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Research paper



Low Temperature Fabrication of Flower-Like Rutile Phased Tio_2 Film towards Methyl Orange Degradation

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Abstract

Pure rutile titanium dioxide (TiO_2) thin film was fabricated at a low temperature of 150°C by using a simple, one step hydrothermal method. TiO_2 thin film was developed on Fluorine doped tin oxide (FTO) by using titanium butoxide (TBOT) as a precursor, hydrochloric acid (HCl) and deionized (DI) water. The assembly of flower-like rutile phased TiO_2 could be controlled by simply changing the amount of precursors. The prepared samples were characterized by using Field Emission Scanning Electron Microscopy, X-ray Diffraction and Energy-dispersive spectroscopy. Most importantly, this pure rutile TiO_2 thin film showed a great significance compared to commercial TiO_2 Degussa P25 on degradation of methyl orange under UV light. The degradation of rutile TiO_2 thin film was up to 65.6 % while P25 thin film was only 8.07 %. From the experiments, it was found that the rutile phased TiO_2 has the higher photocatalytic activity in lower MO concentration and favorable in acidic environment. The enhanced activity might be accredited to the efficient separation of electron-hole pairs and high surface area produced by flower-like rutile phased TiO_2.

Keywords: *Rutile, flower-like, TiO_2, photocatalytic*

1. Introduction

A well-known semiconductor material, titanium dioxide is a chemically stabile material over a wide pH range with high illumination resistance (low photo-corrosion). Despite of being safe and non-toxic, titanium dioxide is relatively abundant [1]. TiO_2 is the most commonly used material for photocatalytic applications due to these characteristics. The preparation of nanostructured titanium dioxide (TiO_2) has received considerable attention from many researchers because of its excellent potential in many applications such as photocatalyst, gas sensor, optical filter, antireflective and dye-sensitized solar cells (DSSC) [2]. Furthermore, nanostructured TiO_2 offers more surface area and has a low electron-hole pair recombination rate compared to nanoparticles TiO_2[3].To fabricate, countless preparation techniques have been conducted such as sol-gel method [4], DC magnetron sputtering [5], spin-coating technique [6], spray pyrolysis deposition (SPD) method [7] as well as hydrothermal method [8]. Among these, a cost-effective hydrothermal method is very capable of producing a homogeneous thin film as compared to others. In general, TiO_2 is present in the form of three minerals, brookite, anatase and rutile [4]. Rutile phase is the main source of TiO_2 and very stable. The other phases of TiO_2 can be easily synthesized and usually the metastable anatase and brookite will form a thermodynamically stable rutile at temperatures above 600°C [9]. This process of calcination leads inevitably to the agglomeration and development of nanocrystalline particles [10]. Moreover, the morphology of the surface has become devastated and has faced difficulties to control[11]. Therefore, these show the importance to prepare a rutile phase of TiO_2 nanostructures by a low temperature hydrothermal method. Previously, anatase phase of TiO_2 acts as a photocatalytic catalyst. However, since rutile has a stable phase and a lower bandwidth than the anatase phase, in some circumstances, rutile has been found to be more active than anatase in photocatalytic activity[12]. The photocatalysis process has been found to be one of the most effective green technologies for the treatment of waste water by removing organic contaminants over the last two decades[13]. The first significant advance of photoelectrochemical water splitting using a TiO_2 anode and a Pt counter electrode is reported by Fujishima and Honda in 1972 [14]. In 1975, when Frank and Bard reported a reduction in CN-in water[15], TiO_2 photocatalysis was first used to remedy environmental pollutants. Photocatalysis can be defined as a " catalytic reaction involving light absorption in the production of a catalyst"[16]. Interac-

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tion with light and sufficient energy in the semiconductor produces reactive oxidizing agent that can help to the photocatalytic transformation of pollutants. In order to achieve the production of reactive oxidizing agent, at least two processes must take place simultaneously during the photocatalytic reaction[17]. In general, a photocatalytic process occurred in the slurry system, but several problems have arisen among them especially after the treatment process between the powder and treated water, the powder is aggregated when applied at high concentrations and the powder form is not recommended for the continuous flow system [18]–[20]. The immobilization of the catalyst thin film offers good condition for photocatalytic activity after separation and overcomes the difficulties. In this study, a low temperature hydrothermal method for about 150^{o}C was used to prepare the rutile TiO_2 film on a fluorine doped tin oxide (FTO) which acts as a substrate. This study was the first report on the photocatalytic application of the rutile thin film for MO degradation. Under UV light radiation, the treatment process with the presence of the rods and flowers nanostructures of the rutile TiO_2 thin film shows a good performance of photocatalytic activity on Methyl Orange (MO) photodegradation. The thin film of TiO_2 rutile phase was characterized by the use of Field Emission Electron Scanning Microscopy (FESEM), X-ray diffraction (XRD), Electron Dispersive Spectroscopy (EDS) and UV Vis spectroscopy. The purpose of this study is to find the most favorable pH and concentration of MO to achieve the highest degradation by film TiO_2 rutile phase.

