Hydrophobic properties of microrods and flower-like rutile phased TiO_2 on FTO glass using hydrothermal method

S. S. TAIB[a], M. K. AHMAD[a,*], N. NAFARIZAL[a], C. F. SOON[a], N. J. YAACOB[a], J. LIAS[a], N. M. RAMLI[a],
A. B. SURIANI[b], A. MOHAMED[b], M. H. MAMAT[c], M. F. MALEK[c], M. SHIMOMURA[d]
[a]*Microelectronic and Nanotechnology – Shamsuddin Research Centre (MiNT-SRC) Faculty of Electrical and Electronic Engineering, Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia.*
[b]*NANO-SciTech Centre (NST), Institute of Science (IOS), Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia*
[c]*NANO-Electronic Centre (NET), Faculty of Electrical Engineering, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia*
[d]*Department of Engineering, Graduate School of Integrated Science and Technology, Shizuoka University, 432-8011, Japan*

Flower-like and micro-rods rutile Titanium Oxide (TiO_2) were fabricated on Fluorine-doped Tin Oxide (FTO) glass substrate by hydrothermal synthesis. TiO_2 was prepared with different volumes of Titanium(IV) butoxide (TBOT). The hydrothermal reaction time and temperature were optimized. The amount of TBOT were varied to be 2, 4, 6, 8, and 10 mL to achieve the property of micro-sized hydrophobicity on its surface. The samples were characterized by using Field Emission Scanning Electron Microscopy (FE-SEM), water contact angle measurement (WCA) and X-Ray Diffraction (XRD). Results from FE-SEM showed the micro-rods and flower-like TiO_2 grown on the FTO substrate. The WCA results of the sample with 8 mL of TBOT revealed an increase in contact angle. It has been proven from XRD data analysis that rutile crystalline micro-rods and flower-like structures were successfully grown on the surface of FTO with the peaks on TiO_2 of the sample.

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1. Introduction

The surface wettability is important for many applications such as industrial application, biological application and self-cleaning application. In the modern technology, wettability is mostly focused in nanoscience and nanotechnology fields due to the appearance of many nanomaterials in the previous two decades. Furthermore, researchers are interested in discovering more in this hydrophobic area because there are many applications that can be used in the future such as solar panel cover [1][2], wind turbines [3][4] and marine ship [5]. Hydrophobic rutile phased titanium dioxide (TiO_2) microstructure was fabricated on glass material which is the best to achieve powerful and suitable surface for self-cleaning application. Titanium dioxide (TiO_2) becomes an important material because of its unique properties that can remove and prevent any dirt or dust on the surface. Dirt on the glass that originated from water can be eliminated. Self-cleaning behavior on the glass surface can be determined with two different mechanisms such as hydrophobic and hydrophilic features. Hydrophobic surface water does not adhere on the roughness of the surface which makes the water droplet bounce and form a round shape that avoids contact with the surface. Contrasting with hydrophilic surface, the water will spread into the thin film. A contact angle less than 90° (low contact angle) usually shows that wetness will spread over a large area of the surface. Contact angles greater than 90° (high contact angle) means that water on the surface will have minimized contact with the surface and form a dense liquid droplet [6]. Both mechanisms are defined by the water contact angle (WCA) [7]. Nonpolar solvents react with hydrophobic molecules that produce an angle above than 90° [8].

Hydrophobicity also occurs when the presence of air pockets under the liquid drop and highly rough surface affect the water contact angle to be even greater than 150° [9]. TiO_2 is known due to the strength of its chemical structure, photocatalytic and optical properties, biocompatibility and good electrical properties. The combination of these properties has brought to the development of unique self-cleaning materials, whose surfaces can be maintained clean with sunlight and rainfall. Interestingly, TiO_2 surface has a sufficiently rough surface suitable to be a hydrophobic surface. In this study, we prepared the rutile phased of TiO_2 micro-rods and flower-like structures to produce a good quality hydrophobic surface.

2. Experiment details

2.1. Substrate cleaning

FTO substrate were cleaned using an ultrasonic machine for 15 minutes. The solution for cleaning process was prepared by adding and mixing chemical solutions in a beaker consist of acetone, ethanol and distilled water with the same ratio of 10 mL. The ultrasonic machine (wise clean Wisb.β) was used to clean the FTO glass substrate from foreign substances.

