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Growth and Characterization of Titanium Dioxide Nanorods Via Hydrothermal Method

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Abstract: Wide band gap semiconductor materials such as titanium dioxide (TiO_2) are of interest in the research field due to their potential application in photovoltaics and sensors. In particular, TiO_2 nanostructures, due to the larger surface area and the ability for bandgap tunability. In this study, titanium dioxide (TiO_2) nanorods were fabricated using the hydrothermal method on fluorine doped tin oxide (FTO) with different variation growth solution parameters at a constant reaction time of 7 hours. The parameter variation in this study were reaction temperature, concentrations of hydrochloric (HCL) acid solution and concentrations of titanium (IV) butoxide (TBOT) solution. The structural analysis of the samples was characterized by using X-ray Diffraction (XRD) while the composition of the sample was obtained by the Energy Dispersive X-Ray (EDX) analysis. The surface morphology of the samples was characterized by Field Emission Scanning Electron Microscopy (FESEM) and Ultraviolet–Visible Spectrophotometer (UV – Vis) were used to characterize the optical properties of the samples. The structural analysis had proven that the TiO_2 nanorods consist of pure rutile phased which can be used in photocatalyst activity. The composition analysis showed that TiO_2 compounds had been fabricated on the substrates. From the surface morphology and optical properties analysis, the best sample was found to be fabricated at a reaction temperature of 150 ℃ with the precursor solution of 30 ml of HCl acid solution and deionized (DI) water with a volume of ratio was 1:1 and the volume of TBOT at 1.5 ml for 7 hours. The sample shows rod-like structure formation and uniform thickness while the band gap obtain was 3.85 eV.

Keywords: TiO_2, Nanorods, Hydrothermal thermal, XRD, FESEM, UV-Vis

1. Introduction

Titanium dioxide (TiO_2) have been extensively studied by many previous researchers and is considered one of the promising materials since it has unique characteristic and properties such as non-toxicity, high refractive index, chemical stability and high dielectric constant [1]. The characteristics and properties of the TiO_2 differ depending on the formation of the structure. Nowadays, nanostructured

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material has been getting a lot of attention due to the fact this material can produce structures in the size of nanoscale which can be used in a wide range of areas that are involved with nanotechnology. The TiO_2 nanostructures exhibit tuneable optical properties, powerful oxidation strength, chemical stability and non-toxic depending on their shape and morphology [2]. There is a lot of variety of nanostructures such as nanowires, nanorods, nanoparticles and nanoflowers [3]. Hence, it is essential to understand the ability to engineer for the application's specific needs. For example, for the high surface-to-volume ratio nanorods with a small diameter with higher lengths are required in applications such as sensors and photovoltaics. One of the main ways to engineer the characteristics and properties of TiO_2 nanostructures is by the methods used for synthesizing TiO_2 and manipulating the parameters.

There are numerous methods approaches for the growth of titanium dioxide (TiO_2) nanomaterials such as solution-based synthetic approaches, vapor-based approaches, templated growth and top-down fabrication techniques[4]. Many researchers have been trying to find and develop the optimum synthesis method for producing particles with suitable characteristics for environmental remediation or other application interest [5]. Even though there are various kind of synthesis method to produce titanium dioxide (TiO_2) nanomaterial, the most frequent method that has been done for research are the hydrothermal method. Hydrothermal is a method that is able to produce crystallization of a substance that relies on the solubility of the aqueous solution or mineral under high pressure and temperature [6].

Several parameters impact the size and properties of the TiO_2 particles fabricated by the hydrothermal method. The parameters that greatly influence the hydrothermal method process should be controlled so that the desired result will be achieved. It has been proven that there are some parameter that plays major roles compared to others parameters [7]. In this work, the growth of TiO_2 nanorods were conducted by changing some of the parameters that are used such as different reaction temperature, different concentration of hydrochloric (HCl) acid solution and titanium (IV) butoxide (TBOT) solution. These parameters that are being changed were improved and optimised to find the best ratio for the growth of TiO_2 nanorods. The characteristic analysis such as the structural analysis, surface morphologies and optical properties were characterized by using XRD, FESEM and UV- Vis spectrophotometer for each category specifically.

