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Effect of Hydrothermal Reaction Time and Etching on Nanorod TiO_2 Thin Film

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ABSTRACT

Titanium dioxide (TiO_2) has the most potential function in numerous research domains because of its various advantages. Among the variety of ways, TiO_2 nanorods (TNRs) are one of interest nanoparticle structures due to their superior delocalisation of the electron holes pair and lower charge recombination. However, TNRs inhibit solar spectrum absorption and have a high resistivity. In this study, etching treatment is introduced to increase the specific surface area and reduce resistivity. The effect of reaction time was investigated on TNRs thin film by using the hydrothermal method. From the findings, the 8-hour reaction time of TNRs thin film revealed the most striking characteristics. The preferred (101)-orientation of TNRs was observed and the diameter of rods increased along with reaction time. As the reaction time rises, the bandgap energy of TNRs approaches the value of 3.0 eV and presents a compact surface. After etching treatment, the peak intensity of (101)-orientation of TNRs increases indicating high crystallinity. The morphology of nanorods changed into smaller rods, apparently a nanowire with deeper depth. The surface roughness and band gap increased due to the surface area affected by etching. The electrical properties of etched-TNRs thin film after showed a reduction of resistivity aligning to thickness decrement. Thus, hydrothermal etching treatment showed effectiveness in enhancing TNRs properties in terms of crystallinity, surface morphology and reducing resistivity.

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1. Introduction

Titanium dioxide (TiO_2) has piqued the interest of researchers due to its use in various solar cell applications [1]. TiO_2 has the most potential function in numerous research domains because of its high-efficiency photocatalytic activity [2], mechanical flexibility, chemical stability [3], high refractive index, superior conductivity and photo-corrosion resistance [4]. TiO_2 has high photocatalytic activity because its conduction band is well above the standard potential and its valence band is well below the standard potential of reactive oxygen species [5]. TiO_2 has been synthesised using a variety of techniques [6], including sol-gel [7], chemical vapour deposition [8] and hydrothermal [9]. TiO_2 is composed of three crystalline phases: anatase, rutile and brookite [10]. The characteristics of charge and electrical structure will be affected by the different crystalline phases [11]. The rutile phase is more chemically stable than anatase and has the highest photo-reactivity [12].

The manufacturing of TiO_2 nanorods (TNRs) has since become a significant research area. The hydrothermal technique is employed in this study to fabricate TNRs on fluorine-doped tin oxide (FTO) glass substrates [13]. TNRs may be nanostructured in a variety of ways, including nanoparticles, nanorods, nanobelts, nanowires and nanoflowers [14] but the nanorods were chosen over other nanoparticle structures due to their superior delocalisation of the electron holes pair and lower charge recombination [15]. TNRs material has been proven to be an excellent candidate for the applications due to its stability in solution, optimum surface area and environmental endurance. TNRs have a high surface area of nanorods, which can improve electron transfer and the efficiency of various applications [16]. The hydrothermal approach, on the other hand, is employed because it is a straightforward and low-cost method for manufacturing TNRs [17].

However, TNRs have a disadvantage because the limitation of TNRs is that the bandgap of TNRs restricts solar spectrum absorption and has high resistivity. Due to the low surface area and resistivity that limit the fabrication efficiency of the next layer, an etching treatment using the hydrothermal method for TNRs is introduced to improve the surface area and lower its resistivity [18]. Several studies and testing demonstrated that the photocatalytic activity of TiO_2 was affected by a variety of conditions such as surface area crystallinity level, morphology properties, crystal composition and thickness of the thin film [19].

Hence, the parameter used which was the effect of the reaction time was used in fabricating TNRs by the hydrothermal method and the results of the process will be investigated to obtain a good sample before conducting hydrothermal etching treatment. The effect of hydrothermal reaction time on TiO_2 thin film is still unknown to optimise TNRs thin film for etched-TNRs thin film. This study aims to examine the effect of hydrothermal reaction time on TNRs thin film for etched-TNRs thin film to characterise structural, morphological, topological, optical properties and electrical properties.

2. Methodology

The hydrothermal method is employed in this experiment to create TNRs and the same approach is used for the subsequent etching treatment process. TNRs fabrication, etching process and characterization are the three major steps of experimental procedures.

2.1 Fabrication of TNRs

In this investigation, TNRs were fabricated by using hydrothermal method on the FTO glass substrate. Initially, the conductive side of the FTO glass substrate was assessed using a multimetre. Upon identifying the conductive side, a slight mark was made by scratching that side of the FTO glass

substrate. Subsequently, the FTO glass substrate underwent a cleaning process using acetone, ethanol and deionized water in sequential steps, each lasting five minutes in a digital ultrasonic cleaner. The conductive portion of the FTO glass substrate faced upward during this cleaning procedure. This meticulous cleaning protocol was essential to ensure the substrate's freedom from contaminants and to eliminate any undesired particles and oxide layers from its surface.

Initiating the TiO_2 solution preparation, 60 ml of hydrochloric acid (HCl) (36.5%-38% by weight) was dissolved in 60 ml of deionized (DI) water within a beaker. To achieve thorough blending, the liquid was stirred using a magnetic stirrer for 5 minutes. After that, 3 ml of titanium butoxide (TBOT) was incrementally added to the mixture using a disposable pipette. The stirring process continued for approximately 10 minutes until a clear solution was obtained, devoid of any precipitate formation.

Subsequently, the cleaned FTO glass substrate was positioned inside a Teflon-lined autoclave, with the conductive side facing downward and fully immersed in a TiO_2 solution. The autoclave was then placed in an oven set at 150°C, with varying reaction times of 7, 8, 9 and 10 hours. Following the designated reaction time, the autoclave was removed from the oven and the sample was rinsed with 5ml of DI water twice in separate beakers, each rinse lasting for 5 minutes. Then, the substrate was left to air-dry naturally in ambient conditions.

