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Preparation of Free Standing TiO_2 Nanowires (FSTNW) with Super Hydrophilic Properties

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Abstract. TiO_2 is the most widely used photocatalyst with wide range of application. In order to extend its properties for desired application, the morphology modification often use as one of the self-modify approaches. In this paper, the free standing TiO_2 nanowires (FSTNW) were synthesized via alkaline hydrothermal process with oxidizing agent assisted. Acetamide and acetone were used in combination with 10 M NaOH for hydrothermal reaction at 180ºC for 18 hours. The results indicate that acetone perform better in assisting the TiO_2 formation during the hydrothermal process compared to acetamide. By the synergetic combination of acetone and NaOH the FSTNW were formed through several mechanism with end result possessing super hydrophilic properties that can be utilize for many new applications.

Keywords: free standing TiO_2, nanowires, super hydrophilic

INTRODUCTION

Self-modify TiO_2 with various methods including morphology and surface modification often used to improve the existing properties or even extend the properties for desired application. TiO_2 is the most widely used photocatalyst, as it has high photocatalytic activity, high stability, non-toxic, and relatively cheap [1]. It potential applications widely range from water treatment, energy conversion, devices with enhancing electrochromic, photovoltaic, and antifogging, smart surface coatings and for oil-water separation [2].

Advanced research has proved that TiO_2 can be engineered in various types such as 0, 1, 2 and 3 dimensional nanostructures. The widely used 0D nanostructured TiO_2 (powder) is having some drawback such as fast recombination of electrons and holes, and slow charge carrier transfer. Meanwhile the synthesis of 2D and 3D nanostructured materials was comparably complex and required high maintenance experimental conditions. Recently, 1D nanostructure has been extensively studied due to its unique advantages. It had a high aspect ratio with the diameter ranging from 1 to 100 nm, in the form of tube, rod, wire, fiber or belt/ribbon-shape. 1D TiO_2 nanostructured materials possess all the typical features of TiO_2 nanoparticles and displayed a large specific surface area which favorable for photo-generated carriers transfer and photocatalytic activity [3–5].

Methods that have been developed to prepare 1D TiO_2 nanostructures are hydrothermal, solvothermal, Electrochemical anodization, Chemical vapor deposition (CVD), Electrospinning, Template-assisted and sol–gel. Hydrothermal method is the most common methods used for the fabrication of 1D TiO_2 nanostructures. It is usually conducted in a stainless-steel vessel with moderately high temperature and pressure. The hydrothermal method has attracted much attention due to its simple procedure and low production cost. Kasuga et al. reported the fabrication of TiO_2-based nanotubular materials by the hydrothermal method for the first time in 1998 [6]. In this process, amorphous TiO_2 powder was treated at high temperatures in a highly concentrated NaOH solution. This method can 100% convert the precursors to 1D TiO_2 nanostructured materials such as tube, wire, rods, belt and plate [4,5,7,8]. In

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this paper the synthesis of Free standing TiO_2 nanowires via alkaline hydrothermal methods with oxidising agent assisted were investigated.

MATERIALS AND METHODS

Free standing TiO_2 nanowires (FSTNW) were synthesized by adding a cut size 20 mm x 20 mm x 0.25mm of titanium foil 99% (BTMM Co. Ltd.) into mixture of 30 ml 10 M NaOH and oxidising agent acetone/acetamide (5,10,15% v/v) in Teflon hydrothermal autoclave (volume 50 mL). Prior the submision, the foil were cleaned in the beaker glass contain DI water and then placed in the ultrasonic bath for 10 min. The Teflon hydrothermal reactor were heated for 18 hours with temperatures 180ºC inside the oven. The post treatment after hydrothermal process consist of cooling until ambient temperature followed by several washing with DI water, and drying in oven at 110ºC for 2 h and finished by calcination for 2 h at 500ºC in the furnace.

X-Ray Diffraction SHIMADZU XRD-7000 were used for crystal structures analysis meanwhile for the surface morphology characterization were conducted using SEM-EDX JEOL JSM-6510LA. The surface wettability of the sample were analysed by interpreting the contact angle result of the sample that resulted from the Contact Angle and Surface Tension Measurement (OCA 25).

RESULTS AND DISCUSSION

This study observed the effect of NaOH addition in the process of FSTNW layer formation as well as variations in the addition of oxidising agents acetone and acetamide (5.10 and 15%) with the optimum operating conditions in previous work [9,10]. Comparison of visualization results can be seen in Figure 1. A white layer is seen in the sample that is queued using acetone. While in the sample with the addition of acetamide the color changed to dark brown. The resulting layer is very different from the initial treatment which only adds oxidising agent.