2. Methodology

2.1. Catalyst preparation and characterization

FTO substrate, titanium (IV) butoxide, acetone and ethanol were purchased from sigma Aldrich. Hydrochloric acid was purchased from J.T Baker (USA) and TiO_2 P25 was purchased from Evonik Industries AG (Germany). Fluorine-doped SnO_2 (FTO) with a thickness of 0.5 µm coated on the glass was used as substrate. Ethanol, acetone, hydrochloric acid (HCl), deionized (DI) water and titanium (IV) butoxide (TBOT) were used for the preparation of solution. The FTO coated glass was cut into the desired dimension of 35 mm x 35 mm and cleaned using sonication method by applying acetone, ethanol and DI water with the volume ratios of 1:1:1 for 10 minutes followed by air drying. For the rods and flowers layer, the chemical solution for hydrothermal process was prepared by dissolving 80 ml concentrated HCl (36.5 %~38 %) in 80 ml of DI water. The mixture was stirred for five minutes and then the volume of TBOT was varied to 5 ml, 7 ml, 10 ml and 12 ml. TBOT was added by drop wise using a capillary tube. After stirring for 10 minutes, the solution was put into a steel made autoclave with Teflon made liner (300 ml) for hydrothermal process in which the FTO glass substrates are set with a conducting FTO surface facing upward. The temperature was set at 150^{o}C and the reaction time was fixed for 10 hours. After this hydrothermal process, the autoclave was taken out from the oven and cooled down to room temperature. The prepared samples were rinsed with DI water and dried at 60˚C for 10 minutes. FESEM and EDX (JEOL JSM-7600F) were used to observe the morphology and to identify the element content in rutile TiO_2 thin film, respectively. XRD (PANalytical X'Pert3 Powder) was used to characterize the crystalinity of TiO_2 over the 2θ range of 20^{o} to 80^{o} by using copper radiation CuKα (λ=0.15406 nm). UV-vis spectroscopy (Shimadzu UV-1800) was used to determine the absorbance of methyl orange in photocatalytic analysis.

2.2. Photocatalytic degradation of Methyl Orange

Photocatalytic analysis was conducted to investigate the efficiency of the fabricated TiO_2 in waste water treatment. Methyl orange (MO) was used to evaluate the photocatalytic activity of TiO_2 film with different parameters. MO with 5 ppm concentration was used in this experiment. The rutile TiO_2 thin film was immersed in 100 ml of MO solution under vigorous stirring. The whole system was covered in a black box to refrain it from the interference of light. Before the reaction begins, the solution was stirred in the dark for 15 minutes to promote the adsorption-desorption within MO solution and rutile TiO_2 thin film. The system was illuminated with UV lamp (25 W RS Company). At constant time interval, 4 ml of MO solution was withdrawn for sampling. The concentration of MO was observed from the absorbance value at wavelength of 465 nm.

3. Result and discussion

3.1. Surface morphology and elemental property

EDX was used to check the elemental property of the prepared samples. The result from the EDX spectra has proven the presence of titanium (T) and oxygen (O) elements in all tested samples. No foreign substance was detected on the TiO_2 rutile phased thin film. FESEM was used to investigate the morphologies of the samples. Figure 1 shows the result for different volumes of precursor for 5 ml to 12 ml.