2.2. Preparation of the TiO_2 thin film

This experiment used hydrothermal method to produce micro-size rutile-phased TiO_2. The solution contains 120 mL distilled water, 120 mL of hydrochloric acid, and titanium butoxide (TBOT) which was used as a precursor solution to produce TiO_2. TBOT volume was varied to be 2, 4, 6, 8 and 10 mL. Table 1 concludes the summary of the solution preparation. All solutions were stirred for 10 minutes to ensure that the solution are completely dissolved. FTO glass substrate was put into Teflon lined autoclave. The autoclave is filled with the precursor solution and put into the oven set at 150°C. This hydrothermal synthesis was conducted at a constant temperature for 16 hours. After synthesis, the FTO film was taken out and rinsed with deionized water before drying at 60 °C in an oven for 10 minutes.

Table 1. Summary of solution preparation of TiO_2 microstructures

Sample	Chemical Solution	
	Constant	TBOT (mL)
1	Deionized Water (DI) : 120 mL Hydrochloric acid (HCL): 120 mL	2
2	Deionized Water (DI) : 120 mL Hydrochloric acid (HCL): 120 mL	4
3	Deionized Water (DI) : 120 mL Hydrochloric acid (HCL): 120 mL	6
4	Deionized Water (DI) : 120 mL Hydrochloric acid (HCL): 120 mL	8
5	Deionized Water (DI) : 120 mL Hydrochloric acid (HCL): 120 mL	10

