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Investigation of the effect of Anodized Duration toward Photocatalytic Performance of Nb_2O_5

Ahmad Sabirin Zoolfakar[1], Nurul Atiqah Mokhtar[1], Rozina Abdul Rani[2], Nur Samihah Khairir[1], Mahzaton Aqma Abu Talip[1], Mohamad Hafiz Mamat[1], Rosmalini Abdul Kadir[1], M. Rusop[2]

[1]Faculty of Electrical Engineering, University Teknologi Mara, 40450 Shah Alam, Selangor, Malaysia

[2]NANO-SciTech Centre, Institute of Science, Universiti Teknologi MARA, 40450, Shah Alam, Selangor, Malaysia

Email: ahmad074@salam.uitm.edu.my

Abstract. Highly oriented Nb_2O_5 nanoporous network produced *via* anodization for photocatalytic activity of methyl orange (MO) is presented. The anodization duration was varies from 0.5 to 2 hours and the photocatalytic performance is observed by degradation of MO solution. The Nb_2O_5 nanoparticles were added in MO solution and were exposed to the solar simulator for 3 hours. The morphology of Nb_2O_5 nanoporous and the photocatalytic performance are characterized in Field Emission Scanning Electron Microscopy (FESEM) and UV-Vis spectrophotometer, respectively. The result shows that different duration of anodized produce different sizes of nanoporous diameter that will significantly affect the photocatalytic performance. The 1.5 hours of anodized has the largest diameter size of nanoporous and exhibited the best photocatalytic performance

1. Introduction

Wastewater is one of the main issues in Malaysia due to the water contamination produced by the industries that produce leather, textiles, plastic and other dying industries [1]. Dyes have negative impact to many types of life for both esthetical and toxicological reasons [1]. Dyes used in industries for various field namely textile to color their products. These industries produced large amount of colored wastewater and will caused water pollution. It is estimated from 40,000 to 50,000 tons of dye are wasted to surface water every year [1].

Public awareness towards these type of pollution have caused the scientists to develop numerous treatment technologies for dyes cure such as adsorption, filtration, photocatalytic degradation and many more [2]. One of the treatment technologies that has obtained huge attention is photocatalytic because its speed, high efficiency and no side pollution [3, 4].

The photocatalytic using niobium pentoxide (Nb_2O_5) is considering as favourable material because of its chemical stability and environmental friendly [5]. It is an important semiconductor with a bandgap of ~3.1 eV and has been discovered to potentially serve in various applications such as photocatalysis, catalysis and sensors [6, 7]. In this research, the Nb_2O_5 nanoparticles were used instead of the thin film. The nanoparticles of Nb_2O_5 are obtained after anodized of Nb_2O_5 thin film. Anodized is a commonly used method in nano-fabrication because of its capability to produce highly porous and ordered oxide morphologies [8, 9]. Usually the anodized process includes two electrodes which are cathode (negative electrode) and anode (positive electrode) [10]. Both of the electrodes are both

immersed in the liquid electrolyte and when voltage or electrical current is turned on, the electrochemical reactions will take place on the surface of anode electrode [11].

There are many research have been published on investigating factors that affect photocatalytic performance but no research has been focus on the effect of anodized duration on photocatalytic of Nb2O5 nanoparticles performances. Therefore, it is necessary to investigate this parameter in order to treat the dye wastewater. The aim of this research is to investigate the effect of anodized duration toward photocatalytic performance of Nb_2O_5 nanoparticles. Variation of anodized duration caused change in size of Nb_2O_5 nanoporous that will affect the photocatalytic performance of Nb_2O_5 nanoparticles. Thus, the photocatalytic performance of the Nb_2O_5 nanoparticles is determined with degradation of methyl orange solution that is observed by the value of transmittance during photocatalytic activity.

2. Methodology

2.1. Fabrication of Nb_2O_5 nanoparticles

The niobium foil with a thickness of 0.25 mm was cut into smaller pieces 1.0 cm X 2.5 cm. The surface of each sample was cleaned ultrasonically with acetone, ethanol, distilled water and blow with nitrogen gas to avoid any contaminates. The electrolyte for anodized was prepared with 0.5g NH_4F powder, 50 ml ethyl glycol, and 4% from ethyl glycol of distilled water (2 ml). The electrolyte was stirred on the hot plate and kept the temperature of 50℃. Two electrodes of cathode (platinum) and anode (Nb_2O_5 thin film) was set up as shown in Figure 1. The anodized duration was varies to 0.5, 1.0, 1.5 and 2.0 hours. Thus, four samples of Nb_2O_5 thin films with different duration of anodized were obtained. The samples were annealed after the anodized with temperature 440℃ for 20 minutes with steady ramp up and ramp down of 2℃/min to improve crystallinity. After that, the Nb_2O_5 nanoparticles were prepared by using a cleaned razor blade to scrape the oxides nanostructures from the Nb foil substrates. The flow chart of the anodization of Nb_2O_5 steps have been summarize in Figure 2.