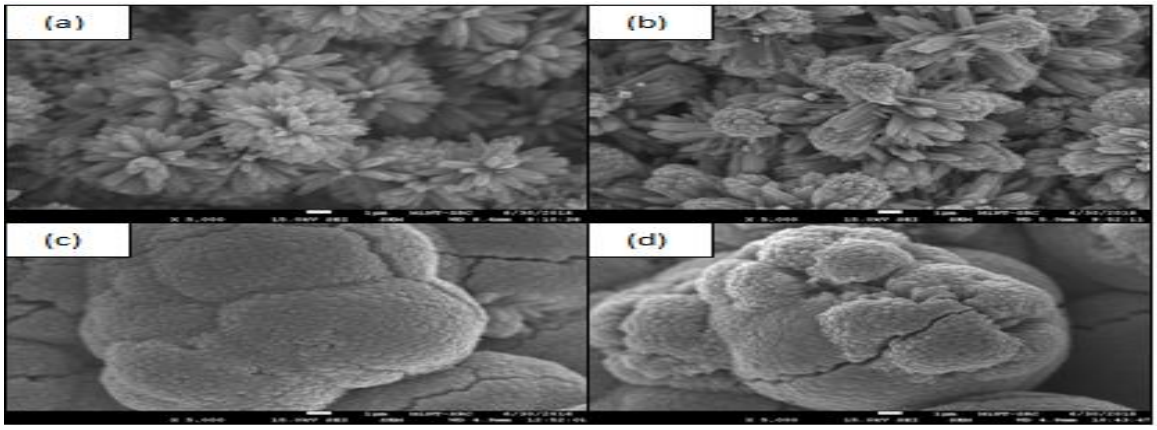


Fig. 1: FESEM images for the different volume of precursor (TBOT). (a)5 ml , (b) 7 ml (c) 10 ml (d) 12 ml

At 5 ml volume of TBOT, the FESEM images shows the TiO_2 is produced in a flower like structure and rods at the bottom of the flowers. The size of the rods for 5 ml TBOT is in the range between 290 nm to 320 nm. The flower consists of rods growing radially from the center within the 500 nm diameter. At 7 ml volume, the TiO_2 produced is still in flower like shape but contains branches along the rods. The size of the rods for 7 ml TBOT is in the range between 330 nm to 400 nm. At 10 ml and 12 ml TBOT volume, the morphology of flower like structure is diminished. The TiO_2 produced a ball like structure. The density of the rods/flowers is increased when the volume of TBOT is increased. The increasing of the TBOT amount causes rapid hydrolysis and homogeneous precipitation when it is added into solution [9]. Figure 2 shows FESEM images of cross sectional rutile phased TiO_2 thin film. The length of the rods of 5 ml TBOT volume is 2.053 µm. The length of the rod increased when TBOT volume increases to 7 ml. However, when TBOT volume increased to 10 ml, the length decreased to 3.741 µm. The length become shorter when the volume of TBOT reached 12 ml. the length of rods at 12 ml is 2.559 µm. B. Liu et al. reported that when the amount is too high, the probability of the rods colliding together with the neighbour increases, which then stops the

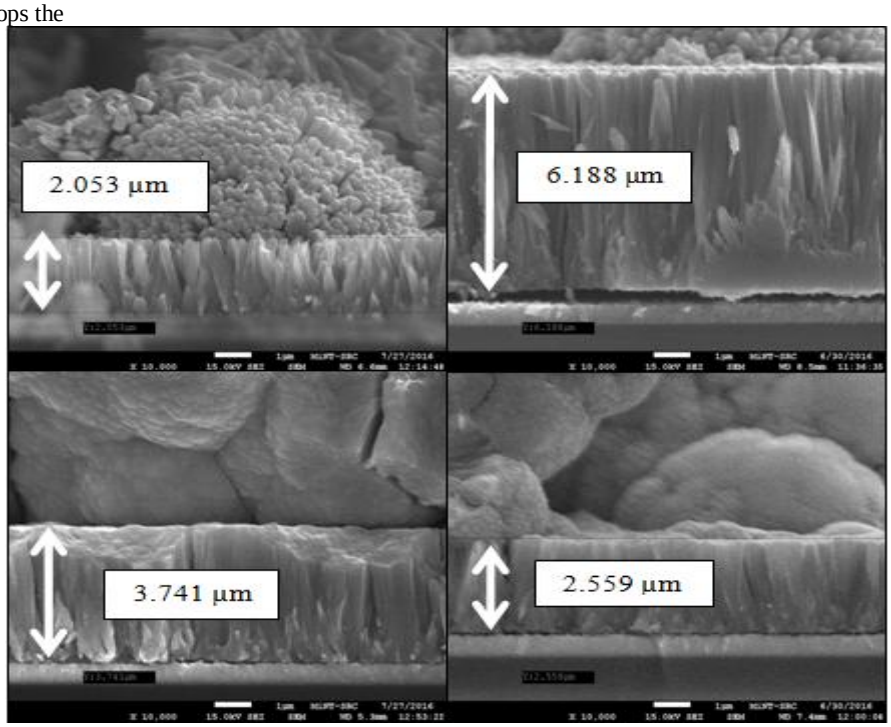


Fig. 2: FESEM cross section image for the different volume of precursor (TBOT). (a) 5 mL, (b) 7 mL, (c) 10 mL (d) 12mL