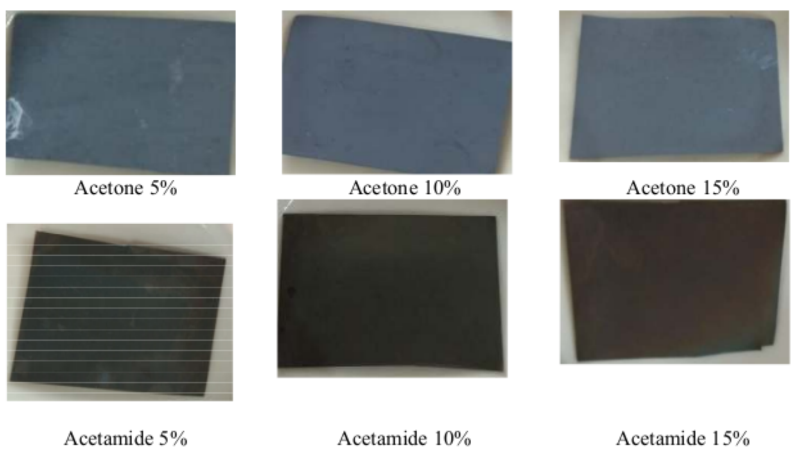


FIGURE 1. Visual comparison of FSTNW samples synthesized using different oxidising agent at various concentration

Samples were also characterized using XRD for the crystal structures identification. Figure 2 shows the XRD pattern for samples synthesized through hydrothermal processes with the addition of NaOH 10 M and various acetone concentrations. Numerous peaks were found such as TiO_2 anatase (JCPDS Card no. 78-2486)), β-TiO_2 (JCPDS 46-1238), $H_2Ti_3O_7$ (JCPDS 47-0561), and the substrate Ti metal. TiO_2 anatase phase has peak at 25.3º with high intensity. Meanwhile β-TiO_2 commonly found at 28º [11], monoclinic of hydrogen trititanate ($H_2Ti_3O_7$) peaks at 11, 24.5, 33, and 48.4º [12]. The synthesis of TiO_2 via hydrothermal process can produce various crystal structures such as TiO_2 anatase and rutile [13]; TiO_2 [2,14]; β-TiO_2 [11,15]; $H_2Ti_3O_7$[5,16] depend on the percusor used in the process as well as the temperature and time operation. In this work the addition of acetone at different concentration, the alkaline solution, temperature and time operation effect the crystal structures formation in the sample.

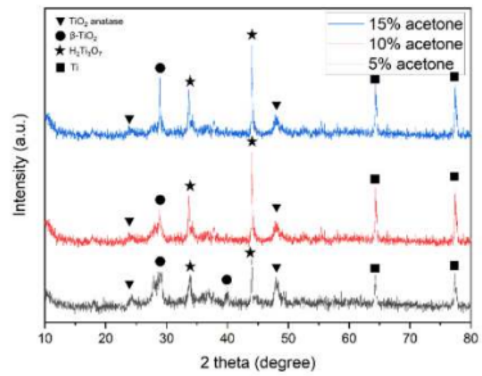


FIGURE 2. XRD pattern of FSTNW synthesized by oxidising agent acetone, at 10M NaOH solution at 180°C for 18 hours

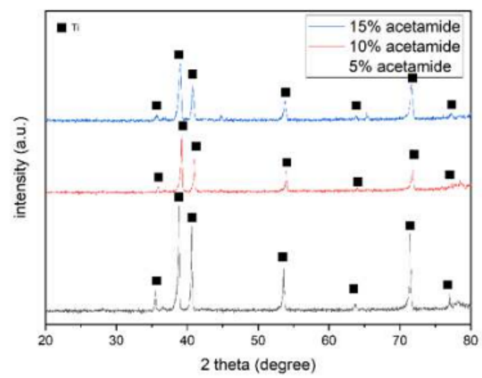


FIGURE 3. XRD pattern of FSTNW synthesized by oxidising agent acetamide, at 10M NaOH solution at 180°C for 18 hours

Meanwhile, Figure 3 shows the XRD pattern for samples synthesized through hydrothermal processes with the addition of NaOH 10 M and various acetamide concentrations. In contrast to the synergy of NaOH and acetone additions, the addition of NaOH and acetamide did not show any influence on the XRD pattern. The figures only show the titanium metal peaks 35.27°, 38.33, 38.56°, 40.32°, 53.14°, 70.23°, 70.76 ° for all of the addition percentage variation and there is only a very weak peak at the 2nd angle position of theta 20-28°, which is a signal of the existence of TiO_2 anatase phase.