2.2. Photocatalytic Process

0.01 g Methyl orange powder was stirred in 100ml of distilled water until dissolved. The 5 milligrams mass Nb_2O_5 nanoparticles was added and stirred. Then the solution was put in a dark solar simulator for 1 hour to ensure that the solution reached equilibrium state. Then, the solar light in solar simulator turned on. The process take placed for 3 hours, but every half hour, the solution was taken out for UV-Vis to observe the change of its decolorization. All of the steps for photocatalytic activity have been summarize in the Figure 3.

2.3. Photocatalytic characterization

In every 30 minutes of the photocatalytic activity in the solar simulator, the solution was removed and observed using UV-Vis equipment. The original solution before photocatalytic process was put first to set as the baseline. The aim of this characterization is to see the reaction of Nb_2O_5 nanoparticles with the methyl orange solution. The transmission data was observed.

3. Result and Discussion.

3.1. Effect of duration of anodized to the Nb_2O_5 nanoporous size.

The anodized Nb_2O_5 layer is formed by transferring a direct current through electrolytic solution. At the cathode which is the negative electrode, hydrogen is formed. Together with hydrogen and oxygen that formed at the Nb anode, a build-up Nb_2O_5 is created. The electrolyte used in anodized process contains fluorine ions and the chemical dissolution of fluorine ions happened during anodized process [12]. When 10 V of power supply connects, the reaction of chemical dissolutions takes place in Nb_2O_5 thin film that acts as an anode. Thus the nanoporous produced in the Nb_2O_5 thin films.

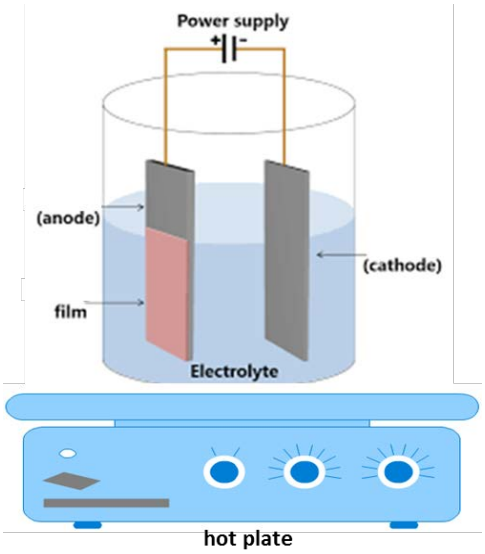

Figure 1. Illustration of anodization set up.

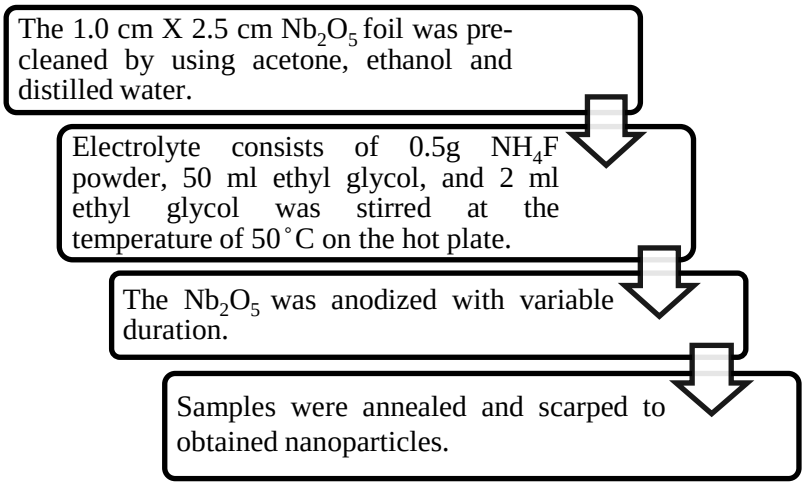

Figure 2. Flow chart of Nb_2O_5 anodization process.

