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Synthesis of free standing TiO_2 nanostructures (FSTNS) via hydrothermal process for organic photocatalytic degradation

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Abstract. The superiority of TiO_2 nanoparticle for photocatalytic degradation of organic pollutant has been acknowledged in many researches. However, the powder form of TiO_2 face new challenge related to its recovery after photocatalytic process. In this paper the synthesis of free standing TiO_2 nanostructures (FSTNS) via hydrothermal process were reported. The effect of hydrothermal processing time at temperature 180°C to the FSTNS properties were observed. The optimum FSTNS was synthesized at 180°C in 18 hours by using acetone as oxidation agent. The synthesized FSTNS was effectively able to degrade the organic pollutant (Bromothymol blue) via photocatalysis under black light illumination.

INTRODUCTION

Almost 80% of wastewater is simply discharged into the environment without further treatment, including domestic waste and 300-400 cubic tons of industrial waste [1, 2]. In Indonesia, industrial wastewater, domestic wastewater and commercial wastewater are the largest contributors of the total wastewater. According to the Indonesian Agency for the Assessment and Application of Technology (BPPT), domestic and industrial wastewater have a high pollution potential due to the lack of affordable technology to be applied in the wastewater treatment system [3].

Wastewater contains various components such as colloidal particles, pathogenic microorganisms, inorganic pollutants and organic pollutants. Domestic and industrial wastewater both small and medium contain more organic components with a COD value of 7000-10,000 ppm [3]. Organic components include dyes, pesticides, fertilizers, hydrocarbons, phenols, plasticizers, biphenyl, detergents, oils, fats, pharmaceutical ingredients, proteins and polysaccharides [4-6].

At present, organic wastewater treatment still relies on biological methods such as aerobic and anaerobic processes. This process can degrade organic pollutants, but the time required is very long and this process is very vulnerable to environmental changes [5, 6]. Advanced oxidation processes (AOPs) are relatively new destructive technologies and can be used as an alternative for wastewater treatment processes that contained organic components. The basic principle of this process is the formation of hydroxyl radicals (• OH) which can degrade organic pollutants to form minerals. One of the technologies categorized as AOP is photocatalysis with semiconductor material TiO_2. In photocatalytic oxidation process UV / TiO_2 hydroxyl radicals (• OH) are generated by the illumination of ultraviolet light into the surface of TiO_2 [7, 8]. TiO_2 has high photoreactive properties and chemical stability compared to other materials [9].

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Many studies have proven the effectiveness of TiO_2 nanoparticles as a catalyst for degradation of various types of organic pollutants [10-13]. However, nanoparticle has drawback that is difficult to recover so that the additional separation process is required to prevent new pollution namely TiO_2 in the treated water [14-16]. That makes the application in the industry is still difficult to conduct. Other alternatives such as photocatalyst modification to be immobilized or TiO_2 in the form of free standing can be a solution to the problem [17].

MATERIALS AND METHODS

Titanium foil (99%) dimension 20 mm x 20 mm x 0.25mm were used as substrate (BTMM Co. Ltd.). For cleaning purposes, the foil was treated in ultrasonic bath for 10 min and washed with DI water. The synthesis of FSTNS were conducted in the Teflon hydrothermal autoclave (volume 50 mL) with first the addition of acetone (Merck) (5%v/v) 30 mL as oxygen source followed by the immersion of prepared titanium foil. The Teflon hydrothermal autoclave were then heated inside the oven for 18-68 hours with temperatures varied from 150-180°C. After hydrothermal process, the sample were cleaned with DI water and dried in oven at 110°C for 2 h.

Characterization of crystal structure of the sample were conducted using XRD. Meanwhile, SEM EDX (JEOL JSM-6510LA) were used to observe the sample morphology and chemical component.

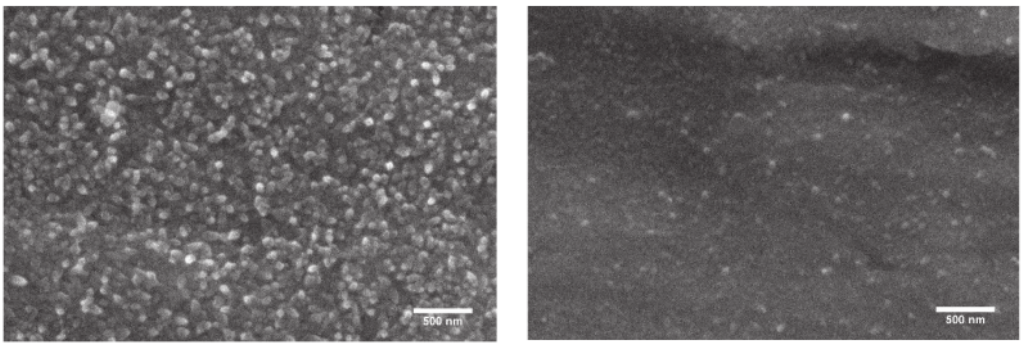
For photocatalytic activity, the sample were immersed in 50mL (5ppm) of Bromothymol Blue solution for 4 hours and irradiated with black light 20W. The concentration of bromothymol blue before and after were determined by the adsorption value at 602 nm evaluated by UV Vis Spectrophotometer.

