

Influence of Hydrochloric Acid Volume on the Growth of Titanium Dioxide (TiO₂) Nanostructures by Hydrothermal Method

(Pengaruh Isi Padu Asid Hidroklorik ke atas Perkembangan Nanostruktur Titanium Dioksida (TiO₂) melalui Kaedah Hidroterma)

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ABSTRACT

Titanium dioxide (TiO₂) with various morphologies has been successfully synthesized by a simple hydrothermal method at 150°C for 10 h using titanium butoxide (TBOT) as a precursor, deionized (DI) water and hydrochloric acid (HCl) on a fluorine-doped tin oxide (FTO) substrate. The influences of HCl volume on structural and morphological properties of TiO₂ have been studied using x-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM), respectively. The result showed that several morphologies such as microsphere, microrods, nanorods and nanoflowers were obtained by varying the volume of hydrochloric acid. The crystallinity of titanium dioxide enhanced with the increasing of hydrochloric acid volume.

Keywords: Acid hydrochloric (HCl); field emission scanning electron microscopy (FESEM); titanium dioxide (TiO₂); x-ray diffraction (XRD)

ABSTRAK

Titanium dioksida (TiO₂) dengan pelbagai morfologi telah berjaya disintesis melalui kaedah hidroterma pada 150°C selama 10 jam dengan menggunakan titanium butoksida sebagai perintis, air ternyahion (DI) dan asid hidroklorik (HCl) pada substrat fluorin-terdop timah oksida (FTO). Pengaruh isi padu HCl pada sifat struktur dan morfologi TiO₂ telah dikaji menggunakan pembelauan sinar-X (XRD) dan medan pelepasan mikroskop elektron pengimbas (FESEM). Hasil kajian menunjukkan beberapa morfologi seperti mikrosfera, mikrorod, nanorod dan bunga nano diperolehi dengan mengubah isi padu asid hidroklorik. Penghabluran daripada titanium dioksida dipertingkatkan dengan meningkatkan jumlah asid hidroklorik.

Kata kunci: Asid hidroklorik (HCl); medan pelepasan mikroskop elektron pengimbas (FESEM); pembelauan sinar-x (XRD); titanium dioksida (TiO₂)

INTRODUCTION

Titanium dioxide (TiO₂) is known as a crucial material as important transition metal oxides. It has a numerous application in photocatalysis, photovoltaic, electrochromic device, gas sensor and solar cell (Ahmad et al. 2010). This was due to its high transparency and high refractive index and also its chemical durability in the visible and near IR region. TiO₂ thin film can be fabricated using many different techniques such as sol-gel (Biju & Jain 2008), DC magnetron sputtering (Domaradzki 2006), spin-coating (Diebold 2003) and spray pyrolysis deposition (SPD) method (Shinde et al. 2008) electrically conducting substrates (fluorine doped tin oxide on glass). Titanium dioxide occurs in nature as minerals rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Among these minerals, rutile phased display a good expertise in light scattering efficiency, opacity, high refractive index, chemical inertness and photocatalytic effect (Zhou et al. 2011). In addition, rutile phased also has a good electron mobility which is an important factor used in the many applications.

Generally, rutile phase TiO₂ is obtained at high temperature after the calcination of anatase phase. The morphology of the TiO₂ will be devastated after the calcination treatment (Zhou et al. 2011). Thus, the specific morphology of rutile phase TiO₂ will face difficulty to produce. The complicated processes and usage of catalyst or template were used to fabricate the specific morphologies of rutile phased. Andrea Testino reported that surface morphology can act as an important role in determining the efficiency in specific application (Testino et al. 2007). Due to this problem, the preparation of rutile phased with different morphologies by varying the HCl volume at low temperature by simple hydrothermal method is approached to fabricate TiO₂ thin film to protect the surface morphology from devastated.