growth and shorten the length of TiO_2 produced [9]. For P25 thin film, the FESEM images are shown in Figure 3. The average size of nanoparticle was 25 nm to 27 nm since Degussa P25 is used. The particle seems to agglomerate with each other. The height of the P25 thin film is only 2.091 µm. The height of the P25 thin film is shorter than rutile phased TiO_2 thin film. Further explanation about the correlation between surface morphology and photocatalytic performance will be discussed in the photocatalytic analysis section.

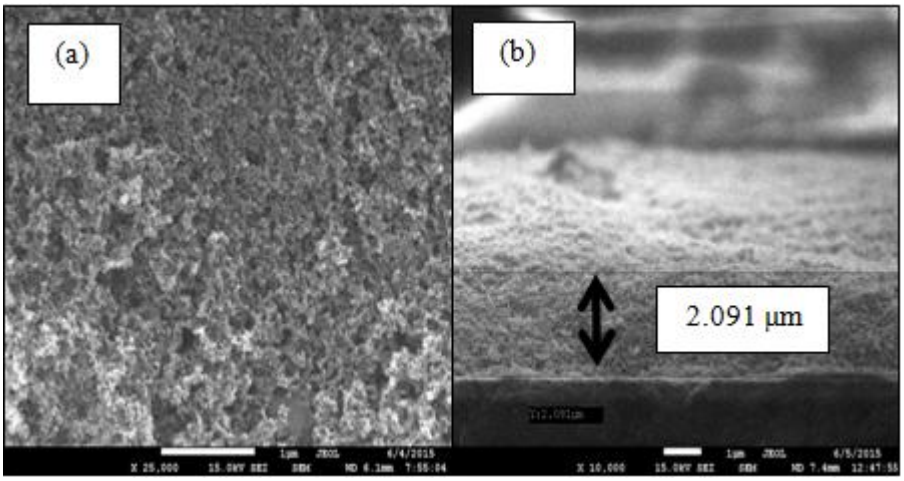


Fig. 3: FESEM images for P25 (a) surface morphology and (b) cross section

3.2. Structural property

XRD is used to determine the phase composition of TiO_2. Figure 4 shows the XRD pattern for different amount of TBOT volume with P25 thin film. The result shown no anatase peak was found for rutile phased TiO_2 thin film. The peak at 2θ value of 27.38°, 36.10°, 41.24°, 54.28°, and 62.67° match well with the (110), (101), (111), (211) and (002) planes of rutile phased TiO_2 respectively (JCPDS no 98-005-1933). For P25 film, the peak at 2θ value appeared at 25.35°, 37.6° and 47.76° fit well with (101), (101) and (111) respectively (JCPDS no 98-008-2082) was confirmed anatase phased. The intensity of diffraction peak at plane (110) decreased gradually with the

increase of TBOT volume. This was indicated by the decrement of growth of TiO_2 on the FTO substrate. When TBOT volume is increased, the formation of TiO_2 become restricted due to the high concentration of TBOT solution and amorphous phased is approached.

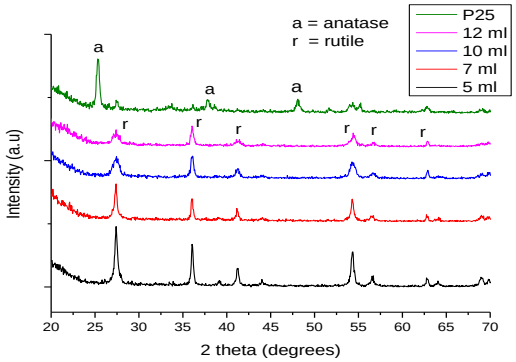


Fig. 4: XRD pattern for different TBOT volume and P25

3.3. Photocatalytic activity

In order to investigate the efficiency of the rutile-phased TiO_2 thin film towards MO degradation, photocatalytic analysis was conducted. The percentage dye degradation was calculated by using Equation (1):

$$\text{MO degradation (\%)} = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