The duration of the hydrothermal reaction is a crucial parameter influencing the growth mechanism and properties of TNRs, thereby impacting the characteristics of the prepared samples. The samples synthesized at different reaction times are denoted as RT7, RT8, RT9 and RT10, where "RT" signifies the hydrothermal reaction time and the numerical value indicates the duration taken to synthesize the TNRs thin film. Parameters of the as-prepared samples are tabulated in Table 1.

Table 1
The conditions of the as-prepared samples hydrothermally grown at different reaction times

Sample	Reaction times (hours)
RT7	7
RT8	8
RT9	9
RT10	10

2.2 Hydrothermal Etching Treatment

Following the fabrication of TiO_2 nanorods on the FTO substrate, the samples underwent an etching treatment aimed at altering the structure of the TNRs. The etching process utilized a high-acidity medium, employing hydrochloric acid (HCl) and deionized water to generate a transparent solution [20]. This solution, with a concentration of 0.03M, was prepared by blending deionized water and HCl. Subsequently, the sample was placed inside a Teflon-lined autoclave, with the conductive part facing upward and the Teflon inner was filled with the HCl solution. The sample was immersed in the solution. The HCl etching treatment was conducted at a reaction temperature of 150°C for 5 hours. Following cooling to room temperature, the substrates were removed from the autoclave, thoroughly rinsed with deionized water and allowed to naturally air-dry in ambient conditions.

2.3 Characterization

Characterization was a critical step in investigating and understanding thin film properties. In this study, all the parameters will be studied to characterize the structural properties-X-ray diffractometer (XRD), morphological properties-field emission scanning electron microscopy (FE-

SEM), surface topology analysis-Atomic Force Microscopy (AFM), optical properties-ultraviolet-visible spectrophotometry (UV–Vis) and electrical properties-four-point probe of TNRs. Illustration of experimental procedures for fabrication of TiO_2 nanorods is shown in Figure 1.

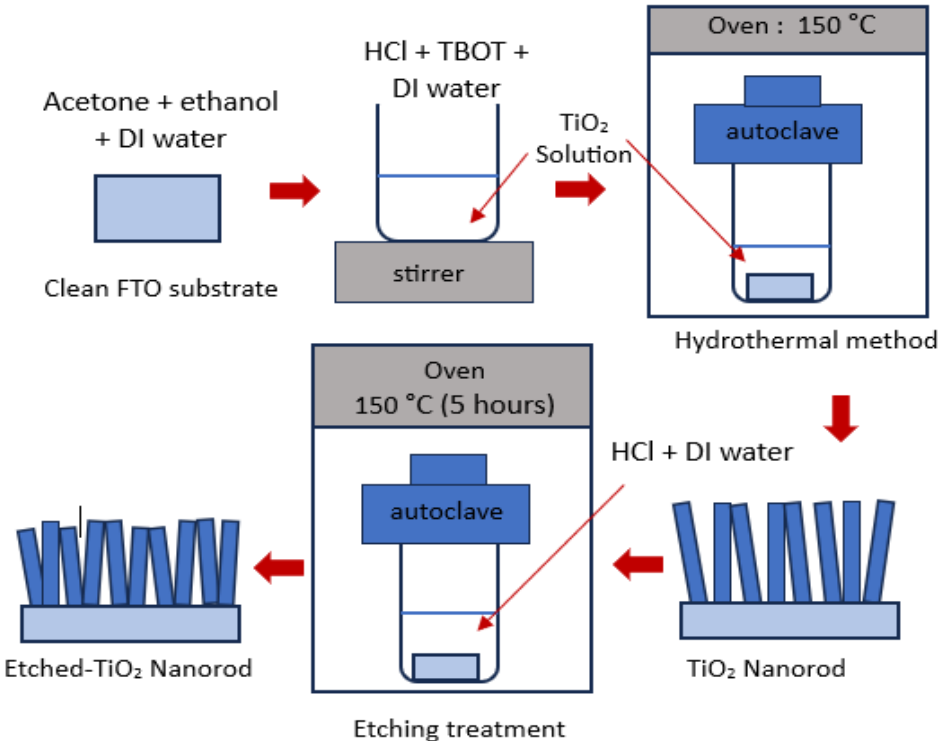


Fig. 1. Illustration of experimental procedures for fabrication of TiO_2 nanorods

3. Results

3.1 Fabrication of TNRs on FTO Glass Substrate

This section described the analysis and discussion for each of the samples from the experiment conducted by varying the reaction time at a constant hydrothermal process temperature of 150°C. The reaction time is an important parameter that could control the growth mechanism of the TiO_2 structure and affect the properties of the prepared samples. The as-prepared samples are represented as RT7, RT8, RT9 and RT10, respectively. In this case, RT is hydrothermal reaction time and the number refers to the duration taken to synthesise the TNRs thin film.

3.1.1 Structural properties

According to the standard JCPDS file number: 77-0452, the (101) diffraction peak has the highest intensity, whereas the remaining peaks have weak and wide intensities. All TiO_2 is polycrystalline by nature. The absence of any extra peak in the XRD pattern that would be linked with the other phases of TiO_2, such as anatase or brookite, confirms the synthesis of high-purity rutile phase TiO_2.

Figure 2 depicts the XRD patterns of TNRs generated by varying the hydrothermal reaction time. It indicates the crystalline quality and direction of the nanostructure. The nanostructure synthesized showed a crystalline nature with diffraction peaks lying at 2θ = 36.1, 41.5, 54.4, 65.0 and 71.2° can be indexed to (101), (111), (211), (002) and (301) crystal planes, respectively. When the plane (110) was present at 27° at RT8, suggesting more TiO_2 growth, the pattern suggests that increasing the reaction time enhanced the crystallinity of the film formed.