2. Materials and Methods

2.1 Substrate cleaning

Fluorine dope tin oxide (FTO) glass substrate was used in the fabrication process of TiO_2 nanorods. The FTO substrates were cut with a size measurement of 2.5 cm × 1.5 cm and ultrasonically cleaned in the solution of acetone, ethanol and deionized (DI) with a volume of the ratio were 1:1:1 of 10 ml each respectively for 10 minutes. After that, the cleaned substrates were rinsed with DI water and dried in the oven for 30 minutes at a temperature of 110℃.

2.2 Sample preparation

TiO_2 nanorods were synthesized by hydrothermal method. The precursor solution was first prepared by mixing the solution 30 ml of HCl and deionized (DI) water with a volume of the ratio of 1:1 and stirred with a magnetic stirrer at 370 rpm for 15 minutes. Titanium (IV) butoxide (TBOT) of 1.5 ml solutions was added dropwise using a capillary tube and constantly stirred until a clear solution was obtained. Before transferring the precursor solution into the Teflon-lined stainless-steel autoclave (100 ml), the glass substrates were checked using a multimeter so that the conducting FTO substrates surface were facing upward in the Teflon at an angle of 45° vertically against the wall. The hydrothermal synthesis was fabricated at three reaction temperatures which were 150 ℃, 170 ℃ and 180 ℃ keeping all other parameters constant for 7 hours. Further, the fabrication was carried out at two different concentrations of HCl solution such as 15 ml and 35 ml. The fabrication was then lastly observed at two different concentrations of TBOT solution such as 1.5 ml and 2.0 ml. The reaction time and temperature for the two parameter changes were kept constant for 7 hours at 160 ℃. After the process of fabrication, the samples were washed with DI water and finally dried at room temperature.

2.3 Sample characterization techniques

The structural analysis of the sample was investigated by obtaining the XRD pattern observed by X-Ray Diffraction (XRD) machine. The composition analysis was carried out by the Energy Dispersive X-Ray (EDX) analysis from the FESEM-EDX. The surface morphologies were observed by using Field-Emission Scanning Electron Microscopy (FESEM). Lastly, the optical properties of the samples were observed and analysed by using the Ultraviolet-Visible Spectrophotometer (UV-Vis).

3. Results and Discussion

3.1 Structural and Composition Analysis of TiO_2 Nanorods

The crystallinity of the TiO_2 nanorods arrays was observed by looking into the XRD pattern of the results obtained. In this analysis, the sample that was used to characterize is based on the parameter of different reaction temperatures of TiO_2 nanorods which the temperature was 150°C. From the pattern, strong diffraction of rutile peaks at 36°, 41°, 54°, 63° and 70° indicates that the Titanium Dioxide (TiO_2) were in the rutile phase with a crystal plane corresponds to (101), (111), (211), (002) and (301) as shown in Figure 1. The experimental XRD patterns were compared with standard diffraction data of rutile-phased TiO_2 cited from the 1998 Joint Committee on Powder Diffraction Standards- International Centre for Diffraction Data (JCPDS) which index to the tetragonal crystal structure (JCPDS card No. 01-82-0514) [8]. Overall, the peaks from the results obtained show that there was no broad peak produced since the peaks consist of strong, sharp diffraction which indicates the characteristics of good crystallinity of the sample.

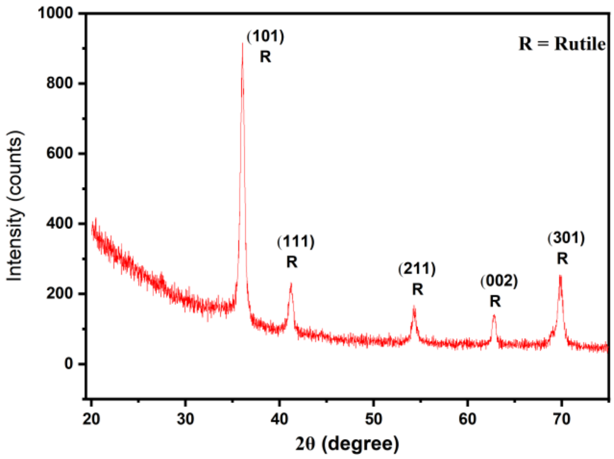


Figure 1: XRD patterns result of TiO_2 nanorods for reaction temperature of 150°C

As tabulated in Table 1 the value of FWHM shows the lowest at the peak positions position 36°, 54° and 63° which indicates that it has high crystallinity compared to other peaks. The full width at half maximum (FWHM) of XRD patterns of materials is observed to determine the material properties and surface integrity features which concern about the grain distortion, residual stresses and dislocation density [9]. The value of FWHM recorded can determine the crystallinity of the properties of the material, it showed that high crystallinity of materials had a low value of FWHM.

