Abstract: In this study titanium dioxide nanotube (TNT) were prepared by anodization method. Photocatalytic activity of the TNT films was evaluated in terms of the degradation of methylene blue in aqueous solution under UV light irradiation. The effects of the temperature, time and voltage on the anodization process were investigated in detail. The results showed that the optimization of temperature, time and voltage on anodization process were 45°C, 240 min and 30 V, respectively. Consequently, these results indicate that the optimization of anodization process is critical to achieve the high performance of photocatalytic reaction.

Key Words: Titanium dioxide nanotube/ Anodization/ Photocatalytic activity

1. INTRODUCTION

Titania (TiO₂) is well known as a semiconductor with photocatalytic activities and has great potential in many areas, including environmental purification, gas sensors, photovoltaics, immobilization of biomolecules, and generation of hydrogen gas [1]. To date, TiO₂ nanotubes have been synthesized by various methods, including the sol–gel method, hydrothermal method, template synthesis and electrochemical anodization. Among these methods, direct electrochemical anodization of titanium is considered to be the most ideal method to fabricate highly oriented TiO₂ nanotube arrays because the process is very simple and the morphology can be easily controlled by the anodization conditions [2]. The various anodization variables such as electrolyte concentration, pH and voltage have been studied for the formation of TiO₂ nanotube arrays by many researchers [3-5], resulting in uniform TiO₂ nanotube arrays with various pore sizes and lengths.

Photocatalytic degradation of organic compounds has also generated great interest for its potential to eliminate the hazardous chemical substances in water. A number of studies have demonstrated that the complete mineralization, i.e., oxidation to CO₂ and OH, of a variety of chlorinated aromatics occurred via heterogeneous photo-oxidation over titanium dioxide (TiO₂). For the degradation mechanisms of TiO₂ photocatalysis, a number of studies have indicated that OH was formed on TiO₂ during the photochemical reactions [6]. The objective of this study was to examine the effect of temperature, time and voltage on photocatalytic activity of TiO₂ nanotube prepared by anodization method.

2. EXPERIMENTAL

In this work, titanium foils (250 μm thick, 99.7% purity, Sigma-Aldrich) were used as Substrate to grow TNT. Before anodization Ti foil was degreased by ultrasonication with acetone and ethanol, rinsed with de-ionized water and then dried in air. The anodization was performed in a two-electrode configuration with titanium foil as the working electrode and platinum foil as the counter electrode under constant voltage. Ethylene glycol electrolyte with the addition of NH₄F (0.3 wt.%) and de-ionized water (2 vol.%) was used. The experiments were varied temperature at 25, 30, 35, 40 and 45°C, times at 30, 60, 120, 180 and 240 min and voltage at 20 and 30 V. After that, an anodized TiO₂ nanotube array was washed by ultrasonication with de-ionized water and dried in air. After that the anodized samples were annealed at 450 °C for 3 h in air at a heating rate of 4 °C min⁻¹.

The annealed samples were used for the photocatalytic activity decomposition of methylene blue (MB) solution with a concentration of 1x10⁻⁵ M 10 mL under the illumination of the five 10-W 365 nm UV lamps. The concentration of methylene blue was determined by an UV-vis spectrophotometer (Thermo
3. RESULTS AND DISCUSSION

Figure 1a, 1b and 1c show the current density versus time behavior during anodization, for the ethylene glycol electrolyte with 0.3 wt.% NH₄F and 2 vol.% de-ionized water. From these figures, they are apparent that all curves exhibit a similar behavior with the time. In the early stages of the anodization process, a thin oxide layer is formed on the surface of the titanium sheet.

This compact oxide layer on the titanium surface leads to a rapid reduction in the current density due to its poor electrical conductivity. The current density then reaches a quasi-steady state due to the chemical dissolution of the oxide layer forming soluble fluoride.

As a result fine pits or pores are formed at the surface. Under sufficient applied voltage magnitude, field-assisted oxidation occurs at the TiO₂/Ti interface, where the oxygen ions (O²⁻) are transported from the solution to the oxide layer. At the same time, titanium ions (Ti⁴⁺) are transported from the titanium to the oxide/solution interface and dissolve into the solution, leading to a continuous increase in the depth of the porous structure and thus the formation of ordered nanotubes oriented vertically to the substrate[7].

3.1 Effect of anodization temperature on photocatalytic activity of TiO₂ nanotube

The photocatalytic activity of TiO₂ nanotube were evaluated by photocatalytic decolorization of MB aqueous solution under UV light for 4h. Figure 2 shows the relative concentration of MB aqueous solution under photocatalytic activity of TNT prepared by anodization method at 25-45°C, 30 min, 20 V and followed by anneal at 450 °C for 3 h in air at a heating rate of 4 °C min⁻¹. The highest photocatalytic decolorization of MB aqueous solution were found from the anodization temperature of TiO₂ nanotube at 45°C. From this result indicated that TiO₂ nanotube synthesis was affected by the electrolyte temperature. It may be due to fluorine ion mobility in the viscous electrolyte (ethylene glycol) was increased when increased the anodization temperature.

3.2 Effect of anodization time on photocatalytic activity of TiO₂ nanotube

The effects of time on anodization method were investigated. Figure 3 shows the relative concentration of MB aqueous solution under photocatalytic activity of TNT prepared by anodization method at 45°C, 60-240 min, 20 V and followed by aneal at 450 °C for 3 h in air
at a heating rate of 4 °C min⁻¹. The highest and lowest photocatalytic decolorization of MB aqueous solution were found from the anodization time of TiO₂ nanotube at 240 and 60 min, respectively. The SEM images of

3.3 Effect of anodization voltage on photocatalytic activity of TiO₂ nanotube

The effects of voltage on anodization method were studied also. Figure 5 shows the relative concentration of MB aqueous solution under photocatalytic activity of TNT prepared by anodization method at 45°C, 240 min, 20 and 30 V and followed by anneal at 450 °C for 3 h in air at a heating rate of 4 °C min⁻¹. The highest photocatalytic decolorization of MB aqueous solution were found from the anodization voltage of TiO₂ nanotube at 30 V. The largely enhanced electrical field induced etching of TiO₂ at elevated anodization potential, although the electrochemical oxidation speed was also increased at higher anodization potential.

4. CONCLUSION

The TiO₂ nanotubes were succesfully prepared by anodization method. The optimization of process parameter of temperature, time and voltage on anodization process were 45°C, 240 min and 30 V, respectively.

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6. REFERENCES