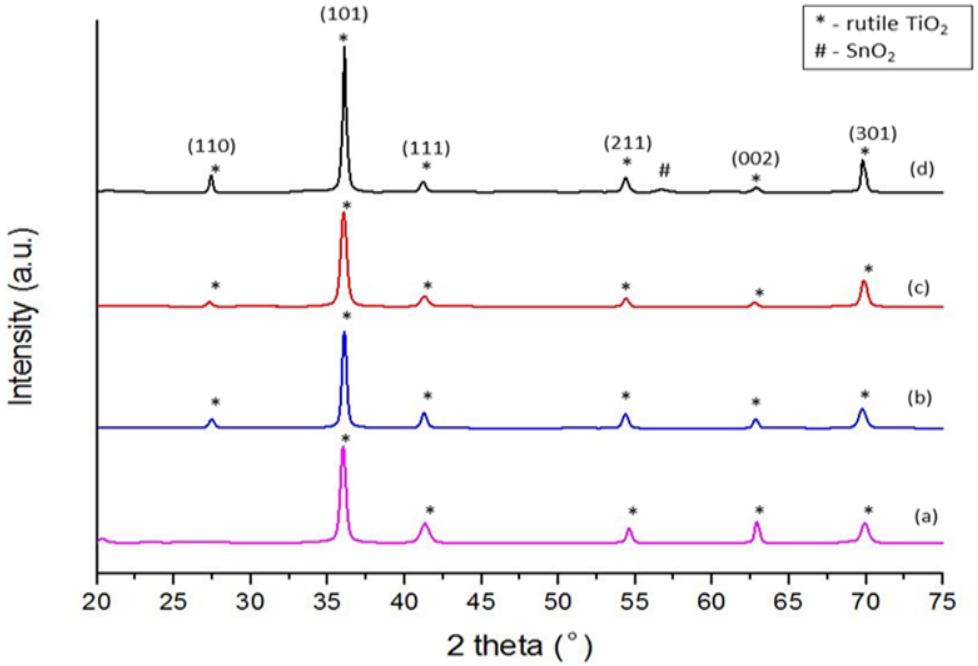


Fig. 2. XRD patterns of samples (a) RT7 (b) RT8 (c) RT9 (d) RT10 respectively

The preferred orientation (101) is detected and recognised as the most intense peak in all of the samples. Because XRD patterns reveal the similarity of the intensity crystal plane growth, the samples RT7, RT8 and RT9 are stable in our investigation. The peaks are likewise narrow and sharp, indicating that an excellent TNRs film was produced. The TiO_2 peak characteristics of sample RT10 are smaller, sharper and have the maximum intensity at (101) plane orientation, indicating better crystallinity. Nevertheless, the presence of SnO_2 peaks in sample RT10 indicates the persistence of FTO substrate remnants. This observation suggests that extending the hydrothermal reaction time beyond 10 hours may have detrimental effects on the synthesis of the film.

The average crystallite size of TiO_2 is calculated using the Scherrer equation by calculating the FWHM in radians corresponding to (110) peaks. Table 2 displays the results where FWHM values are crucial in determining crystallite size. The crystallite size for sample RT7 was almost 77.0 nm and increased to 94.6 nm for sample RT8. The crystallite size of sample RT9 was found to be 50.6 nm, whereas the crystallite size of sample RT10 was determined to be 30.5 nm. The decrement crystallite size is believed due to peak broadening, which indicated its rapid size reduction when elevating the hydrothermal reaction time. In conclusion, the study suggested that the crystallite size of the resultant rutile grew with increasing reaction time, before decreasing when equilibrium states were reached for samples hydrothermally produced for more than 9 hours.

Table 2
Full-width half maximum and crystallite size of the sample fabricated with different reaction time

Sample	2θ (°)	FWHM, β	Crystallite size, D (nm)	Plane (hkl)
RT7	36.02	0.1378	77.0	101
RT8	36.02	0.1181	94.6	101
RT9	36.02	0. 1968	50.6	101
RT10	36.02	0. 3149	30.5	101

3.1.2 Morphological properties

In analysing the morphological properties of the TNRs, FE-SEM is used to observe the nanostructured TiO_2 grown on the FTO as shown in Figure 3(a) to 3(b). On the FTO surface, the nanorods have grown uniformly. As time passed, the development of both nanostructures intensified, becoming more packed and denser and occupying nearly the whole FTO substrate. It was revealed that the diameter of the rods expanded continuously throughout the early response periods but changed somewhat as time proceeded.