Table 1: The Peak list of XRD data analysis

Position (2θ)	FWHM (2θ)
36.04049	0.39360
41.24157	0.47232
54.31772	0.39360
62.95120	0.39360
69.96835	0.43296

The EDX elemental analysis of TiO_2 nanorods sample for 150°C was shown in Figure 2 and confirms the presence of five compounds which were carbon (C), oxygen (O), chlorine (Cl), titanium (Ti) and tin (Sn).

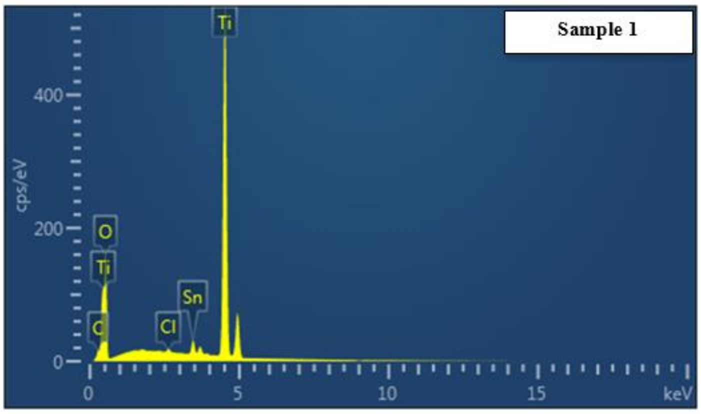


Figure 2: The EDX analysis graph of TiO_2 nanorods for a reaction temperature of 150°C

Table 2 shows the elemental concentration for each element in the sample for TiO_2 nanorods. The titanium (Ti) and oxygen (O) elements had high concentrations compared to other elements, this confirms that the TiO_2 compound was being fabricated on the FTO glass substrates surface. Other elements such as tin (Sn), chlorine (Cl) and carbon (C) were found in the sample, possible explanations for this were may due to some factors. The existence of the tin (Sn) element was due to the FTO glass substrates that had been used in the fabrication process and the element chlorine (Cl) was possibly because of the precursor solution that had been used in the hydrothermal method. The carbon (C) peak may occur due to environmental contamination from the surroundings.

Table 2: The EDX analysis of TiO_2 nanorods for a reaction temperature of 150°C

Element	Elemental Concentration
C	139.35
O	2182.18
Cl	28.36
Ti	5307.93
Sn	371.07

3.2 Surface Morphology Analysis of TiO_2 Nanorods

Figure 3 (a), (c) and (d) shows the resulting images of surface morphology for TiO_2 nanorods arrays with different reaction temperature of 150 ℃, 170 ℃ and 180 ℃. Figure 3 (b) indicates the cross-sectional area for a reaction temperature of 150 ℃. The result for the reaction temperature showed that the diameter and thickness of the TiO_2 nanorods increased as the temperature increased. Moreover, the surface morphology of TiO_2 nanorods was found to be formed in a tetragonal shape with square top facets but as the reaction temperature increases it shows step edges on uneven top facets as shown in Figure 3 (a), (c) and (d) respectively. Previous studies carried out by Liu et al. [10], have demonstrated that the parameters used for the precursor solution affect the growth of each unit of rods and its top facet may differ from one another. Figure 3 (b) shows that the side walls become clustered and many slender and shorter nanorods were formed. Yuxiang et al. [11], stated that a possible explanation for this might be because the growth units rate of TiO_2 essentially adsorb onto the surface of long nanorods and hardly diffuse into the inter- spaces between the nanorods, so it occurs to be some units parts to fabricated short nanorods at a slower rate.

