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# Influence of Reaction Time and Hydrochloric Acid Volume on Rutile Titanum Dioxide Nanorods Thin Film

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**ABSTRACT**

Titanium dioxide ($TiO_2$) nanostructured materials have attracted attention due to their application at various fields such as photocatalysis, solar cell and photochemical applications. Whereas $TiO_2$ could exhibit high efficiency of solar cell and economical than traditional silicon solar cells. In this study, hydrothermal method demonstrated to synthesis $TiO_2$ nanorods properties at different hydrothermal reaction times and various hydrochloric acid volumes. Increasing the reaction time could influence the thickness towards high crystalline rutile formation while modifying the hydrochloric (HCl) acid concentration favours a great influence on the morphologies and alignment of the nanostructure. The result is beneficial for improvements thin film power conversion efficiency.



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## 1. INTRODUCTION

$TiO_2$ is an n-type metal oxide semiconductor with wider band gap of more than 3.0 eV, comes in three major types of nature, which are anatase, rutile and brookite. Rutile $TiO_2$ is known as the most stable phase compare to anatase and brookite.[1] Presently, the interest towards nanostructures become popular because of its outstanding features such larger exposure area to sunlight, high surface-to-volume ratio, non-toxicity, uniquely photochemical and photo-physical properties and also for their electron-transport properties.[2] Therefore, variety of $TiO_2$ nanostructures such as nanoparticles, nanotubes, nanorods, nanofibers, and nanoflowers has been prepared. These structures can be synthesis through sol-gel process [3] template-assisted,[4] hydrotherma, chemical bath deposition [5] spray pyrolysis and anodization.[6] Hydrothermal process is a promising approach due to its simple process, fast reaction velocity and low cost.[7] $TiO_2$ nanorods has paid much attention in this study due to the superior electrical transport performance, excellent chemical stability, high refraction index, and low production cost. In this article, hydrothermal method demonstrated to synthesis $TiO_2$ nanorods morphology under various reaction times and different hydrochloric acid volumes to have an optimum parameter.

## 2. RESEARCH METHOD

### Preparation of $TiO_2$ nanorods

Fluorine-doped $SnO_2$ (FTO) glass (7 Ω/sq) with a thickness of 2.0 mm was cut into pieces of 15 × 25 mm in dimension as substrates. These substrates were cleaned ultrasonically in acetone, ethanol and de-ionized water for 10 minutes each. In a typical synthesis, 60 mL deionized water and 60 mL concentrated hydrochloric acid (36.5 – 38% by weight) stirring for 5 minutes before a certain amount of titanium(IV) butoxide (TBOT) was added wisely and stirring for another 10 minutes. The mixture solution was poured into a Teflon-lined autoclave where the FTO substrates were placed against the Teflon wall with an active side facing downward. Then the autoclave was sealed completely and hydrothermal synthesis was carried out at temperature 150°C for 5 to 10 hours, respectively and manipulating the volume of acidity medium (40 – 80 mL). After cooling down to ambient temperature, the substrates were taken out, rinsed extensively with deionized water and allowed to dry naturally in ambient air. To investigate the effect of synthesis duration, the samples were designated as 'RT*t*' which RT refers to reaction time and *t* corresponded to the duration taken to synthesis the $TiO_2$ film. Whereas in acidity investigation, the samples are denoted as 'HC*v*' where 'HC' is the abbreviation for hydrochloric acid (HCl) and '*v*' is corresponded to HCl volume.