Here, C_o is the initial concentration of MO solution and C_t is the concentration of MO solution at time t. The degradation percentage of MO is plotted against time to observe the photocatalytic efficiency of TiO_2 thin film. The direct photolysis of MO in the absence of the catalyst did not show any significant degradation. A commercial catalyst Degussa P25 thin film was used as a control experiment as benchmark to compare with improved TiO_2 photocatalyst. Figure 5 shows the percentage of MO degradation result for various TiO_2 loading versus time irradiation under UV light. The degradation results for different TBOT amount were compared with the commercially available TiO_2 Degussa P25 as a reference. The MO degradation efficiencies of TiO_2-5 ml, TiO_2-7 ml, TiO_2-10 ml, TiO_2-12 ml and P25 were 2.5%, 65.6%, 42.7%, 48.93% and 8.46% respectively, estimated at 10 hours as shown in Figure 5. The highest photocatalytic degradation was observed at 7 ml TBOT volume. The photocatalytic ability strongly depends on the number of electron-hole pairs during photocatalytic activity in the semiconductor. During the process, radical species were attacked by the organic substance and produce carbon dioxide and water which are harmless to environment.

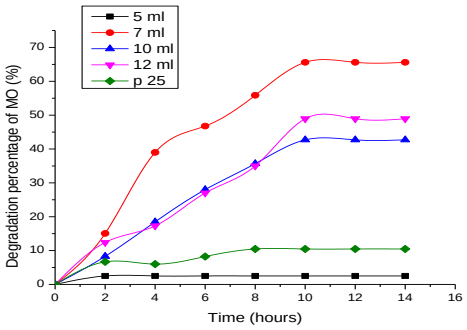


Fig 5: Percentage degradation of MO for different amount of TBOT volume and P25

FESEM images shows 7ml TBOT volume surface morphology has flower-like morphology and has the highest rods. This flower-like structure provides a larger surface area than the other amount of TBOT volume and P25. The larger surface area could provide more active sites and produce more radical species in photocatalytic activity as well as enhance degradation process. The height of the rods will help to avoid the electron to recombine back with the hole at valence band. Pauly et al. claimed that the nanorods within the nanoflowers has a significant effect which helps in light scattering and can cause the light to multiply absorption during transporting process [21]. This can cause absorption of photons and improved the production of photocarries. The prepared rutile phased TiO_2 sample with narrower band gaps could absorb more light than Degussa P25. Several factors can influence photocatalytic activity such as high crystalinity, different phases, narrower band gap, large surface area and small crystallite size [22]. These factors play an important role in enhancing the photocatalytic activity. When TBOT volume increased to 10 ml TBOT volume, the TiO_2 become ball-like structure and reduce the active site area and hence reduce the degradation of MO. This can be rationalized by the change of surface morphology. At high TBOT volume, the TiO_2 become clotted and cause the limitation of UV light to pass through [23]. High crystallinity might play a crucial role in enhancing the degradation of photocatalytic as well. With high crystallinity, few defects occurred in the photocatalytic activity. The defects can be contributed to the recombination between electron and holes occurred and decreased the photocatalytic activity of TiO_2. In some of the cases, the poor photocatalytic activity of rutile TiO_2 synthesized by high temperature may attribute to the low surface area, although the band gap for rutile is low and has good crystallinity. This can be one of the factors that the degradation of MO decreased when the TBOT volume is increased.

3.3.1. Effect of MO concentration

The effect of MO concentration on the percentage degradation was tested by varying the concentration from 5 ppm to 15 ppm. The result is shown in Figure 6. The best degradation rate at 65.6 % was obtained at 5 ppm concentration of MO, followed by the degradation of 10 ppm of MO concentration which was 7.86 % and 15 ppm of MO concentration was 1.16 %. The concentration of MO increased with the decreasing degradation rate of MO. The rutile phased TiO_2 thin film is more suitable for low concentration of MO. Siham et al. proved that MO degradation rate reaches a saturation limit when at high concentration of reactant [24]. In high concentration, the path length of the photon in the solution was decreased and reversed effect is observed in low concentration of MO. This phenomenon will caused the number of photons to decrease and effect the photocatalytic activity performance in high concentration [25].