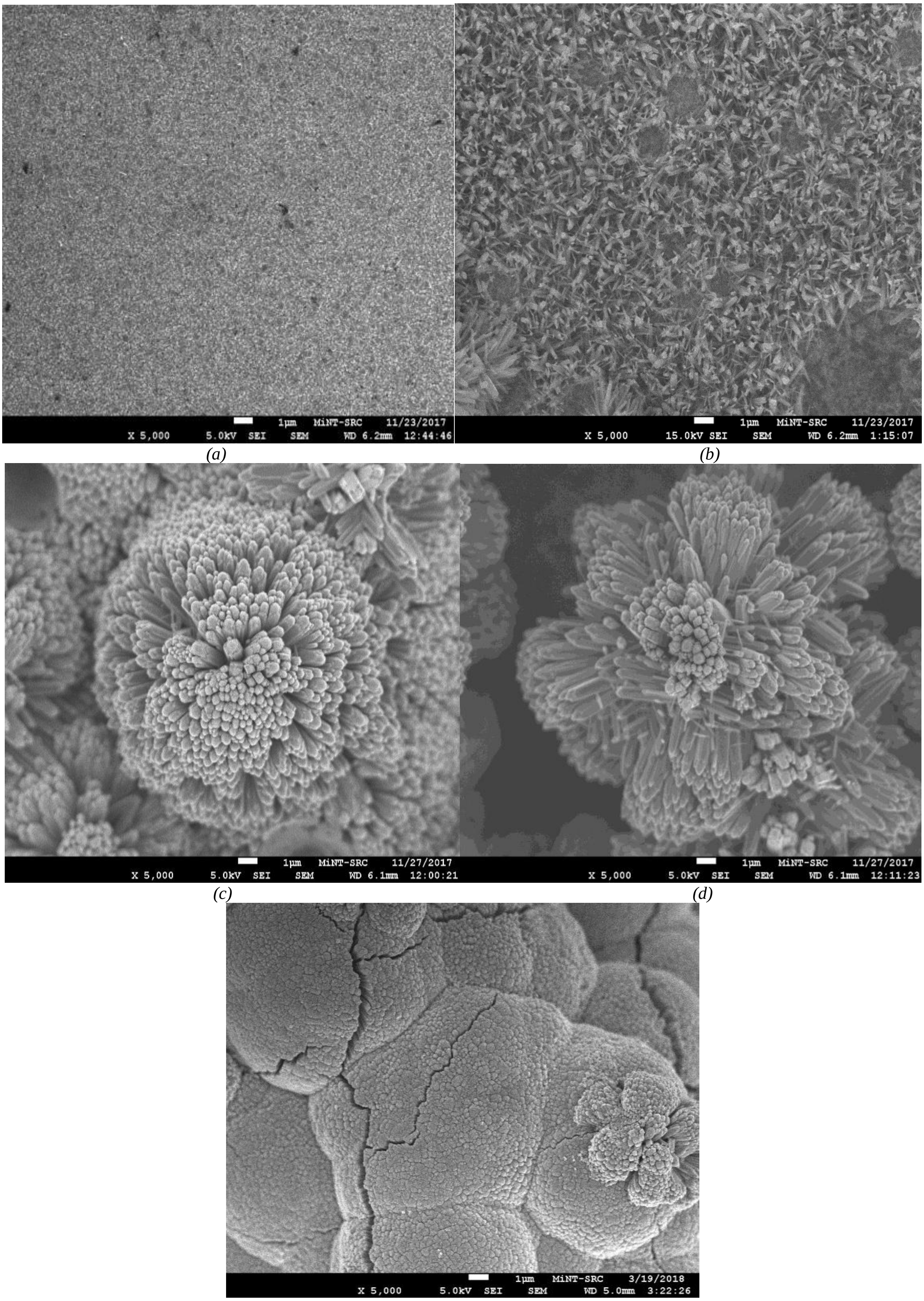
2.3. Characterization and analysis

The film properties were analysed by three characterization methods which is Field Emission Scanning Microscopy (FE-SEM JEOL, model JSM-7600F), X-Ray Diffraction Analysis (XRD) and Water Contact Angle Measurement (VCA-Optima model). FE-SEM and XRD were used to study the morphological and structural properties. Contact angle measurement is to measure the wettability of the sample by dropping water on the surface using the sessile drop method.

3. Result and discussion

3.1. Morphological properties of TiO_2 thin films

The surface morphology properties of the TiO_2 micro-size sample characterized by the field emission scanning electron microscopy was shown in Fig. 1 and Fig. 2. There are a few main concerns in the surface morphological properties of the samples which are the microstructure that develops on the sample, micro-rods and flower size, the shape of micro-rods and flower and lastly, the thickness of the deposited micro-layer on the samples using the cross-section. At 2 mL of titanium butoxide, the figure shows a layer of oriented rod has without any flower-like growth in this condition. Then, Fig. 2 b) shows the cross-section for 4 mL, which shows a smallest average micro-rod on the surface measures at 2.3 µm and flowers-like growth with thickness of 3 µm. It clearly shows that flower-like growth is up on top of the micro-rods. For the third sample with 6 mL of titanium butoxide, the figure depicted that micro-rod and flower size have rapidly increased in size which is from 2.3 to 7 µm and 3 µm to 9.2 µm in the cross-section image in fig 2. c). Then, for the fourth sample at 8 mL of TBOT, fig. 2 d) shows the size of micro-rods at 7.45 µm and the thickness for flower at 15.3 µm. Lastly, Fig. 2 e) of the sample with 10 mL of TBOT, micro-rods and flower sizes increased to 8.95 and 17.15 µm respectively.