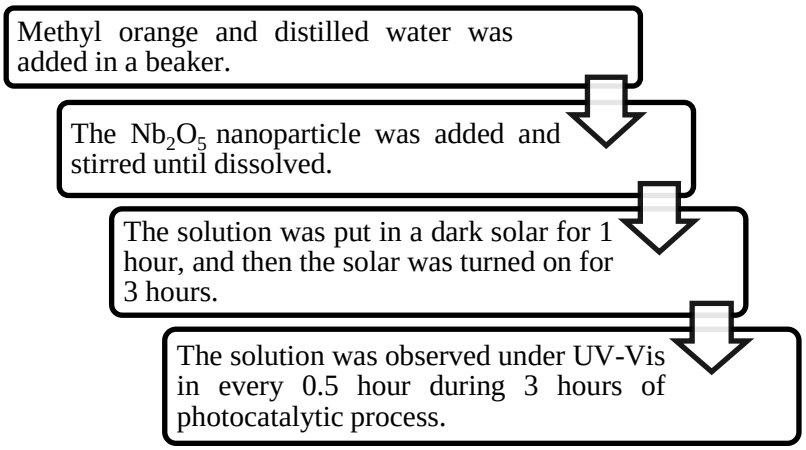

Figure 3. Flow chart of photocatalytic process

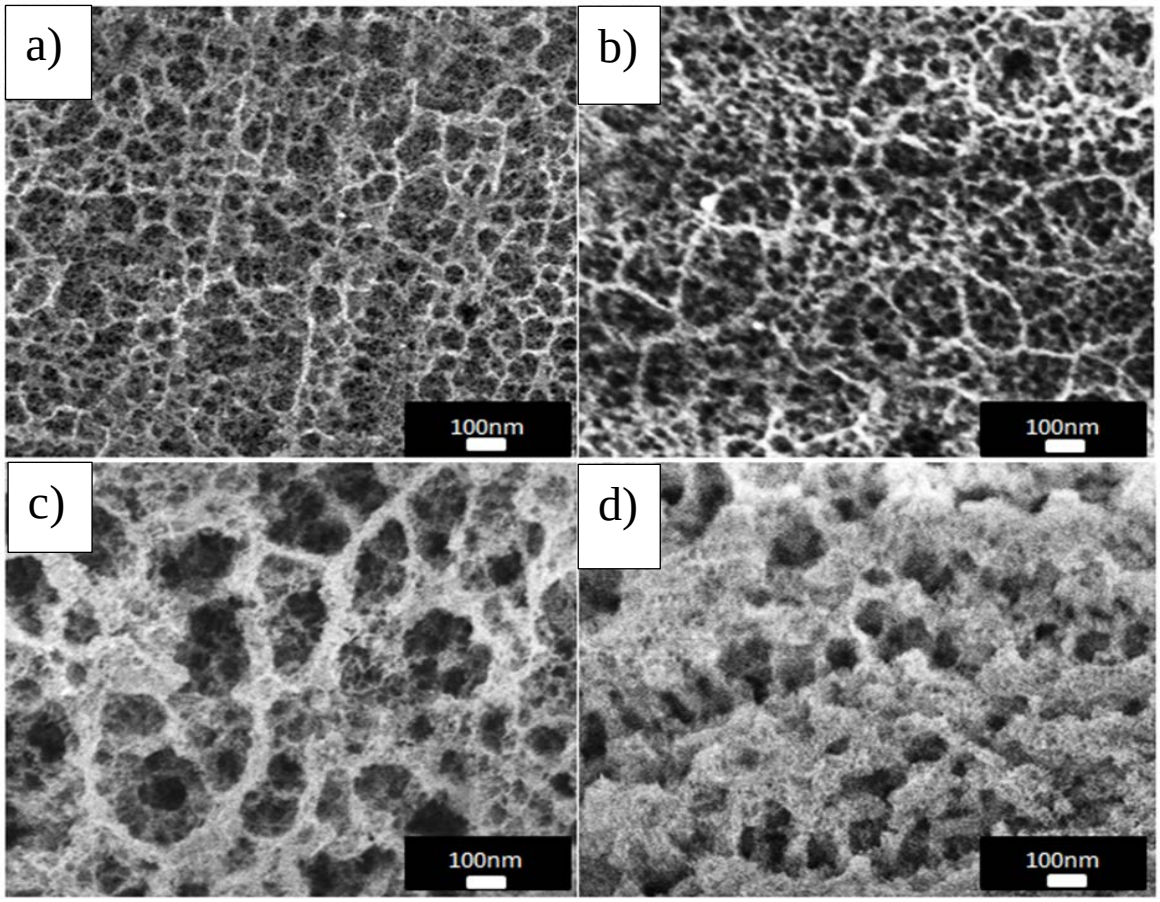

Figure 4. FESEM images of Nb_2O_5 nanoporous prepared in different time of anodized, (a) top view of anodized Nb_2O_5 at 0.5h, (b) Nb_2O_5 at 1.0h, (c) Nb_2O_5 at 1.5h, (d) Nb_2O_5 at 2h.