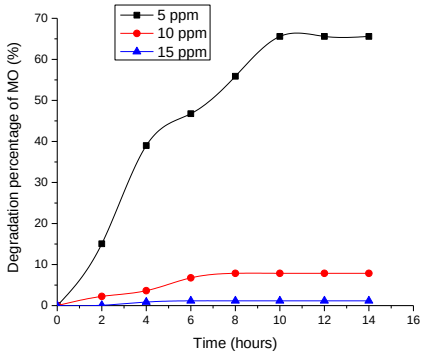


Fig 6: Percentage degradation of MO for different MO concentration

3.3.2. Effect of changing pH

pH of the solution plays an important role in the adsorption process in photocatalytic activity. The surface charges of TiO_2 influenced by the pH solution. The photocatalytic performance of rutile phased TiO_2 was studied in pH range of 3 to 10. Figure 7 shows the degradation percentage of photocatalytic activity gradually decreased with the increasing pH. The best degradation was obtained at pH 5 which is 65.6%. At pH 3 the degradation is only 5.46 %. At neutral pH which is pH 7, the degradation is 1.44 %. At higher pH which is pH 10, no degradation is observed. The highest degradation is favourable in acidic environment. This phenomenon can be explained by the zero point charge (ZPC) of rutile phased TiO_2 and the anionic nature of MO [26]. The ZPC of rutile phased TiO_2 is proven by the previous study is pH 5.4 to 5.5 [27]. This indicates that the surface of rutile phased TiO_2 has a positive charge below pH 5.4. This environment is favourable to anionic nature of MO solution and enhanced the photocatalytic activity in acidic environment. In addition, in alkaline range, the opportunity of hydroxyl radical to attack the dye or waste water is limited because the hydroxyl radical is scavenged rapidly [28].

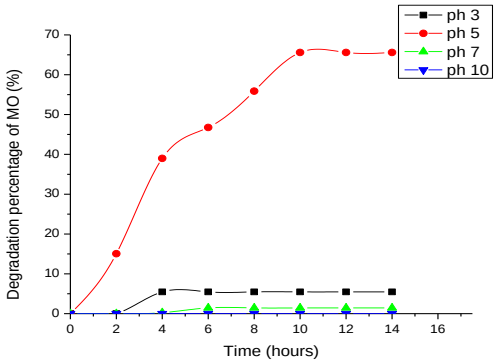


Fig 7: Percentage degradation of MO for different pH

3.4. Possible formation process of rutile phased TiO_2 thin film

The possible growth process of rutile phased TiO_2 can be proposed as follows. From the hydrothermal process, $[Ti(OH)_4]$ is produced from TBOT in the solution and becomes the important point of growth in the TiO_2 on the FTO (SnO_2) substrate. Since the SnO_2 layer also has the rutile phased crystallinity resulting in an epitaxial growth of the rutile phased TiO_2 [29]. SnO_2 and rutile phased TiO_2 has a similar tetragonal crystal and the lattice parameter for SnO_2 and rutile TiO_2 is SnO_2 a= 4.687Å, c=3.160Å and rutile TiO_2 a= 4.594Å, c=2.959Å, respectively. $[Ti(OH)_4]$ also set off the growth of TiO_2 in the solution. The growth of the rutile phased TiO_2 could be originated from a high concentration of HCl. In high acidic solution, pH < 0, TiO_2 becomes soluble, which suggests that a dissolution-precipitation process can occur rapidly. Since the hydrothermal condition under the free space, the flourish rutile flower are grown and deposited on the top of the rutile rod TiO_2 due to gravity. Figure 8 show the growth mechanism of rutile phased TiO_2 using hydrothermal method.

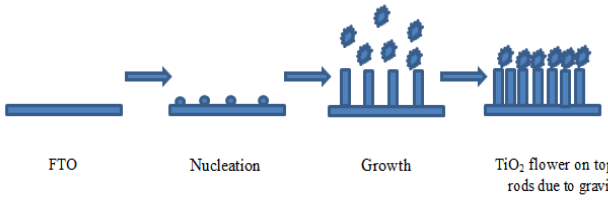


Fig 8: The growth mechanism of rutile phased TiO_2 by hydrothermal method

4. Conclusion

Rutile phased TiO_2 was successfully fabricated by using a simple hydrothermal method. 7 ml TBOT volume has the highest degradation of MO. The degradation was up to 65.6 % while P25 thin film was only 8.07 %. Their high photocatalytic activity could be attributed to their narrow band gap, large surface area, and high crystalinity.
The highest degradation of MO was obtained at lower concentration. At higher concentration, the numbers of photon to pass through become limited and inhibit the photocatalytic activity. The rutile thin film was suitable at acidic pH than alkaline pH. This phenomenon may be due to the zero point charge (ZPC) of rutile phased TiO_2 and the anionic nature of MO. This study provides a simple and inexpensive method to prepare rutile phased TiO_2 by using hydrothermal method.

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