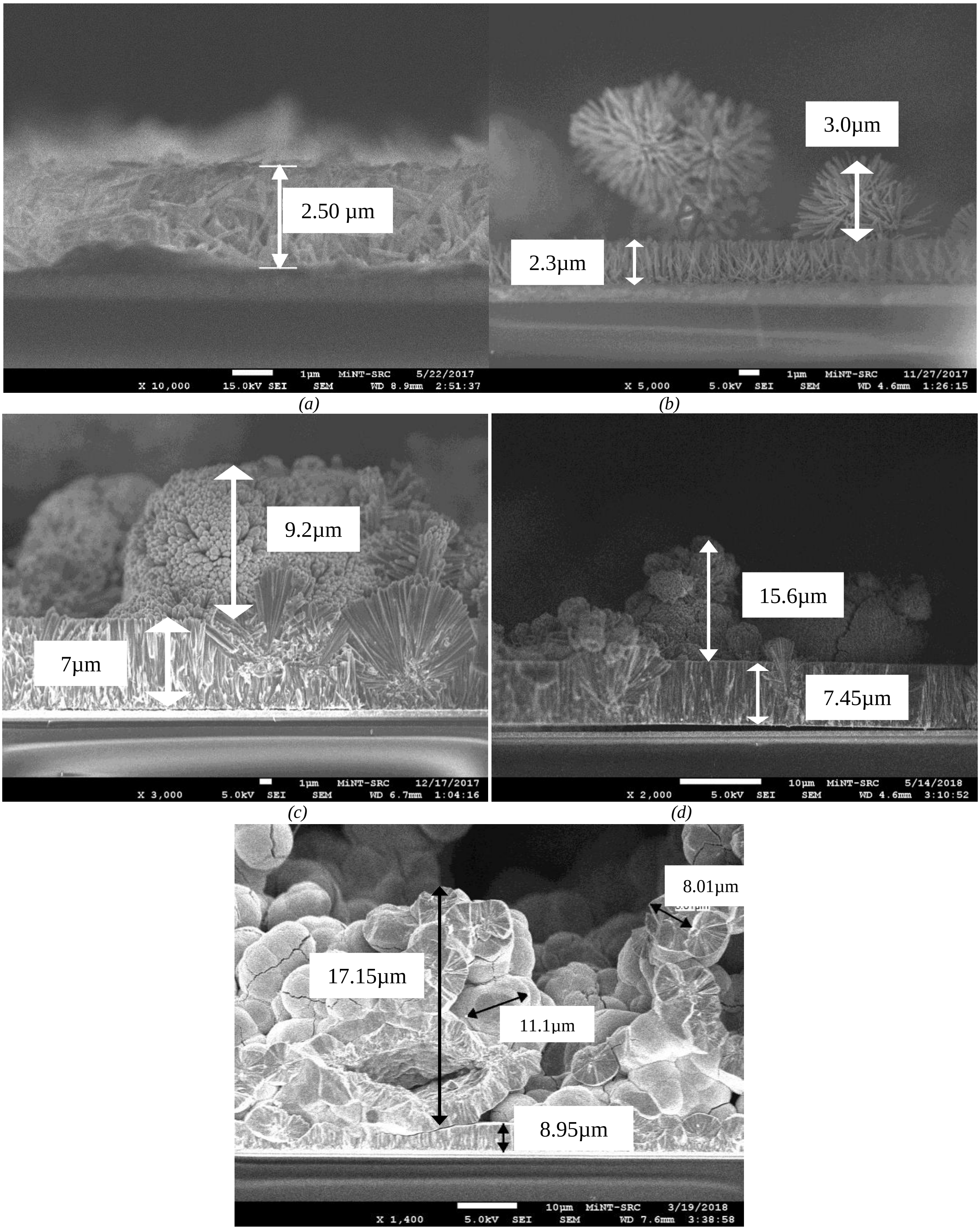


(a) *(b)*

(c) *(d)*

(e)

Fig 1. FE-SEM images of TiO_2 grown on FTO substrate with a) 2 mL, b) 4 mL, c) 6 mL, d) 8 mL and e) 10 mL of TBOT with 5K magnification



(a) *(b)*

(c) *(d)*

(e)

Fig 2. FE-SEM images of TiO_2 grown on FTO substrate with a) 2 mL, b) 4 mL, c) 6 mL, d) 8 mL and e) 10 mL of TBOT (cross section view)

The size difference between micro-rod thicknesses is due to the hydrothermal condition, in which the microstructure will continue to grow at different times. Besides, FE-SEM results also showed no space between micro-rod when the solution for TBOT increased. In addition, the sample with 10 mL of TBOT sample had the highest concentration and it affected the film in which it peeled off from the substrate. It shows a structure that is denser than the others. Micro-rods and flower size greatly affected the surface area measurement. However, it can be concluded from the FE-SEM images that the thickness of the micro-rods and flower could be varied by changing the titanium precursor concentration during hydrothermal synthesis. The thickness of the micro-rods and flower could be varied by increasing the titanium butoxide during hydrothermal synthesis from 2 mL to 10 mL. From the observation, the micro-rods were not aligned when the precursor titanium concentration is low and micro-rods growth flourished when titanium precursor is higher. The rod-shaped TiO_2 is narrow due to the high density of active site available for surface reaction as well as a high interfacial charge carrier transfer rate which is good for any application. The increase in precursor of titanium was suitable in the invention of hydrophobic TiO_2 microstructure for self-cleaning.

3.2. Structural properties of TiO_2 microstructures

Fig. 3 shows the change of intensity versus angle (θ) of the rutile phased TiO_2 micro-size with different volumes of titanium (IV) butoxide. Volumes of titanium (IV) butoxide were varied for 2, 4, 6, 8 and 10 mL.

Fig. 3 shows the graph of XRD analysis on micro-sized TiO_2 deposited at 150° substrate temperature with various volume of Titanium (IV) Butoxide. The X-ray diffraction patterns of pure rutile phased TiO_2 were illustrated in Fig.2. Rutile structure was confirmed by plane (110), (101), (200), (111) and (210) diffraction peaks [10]. The XRD patterns of rutile phased TiO_2 have the main peak at $2θ=27.4°$ due to the (110) planes. Therefore, rutile phased TiO_2 has been detected in characterizations. All planes showed from the rutile peaks and no anatase peak can be seen in the XRD pattern. The graph of intensity for sample 1 have all the peaks identical to the features of rutile phase. This is due to the three peaks for rutile phase at 27.43 (110), 36.11 (101), 41.25 (111).