Figure 4 shows the FESEM images that show the surface morphology of the anodized Nb_2O_5 nanoparticles. The top view shows the structure of the Nb_2O_5 nanoparticles. As shown in the figure, a highly uniform pore distribution can be seen with nanosized pores. The sizes of nanoporous are depending on duration of anodized. The longer duration caused more chemical dissolution on the thin film and size of the nanoporous will increase until it reaches the optimum period of anodization. The size of nanoparticles for anodized in 1.5 hours is the largest compared to 0.5, 1.0 and 2.0 hour anodized. 1.5 hour of anodized is the optimum duration where the size of nanoporous is the largest and highly oriented nanoporous. However, the sample when undergo 2 hours anodized shows that the film is partially ruptured. When the anodized duration exceed more than 1.5 hours, the chemical dissolution of fluoride ions in the electrolyte still keep going and it will become excessive as the time increase. Fluoride ions have a crucial part on the surface morphology of the porous. It has been reported by *Gong et al.* that the fluoride ion concentration changes the formation and morphology of titania samples after undergo anodization process [12].

The concept can also be applied to niobium which is the dissolution of fluorine ions affect the formation of morphology. The oxide layer will fail to form uniformed pores if the quantity of fluorine ions in the electrolyte is insufficient [12]. In this case, the quantity of fluorine ions have become excessive .This situation has caused the thin film's surface become partially ruptured and the size of nanoporous no longer increase. The anodized duration after 1.5 hours does not effective anymore. It can be observed that the 1.5 hours duration of anodization is the optimum condition to obtain the largest size of nanoporous.

3.2. Effect of Nb_2O_5 nanoparticles' size to the photocatalytic performance.

There are so many factors that can affect the photocatalytic performance and one of the factors is the absorption surface area of material [13]. Absorption surface areas which are the nanoporous play important role in photocatalytic because the absorption and diffusion of molecules occur at the nanoporous [13]. The larger sizes of nanoporous increase the efficiency of absorption and diffusion of molecules of dye which is the methyl orange solution so that a better photocatalytic performance can be achieved. The photocatalytic process is done in a solar simulator by exposing the solution with solar light with the range of 400 to 800 nm wavelength. Before the solar light turn on, the solution must keep in the dark to ensure the absorption-desorption equilibrium. The photocatalytic performance in this research is shown by measuring their transmittance. Transmittance is a measurement quantity of light absorb by a substance [13]. If a sample has 100% transmittance means there are no light absorption occurs. The increase of light absorption will cause the decrease in transmittance.

Figures 5, 6, and 7 are representing the transmittance of sunlight over wavelength for different periods of photocatalytic activity for the sample that undergoes anodization period for 0.5 hour, 1.5 hour and 2 hours respectively. In every 30 minutes of photocatalytic activity, the methyl orange solution is characterized by using UV-Vis spectra to observe the change of transmittance.

Figure 8 shows the comparison of magnitude transmittance percentage for different duration anodized of Nb_2O_5 nanoparticles. This figure shows that the photocatalytic performance increases from 0.5 and 1.0 hour of anodized. The larger size of nanoparticles means the larger absorption surface area toward methyl orange ion [14]. The larger absorption of surface area can absorb more negative charge (MO^-) comparing to the small surface area in the same time interval. The larger sizes of nanoporous increase the efficiency of absorption and diffusion of molecules of methyl orange and give the better photocatalytic performance. In contrast, the performances for Nb_2O_5 that undergo anodized for 2 hours become the worst. This happen because the structure of Nb_2O_5 nanoparticles is ruptured. So the reaction between Nb_2O_5 powders with methyl orange already disturbed and cannot absorb many negative charge of methyl orange. These results has been supported with the surface morphology of these Nb_2O_5 nanoparticles which is 2 hours anodized sample has the worst morphology compared to others. Thus it can be said that, the nanoporous sizes really affect the photocatalytic performance. The best size of nanoporous which is the largest, give the best performance of photocatalytic as it has the largest absorption surface area to absorb more negative charge (MO^-) during photocatalytic activity.