### Characterization techniques

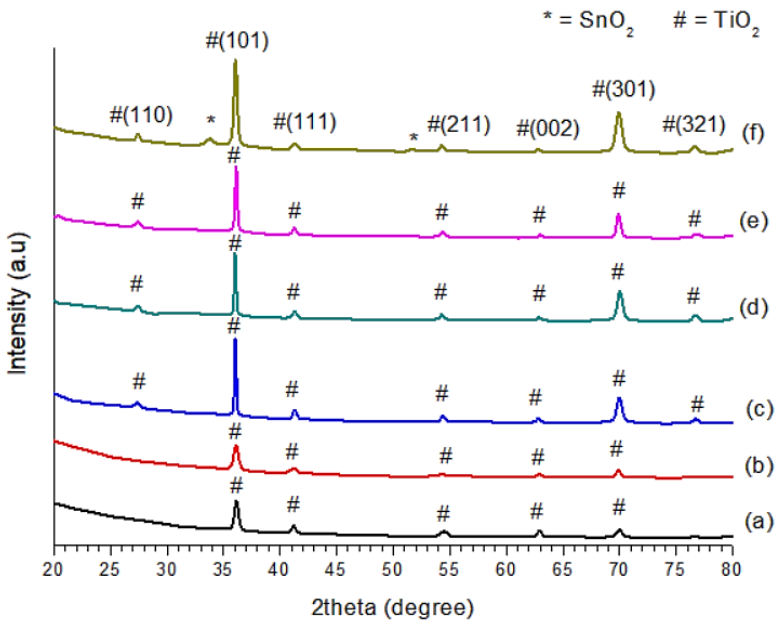
The crystal structure of the as-synthesized films was examined by PANanalytical X-Pert$^3$ Powder X-ray diffraction (XRD) with CuKα radiation (λ) 1.5406 Å in the Bragg angle ranging from 20° to 80° at a scanning speed of 2°min$^{-1}$ and the type of slit used was fixed divergence slit. X-ray tube voltage and current were set at 40 kV and 40 mA, respectively. The morphology and microstructure of the samples were examined by field emission scanning electron microscopy (FE-SEM, JOEL, JSM-7600F). The absorbance spectra were recorded in a range of 300 – 800 nm on a UV–Vis spectrophotometer (Shimadzu-UV 2600) to find the wavelength absorption.

## 3. RESULT AND DISCUSSIONS

### 3.1. Univariat

### Influence of hydrothermal reaction time

Fig. 1: XRD patterns of the as-synthesized samples (a) RT5 (b) RT6 (c) RT7 (d) RT8 (e) RT9 and (f) RT10 at 150 °C, respectively




The XRD pattern provides the information of crystalline quality and the orientation of the nanostructure. Fig. 1 illustrates the XRD pattern of nanorods $TiO_2$ film at different hydrothermal reaction time and conveys an increasing behaviour of crystalline as the time increase. The nanorods $TiO_2$ nanostructure showed crystalline nature with diffraction peaks lying at 2θ = 37.0, 41.0, 54.1, 62.7 and 70° can be indexed to (101), (111), (211), (002) and (301) crystal planes, respectively. A good crystalline of film synthesized could be improved by increasing the hydrothermal reaction time when two peaks existed at 27 and 77° corresponding to (110) and (321) plane, suggested more $TiO_2$ nanorods structure grown in various

planes. However, several $SnO_2$ peaks could be observed in a sample RT10 suggested that elevating the time could improve the film synthesized and no experiment conducted more than 10 hours.