METHODS

For this experiment, hydrothermal method was chosen to fabricate the thin film because of its low growth

temperature, low cost and good potential to scale up (Zhou et al. 2011). Fluorine-doped SnO_2 (FTO) with a thickness of $0.5 \mu\text{m}$ coated on glass was used as substrate. The FTO coated glass was cut into the desired dimension of $10 \times 25 \text{ mm}$ and cleaned by sonicating method in acetone, ethanol and deionized (DI) water with the volume ratios of 1:1:1 for 10 min followed by drying in air.

For the rods and flowers layer, the chemical solution for hydrothermal process was prepared by controlling (20120 mL) concentrated HCl (36.5 %~38 %) in 80 mL of DI water. The mixture was vigorously stirred for 5 min and then 3 mL of titanium butoxide (TBOT) was added

by drop wise using a capillary tube. The solution was stirred until it was clear. Next, the solution was put into steel made autoclave with Teflon made liner (300 mL) for hydrothermal process in which the FTO glass substrates were set with a conducting FTO surface facing upward. The hydrothermal process was performed at 150°C for 10 h. After this hydrothermal process, the autoclave was taken out from oven and cooled down to room temperature. The prepared samples were rinsed with DI water and dried in the oven at 150°C for 10 min.

Next, surface morphology and structural property sample will be studied in this stage. The morphological