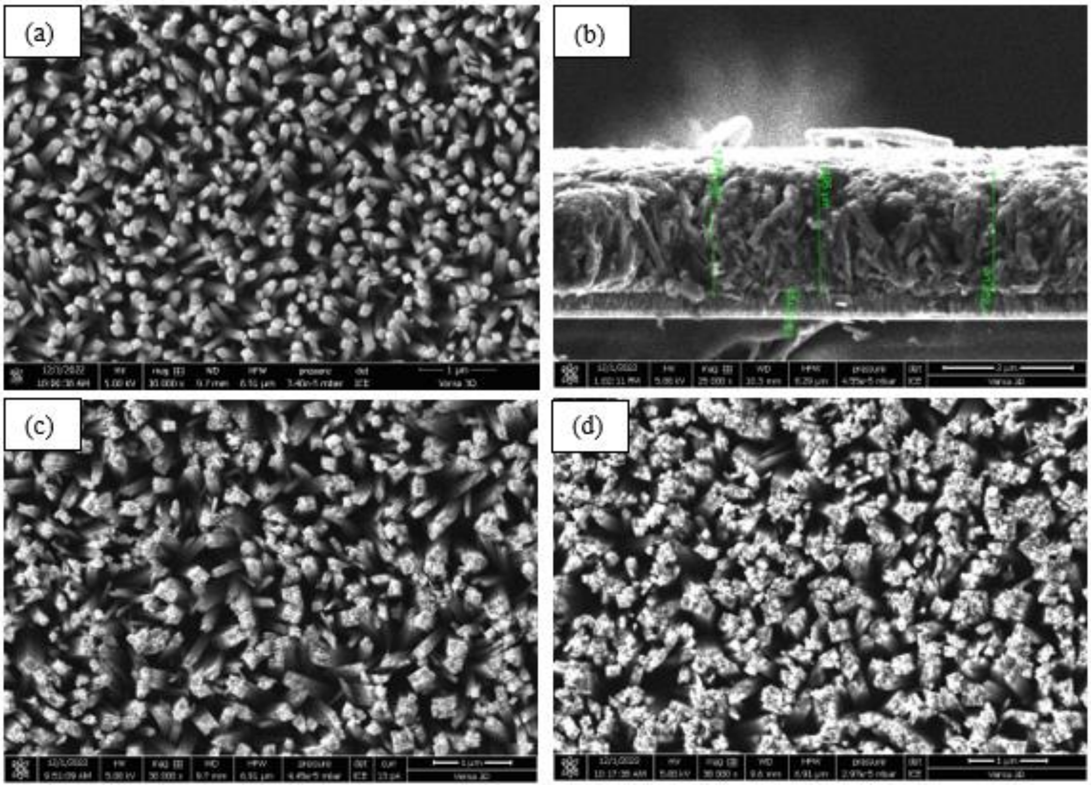


Figure 3: FESEM results of TiO_2 nanorods surface morphology for (a) 150 ℃ (c) 170 ℃ and (d) 180 ℃ while (b) cross-sectional image for 150 ℃

Figure 4 (a) and (b) shows the surface morphology for different concentration of HCl at 15 ml and 35 ml respectively. The result showed that the surface morphologies of TiO_2 were influenced by the HCl concentration. Surprisingly, the image shown in Figure 4 (a) for 15 ml concentration of HCl forms a cauliflower type like of TiO_2 and there was no formation of rod–like structure of TiO_2. It was expected that the surface morphology at an HCL concentration of 35 ml in Figure 4 (b) will be formed with less diameter rods but the thickness of the nanorods remains constant. In prior studies conducted by Hamed et al. [12], there was slight growth of rods on the concentration of HCl at 20 ml but when the volume of HCl increases, the nanorods were able to obtain.