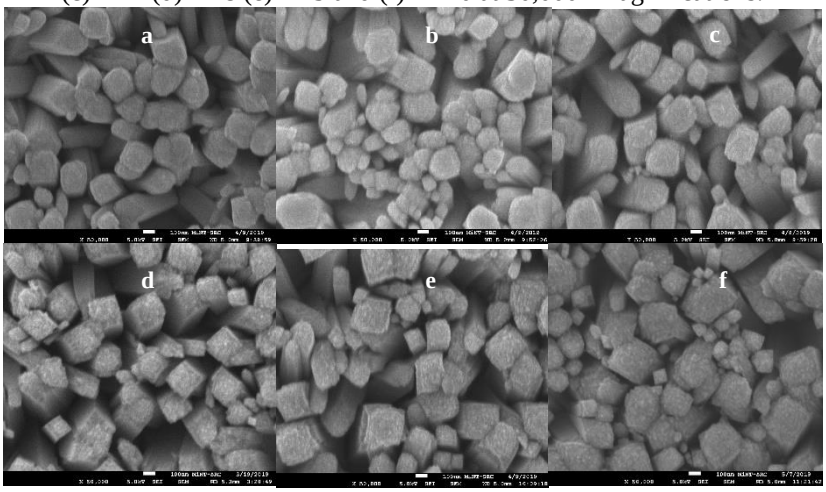
The preferred orientation corresponding to the plane (101) is observed and identified as highest intense peak in all of the samples. In this work, the sample RT7, RT8 and RT9 are exhibited stability because the XRD patterns show the similarity of the crystal plane growth. The peaks are also in thin and sharp shape indicating a good $TiO_2$ film produced. All the peaks in the XRD patterns can be assigned well as tetragonal rutile phase of $TiO_2$ and the diffraction data were in good compliance with JCPDS files no. 21-1276.[8] No peaks corresponding to other phases of $TiO_2$ such as anatase and brookite or any impurities were detected confirming the formation of high purity and stable rutile phase $TiO_2$.

Table 1: Full-width Half-Maximum and crystallite size of sample fabricated with different reaction time.

| Sample | 2θ (°) | FWHM, β | Crystallite size, D (nm) | Plane (h k l) |
|---|---|---|---|---|
| RT5 | 36.08 | 0.4723 | 20.1 | 101 |
| RT6 | 36.12 | 0.3936 | 24.2 | 101 |
| RT7 | 36.02 | 0.1378 | 77.0 | 101 |
| RT8 | 36.05 | 0.1181 | 94.6 | 101 |
| RT9 | 36.09 | 0.1968 | 50.6 | 101 |
| RT10 | 36.04 | 0.3149 | 30.5 | 101 |

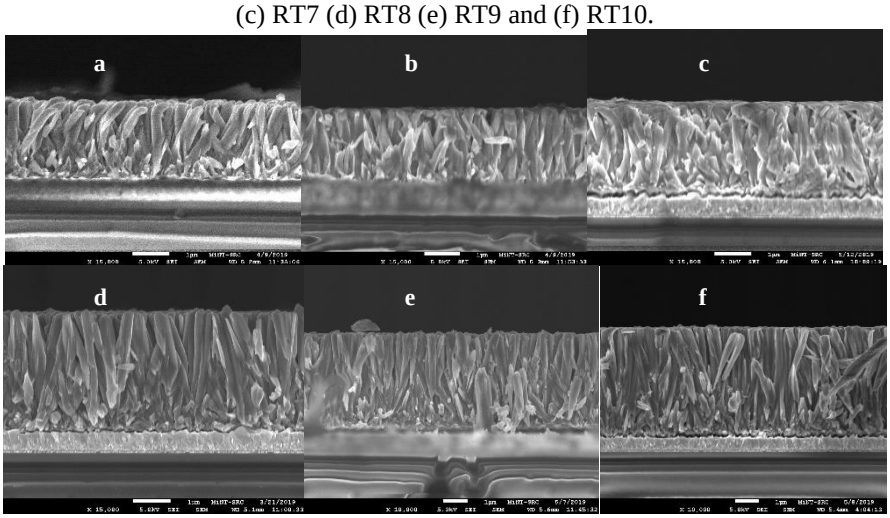
The crystallites sizes are shown in Table 1 and obtained using Scherrer formula where FWHM is significant in determine the crystallite size. Sample RT8 shows a lowest FWHM indicating a higher degree of crystallinity of $TiO_2$ film. From the table, it could be suggested that crystal structure sizes of the resulting rutile increased with increasing the reaction time before decrease as the equilibrium states is achieved for the samples were carried out for more than 9 hours.