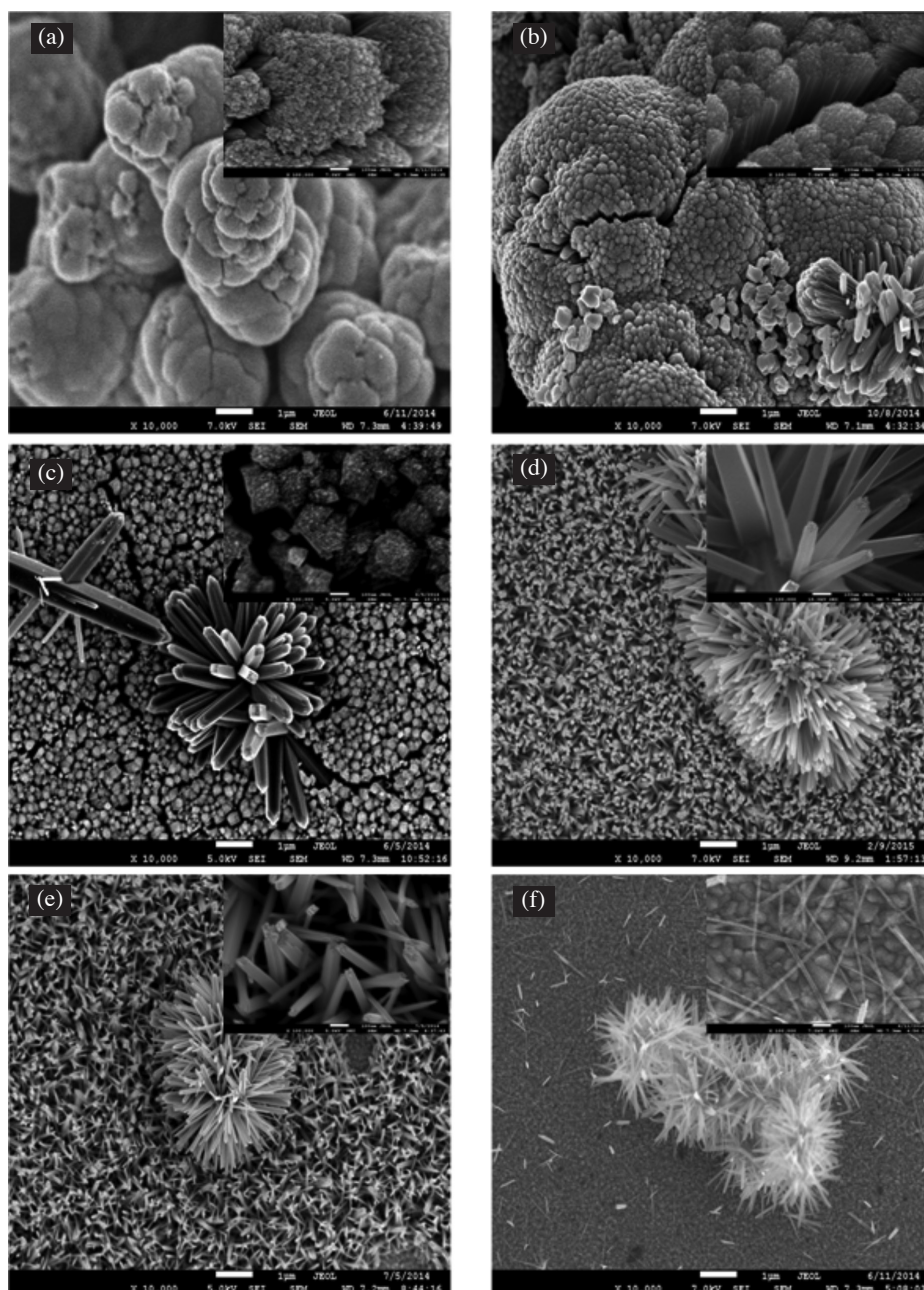


FIGURE 1. Fesem result showed the different morphology by varying the HCl volume (a) 20 mL HCl, (b) 40 mL HCl, (c) 60 mL HCl, (d) 80 mL HCl, (e) 100 mL HCl and (f) 120 mL HCl

and structural properties will be characterized using field-emission scanning electron microscopy (FESEM) and x-ray diffraction measurement (XRD), respectively.

RESULTS AND DISCUSSION

The different morphologies obtained are microspheres, microrods, nanorods, and nanoflowers. Figure 1 shows the result from the FESEM image. The result showed that morphologies of TiO_2 were affected by the volume of hydrochloric acid. For 20 and 40 mL, TiO_2 microspheres composed of rods were obtained. For 40 mL, the size of the spheres becomes larger and the splitting of the sphere is shown clearly. This splitting shows that the spheres started to form the flower like TiO_2 . Then, 60 mL shows the forming of dense rod structure on top of FTO substrate and the branch of flowers of microflower was obtained. The size of the rods was in range 210 to 270 nm. Next, the nanorods and nanoflowers were obtained at 80 mL of HCl volume. The size of the rods for 80 mL of HCl volume was in 90 to 100 nm range. The result for 80 and 100 mL were the same in which nanorods and nanoflowers were obtained and when the HCl volume increased, the size of the rods and flower become smaller to nanometer size which lead to surface area improvement. For 100 mL of HCl volume, the size of the rods was in 80 to 100 nm range. By adding the acid volume, the concentration of $[\text{Cl}^-]$ ions in the solution increases. $[\text{Cl}^-]$ ions around the titanates nucleus lead to the improvement for the length of the single nanorods (Links 2012). This phenomenon will dramatically change rods from micro size to nano size and improves the surface area. However, when the HCl volume is too high at 120 mL and $[\text{Cl}^-]$ ions become very concentrated, the hydrolysis of titanium becomes restricted and restrains for nucleations (Guo et al. 2012). This was supported by the result for 120 mL of HCl volume. FESEM result showed that the distribution of TiO_2 nanorods diminished on the FTO substrate and only nanoflowers left on the substrate.

The rod shaped TiO_2 has higher surface to volume ratio and this would guarantee a high density of active site available for surface reaction as well as a high interfacial charge carrier transfer rate which is good for many applications. Moreover, it was expected to reduce the recombination of electron-hole pair because of the delocalization of electrons in the rod, making them free to move throughout the length of the crystal.

The XRD pattern in Figure 2 shows that the TiO_2 were well crystallized. All planes show rutile peak and no anatase peak can be seen in the XRD pattern. For 20 mL HCl (JCPDF no. 98-016-5922), rutile phase was obtained. The peaks in XRD pattern were observed at 2 theta values of 27.45° , 36.05° and 41.25° were related to 110, 101 and 111 planes. When the volume of HCl increases, the peaks become narrower and sharper. This shows for better crystallinity.