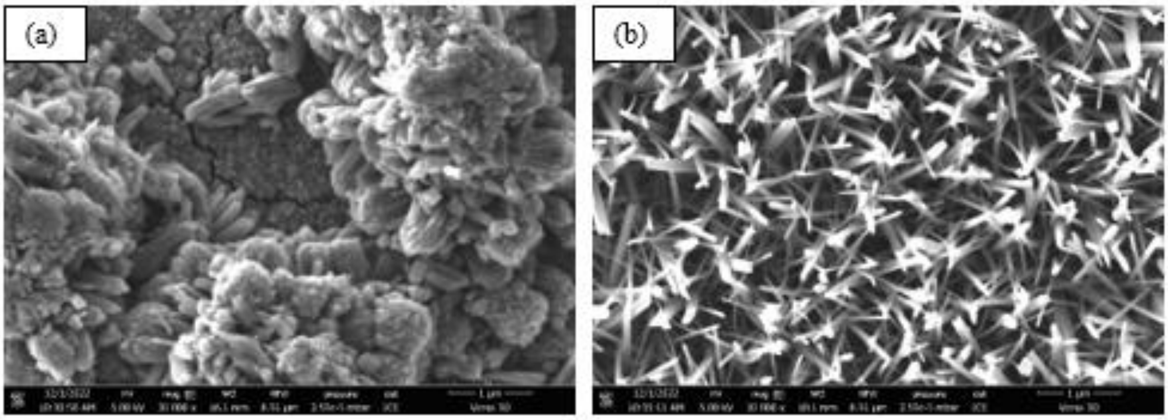


Figure 4: FESEM results of TiO_2 nanorods surface morphology for (a) 15 ml concentration of HCl and (b) 35 ml concentration of HCl

Figure 5 (a) and (b) show the TiO_2 nanorods arrays surface morphology image at 1.5 ml concentration of TBOT and 2.0 ml concentration of TBOT respectively. The other precursor solution was fixed with the ratio of 1:1 which were 30 ml of HCl solution and 30 ml of DI water. The result showed that the surface morphology of the TiO_2 was influenced by the concentration of TBOT. As seen in Figure 5 (a), the diameter and length of nanorods are much smaller compared to Figure 4 (b). This finding was consistent with Prathan et al. [13], who found in the studies that the initial nucleation and the growth rate of TiO_2 nanorods were higher when the percentage concentration of the TBOT molecules was increased. Figure 5 (a) showed that the substrates that were covered were not vertically aligned which influenced to misoriented nanorods. A possible explanation for this might be because the hydrolysis and precipitation reaction of the growth solution was influenced by the TBOT precursor. So when the amount of TBOT precursor is lesser, the dimension of TiO_2 nanorods percentage became lower [10]. In Figure 5 (b) the diameter and length of the nanorods were much larger in dimension but contrary to expectations the growth rate of the single unit rods was not uniform in diameter. The inconsistency may be due to the initial nucleation sites region were not large enough so the growth reaction time may be differed from one unit to another unit, so that may be the reason there were some diameters of nanorods that were smaller in size.

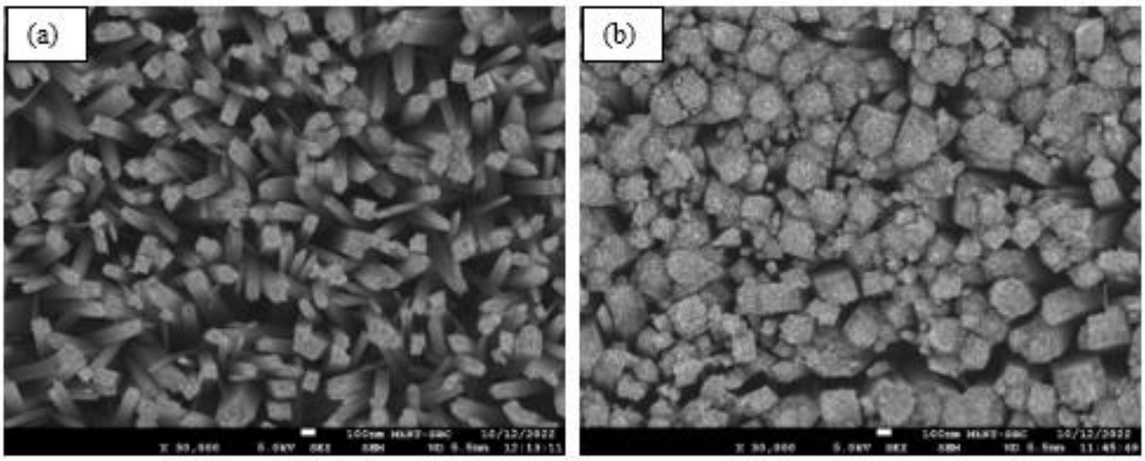
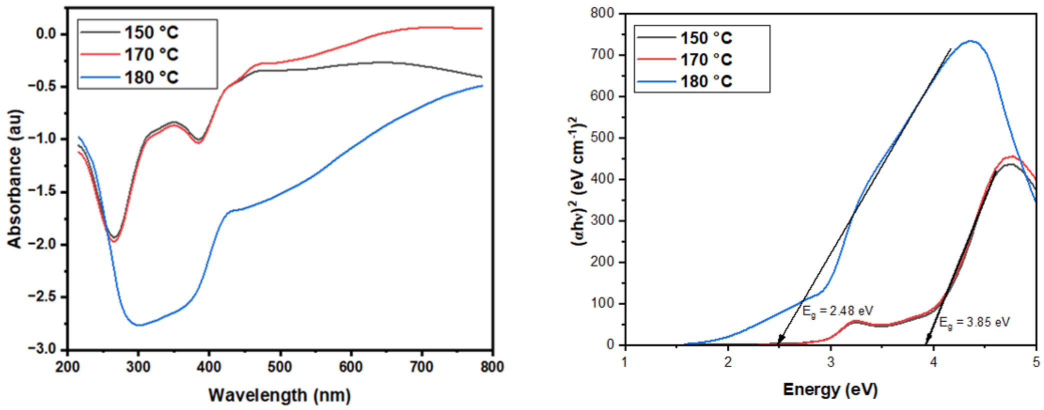