RESULTS AND DISCUSSIONS

Comparative color of nanostructures growth on titanium foils at 180°C with different time is shown in Figure 1. The color of the samples was changed from metallic to dark gray (18 hours) and dark brown (24-68 hours). The uniform color change in all titanium foil surface at different hydrothermal processing time can be the noted as a sign of the formation of new layer on titanium surface due to some reaction that occurred during the process and the existence of different morphology with an absence of well-ordered nanostructures [18].

The most noticeable color change occurred at the surface of FSTNS synthesized at 180°C with the processing time of 18 and 68 hours. Deeper observations were made by taking surface images of FSTNS with SEM. The result of SEM analysis can be seen in Figure 2. It is obviously seen that FSTNS produced at 18 hours formed a nanorods morphology with the diameter 30-50 nm and the nanorods growth is almost evenly distributed throughout the surface of the titanium foil. During hydrothermal process at 180°C, the water solvent in the reactor evaporates and the vapor pressure inside theoretically around 9.9753 Bar. High pressure environment and the present of acetone as an oxygen source will force titanium to oxidized and form rods type of structure [19-21]. Prolonged the processing time to 68 hours is likely destructed the newly formed nanorods due to high pressure from various reactor angles [22], that is only a few nanorods were found on the surface of the titanium foil, as shown in Figure 2b.

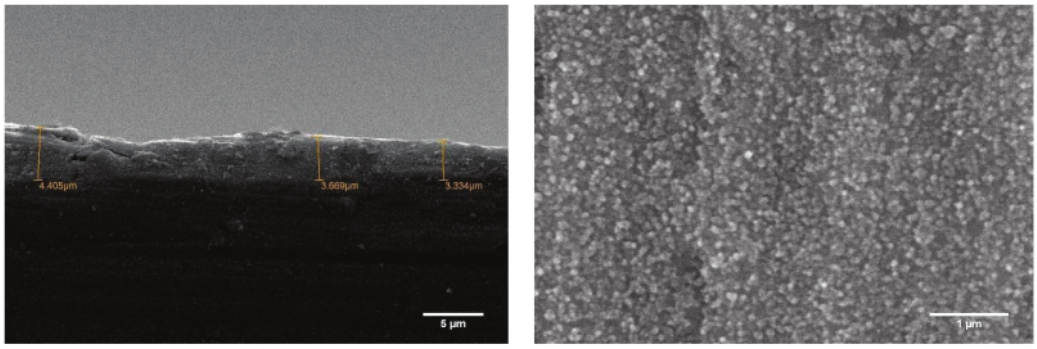
FIGURE 1. The photograph of FSTNS synthesized at temperature 180°C with different time



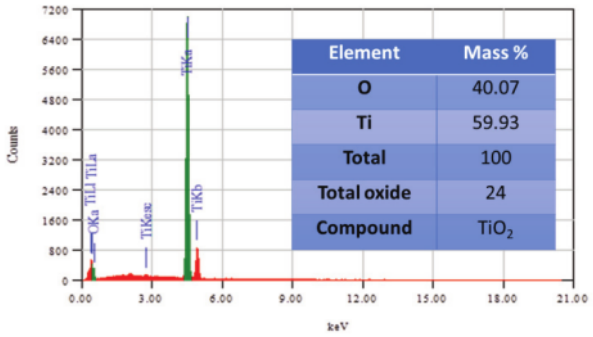
(a) (b)

FIGURE 2. SEM images of FSTNS synthesized at (a) 180°C 18 hours and (b) 180°C 68 hours

SEM analysis is also used to determine the thickness of the oxide layer. Figure 3a shows the thickness of the oxide layer of FSTNS sample synthesized at 180°C for 18 hours ranges from 3.3 to 4.4 microns. This vertical growth occurs due to oxidation of titanium during the hydrothermal process in the presence of carbonyl groups of acetone as a source of oxygen [23, 24]. Figure 3c shows the results of the SEM-EDX analysis on the surface of the FSTNS synthesized at 180°C 18 hours, which confirmed the presence of TiO_2 oxide components on the surface of the sample.