This can be explained by the difference of energy bonding on each oxidising agent. Acetone requires about 84 kcal/mol[17] to be dissociated and donating oxygen to titanium. While Acetamide needed about 112 kcal/mol [18,19]. In acetamide-NaOH system the oxidation process of titanium into TiO_2 requires more energy compared to acetone-NaOH system. NaOH itself will be able to effectively help the process of dissolving and recrystallization of TiO_2 that is hit by TiO_2 anatase when there are many TiO_2 formed due to oxidation process.

Hydrothermal processes involving oxidizing agents and NaOH 10 M in general can be stacked with several stages of the process, namely (i) oxidation of titanium layer into titanium dioxide with the help of oxidizing agent; (ii) titanate layer formations involving NaOH; re-dissolving, recrystallization as well as the process of ion exchange. The process of dissolving TiO_2 formed generally follows the following reactions [20,21]:

$3TiO_2 + 2NaOH \rightarrow Na_2Ti_3O_7 + H_2O$ (1)

$Na_2Ti_3O_7 \rightarrow 2Na^+ + Ti_3O_7{}^{2-}$ (2)

$2Na+ + Ti_3O_7{}^{2-} + H^+ + OH^- \rightarrow H^+ + Ti_3O_7{}^{2-}$ (3)

$2H^+ + Ti_3O_7{}^{2-} \rightarrow H_2Ti_3O_7$, after calcination will form TiO_2 with different morphology (4)

SEM images in Figure 4 shows the morphology of the samples treated using acetone as oxidising agent that proven to have TiO_2 anatase crystal structures in the XRD characterization. Microsphere type of morphology with the size 1-2 microns on the irregular surface of the foil were produced via hydrothermal in the 10 M NaOH solution with 5% acetone treatment. The base were like nanowire network. The temperature and hydrothermal reaction time triger the disolution of TiO2 that previously produced, and then fused to each other and regrew to create microsphere morphology [22]. Meanwhile, more urchin like shaped morphology in the smaller size 0.5-2 microns were found in the sample treated in 10 M NaOH solution with 10% acetone with the same base nanowire network. Smooth base of nanowire network with size 50-100 nm in diameter and several microns long were produced in the environment of NaOH 10 M with acetone 15%. The presence of acetone as an oxygen source will drive titanium to form oxide and form various morphology such as rods [9,23,24]. It also explained elsewhere that the carboxyl groups, acetone functional group favour the vertical growth of the nanorods that follows the oxidation process of titanium [25,26].

