Photoelectrochemical Performance of TiO$_2$/Ti Electrode for Organic Compounds

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Abstract. Photoelectrochemical performance of TiO$_2$/Ti electrode was investigated by using organic compounds. The TiO$_2$/Ti electrode was prepared by anodic oxidation at a potential bias of 25 V for 4 h then calcined for 450 °C to obtain the anatase polymorph. Subsequently, it was characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX). The XRD pattern showed that TiO$_2$ has anatase phase as confirmed by 2θ peaks at 37.93°, 63.00°, and 83.00°. Using SEM-EDX data the TiO$_2$ layer was formed on Ti plate with the composition of Ti (4.5 keV) and O (0.5 keV) elements. Furthermore, the photoelectrochemical sensing on the three organic compounds (ascorbic acid, glucose, and titan yellow) with the electrolyte addition showed that the linearity of TiO$_2$/Ti electrode were 0.937, 0.968, and 0.938, meanwhile without the electrolyte were 0.998, 0.989, and 0.923, respectively.

Keywords. Electrode, organic compounds, photoelectrochemical, and TiO$_2$/Ti.

1. Introduction

The organic compound is a class of compounds composed of carbon and hydrogen atoms and can contain other elements such as nitrogen, oxygen, phosphor, and sulfur. Organic compounds which often cause a variety of environmental pollution problems, especially disposal of organic wastes, are ascorbic acid, glucose, and titan yellow. One of the alternatives in the process of overcoming environmental pollution due to organic compounds in the process of organic compounds degradation or decomposition using titanium dioxide (TiO$_2$) photocatalyst [1, 2].

The last few decades, the utilization of TiO$_2$ has been widely developed among others as the process of the photocatalyst, sensing, photoelectrolysis, photovoltaic, solar cells, filtration and biomedicine [3, 4]. The utilization of the TiO$_2$ compound in the photocatalyst field is generally to degrade organic pollutant perfectly that produces carbon dioxide (CO$_2$) products in aquatic environment [5, 6]. Maulidyah et al (2016) reported the utilization of TiO$_2$ photoelectrocatalysis to
degrade the amino acid waste and Zhao et al (2004) reported the improved performance of TiO$_2$ photocatalyst with the ability to degrade various types of organic substances and surface capacity of TiO$_2$ in absorbing organic substances [7, 8].

Common methods used to produce TiO$_2$ materials include hydrothermal, sonochemistry, and coprecipitation methods. Another method is an electrochemical method known as anodizing method [9, 10]. This method can form a nanotube structure on thin layer of titanium metal [11]. Along with the development of photocatalyst utilization in degrading organic compounds, it still has deficiency such as relatively low efficiency because it can lead to electron-hole recombination [12, 13].

One of the alternatives that can prevent electron-hole recombination is the electric field formation in the electron-hole area [14, 15]. The electric field can occur in the presence of potential difference. This potential difference will be formed when there is electron current in an electrochemical cell that will occur by utilizing electrons formed from the degradation process of organic compounds [16, 17]. Therefore, to improve the performance of photocatalysis, the combination between the process of photocatalyst and electrochemical, which is called as photoelectrocatalysis process, is required [18]. It utilizes photoelectrocatalysis as the main factor in the manufacture of COD sensors. Sensitivity of the sensors to the water-soluble organic compound is the sensitivity effect of thin TiO$_2$ layer on the indium tin oxide (ITO) glass used as the working electrode.

Based on the above description, then an electrochemical sensitivity test was performed using TiO$_2$/Ti nanotube electrodes and photocurrent response test with ascorbic acid, glucose, and titan yellow photometry profile testing. The results of this study are expected to be applied to determine the electrochemical profile of various organic compounds electrochemically.

2. Materials and methods

2.1. Fabrication of TiO$_2$/Ti electrode

The fabrication of TiO$_2$/Ti electrode has been made by using Maulidiyah et al (2015) method. The Ti plate was cleaned and shined. Subsequently, it was inserted in the probe which was filled with the electrolyte solution in the form of 0.27 M NH$_4$F and distilled water with a 98 % glycerol. The electrolyte solution was produced by dissolving 0.99 g of NH$_4$F using 4 mL of distilled water and 96 mL of 98 % glycerol. Anodizing process was done by placing the Ti plate as anode and Cu plate as a cathode, using a magnetic stirrer. A potential bias of 25 V was applied by connecting to a power supply. This anodizing process was carried out for four hours. The final stage was the calcinations of Ti plate for 1.5 h at a temperature of 500 °C to obtain TiO$_2$ anatase crystal which has better activity than other types of TiO$_2$ crystals [5].