(a) (b)



(c)

FIGURE 3. SEM images of FSTNS synthesized at 180°C 18 hours (a) cross section (b) surface; and (c) EDX result

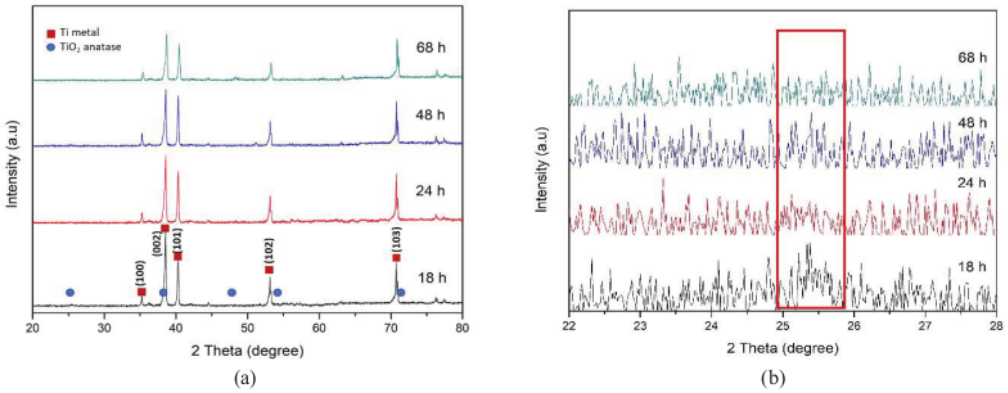


FIGURE 4. XRD Pattern (a) 20-80° (b) 22-28° of FSTNS synthesized at 180°C with different processing time

In order to find out the crystal structure, the sample then characterized by XRD analysis. As shown in Figure 4, the peak is dominated by titanium metal which was the substrate of the sample. However, if it is draws closer at the angle position of 2 theta 20-28° especially in the sample synthesized at a temperature of 180°C 18 hours, a peak at the angle of 25° is shown which is a sign of the presence of anatase phase TiO_2. The anatase phase has peaks of 25,367°, 37,053°, 37,909°, 38,667°, 48,158°, 54,051°, 55,204°, 62,867°, 68,976°, 70,479°, and 75,303° which define the crystal structure 101, 103, 004, 112, 200 , 105, 211, 204, 116, 220, 215, and 224 (Anatase XRD JCPDS Card no. 78-2486)[25]. These XRD results also support the results of SEM EDX analysis which shows the presence of a titanium oxide grows on the surface of the titanium substrate.

All the FSTNS sample synthesized at different time were used as catalyst for photocatalytic degradation of bromothymol blue as the representative of organic pollutant. Prior photocatalytic process, 5 ppm blue bromothymol solution was tested for its photolysis activity. The result shows that there is no change in color and in the concentration of bromothymol blue after photon radiation for 4 hours, meaning that the compound is stable under UV radiation. Meanwhile, photocatalysis test results shows a change in the color and concentration of the bromothymol blue solution before and after the photocatalysis process as depicted in Figure 5. The FSTNS synthesized at 180°C for 18 hours demonstrate higher photocatalytic activity compared to the other sample. The photocatalytic activity of a catalyst is mainly governed by TiO_2 crystallinity, active site and specific surface area [26]. Thus, FSTNS synthesized at 180°C for 18 hours is having higher TiO_2 crystallinity than the rest of the sample.

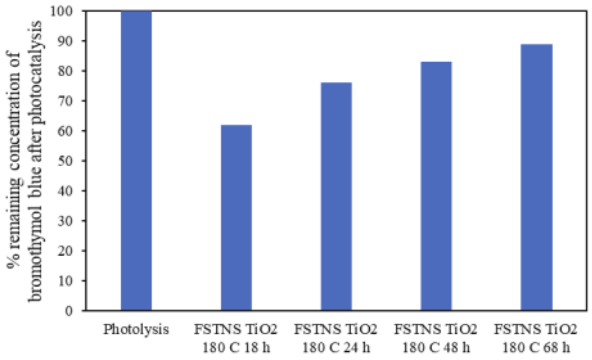


FIGURE 5. Photocatalytic activity of FSTNS synthesized at 180°C with different processing time

CONCLUSIONS

The hydrothermal process in the presence of acetone has been successfully applied for the formation of FSTNS. By conducting the hydrothermal process at 180°C for 18 hours, the nanorods type morphology grows on the surface of titanium foil to the vertical direction in the form of oxide layer in a favor of acetone as an oxygen source. The sample also successfully degrade almost 40% of bromothymol blue in the black light irradiation, confirming its effectiveness as photocatalyst.

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