Figure 5: FESEM results of TiO_2 nanorods surface morphology for (a) 1.5 ml concentration of TBOT and (b) 2.0 ml concentration of TBOT

3.3 Optical properties of TiO_2 Nanorods

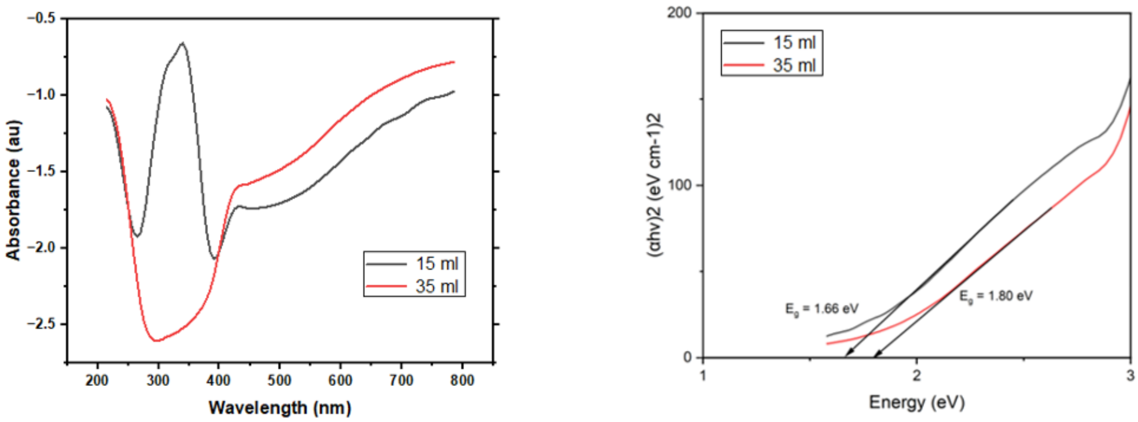
The absorbance spectra of TiO_2 nanorods with different reaction temperatures which were labelled as 150 °C, 170 °C and 180 °C respectively are shown in Figure 6 (a), The absorbency increased with increasing the incident wavelength. However, at 180 °C showed the absorbance value suddenly drops around 300 nm to 400 nm but after that, it showed an increasing value in absorbance. The energy band gap of the TiO_2 nanorods that were based on the different reaction temperatures was obtained in Figure 6 (b). Based on the energy band gap, the reaction temperature at 180 °C showed the band gap obtain was 2.48 eV whereas the band gap obtains for 150 °C and 170 °C shares the same value of band gap which was 3.85 eV. This result may be explained by the fact that when the crystallization of rutile TiO_2 nanorods increases with the reaction temperature, it decreases the bandgap energy [14].



(a) (b)

Figure 6: (a) UV – Vis absorbance spectra of TiO_2 nanorods and (b) optical band gap of TiO_2 nanorods with different reaction temperatures from 150 °C, 170 °C and 180 °C

In Figure 7 (a) the absorption spectrum of TiO_2 nanorods with different concentrations of HCl had been observed. There were two different concentrations were used which were a 15 ml concentration of HCl and a 35 ml concentration of HCl. The analysis had shown that the higher the concentration of HCl, the higher the absorbance rate. The band gap of the TiO_2 nanorods for 15 ml concentration of HCl was 1.66 eV whereas for 35 ml concentration of HCl was 1.80 eV as shown in Figure 7 (b). Both band gap energy showed a value below 3.0 eV, the value of the energy band gap for the rutile phase must be around 3.0 eV [15]. This finding was unexpected and suggests that the concentration of HCl must be increased to get the range value of the energy band gap for the rutile phase.