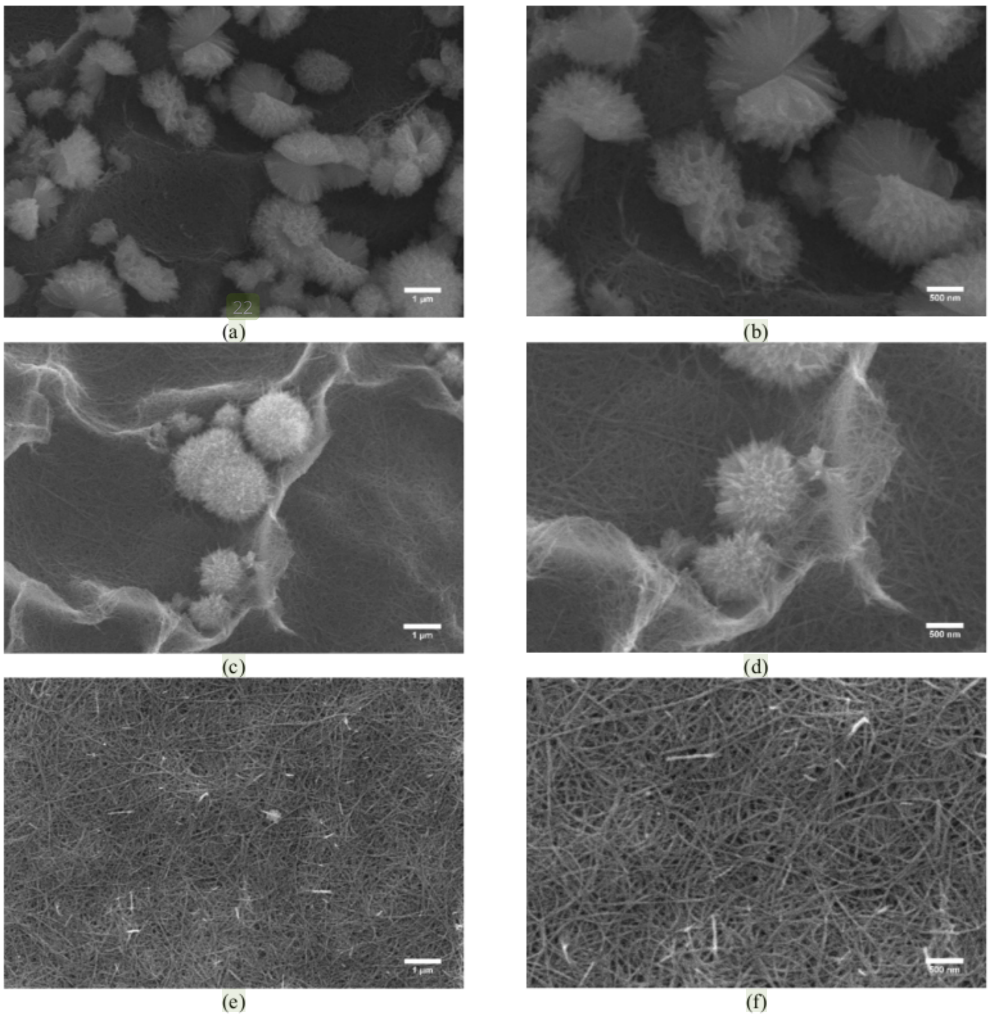


FIGURE 4. SEM result of FSTNW using acetone 5% (a-b); 10% (c-d); 15%(e-f)

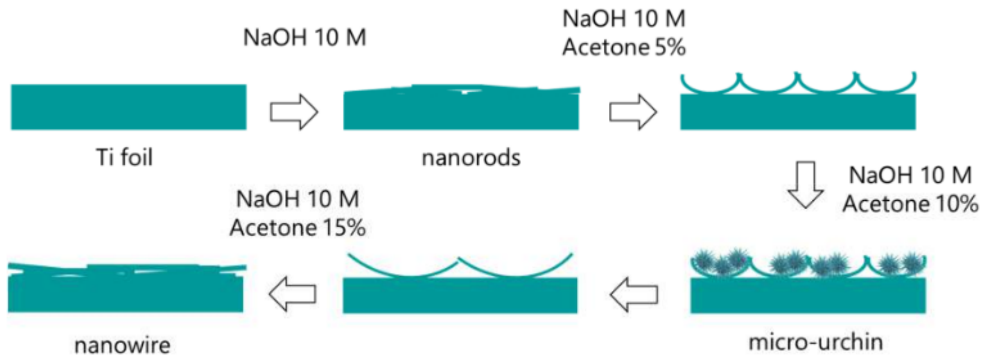
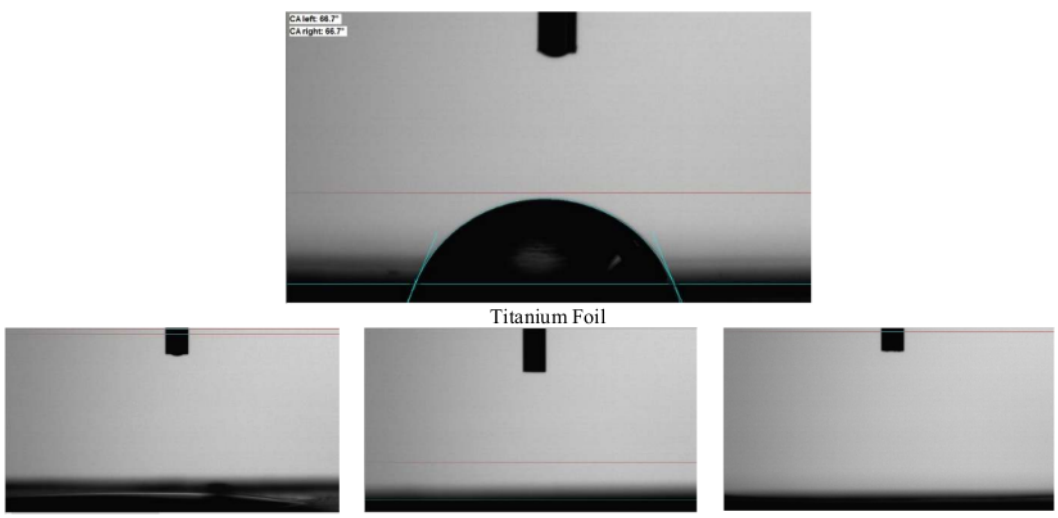