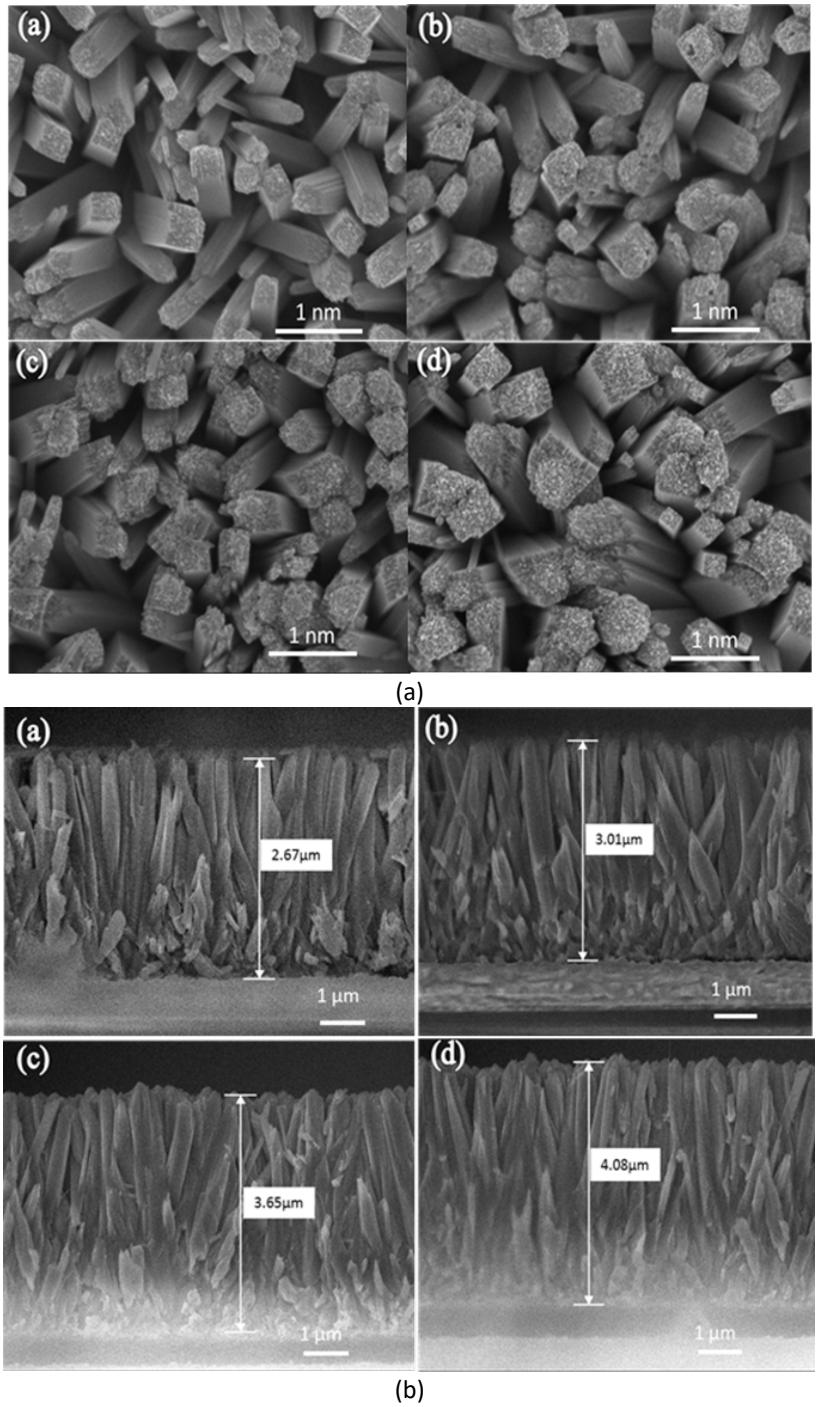


Fig. 3. (a) The surface morphology images of TiO_2 samples (i) RT7 (ii) RT8 (iii) RT9 (iv) RT10 respectively (b) The cross-sectional images of TiO_2 samples (i) RT7 (ii) RT8 (iii) RT9 (iv) RT10 respectively

The diameter of the rods increases with time increases. The characterization was conducted at 15,000 and 50,000x magnification for each sample. The overall picture indicates that the nanorods developed perpendicular to the substrate with a length of as given in Table 3. The well-aligned nanorod arrays that make up the sample's morphology were developed on the FTO substrate's active surface throughout a range of reaction times from 7 to 10 hours. With a reaction time of more than three hours, the nucleation has just started. In this study, even after 10 hours, the sample's adhesion to the FTO substrate remained strong. No occurrences of lifted film during the experiment indicate that the appropriate amount of the material was used within the process.

Table 3
Size variation of TNRs

Sample	Reaction Time (hour)	Average Diameter (nm)	Thickness (μm)
RT7	7	179.75	2.67
RT8	8	190.82	3.01
RT9	9	203.75	3.65
RT10	10	278.00	4.08

In this investigation, it was found that the diameter of the rods increased along with the hydrothermal reaction time. Additionally, it was clear to see that as time went on, the distance between the rods became smaller and closer together. It may be concluded that the size of nanorods generally increases with the reaction time and enhances the crystal orientation to the well-perpendicular alignment of the nanorod's growth [21].

Therefore, it can be suggested that increasing the reaction times, enhances the TNRs orientation as confirmed by the XRD pattern that the sample conducted at more than 7 hours has two excessive peaks. This is suggested that prolonging the reaction time favours the nucleation of TiO_2 where the seed could grow in many planes thus improving the crystalline of the film synthesized. Hydrothermal reaction time for more than 10 hours was not continued in this experiment since the SnO_2 peak was confirmed in the sample RT10.

3.1.3 Surface topology analysis

The surface topological pictures of TNRs deposited relatively treated at different reaction times are shown in Figure 4.

The RMS roughness of the TNRs samples was found to be 81.13 and 71.12 nm for the 7 and 8 hours of reaction time, gradually decreasing as illustrated by Table 4. The value of RMS roughness was slightly lower and found to be 64.20 and 52.30 nm for the samples RT9 and RT10, respectively. It could be observed that the RMS roughness was maximum in the value and consistent for the samples with the reaction less than 9 hours due to uniform distributions of TNRs. The samples synthesized at 9 or more than 10 hours of reaction time show decrement behaviour in the value of RMS roughness. This phenomenon can be attributed to the reduction in the distance between the rods, causing them to become closer together. This results in a more compact surface, leading to lower roughness as depicted in Figure 4 (c) to 4(d) with increasing reaction time.