(a) (b)

Figure 7: (a) UV – Vis absorbance spectra of TiO_2 nanorods and (b) optical band gap of TiO_2 nanorod with different concentrations of HCl from 15 ml and 35 ml

The absorbance spectra of TiO_2 nanorods with different concentrations of TBOT were analysed in Figure 8 (a) with the concentration of TBOT of 1.5 ml and the concentration of TBOT of 2.0 ml. Based on the analysis, the higher the concentration of TBOT, the lower the absorbance value observed. These results match those observed in earlier studies which stated that the lower concentration of TBOT will affect the surface roughness and more photon energy can be absorbed [16]. Figure 8 (b) showed that the band gap energy for 1.5 ml concentration of TBOT was 4.24 eV whereas, for 2.0 ml concentration of TBOT, the value obtained was 4.31. eV. The lower the band gap, the higher the conductivity, these results reflect those conducted by Puteri Sarah et al. [17], which stated that the concentration of TBOT decreases the optical band gap and is attributed to the improvement in surface roughness of surface morphology.

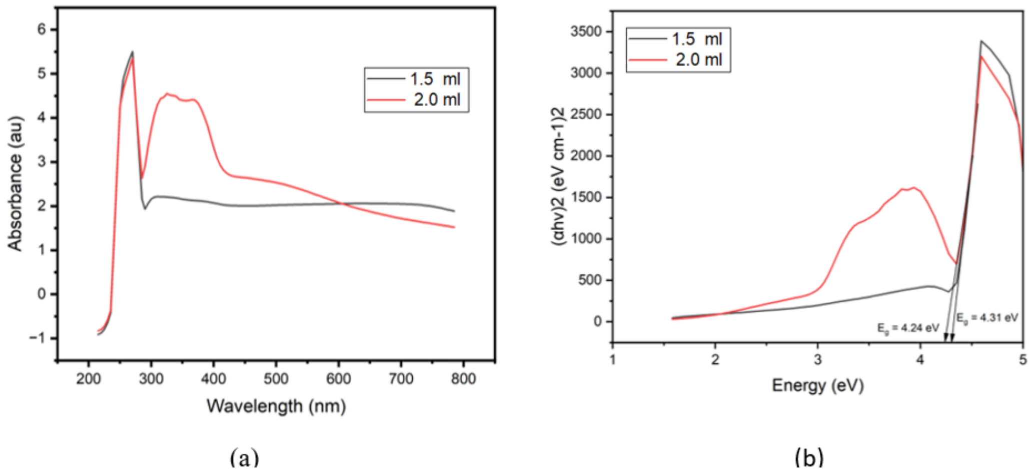


Figure 8: (a) UV – Vis absorbance spectra of TiO_2 nanorods and (b) optical band gap of TiO_2 nanorods with different concentrations of TBOT from 1.5 ml and 2.0 ml

4. Conclusions

Through this study, the objective of the research has successfully been achieved which was fabricating the TiO_2 nanorods with different growth solution parameter changes by the process of hydrothermal method on FTO conducting glass substrates. The structural analysis result from the XRD pattern showed that the TiO_2 nanorods that had been fabricated consisted of a pure rutile phase. The preferable growth of TiO_2 nanorods was oriented along the (101) plane as it has high intensity of rutile peak. The surface morphology analysis by FESEM showed that each sample had a different surface morphology analysis. The growth parameter solution influenced the diameter, thickness, length, shape and the orientation of growth of the nanorods. Therefore, all parameters for hydrothermal synthesis greatly affect the preferable growth of TiO_2 nanorods. The optical properties of the research were characterized by using the UV – Vis spectroscopy and the absorbance spectrum of the sample was observed based on the main parameter changes. The results show that when the absorbance rate decreases, the band gap of the sample increases. Overall, from the surface morphology analysis and optical properties, the reaction temperature at 150 °C with the precursor solution of 30 ml of HCl acid solution and deionized (DI) water with a volume of ratio was 1:1 and the volume of TBOT at 1.5 ml for 7 hours had proven to be the best overall optimization when it comes to properties and characteristics of TiO_2 nanorods with rods – like structure formation and uniform thickness while the band gap obtain was 3.85 eV.

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