Then, for 80 to 120 mL (JCPDF no. 98-005-1930), the FTO structure immersed in the XRD pattern. This was because the thickness of the rods was decreased. The result was shown in Figure 3. The thickness of 80 mL HCl volume was $3.875 \mu\text{m}$ and decreased to $1.125 \mu\text{m}$ when 120 mL of HCl volume was used. Moreover, at 120 mL HCl volumes (JCPDF no. 98-009-1517), the crystallinity of rutile phase was gone and FTO phase has approach. This was caused by the limited growth of TiO_2 at higher HCl volume due to the hydrolysis rate of TBOT. The result was supported by the FESEM result above. This study was conducted to improve the crystallinity of rutile without offering a calcination process that will lead to surface morphological damages. The rutile phase exhibits an excellent combination of physical properties, including exceptional light scattering efficiency, a high refractive index, opacity, chemical inertness and photocatalytic properties (Zhou et al. 2011).

Based on the experimental result previously, the possible growth mechanism of rutile nanostructures was discussed. Generally, the nucleation and growth can be

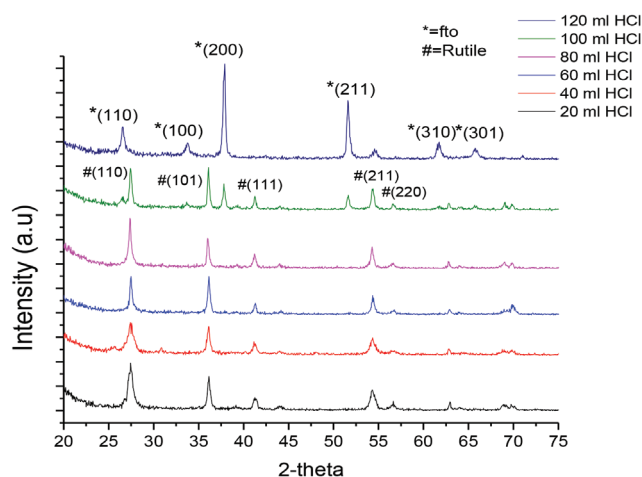


FIGURE 2. The peak of XRD pattern of varying HCl volumes

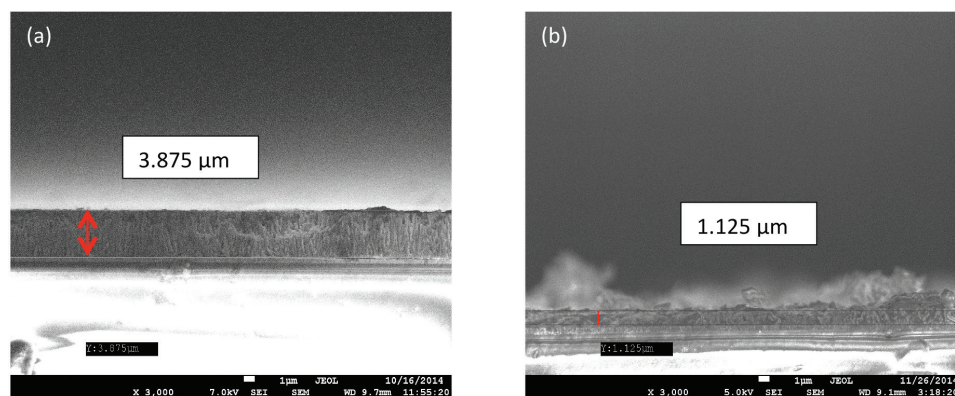


FIGURE 3. Fesem result showed the cross sectional images (a) 80 mL HCl and (b) 100 mL HCl