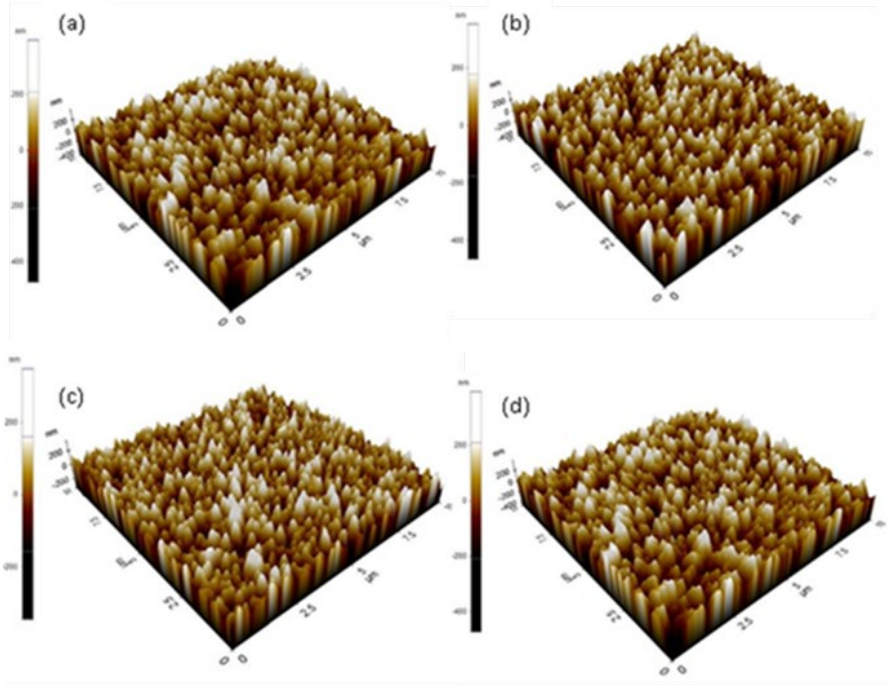


Fig. 4. Topology surface of the TiO_2 sample (a) RT7 (b) RT8 (c) RT9 (d) RT10 respectively

Table 4
RMS roughness of the samples

Sample	Roughness, Rq
RT7	81.13
RT8	71.12
RT9	64.20
RT10	52.30

The roughness is decreasing, indicating that the longer reaction time during manufacture reduces TNR roughness. AFM also indicates a compact surface on the substrate; these findings are consistent with previous FE-SEM images. The surface morphology revealed that the FTO substrate was entirely covered by a thin layer of TiO_2. The roughness of the films diminishes due to an increase in grain size [22]. The RMS roughness of thin films influences photocatalytic activity. Photocatalytic activity is boosted in samples with a large surface area and a high surface roughness [23]. As a result, it may be stated that hydrothermally grown TiO_2 nanorods are encouraged to lower grain size, reducing the roughness of the film.

3.1.4 Optical properties

UV-Vis spectroscopy was used to determine the optical transmittance and absorbance as well as the band gap energy of the n-TiO_2 thin film. The wavelength used was fixed between 300 to 800 nm at room temperature. The band gap increases with the decreasing particle size and the absorption edge are shifted to a higher energy with decreasing particle size.

The band gap numbers confirm the crystallite size results, as smaller crystallite sizes should have a higher band gap due to the shorter reaction time. Meanwhile, as the reaction time increases, bigger crystallites should have a narrower band gap. The graphs in Figure 5 demonstrate that the behaviour of TNRs band gap nanostructures decreased as the reaction time rose. As the reaction time rises, the bandgap energy of all the samples approaches the value of 3.0eV for bulk TNRs [24]. The bandgap

numbers confirm the crystallite size results since smaller crystallite sizes should have larger bandgaps due to faster response times. A greater crystallite size should result in a narrow bandgap as the reaction time increases. This is supported by the crystallite size of the XRD pattern.

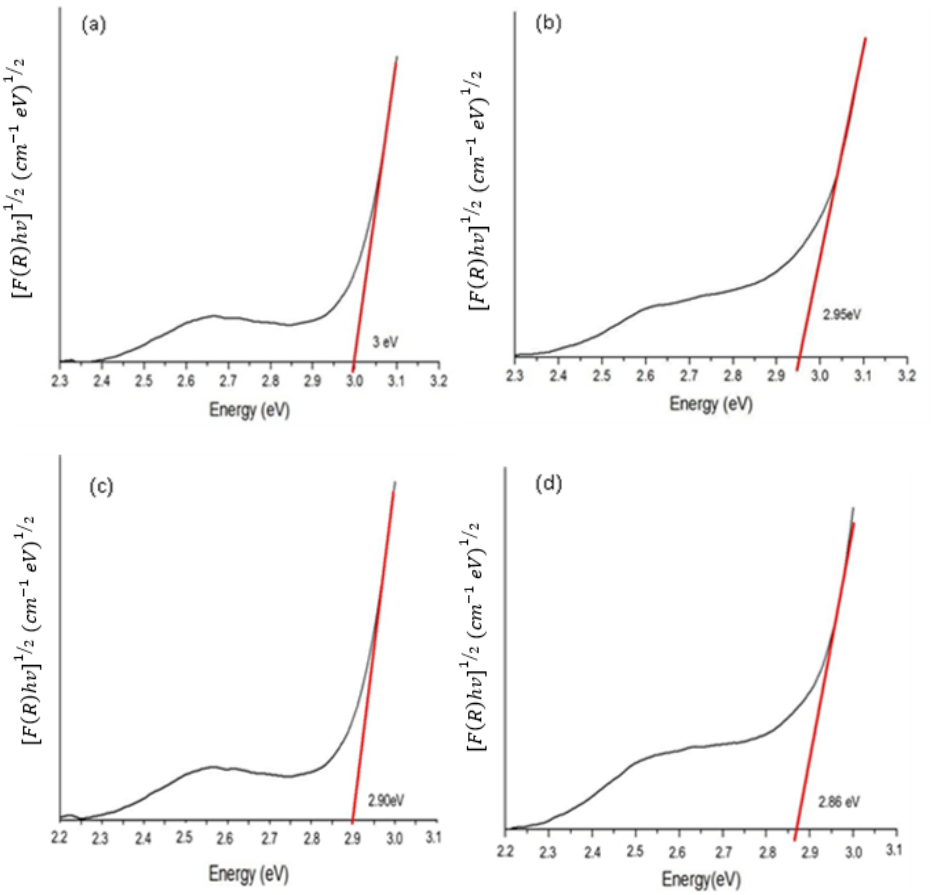


Fig. 5. Band gap estimation for the sample (a) RT7 (b) RT8 (c) RT9 (d) RT10 respectively