FIGURE 5. Proposed mechanism of FSTNW synthesis via alkaline hydrothermal process with acetone as an oxidising agent

Other researcher reported the vertical growth of nanowire can be achieved by using titanium (IV) butoxide as percusor via hydrothermal reaction in the acid condition [27], or calcinating Ti foil inside furnace with KOH atom nebulizer in the two step heating can create nanowires with length up to 500 nm and diameter 50 nm [28]. Meanwhile, the high pressure environment inside the hydrothermal reactor created by NaOH 10M solution with theoretical calculation that can go up to 7.5 bar at 180°C, suppress the vertical growth and increase the energy on the surface. Those high amount of energy circulated in the small space creates rolling effect on the oxide layer to create ball shape or urchin type of morphology [29,30]. Meanwhile the uneven base was force to growth axially to form longer nanowires as depicted in proposed mechanism Figure 5.

The wettability property of FSTNW is measured by observing the water contact angle between the surface of FSTNW and a droplet of water. Figure 6 and Table 1 illustrate the wettability properties of Ti foil as the sample substrate and FSTNW synthesized with the assistance of acetone 5-15%. Initial water contact angle of pristine Ti foil was 66.7°. After the growth of TiO_2 nanowires on the surface the water contact angle measured 0° for all of the acetone concentration addition. Surface wettability are categorized into 4 category, (1) superhydrophobic (water contact angle $\geq 150^0$); (2) hydrophobic (water contact angle 90°-150°); (3) hydrophilic (water contact angle of $\leq 90^0$); and (4) super hydrophilic (water contact angle approaching 0^0) [31,32]. This means the FSTNW possess super hydrophilic properties.



Titanium Foil

Acetone 5% Acetone 10% Acetone 15%

FIGURE 6. Water contact angle visualization of FSTNW in comparison with the pristine Ti foil

TABLE 1. Wettability properties of FSTNW

Sample	Water Contact Angle	Wettability Properties
Ti foil	66.7^o	hydrophilic
FSTNW-Acetone 5%	0^o	super hydrophilic
FSTNW-Acetone 10%	0^o	super hydrophilic
FSTNW-Acetone 15%	0^o	super hydrophilic

Star-like TiO_2 prepared by hydrothermal methods (190^{o}C for 3 h) using titanium isopropoxide (TTIP) as percusor possess hydrophilic wettability properties with contact angle 41-48^o [2]. Meanwhile, TiO_2 nanowire with super hydrophilic properties (contact angle 0^o) synthesized using TiO_2 nanoparticles as starting material via alkaline hydrothermal (200^{o}C for 8 h) [33]. Similar result of 0^o contact angle also found in the TiO_2 nanowire produced via chemical vapor deposition methods [14]. The incorporation of TiO_2 nanowire in other materials such as stainless steel mesh also creates the opposite properties from hydrophobic into super hydrophilic in the measurement of water contact angle [34]. It is speculated that either the shape of nanowire that creates the superhydrophilic effect or the synergetic effect of nanowire morphology as well as TiO_2 as semiconductor materials with photocatalytic properties. In addition by the extended properties of FSTNW which is superhydrophilicity will expand the oportunity of this material to be used in many new application.

CONCLUSION

Free standing TiO_2 nanowires (FSTNW) has sucessfully synthesized via hydrothermal routes in the alkaline environment with 15% (v/v) acetone assisted at 180^{o}C for 18 hours. The nanowires observed to have TiO_2 anatase, β-TiO_2 and $H_2Ti_3O_7$ crystal structures with almost zero water contact angle by means possess superhydrophilic properties. The synergetic effect of acetone as oxidising agent that favor the oxidising process and high pressure condition generated by the alkaline condition at at 180^{o}C for 18 hours develop the FSTNW from rods, microsphere, urchin type and finally nanowire morphology. With the addition of super hydrophilic properties, further research in the use of FSTNW material in many new application can be conducted.

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