2.2. Degradation test of organic compounds

The measured photocurrent in this study was identified from the photoelectrochemical circuit using the bath system. This procedure was a simple system in which three electrodes i.e. working, reference and comparison electrodes. The electrodes were immersed in a beaker containing test solution in the form of organic compounds such as ascorbic acid, glucose, and titan yellow with the addition of NaNO$_3$ as an electrolyte. The photocurrent was measured using a potentiostat with a potential bias of 0.5 V and a measurement time of 60 s. At the beginning of the measurement, UV lamp was off and started up at 10 s. Measurement for 60 s was carried out by using UV radiation [3, 19].

Dye degradation test of organic compounds for (1, 3, 5, and 7) ppm was added by 0.1 M NaNO$_3$ then analyzed using the Multi-Pulse Amperometry (MPA) with a ten-minute duration and a potential bias of 0.5 V in a dark and UV irradiation.
3. Results and discussion

3.1. Characterization of TiO$_2$/Ti electrode

3.1.1. X-Ray Diffraction (XRD)
The crystallinity and phase of TiO$_2$/Ti were characterized using XRD. The ability of diffraction methods is used for the determination of crystalline structure, quantitative phase, qualitative analysis, phase transformation, crystal texture, and crystal size [20]. The crystallinity and phase of crystalline TiO$_2$/Ti are shown in the diffractogram in Figure 1. It is shown that there are peaks at 2θ of (37.93°, 63°, and 83°) which indicates the formation of crystalline TiO$_2$ with anatase phase. Based on the works of Han, et al. (2004) and Khanna et al (2007), anatase TiO$_2$ can be observed from the peaks at 2θ = (25.3°, 37.9°, 48.4°, 54°, 63°, 70°, 75°, and 83°) [21, 22].

![Figure 1. XRD pattern of TiO$_2$/Ti electrode](image)

3.1.2. Scanning electron microscope-energy dispersive x-ray (SEM-EDX)
Characterization using SEM-EDX aims to determine morphology, particle size, and material composition. The characterization results of SEM-EDX of TiO$_2$/Ti anodizing results can be observed in Figure 2. The morphology of TiO$_2$/Ti anodizing results indicates the presence of 10 μm particles (Figure 2.a), which are fairly evenly on all surfaces indicating the dispersed TiO$_2$ particles on the Ti plate surface. SEM-EDX also generates additional data in the form of X-ray energy graph. The peak position of an element in EDX depends on the energy of the element. The element will be detected at its typical energy point with intensity value on Y axis. Y-axis shows quantity values of elements in the whole sample which is later confirmed in wt%. Based on Figure 2.b the TiO$_2$/Ti anodizing results has the composition of O (oxygen) element of 22.34 wt% or 46.27 at% and Ti (titanium) element of 77.66 wt% or 53.73 at%.

![Figure 2. Analysis by using SEM-EDX; (a) morphology of TiO$_2$/Ti electrode (b) EDX spectrum of TiO$_2$/Ti electrode](image)
3.2. Photocurrent response against organic compounds

In this study, ascorbic acid is an organic compound with the molecule formula of C$_6$H$_8$O$_6$ as test compound caused it has three hydroxyl groups allowing readily adsorbed on electrode surface and can produce a high photocurrent response. This may occur as a result of negatively charged hydroxyl group on ascorbic acid will attract with positively charged TiO$_2$ surface in solution. The ascorbic acid photocurrent response can be seen in Figure 3.

![Figure 3. Photocurrent response of ascorbic acid, (A) non-electrolyte (B) addition of electrolyte](image)

The photocurrent responses of ascorbic acid as shown in Figure 3.a and Figure 3.b show the differences in photocurrent intensities. The current response generated by both non-electrolyte and electrolyte ascorbic acid show greater current responses than NaNO$_3$ blank solution response. This is due to ascorbic acid is more readily adsorbed on the surface of photocatalyst, but it can be seen that the curve of electrolyte ascorbic acid response does not coincide with the curve of NaNO$_3$ [10]. This indicates that ascorbic acid is not completely degraded by photocatalysts.

The differences in photocurrent intensity show differences in non-electrolyte and electrolyte glucose response, as shown in Figure 4. The current response produced by electrolyte glucose is greater than the current response produced by non-electrolyte glucose. This is due to the NaNO$_3$ electrolytes that serve as conductors of electrons.