3.1.5 Electrical properties

The electrical characteristics of the TNRs thin film are measured using a four-point probe to quantify the samples' resistivity. In this study, the sheet resistance (R_S) was calculated as the mean of at least five measurements taken at various sizes throughout the sample. Table 5 shows that the R_S rises as the reaction time during the fabricating of the TNRs films increases. The resistivity of the TNRs structure is strongly influenced by the thickness of the thin film formed. When the length of the hydrothermal process is increased, the thickness of TNRs increases, generating a strong barrier to electrons while lowering sample conductivity. As a consequence, a suitable thickness of the TNRs layer should be produced to improve electron transmission.

Table 5
Electrical properties of as-prepared samples

Sample	Resistivity, ρ (Ω.cm)	Sheet resistance, R_S (μm)	Film thickness (μm)
RT7	0.34	8.98	2.67
RT8	0.40	13.20	3.01
RT9	0.50	18.03	3.65
RT10	0.57	22.30	4.08

3.2 Hydrothermal Etching Treatment

This section discussed the structural, morphological, topological, optical and electrical characteristics of as-deposited TNRs and etched-TNRs thin films. As-deposited TNRs used RT8 as the optimum hydrothermal reaction time because the RT8 sample revealed the most striking characteristics.

3.2.1 Structural properties

Figure 6 depicts the changes in the XRD pattern of as-deposited TNRs and etched-TNRs thin film prepared by the concentration of 0.03M HCl based on the standard JCPDS file no: 77-0452, all TiO_2 samples are naturally polycrystalline (101) diffraction peak is noticeably found to have the most vigorous intensity, whereas the intensity of the other peaks is noticeably weak and broad [25]. The rutile phase is present in all planes and no other peak can be recognized in the XRD pattern [26].

When the sample was etched with 0.03M of HCl, six rutile peaks were seen at 2 values of 27.3, 36.1, 41.3, 54.4, 63 and 71.2, which reflected (110), (101), (111), (211), (002) and (301) planes, respectively. The etched-TNRs peaks were smaller, sharper and more intense at (101) plane orientation, indicating better crystallinity [27]. After the etched treatment, the peak intensity of the (101) plane increases [28]. This is possible because sufficient HCl can promote nucleation development and enhance the rate of hydrolysis. One explanation is that the Cl ions, on the other hand, adsorb and prevent the formation of (101) planar surface [29]. Even after the etching procedure, the properties of TNRs at the orientation planes did not change. This demonstrates that the etching process has no effect on the rutile structure, independent of the peak intensity.

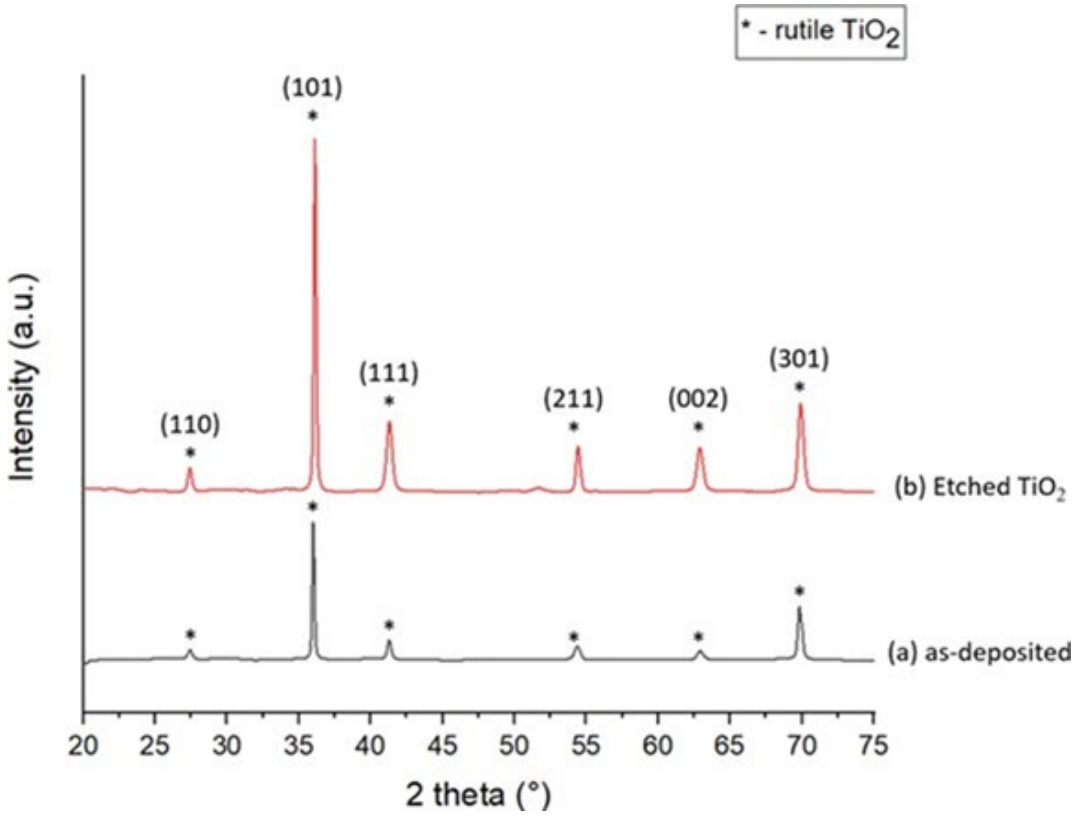


Fig. 6. XRD patterns of (a) as-deposited (b) etched TNRs

3.2.2 Morphological properties

Figure 7 and Figure 8 show surface morphology pictures of as-deposited TNRs and etched-TNRs at 15,000x and 50,000x magnification for each sample. Each sample was examined and it was determined that the sample of TNRs deposited is in nanorod structure and the thickness of the TiO_2 nanorod deposited is 3.03µm, as shown in Figure 6.