Fig. 2: FESEM images of the sample (a) RT5 (b) RT6 (c) RT7 (d) RT8 (e) RT9 and (f) RT10 at 50,000x magnifications.




The morphology of nanostructured $TiO_2$ grown on the FTO was observed using FESEM as shown in Fig. 2. The nanorods have grown uniformly on FTO surface. All the samples show that the rods are in rough morphology on the top surface with relative smoothness on its sides. This rough square shaped top is affirmed to support the expected formation of tetragonal rutile phase crystalline structure. As the time elevated, the growth of both nanostructures becomes increases, more pack and denser and almost occupied on the whole of the surface. The size variation of nanorods $TiO_2$ prepared by manipulating hydrothermal synthesis duration is ranging from 100 to 400 nm. It was observed that at the initial reaction times, the diameter of the rods was grown constantly but slightly change when time rise. The diameter of the slender rods became smaller while the wide rods were expanded in sizes.

Fig. 3: FESEM cross-sectional images of the sample (a) RT5 (b) RT6 (c) RT7 (d) RT8 (e) RT9 and (f) RT10.




The images of cross-sectional area are composed of well-align nanorods arrays grown on the active surface of FTO substrate under various reaction times ranging from 5 to 10 hours. The nucleation has just begun at more than 3 hours. In this study, 5 hours is chosen because it is an enough time to grow the nanorods structure.[9] This nanorods structure is believed to be very beneficial in providing conductive path for electron.[10] The length of the rods is increased as the time elevated from 5 to 10 h and showed a constant growth rate with approximately 0.3 µm for every one hour of the first four samples. The lengthy of the film are found to be 2.03, 2.30, 2.61, 2.98, 3.61 and 4.16µm for samples RT5, RT6, RT7, RT8, RT9 and RT10, respectively as illustrated in Fig. 3.

Fig. 4: UV–Vis absorbance spectra of sample (a) RT5 (b) RT6 (c) RT7 (d) RT8 (e) RT9 and RT10 of $TiO_2$ thin film, respectively.

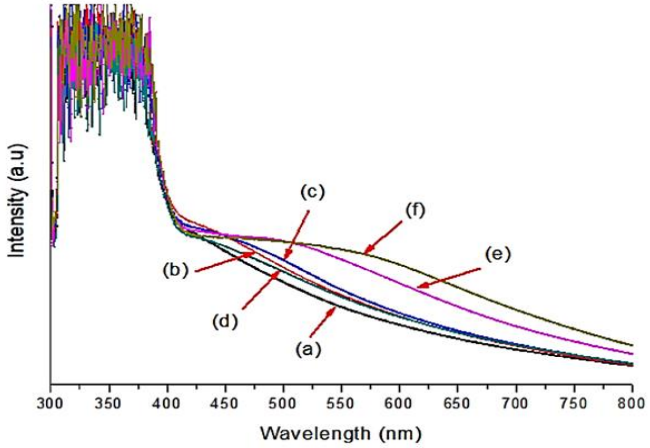



Fig. 4 shows the UV-vis absorbance spectrum of $TiO_2$ nanorods structure. The absorption band edges were estimated around 400 nm slightly higher than normally reported of $\lambda$ = 388 nm $TiO_2$ that was obtained by the following equation:

$$(h\upsilon\alpha)^n = A(h\upsilon - E_g) \quad (2)$$

where $h\upsilon$ is the photon energy, $\alpha$ is the absorption coefficient, $E_g$ is the absorption band gap, A is constant, n depends on the nature of the transitions and n = ½ in this case for indirect allowed transition.[11] The $E_g$ can be determined by Tauc plot which is calculated from the equation (2). The intercept of the tangent to the plot $(h\upsilon\alpha)^2$ versus $(h\upsilon)$ gives a good approximation of the $E_g$ as presented in Fig. 5. The band gap energies of as-prepared $TiO_2$ film are nearly the value of 3.0eV for the bulk rutile $TiO_2$ [12] as the reaction time elevating. The $E_g$ increases with decreasing particle size and the absorption edge is shifted to a higher energy with decreasing particle size. The $E_g$ values validate the crystallite size results according to which smaller crystallite size due to shorter reaction time should have larger band gap. Meanwhile, large crystallite size should have smaller band gap when increasing the reaction time.