Based on the figures 5, 6, and 7, one should observe that the degradation of methyl orange increase as the time increase. The degradation of methyl orange can occurs because surface charges of Nb_2O_5

absorb the negative charge (MO^-) during photocatalytic activity. As the duration of photocatalytic increase, more negative charge (MO^-) can be absorbed by Nb_2O_5 nanoparticles. As a result the photocatalytic performances improve. The negative charges (MO^-) can be absorbed because of the excited electron that gain energy from solar light and the excited electron be absorbed into the nanoporous of Nb_2O_5. The longer duration of photocatalytic process that exposed the methyl orange solution to the solar light gives more energy to the electron and caused surface charges of Nb_2O_5 absorb more negative charge (MO^-). The transmittances become lower shows the increase quantities of light absorb by the methyl orange when duration of photocatalytic become longer that will result in better photocatalytic performance as said above.

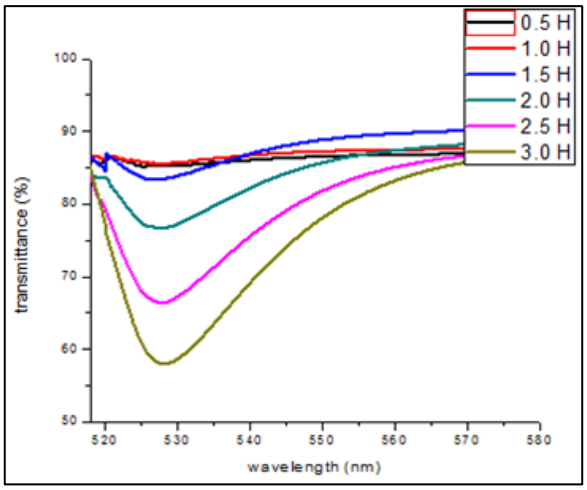

Figure 5. Transmittance of methyl orange for 0.5 H anodized of Nb_2O_5 nanoparticles.

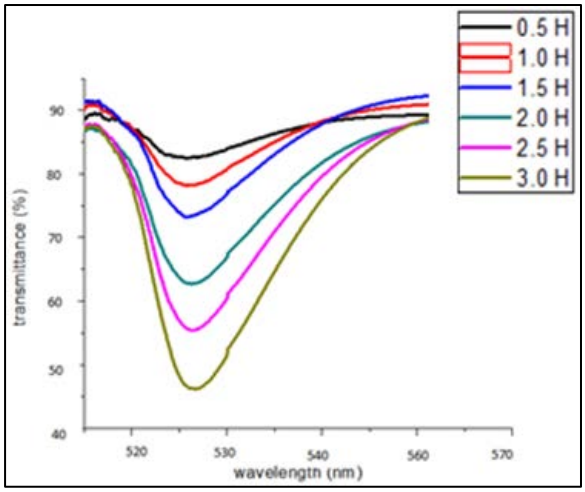

Figure 6. Transmittance of methyl orange for 1.5 H anodized of Nb_2O_5 nanoparticles.

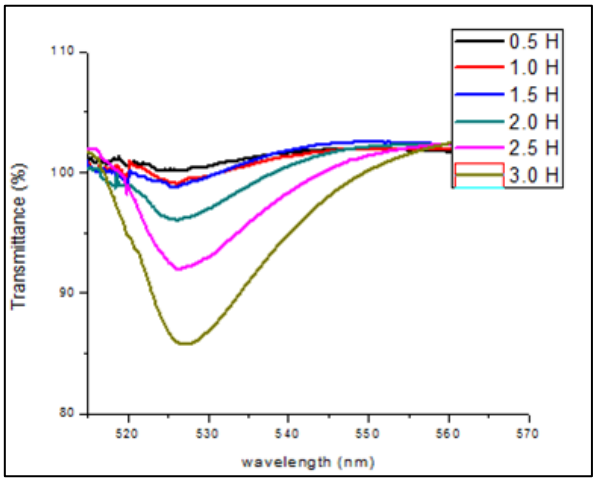

Figure 7. Transmittance of methyl orange for 2.0 H anodized of Nb_2O_5 nanoparticles.