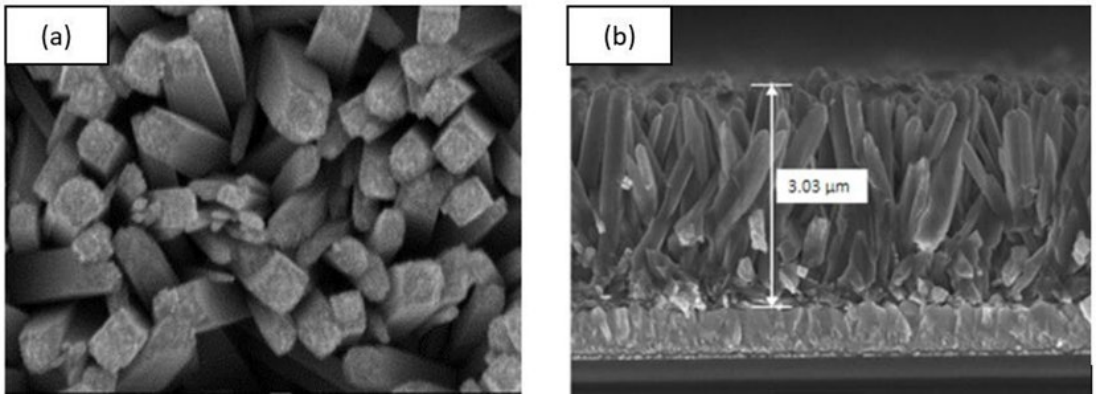


Fig. 7. TNRs deposited samples of the (a) surface morphology (b) cross-sectional image

The FE-SEM picture indicates the transition of the nanorods into smaller rods, apparently a nanowire with deeper depth and the same shape of the sidewall after the sample is etched with 0.03M HCl and the thickness is also reduced to 2.64µm, as shown in Figure 8.

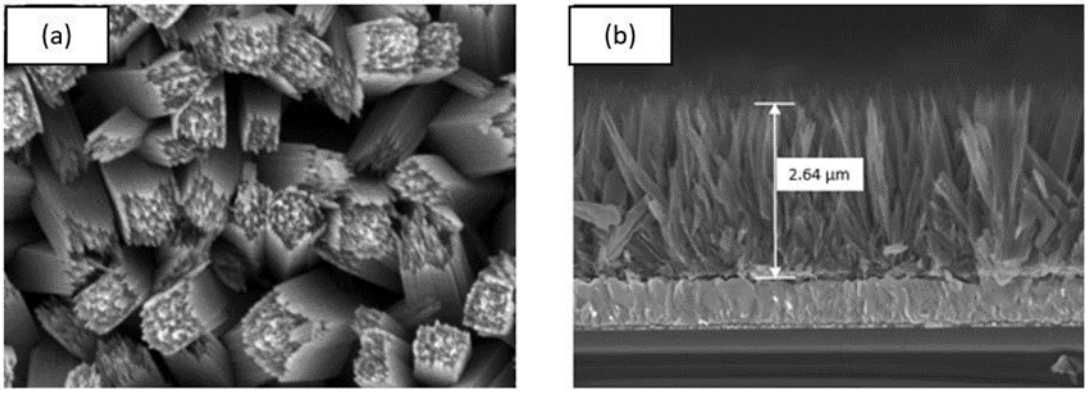


Fig. 8. Etched-TNRs samples of the (a) surface morphology (b) cross-sectional image

Furthermore, the top rod's blunt has disappeared and has become square-like. This is because the etching process, which proved the presence of many tiny particles on the nanorod's surface, disturbed the development and thickness of the TNRs. The densely packed nanorods on the compact structure will be unfastened by the highly acidic etching process. This increases the space between the nanorods, allowing the electrolyte to permeate and facilitating solar cell application [30].

3.2.3 Surface topology analysis

The AFM is used to characterise the change in surface roughness of the TNRs thin film before and after the etching treatment. This examination must be performed to confirm the sample's surface roughness. Figure 9 depicts the RMS roughness of the TNRs as-deposited and etched with a concentration of HCl 0.03M.

