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Preparation of TiO_2-PEG Thin Film on Hydrophilicity Performance and Photocurrent Response

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TiO_2 photocatalytic process has been developed and used in various applications. One of the use of TiO_2 is related to the hydrophilic properties, which is shown with a small contact angle between the surface of object and liquid (<10°). In this study, TiO_2 was coated on a glass surface with the dip coating method. TiO_2 catalyst was prepared by titanium tetraisopropoxide (TTIP) as precursor and polyethylene glycol (PEG) as template calcined at a temperature of 450°C. The addition of PEG was varied to obtain optimal conditions. Measurement of Diffuse Reflectance Spectroscopy UV-Vis (DRS UV-Vis) showed a decrease in the value of the band gap for TiO_2, TiO_2-PEG 200, TiO_2-PEG 400 and TiO_2-PEG 1000 were 3.153 eV; 3.056 eV; 3.012 eV and 2.975 eV, respectively. Results of contact angle measurements have been achieved hydrophilic properties. While, the photocurrent response of the three TiO_2 working electrodes added the PEG 200, PEG 400, PEG 1000 were 2.3×10^{-3} A, 2.2×10^{-3} A and 4.2×10^{-3} A, respectively. Therefore, PEG could improve the performance of TiO_2 catalysts.

Key words: TiO_2-PEG, Thin film, Hydrophilic, Photoelectrocatalytic.

TiO_2 is a transition metal oxide which is chemically inert and stable. TiO_2 has three kinds of crystal structures, namely anatase, rutile and brookite[1]. Anatase type of TiO_2 is more photoactive than rutile because the surface area of anatase is greater than the rutile. So that the active site per unit of anatase is greater than rutile. Brookite structure is the most unstable and most difficult to prepare so it is rarely used in the process of photocatalyst[2].

The preparation of semiconductor thin film is one way to ease the semiconductor applications as a solar cell and photocatalyst in the degradation of harmful chemical compounds[3,4]. Photocatalyst technology is a combination of integrated photochemical and catalytic processes to be able to carry out a chemical transformation reactions. The transformation reaction takes place on the surface of a semiconductor catalyst materials induced by light[5].

Development in the preparation of TiO_2 semiconductor electrochemically is a newer method by combining the photocatalyst with an electrochemical process, known as photoelectrocatalysis[6-8]. Nurdin and Maulidiyah reported in developing photoelectrochemical cell systems, the most important part is the preparation of the nano-sized TiO_2 film[9]. Zhang et al. also reported the synthesis of mesoporous TiO_2 using

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tetrabutyl titanate as precursor as well as polyethylene glycol (PEG) as template[10]. The synthesis result of mesoporous TiO_2 reported is having great surface area and photoelectrocatalytic activities. Many other studies have been conducted with various types of dopants, but dopant with PEG is more interesting than the other dopants, because PEG can improve the performance of the catalyst, and is able to increase the porosity, reduce the size of crystals and reduce the possibility of film cracking during the calcination process[11].

The photocatalytic process when the semiconductor absorbs light energy equal to or greater than the energy of its band gap, there will be a charge separation or photoexcitation in semiconductors. Electrons (e^-) will be excited into the conduction band leaving positive hole (h^+) in the valence band. The positive hole has a high affinity for oxygen in H_2O molecules and form Hydroxyl radicals (•OH). The •OH is a highly reactive species that attacks organic molecules and can degrade into CO_2 and H_2O and halide ions if organic molecules containing halogen[7,12]. Therefore, the positive holes and electrons on the activated titanium can then be used for various applications. One of the application is for self-cleaning materials in a wide range using TiO_2 [9].

The important parameters from the self-cleaning material is the influence of the surface structure, as reported by Xiong et al. that the descend of water contact angle on the surface structure of TiO_2 is caused by the formation of electron-hole, where the hole reacts with oxygen to form the surface of the empty oxygen and the electrons react with metal ions (Ti^{4+}) to form ions (Ti^{3+}) electron traps surface[13]. TiO_2 affects the structure of a surface contact angle and photoelectrocatalytic activity. Several templates of TiO_2 are friendly used for immobilization of TiO_2, PEG that is often used to form pores for the synthesis of porous TiO_2 films formed by hydrothermal method[14,15].