From the result of XRD, we can determine the crystalline phase of these samples. The hydrophobic effect of TiO_2 does not only depends on crystal structure but also is relevant to the specific surface area. When the volume of solution increases, the peaks become narrower and sharper. This shows for better crystallinity. A previous research mentioned that when the results of XRD graph start from zero and have any three diverse peaks within the range of rutile, it proved that the crystalline of the sample is in rutile phase. If the results of the graph start with a high peak, that sample is an anatase crystalline. The synthesis of rutile TiO_2 micro-rods at high temperature is an interesting one and its growth depends mainly on the solution conditions which are temperature, pH and so on [11].

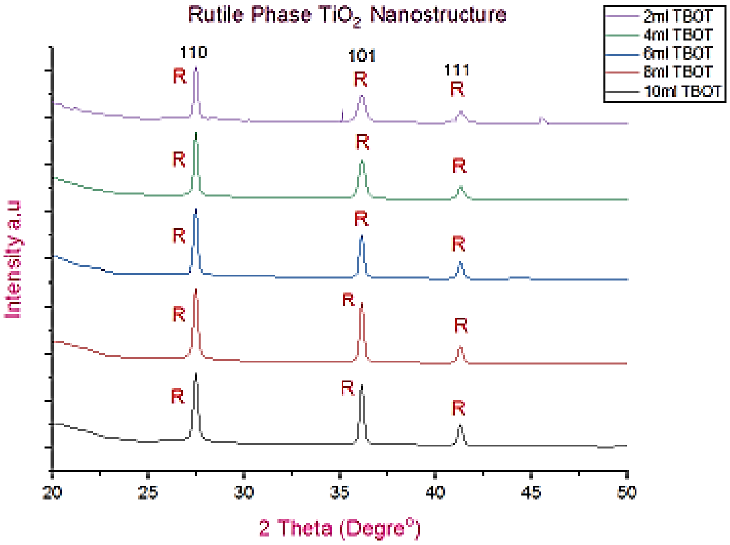
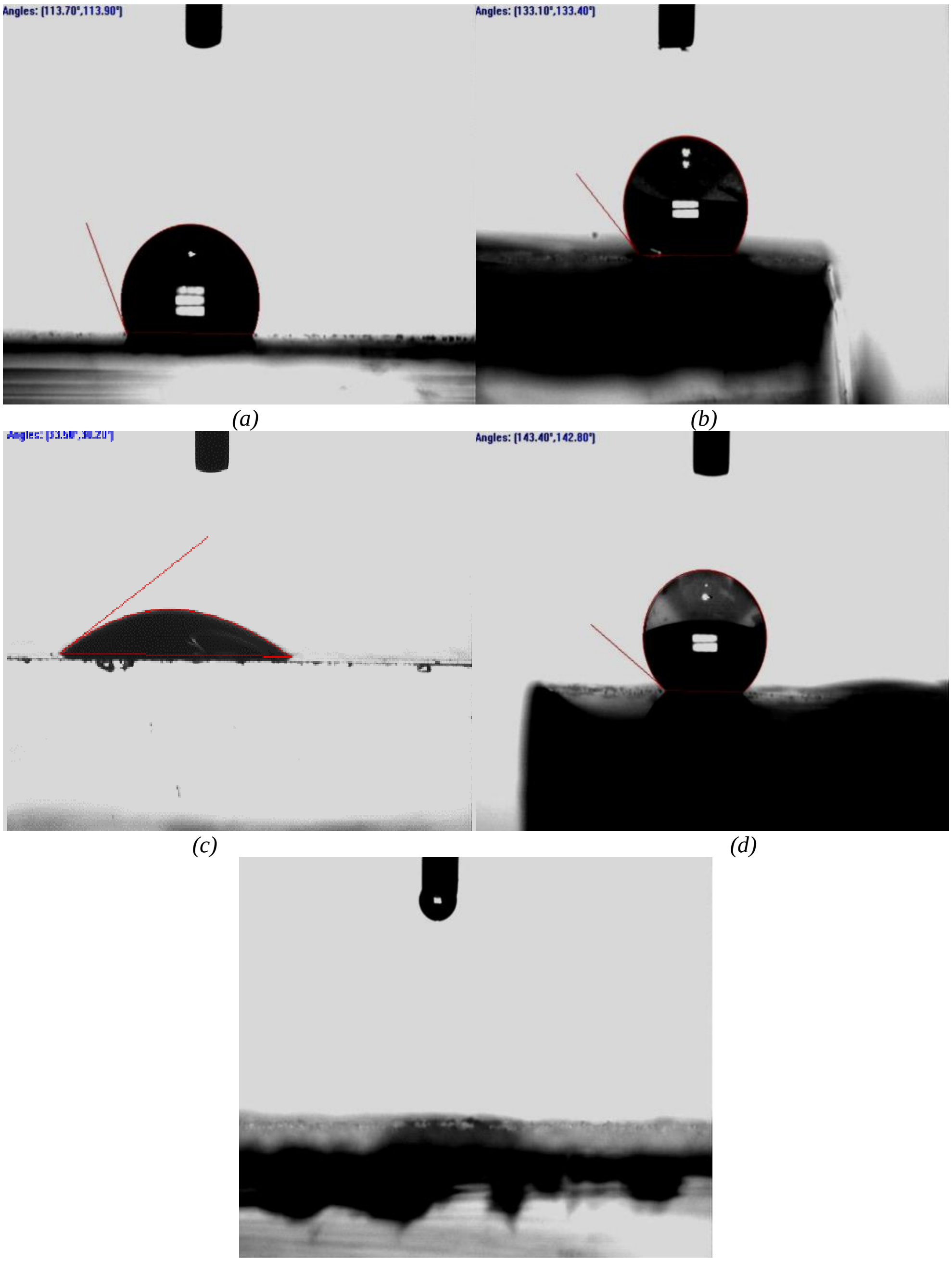