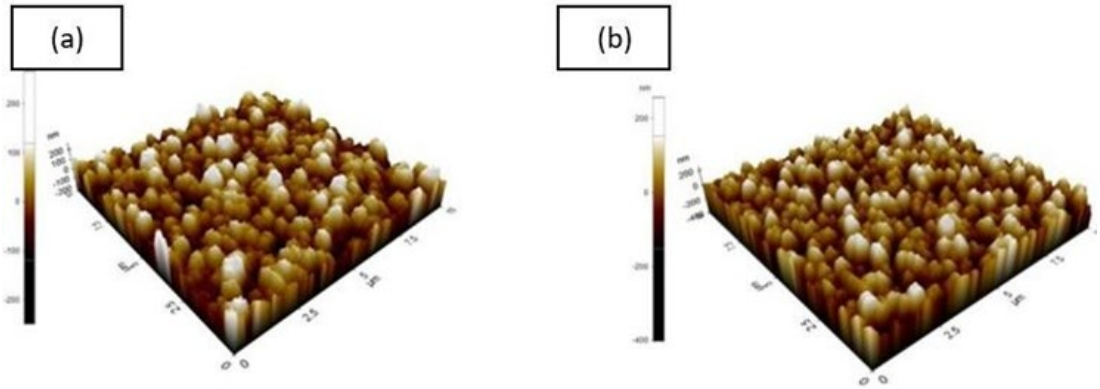


Fig. 9. The RMS roughness of the TNRs samples on the (a) as-deposited (b) etched-TNRs

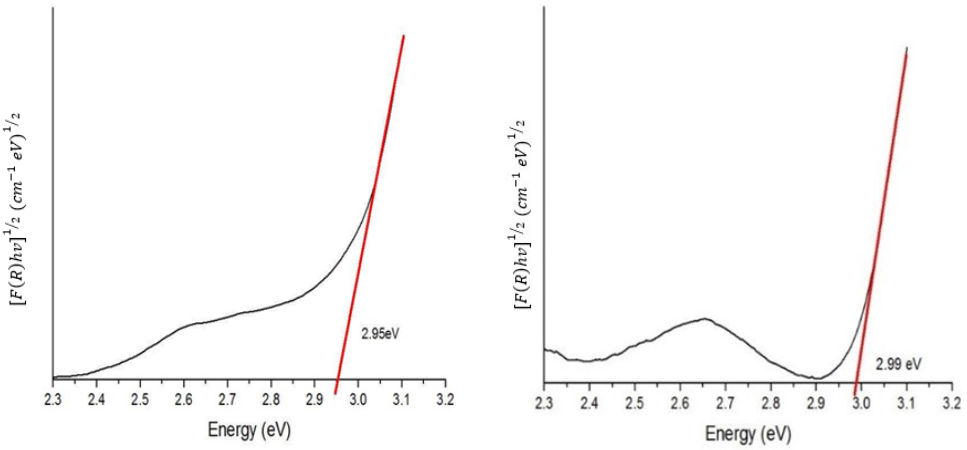
As shown in Table 6, the obtained results indicate that the RMS roughness increases following the etched treatment. The RMS roughness of thin film has a substantial impact on the device's performance. The changes in RMS roughness were verified by the literature, which also shows that RMS roughness rises when exposed to concentration to HCl treatment [31].

Table 6
The film thickness and surface roughness of the as-deposited sample and etched-TNRs sample

Sample	Film thickness (μm)	Rq, (nm)
As-deposited	3.01	71.10
Etched-TNRs	2.64	124.90

3.2.4 Optical properties

UV-Vis spectroscopy was used to determine the band gap value. The obtained results show that the sample's band gap value varies before and after the etching treatment. When the etching treatment is applied, the band gap value slightly increases as shown in Figure 10. The changes in the bandgap value are a result of alterations in the surface characteristics of TiO_2 nanorods. This can be linked to observations in previous studies, indicating that the transformation from nanorods to smaller rods, resembling nanowires, can impact the material properties [32]. This phenomenon is associated with the reduction in particle size, causing a shift in the absorption edge to higher energy levels, consequently leading to changes in the bandgap value [33].



(a) (b)

Fig. 10. Band gap estimation for (a) as-deposited (b) etched-TNRs thin film

3.2.5 Electrical properties

The concentration of HCl had an influence on the thickness of the TNRs layer, which decreased. The decrement behaviour is related to the smaller nanowire structure altered during the etching treatment via the HCl reaction with the help of a moderate hydrothermal temperature [34]. The gap area between the nanorods alters the grain boundary and changes the samples' resistivity, indicating quicker electron transport in the etched-TNRs. This is owing to well-aligned nanorods, which can operate as an effective electron transport channel for electrons in the photoanode and inhibit charge recombination [35].

Table 7
Electrical properties of as-deposited and etched-TNRs

Sample	Resistivity, ρ (μm)	Sheet resistance, R_S (Ω.cm)	Film thickness (μm)
As-deposited	0.40	13.20	3.01
Etched-TNRs	0.25	9.47	2.64

4. Conclusions

In conclusion, the TNRs thin film was successfully fabricated via the hydrothermal method. The effect of hydrothermal reaction time during the fabrication of nanorod film was intensively studied. It can be concluded that the crystallinity of the TNRs increased with time, with the highest peak intensity at 10 hours of fabrication. However, there is a SnO_2 peak observed indicating extending the experiment's duration beyond 10 hours would harm the film's synthesis even though it cannot be clearly seen in FESEM images. Moreover, the nanorod morphology withstands increasing diameter and thickness. The RMS roughness was the best and highest at 81.13nm for the sample RT7 but the plane (110) was not present at 27° at RT7. By comparing the results, the sample of RT8 demonstrated the prominent features in fabricating of TNRs on the FTO glass substrate.

Then, the TNRs thin film was successfully etched using HCl via the hydrothermal method. The hydrothermal etching treatment of TNRs thin film with HCl was accomplished. The properties of etched-TNRs after the process of hydrothermal etching treatment were thoroughly investigated. It is possible to deduce that the crystallinity of TiO_2 increased after the etching treatment, with the

maximum peak intensity at (101) plane orientation being narrower, sharper and had a higher intensity.

Furthermore, the nanorod form may be transposed to smaller rods, apparently a nanowire. The sample after etching had the best and greatest RMS roughness at 124.90 nm. This is followed by a drop in resistivity and sheet resistance after etching treatment, which is reduced. These findings establish that assuming hydrothermal etching treatment on TiO_2 nanorod film provides great behaviour qualities to improve thin film attributions.

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