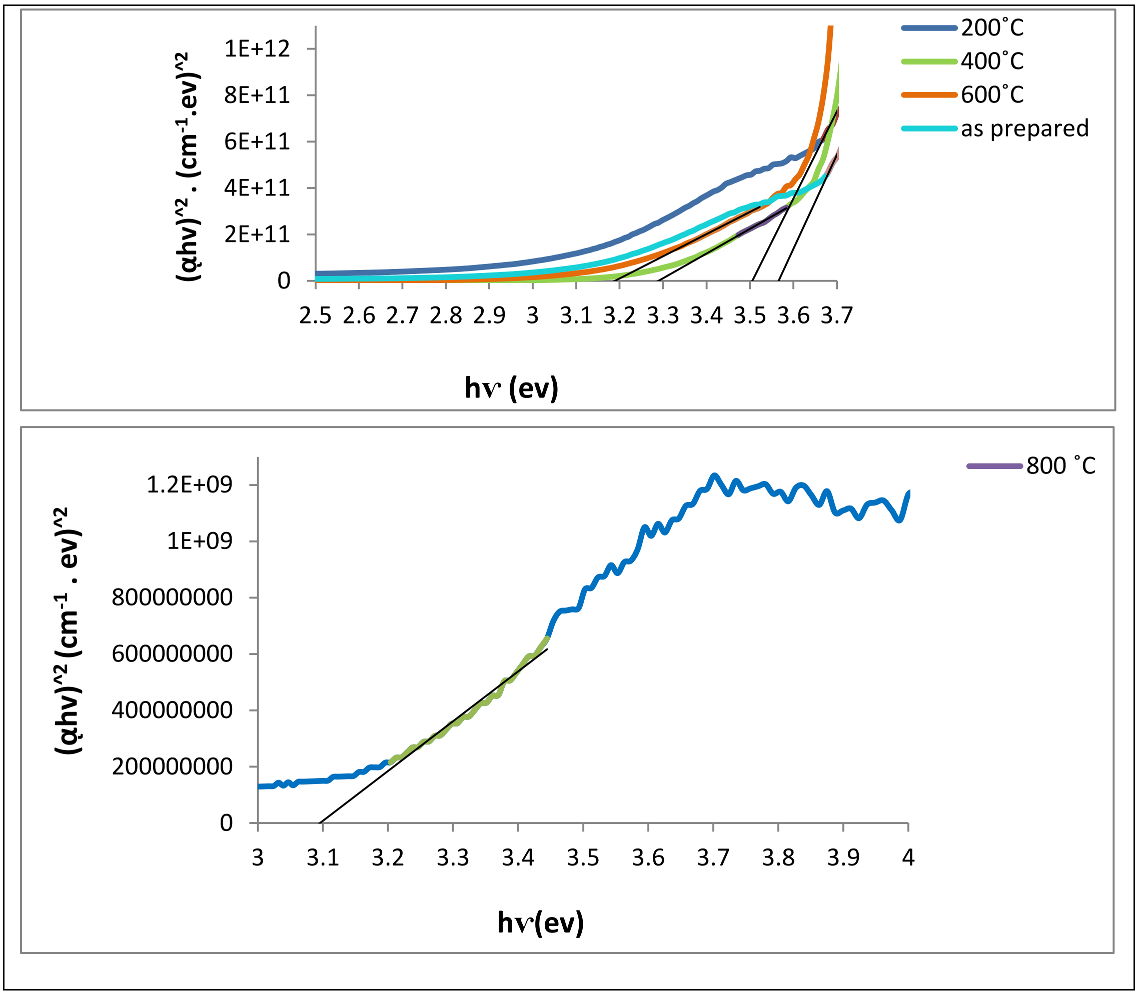

Figure 6- The optical band gap for titanium dioxide (TiO_2) at different annealing temperature (200, 400, 600 and 800°C) for 120 min.

4. Conclusions

Titanium dioxide nanopowders were synthesized by a hydrothermal method. The XRD give the high intensity peak (110) of TiO_2 structure. The AFM study shows that the size range of the nanopowder increase from (69.40 - 92.87 nm) with increase annealing temperature (200- 800°C) for 120 min respectively. The SEM images show that with increasing temperature the morphology of the particles are spherical shape and nanopowders were less agglomerate. The high transmetion when annealing titanium dioxide nanopowders at 600°C and the maximam energy gab of titanium dioxide nanopowders was above 3.2 eV.

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