**Influence of hydrochloric acid volume**

Fig. 5: XRD patterns of the as-synthesized samples (a) HC40 (b) HC50 (c) HC60 (d) HC70 and (e) HC80 at 150 °C, respectively

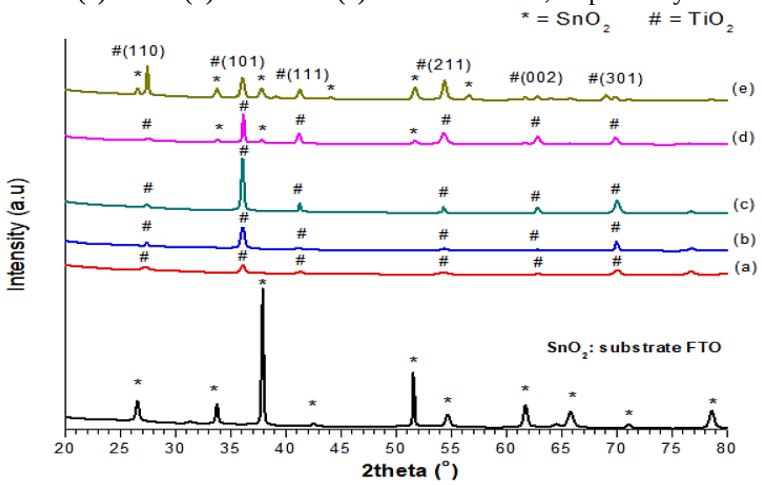


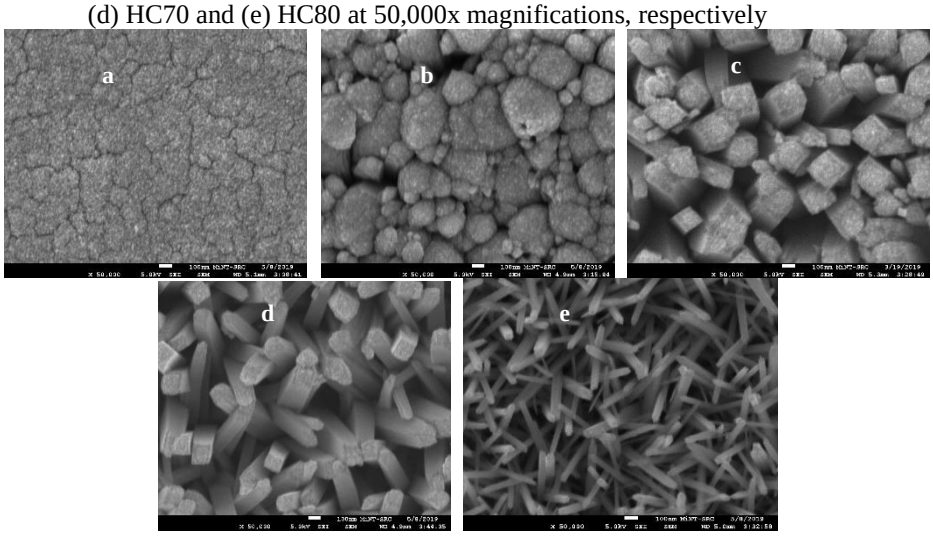

Table 2: Full-width Half-Maximum and crystallite size of sample fabricated with different hydrochloric acid concentrations.