Fig 3. Graph of XRD of Titanium Dioxide (TiO_2) rutile phase (color online)

3.3. Contact angle properties of TiO_2 microstructures

Fig. 4 shows the contact angle analysis. There are 5 samples characterized for their hydrophobic properties which were the structures of TiO_2 with different volume of TBOT precursor 2, 4, 6, 8 and 10 mL. No pattern of water droplet was observed using contact angle measurement. As shown in Fig. 4 a), b), c), d) and e). It is seen that the angle of the water droplet on the sample increases as volume of TBOT increases from 2 to 10 mL.

The figure shows the angle of water droplets on the TiO_2 films with a different angle on every sample. At Fig. 4 a), the contact angle measurement is at about 113.70°, meanwhile for 4 mL of TBOT in Fig. 4 b), the angle increased to 133.16°. Furthermore, in Fig. 4 c), the angle dropped to 50.5°and for 8 mL of TBOT sample, it increased to be the highest contact angle measurement at about 143.40 ° but at 10 mL TBOT, the contact angle is shows 0° which means the water droplet has permeated into the film.



(a) (b)

(c) (d)

(e)

Fig 4. Contact angle of water droplet on TiO_2 *film with a) 2 mL (113.70), b) 4 mL (133.10°), c) 6 mL (33.50°), d) 8mL (143.40) and e) 10 mL (0°) of TBOT FTO substrates*

From this entire figure, it was found that the different volumes of TBOT has affected the contact angle of the samples. The increment of the volume of TBOT during hydrothermal synthesis causes the increase of the contact angle measurement. This can be observed from hydrophobic that is form on the sample verified by using contact angle measurement. The behaviour interpreted in terms of lower free energy for the hydrophobic substrate when there is minimal contact between water and the hydrophobic substrate. In addition, the surfaces are hydrophobic with the apparent contact angle which are greater than 100◦, because air is entrapped between the micro-rods and flower interspaces. At 6 and 10 mL, the angle does not show hydrophobic properties with an angle less than 90°. This condition occurs due to the correlation between the surfactant curvature and affinity of headgroup for the solid substrate. This is because the distance of the microstructures dependence on the force in between which is the water will absorbed and combined between the gaps. The higher the distance of microstructure, the higher the water will be absorbed into the sample.

4. Conclusion

In conclusion, pure crystalline rutile phased TiO_2 was successfully synthesized onto FTO glass substrate. The samples were prepared with various amount of TBOT precursor solution. The effect of TBOT volume on the crystal structure, morphology and the angle of the water and substrate have been studied. Highly hydrophobic aligned TiO_2 micro-rods and flower structure arrays have been successfully synthesized on FTO. The FTO substrate is an important part of TiO_2 growth to achieve the hydrophobic properties for self-cleaning application from the water contact angle measurement.

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* Corresponding author: akhairul@uthm.edu.my