This research developed a preparation method of the TiO_2 catalyst by adding PEG dopant immobilized on Ti plate. Thus, it is expected to improve the performance of the catalyst, and is able to increase the porosity, reduce the size of the crystals and reduce the possibility of film cracking during the calcination process.

METHODS

Synthesis of TiO_2 Sol

TiO_2 sol was prepared by mixing 35 mL of ethanol, 2.4 mL of diethanolamine (DEA), and 7.5 mL of titanium tetra isopropoxide (TTIP). The mixture was stirred at room temperature for 1.5 hours. The mixture was added ethanol: water (4.5 mL: 0.5 mL) and 0.5 mL of PEG 200 and stirred for 1.5 hours. With the same treatment and added 1 mL of PEG 400 and 2 mL of PEG 1000 and stirred for 1.5 hours.

Preparation of TiO_2 Film

TiO_2 sol was used to coat on a preparations of glass substrate with a dip-coating method, then calcined at 450°C for 2 hours.

Contact Angle Measurement

The contact angle of measured glass slide was placed at the back of the plate in a horizontal position. Then water was dripped using a syringe on the preparations surface. Further, the droplet images taken with a digital camera that light and magnification had been set up to obtain images of water droplets in focus. Furthermore, the image obtained was input into a computer to measure its contact angle with software protactor (MB-ruler). Then the contact angle was recorded as the surface contact angle before irradiated by UV. Finally, preparations were irradiated by 18 watt of UV for 1 to 4 hours in a UV reactor. After 1 hour irradiation, this process were repeated. Changes in the contact angle on the surface were compared with every hour irradiation.

Photocurrent Response

Voltammogram was measured with Linear Sweep Voltammetry (LSV) using 0.1 M $NaNO_3$ solution, where 0.85 g of $NaNO_3$ was dissolved in 100 mL flask. LSV testing was conducted on the potential -1 to 1 volt, with a scan rate of $1x10^{-4}$ V/s, in which each of TiO_2 without PEG, TiO_2-PEG 200, TiO_2-PEG 400 and TiO_2-PEG 1000 were tested by illuminating the UV-LED light. The LSV results were used to observe the photoelectrocatalytic activity during the testing process[16].

RESULTS AND DISCUSSION

Determination of Band Gap Energy

Measurement with DRS UV-Vis aimed to determine the character of absorption in the

wavelength range both for UV and Visible (200-600 nm). In Fig. 1, it can be observed that for TiO_2 with additional variations of PEG concentration, it has different reflectance spectrum profile. The reflectance spectrum profile clearly showed that the TiO_2-PEG has an area of absorption in the visible light ($\lambda > 400$nm).

Table 1. Values of Band Gap

Sample	Band Gap (eV)
TiO_2 Degussa	3.4813
TiO_2 Standard	3.1536
TiO_2-PEG 200	3.0565
TiO_2-PEG 400	3.0128
TiO_2-PEG 1000	2.9758

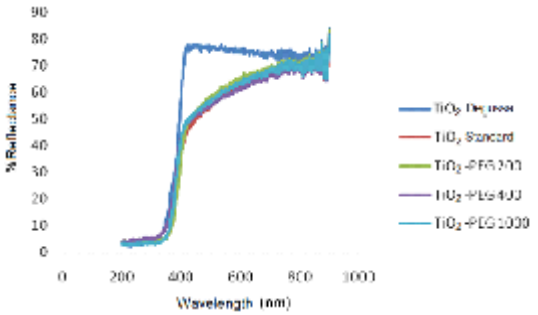

Fig. 1. The spectrum of DRS UV-Vis

TiO_2-PEG has band gap energy values smaller than TiO_2 degussa and TiO_2 standard. With the decrease in the band gap values, the light energy needed by photohole and photoelectron was smaller, simply by using a visible light source[7,16]. Moreover, it can also be seen that the higher concentration of PEG, it proved to have a tendency of decreasing the band gap values although the decrease was not significant, as can be seen on the Tabel 1 that the optimum band gap value was obtained at TiO_2-PEG 1000.