![Figure 4. Photocurrent response of glucose, (a) non-electrolyte (b) addition of electrolyte](image)

The current difference occurs because electrolyte glucose is more readily adsorbed on the photocatalyst surface than non-electrolyte glucose. Thus, on electrolyte glucose current response curve with NaNO$_3$ blank solution curve shows no coincidence. This indicates that glucose is not decomposed or degraded completely by the photocatalyst.

The photocurrent responses of non-electrolytic and electrolyte titan yellow are shown in Figure 5.a and Figure 5.b. The photocurrent responses of electrolyte titan yellow seen as observed in Figure 5.a
shows higher current responses at each concentration variation than non-electrolyte titan yellow responses (Figure 5.a). This tendency occurs because the electrolyte NaNO₃ used in analyte plays an important role in the transfer of electrons in the solution resulting in more optimal current responses. The curve of photocurrent response in Figure 5.b indicates the degradation activity of the titan yellow at concentrations above 5 ppm does not occur perfectly. This is clearly seen on the curve of yellow titan in concentrations of 7 ppm and 10 ppm do not coincide with the NaNO₃ curve which is the blank in the measured test solution. The imperfect process of degradation is due to the saturation on the surface of the photocatalyst thereby inhibiting the degradation process.

**Figure 5.** Photocurrent response of titan yellow, (A) non-electrolyte  (B) addition of electrolyte

3.3. Compared linearity of electrolyte against non-electrolyte

In this study, linearity was obtained by plotting concentration (C) and photocurrent response (Iph) values generated by the test compounds. The linearity of some test compounds with electrolytes is related to the resulting current response in some concentrations. As observed on the graph of Figure 6, the linearity of titan yellow is 0.938 that higher than the ascorbic acid, indicating that the average increase in photocurrent for each titan yellow concentration is more stable than ascorbic acid.

The ascorbic acid curve shows increases in current responses in the concentration range of 0 ppm to 10 ppm. This indicates the higher concentration of ascorbic acid, the higher the resulting current response. It is also experienced by some other test compounds that show increases in current responses as the concentrations increase. Photocurrent responses of glucose and titan yellow also increase along with the increasing concentration but the resulting current response at each concentration variation is lower than on ascorbic acid. The linearity of glucose and titan yellow as shown in Figure 6 are 0.968 and 0.938, respectively.

**Figure 6.** Comparison of photocurrent response (a) using electrolyte, and (b) non-electrolyte
The correlation graph between current response produced and the variation concentration of several non-electrolyte test compounds is shown in Figure 6.a and Figure 6.b. The photocurrent response of ascorbic acid shows increase in each concentration variation with a linearity value of 0.998.

The current response produced by ascorbic acid at each concentration variation is lower than the current response produced by glucose. It shows that non-electrolyte glucose can decompose optimally than non-electrolytic ascorbic acid with a linearity value of 0.998. Unlike the curve of non-electrolyte titan yellow that shows lower photocurrent response value than glucose and ascorbic acid for each concentration variation. It also shows that titan yellow is more difficult to degrade than glucose and ascorbic acid. In addition, the linearity value of non-electrolyte titan yellow of 0.923 is also lower than in the linearity values of glucose and ascorbic acid.

4. Conclusions
Based on the results of this study, it can be concluded that the XRD pattern showed that TiO$_2$ in TiO$_2$/Ti electrode has anatase crystal phase as confirmed by 20 peaks at 37.93°, 63.00°, and 83.00°. From SEM-EDX data the TiO$_2$ layer was formed on Ti plate with the composition of Ti (4.5 keV) and O (0.5 keV) elements. The photoelectrochemical sensing on the three organic compounds (ascorbic acid, glucose, and titi yellow) shows that the photocurrent response is different. Glucose has the highest photocurrent response, followed by ascorbic acid, and then non-electrolyte ascorbic acid with a linearity value of 0.998. Unlike the curve of non-electrolyte electrolyte glucose can decompose optimally than non-electrolytic ascorbic acid with a linearity value of 0.998. Unlike the curve of non-electrolyte electrolyte glucose can decompose optimally than non-electrolytic ascorbic acid with a linearity value of 0.998. Unlike the curve of non-electrolyte electrolyte glucose can decompose optimally than non-electrolytic ascorbic acid with a linearity value of 0.998. Unlike the curve of non-electrolyte electrolyte glucose can decompose optimally than non-electrolytic ascorbic acid with a linearity value of 0.998. Unlike the curve of non-electrolyte electrolyte glucose can decompose optimally than non-electrolytic ascorbic acid with a linearity value of 0.998.

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