generated by the arrangement of the atom at the nucleation site on the substrate and the precursor. In this experiment, TBOT was used as a precursor and producing $(\text{Ti}(\text{OH})_4)$ and became growth point of TiO_2 on the FTO substrates. The FTO substrate has a similar tetragonal structure with the rutile phased. The lattice mismatch between the tetragonal FTO ($a=4.687\text{\AA}$, $c=3.160\text{\AA}$) and rutile TiO_2 ($a=4.594\text{\AA}$, $c=2.959\text{\AA}$) has a small different (Ye et al. 2013). This small lattice mismatch led to the growth of rutile TiO_2 compactly on the FTO substrate. $\text{Ti}(\text{OH})_4$ has generated the growth of TiO_2 in the solution. A high concentration of HCl could be the origin of the growth of rutile phased TiO_2 . TiO_2 became soluble in the high acidic ambience and caused the dissolution-precipitation process to occur instantly. Since the growth progress was under the hydrothermal condition in free space, the nanoflowers were flourishing in the deposition on top of the nanorods layer.

CONCLUSION

TiO_2 was successfully fabricated on FTO glass by simple hydrothermal method at low temperature. TiO_2 nanostructures with different morphologies including microsphere, microrods, nanorods and nanoflowers can be selectively fabricated by adjusting the volume of HCl used. By obtaining different morphologies, it was easier to find the most suitable morphology for the desired application. The possible mechanism of rutile TiO_2 was discussed. In addition, surface morphology and structural property play an important role in determining its efficiency in a specific application.

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REFERENCES

- Ahmad, M.K., Halid, M.L.M., Rasheid, N.A., Ahmed, A.Z., Abdullah, S. & Rusop, M. 2010. Effect of annealing temperatures on surface morphology and electrical properties of titanium dioxide thin films prepared by sol-gel method. *Journal of Sustainable Energy & Environment* 1: 17-20.
- Biju, K.P. & Jain, M.K. 2008. Effect of crystallization on humidity sensing properties of sol-gel derived nanocrystalline TiO_2 thin films. *Thin Solid Films* 516(8): 2175-2180.
- Diebold, U. 2003. Structure and properties of TiO_2 surfaces: a brief review. *Applied Physics A: Materials Science & Processing* 76(5): 681-687.
- Domaradzki, J. 2006. Structural, optical and electrical properties of transparent V and Pd-doped TiO_2 thin films prepared by sputtering. *Thin Solid Films* 497(1-2): 243-248.
- Guo, W., Xu, C., Wang, X., Wang, S., Pan, C., Lin, C. & Wang, Z.L. 2012. Rectangular bunched rutile TiO_2 nanorod arrays grown on carbon 2 fiber for dye-sensitized solar cells. *Journal of the American Mechanical Society* 134(9): 4437-4441.
- Sarkar, D., Ghosh, C.K. & Chattopadhyay, K.K. 2012. Morphology control of rutile TiO_2 hierarchical architectures and their excellent field emission properties. *CrystEngComm* 14: 2683-2690.
- Shinde, P.S., Sadale, S.B., Patil, P.S., Bhosale, P.N., Brüger, A., Neumann-Spallart, M. & Bhosale, C.H. 2008. Properties of spray deposited titanium dioxide thin films and their application in photoelectrocatalysis. *Solar Energy Materials and Solar Cells* 92(3): 283-290.
- Testino, A., Bellobono, I.R., Buscaqlia, V., Canevali, C., D'Arienzo, M., Polizzi, S., Scotti, R. & Morazzoni, F. 2007. Optimizing the photocatalytic properties of hydrothermal TiO_2 by the control of phase composition and particle morphology. *A Systematic Approach* 129(12): 3564-3575.
- Ye, M., Liu, H.Y., Lin, C. & Lin, Z. 2013. Hierarchical rutile TiO_2 flower cluster-based high efficiency dye-sensitized solar cells via direct hydrothermal growth on conducting substrates. *Small (Weinheim an der Bergstrasse, Germany)* 9(2): 312-321.
- Zhou, W., Liu, X., Liu, J., Liu, D., Li, J., Jiang, H., Wang, J. & Liu, H. 2011. Control synthesis of rutile TiO_2 microspheres, nanoflowers, nanotrees and nanobelts via acid-hydrothermal method and their optical properties. *CrystEngComm* 13(14): 4557-4563.

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