Measurement of Contact Angle (Hydrophilic Test of TiO_2 -PEG Thin Film)

Hydrophilic test on TiO_2 catalyst films was measured by contact angle meter. The contact angle measurements were performed by varying the exposure time of 20 Watt UV (0 to 4 hours) and varying the thin film of TiO_2 which was added to the PEG. Fig. 2 shows the contact angle without a thin film of TiO_2 exhibits superhydrophobic wherein the contact angle is greater than 100°, so that the level of wetness is lower. Contact angle is relatively constant despite irradiated by UV light[17]. As for the contact angle measurements without PEG, PEG 200, PEG 400 and PEG 1000 were hydrophilic due to a decrease in the contact angle from 40° to 20°. These showed that the TiO_2 film irradiated by UV light could transform into hydrophilic properties. Similarly, the length of time variation of UV irradiation, the longer the exposure time, the intensity of UV rays on the surface of TiO_2 films was getting bigger, so that the wetting was greater and contact angle of water would decrease.

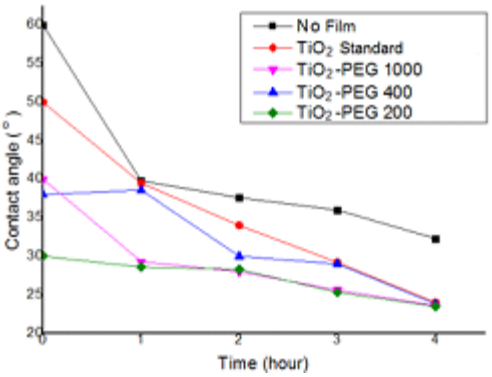

Fig. 2. Contact Angle Measurement

Measurement of Photocurrent Response

Fig. 3 showed the photocurrent increased linearly at low potential and then saturated at higher potential. Photocurrent generated would be increased by the increasing concentration of organic compounds, it showed the increasing rate of photohole capturing, i.e the reacting hole with organic compounds on the surface of TiO_2 film[18]. With the increasing rate of capturing photohole the charge recombination processes on the surface of TiO_2 was reduced and the photocurrent value would increase. According to Maulidiyah et al. there are two factors affect the value of the photocurrent on the photoelectrocatalytic process, namely the transfer of electrons in the semiconductor film and the capturing process of photohole on TiO_2 or solution interface, these two factors are important in reducing the recombination of electron-hole pairs[16,20]

The photocurrent was increased in Fig. 3, the increase of the potential bias given at lower

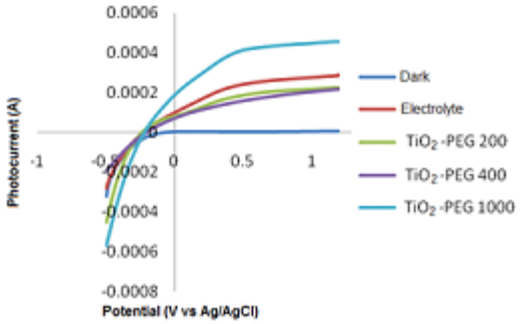

Fig. 3. LSV of TiO_2 + PEG electrode with illumination, an electrolyte solution of 0.1 M $NaNO_3$

potential range when the organic compounds contained in the solution and showed the photocurrent saturation at a higher potential bias. Photocurrent saturation at a higher potential indicates the maximum rate of photohole capturing on the surface of TiO_2. LSV response in Fig. 3 shows that the three TiO_2 working electrodes added to the PEG 200, PEG 400 and PEG 1000 were generated photocurrent. The PEG 200 generated 2.3×10^{-3} A, PEG 400 generated 2.2×10^{-3} A. While PEG 1000 generated photocurrent as high as 4.2×10^{-3}. These showed that the activity of TiO_2-PEG 1000 was better than the TiO_2-PEG 200 and TiO_2-PEG 400.

CONCLUSION

1. The results of hydrophilic tests on the TiO_2-PEG film had been reached the hydrophilic property.
2. The photocurrent measurements value from three TiO_2 working electrodes added the PEG 200, PEG 400 and PEG 1000 were 2.3×10^{-3} A, 2.2×10^{-3} A and 4.2×10^{-3} A, respectively.

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