| Sample | 2θ (º) | FWHM, β | Crystallite Size, D (nm) | Plane, (hkl) |
|---|---|---|---|---|
| **HC40** | 36.08 | 0.4330 | 22.0 | 101 |
| **HC50** | 36.07 | 0.3936 | 24.2 | 101 |
| **HC60** | 36.05 | 0.1181 | 94.6 | 101 |
| **HC70** | 36.13 | 0.1574 | 65.4 | 101 |
| **HC80** | 36.05 | 0.3542 | 27.0 | 110 |

Fig. 5 shows the evolution of XRD pattern of $TiO_2$ thin films prepared in various hydrochloric acid volumes ranging from 40 to 80mL on FTO substrate. As can be seen, all the prepared samples showed the characteristic of peak which related to the rutile phase. For sample HC40 and HC50, there are six rutile peaks were observed at 2θ = 27.1, 36.1, 41.3, 54.4, 63 and 70.1° reflected to (110), (101), (111), (211), (002) and (301) planes, respectively. These facets were believed having the lower surface energy that promoted the nucleation process with fastest growth rate. The broad shape of those peaks came out with a very weak intensity nature indicating a poor degree of crystalline film. Further increase the HCl volume can increase the intensity of the peaks that imply the improvement of the crystalline of the samples.

Sample HC60 exhibited a higher intensity with sharper and thinner peak at (101) plane indicating a smaller FWHM as presented in Table 2. Therefore, (101) plane is identified as a dominant plane due to the highest intensity count and FWHM obtained. HC60 also exhibits high quality of rutile $TiO_2$ since there are no other peaks belong to $SnO_2$, anatase or brookite are detected which suggested a stability of thin film synthesized. Further increasing the amount of HCl volume which referred to HC70, more peaks were observed including the presence of $SnO_2$ peaks. Moreover, it was clearly seen that the preferential plane (101) was weak in the intensity count suggested a poor degree of thin film synthesized. To investigate the effect of HCl addition, the volume has been increased to 80mL. Sample HC80 exhibited significant changes of the peaks growth. The peak growth at (110) plane was increased leaving the (101) peak and the rest peaks to broad and weak shape. The $SnO_2$ peaks presence in high number elucidates the low crystalline of $TiO_2$ growth.

Fig. 6: FESEM images of the sample (a) HC40 (b) HC50 (c) HC60 (d) HC70 and (e) HC80 at 50,000x magnifications, respectively




An excessive HCl amount could retard the hydrolysis rate whereas the insufficient HCl volume could decelerate the nucleation. As suggested by Imran and co-workers, the crystallite size can increase by the increasing of $H^+$ concentration and decreasing of $OH^-$ ions [13] but it is slightly different in this work. The $H^+$ ions that come from HCl and $OH^-$ ions from the water with an equal amount, favours the crystallite sizes growth. From the results obtained, it is suggested that the volume of HCl has strongly influence in the fabrication of $TiO_2$ crystalline structure and preferential planes.

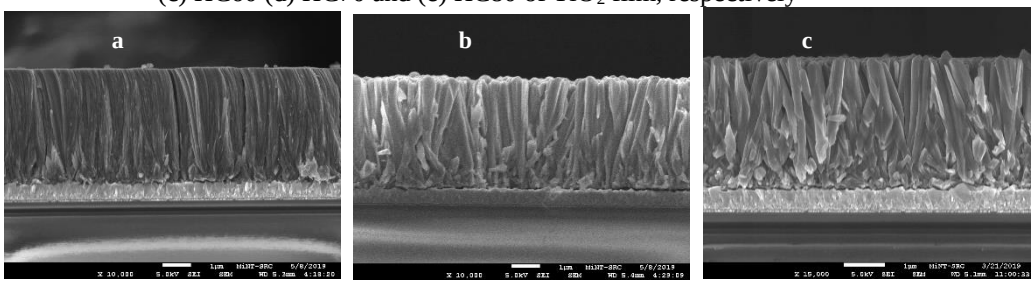
The surface morphological of $TiO_2$ films under various HCl concentrations were observed by FESEM as shown in Fig. 6. The role of HCl as catalyst and chemical corrosive agent for the formation of rutile phase at the same time induce defects on the surface for the origination of $TiO_2$ structures.[14] Moreover, the concentrations of HCl also determine the yielded polymorphs of synthesized $TiO_2$ whether anatase, rutile or brookite phases. In this work, high acidic medium specifically HCl[15] with concentration more than 3M is selected to fabricate a high purity of rutile phase, good agreement as reported by Chaochin Su and co-workers.[16]