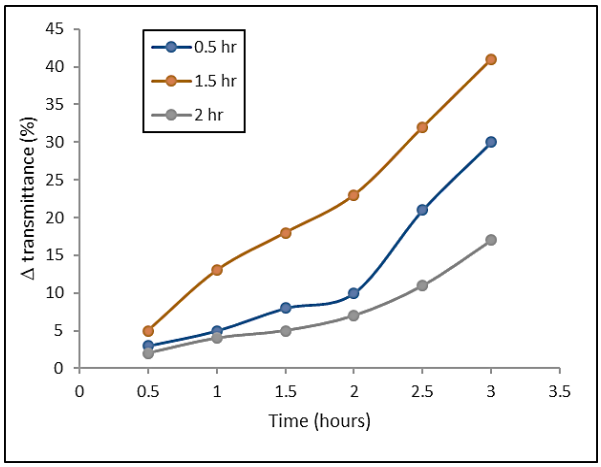

Figure 8. Comparison magnitude transmittance of methyl orange for difference duration of anodized for of Nb_2O_5 nanoparticles.

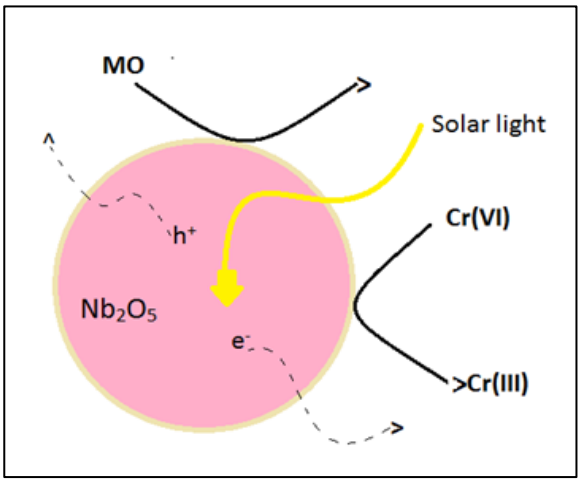

Figure 9. Schematic diagram of charge transfer of photogenerated electrons and holes

3.3. Photocatalytic mechanism.

The photocatalytic activity takes place in solar simulator under solar light. The processes that involve in this activity are reduction and oxidation. In this reaction, the photons have higher or equal energy than the bandgap energy ($hv \geq Eg$).

The mechanism of photocatalytic is shown in Figure 9. The methyl orange solution or dye absorbs the solar light and become excited [15]. As shown in figure 9, the excited dye changes to suitable state whether singlet (^{1}Dye*) or triplet (^{3}Dye*) and releases electron [16]. Afterward, the electron is infused onto the conduction band of the semiconductor particles [17]. At the same time, the dye is transformed to the cation dye radicals (Dye^{+}) that experiences degradation to yield products.

The photocatalyzed reaction is important but may not occur if the recombination of the elctron and hole happen during reaction. When activated electron with an oxidant agent give a product of a reduced product and the generated hole with the reductant agent give the product of an oxidized product, the photocatalyzed will occur

The reaction of photocatalytic can be expressed as shown below (Eqs. (1) – (4)) [18]:

$$\text{Dye} + \text{solar light} \rightarrow {}^1\text{Dye}^* + {}^3\text{Dye}^* \quad (1)$$

$${}^1\text{Dye}^* \text{ or } {}^3\text{Dye}^* + Nb_2O_5 \rightarrow \text{Dye}^{\bullet +} + Nb_2O_5({}^eCB^-) \quad (2)$$

$$Nb_2O_5({}^eCB^-) + O_2 \rightarrow O_2^{\bullet -} + Nb_2O_5 \quad (3)$$

$$\text{Dye}^{\bullet +} \rightarrow \text{degradation products} \quad (4)$$

There are significant impacts of nanoporous surface to area ratio toward photocatalytic performance. As discuss above, the nanoporous size represent the absorption surface area. The larger the surface area, the increase negative charge (MO^-) can be absorbed by Nb_2O_5 nanoparticles compare to small surface area of nanoporous. Thus, the degradation of methyl orange solution becomes increase because of this rapid absorption process.

4. Conclusion

The effects of anodized duration toward photocatalytic performance of Nb_2O_5 nanoparticles have been successfully investigated. When the anodized time increase up to 1.5 hours, the size Nb_2O_5 nanoporous also increase. The increase of anodized process caused the performance of photocatalytic increase too. The performance of photocatalytic shown by the transmittance graphs that decrease in value as the anodized duration increase. When the anodized time exceed than 1.5 hours, the anodized process does not affective anymore as the size of Nb_2O_5 nanoparticles become decrease. The performances of photocatalytic also decrease as the transmittance increase. Overall, the increases of anodized duration up to 1.5 hours cause the performance of photocatalytic also increase..

5. Acknowledgement

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