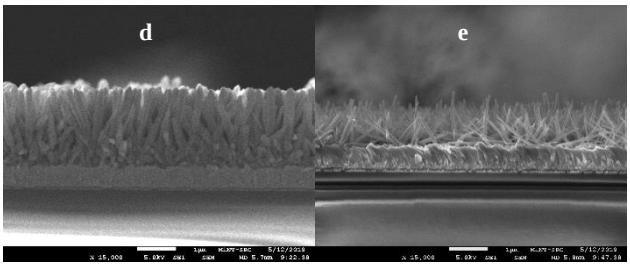
The samples HC40 is composed of barely seen coalescence structure of $TiO_2$ nanorods that agglomerates and sticks to each other closely. This kind of structure is similar in a work done by Lin et al. when they use low concentration of HCl that was 4M.[17] The reason why this structure is coalesced and agglomerated possibly because of the high surface energy that $TiO_2$ molecule possessed favours the attractive forces to hold the molecules together thus eliminated the energy and promoted the agglomeration between the $TiO_2$ molecules.[18]

Increasing the amount of HCl to 50mL denoted by sample HC50, the formation of nearly perfect $TiO_2$ nanorods structure can be observed. The rods are in epitaxial growth in spite of the nanorods are still in coalescence and did not split-up entirely. The cracks also can clearly be seen and suggesting low quality of film when using an inadequate amount of HCl. Nevertheless, the diameter of the rods could be estimated and found to be 50 to 300nm.

### 3.2. Bivariat

Fig. 7: FESEM cross-sectional images of the sample (a) HC40 (b) HC50 (c) HC60 (d) HC70 and (e) HC80 of $TiO_2$ film, respectively



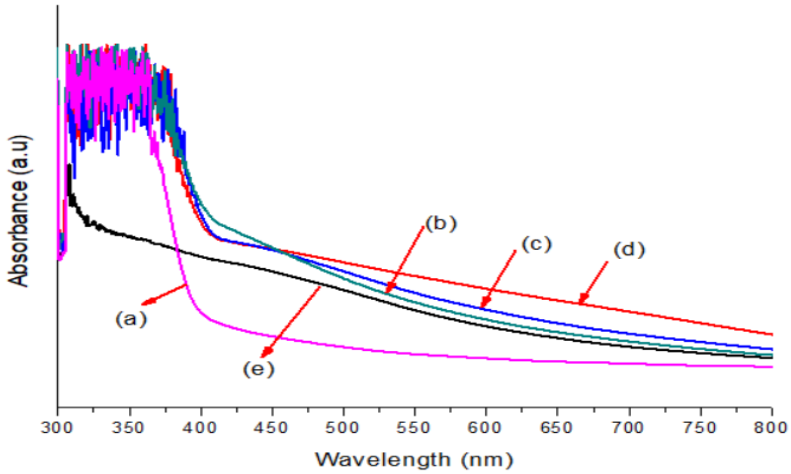



As the amount of HCl is increased to an equal proportion of DI water as designated by the sample HC60, the nanorods structure has enormously changed. The nanorods are standing freely with a gap between them have been developed and grown perpendicular to the FTO substrate. The nanorods surface structure was in tetragonal shape with square top facets consisted of many step edges. In addition, the step edges were served as a seed layer for the subsequent growth of $TiO_2$. The diameter of nanorods was found to be extending from 120 to 230 nm. Further increasing the amount of HCl to 70 mL denoted by sample HC70, the structure of nanorods changed. It was clearly seen that the nanorods structures are getting thinner and standing more freely with a gap between the rods was enlarged. The estimated diameter for minimum nanorods was 80 while 160 nm was the maximum value could be obtained.

The experiment to investigate an excessive amount of HCl in $TiO_2$ nanostructures development has been conducted. The HC80 sample used 80 mL of HCl and shows a great change to the $TiO_2$ nanostructure formed. The nanorods structures are almost in needle like structure, standing randomly in slanting position. The top of the surface was in tetragonal shape with a larger gap between them. The diameter is slightly decreased approximately to 40 to 60 nm. The length of the rods is decreased as the HCl volume was elevated from 40 to 80 mL. The lengthy of the film are found to be 4.08, 3.96, 2.98, 1.93 and 0.92 µm for samples HC40, HC50, HC60, HC70 and HC80 respectively, and illustrated in Fig. 7. From the cross-sectional view of sample HC40 as portrayed in Fig. 7(a), the growth of nanorods was coalescence and perpendicular aligned with FTO substrate. Increasing the HCl volume to 50 mL as represented by HC50, could improve the development of nanorods growth where the rods were standing freely as depicted in Fig. 7(b).

Further increment of the HCl volume of HC60, the rods are standing freely with well-aligned orientation. The lengthy of rods is decreased and some of the rods grown in slanting position as denoted by the sample HC70 treated by 70 mL of HCl creating a small gap between them. Keep raising the HCl volume as sample HC80, the rods changed to a needle-like structure and grown randomly in direction and less aligned to the FTO substrate. All the results indicate that the $TiO_2$ morphology could be adjusted by modifying the amount of HCl content. Furthermore, a moderate temperature during hydrothermal process may helpful in crystallization of $TiO_2$. According to Nguyen and co-workers, a low HCl concentration is primarily assigned to anatase phase formation with nanocubic particles structure.[19] Whereas in strongly acidic medium, the rutile phase is built-up and can be found in many nanostructures such as flower and rod-like morphologies.

Fig. 8: UV–Vis absorbance spectra of sample (a) HC40 (b) HC50 (c) HC60 (d) HC70 and (e) HC80 of $TiO_2$ thin film, respectively. Inset is the band gap estimation of sample HC60



In fact, the abilities of several acid media to obtain a larger of $TiO_2$ particles have been investigated and HCl was identified as the strongest acidic solution when reacting to titanium butoxide as precursor.[20] Hence, the result in this work is quite consistent with the previous literatures. It can be concluded that the insufficient amount of HCl attributed to the agglomeration due to a high energy surface between the molecules. Whereas an excessive of HCl, more chloride ions could preferentially adsorb then tend to contribute in slower hydrolysis rate thus promoted to the decrement of thicknesses and diameter of the nanorods. In this work, an equal volume proportion of $H_2O$ and HCl are chosen for favourable growth of well aligned nanorods.

The study on optical properties of $TiO_2$ nanorods film is conducted using UV-Vis spectroscopy. The optical absorption edge is found to be within wavelength 300 to 400 nm as in Fig. 8. The graph shows the decreasing behaviour for $TiO_2$ band gap as the HCl volume increasing however the energy slightly increased for the sample treated using higher HCl concentration. The $E_g$ of as-prepared $TiO_2$ film is found to be 2.9 eV slightly differ with the value of 3.0 eV for bulk rutile $TiO_2$.

## 4. CONCLUSION

$TiO_2$ nanorods structure has been successfully prepared via hydrothermal method under various reaction hours and regulating hydrochloric acid volumes. The result shows that the reaction time give a high significant to the thickness adjustment of nanorods structure whereas acidity medium is favourable on direction and alignment of nanorods on FTO substrate. It can be suggested that optimum reaction time and HCl concentration are 8 hours and 60 mL in hydrothermal process, respectively since the samples exhibiting excellent properties of $TiO_2$ nanorods film.

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