Synthesis of Nano-Ilmenite (FeTiO3) doped TiO2/Ti Electrode for Photoelectrocatalytic System

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Abstract. Ilmenite (FeTiO3) doped on Ti and TiO2/Ti electrodes were successfully prepared by using the sol-gel method. The structure, morphology, and optical properties of FeTiO3 are characterized by XRD, UV-Vis DRS, and SEM. The FeTiO3 and TiO2 greatly affect the photoelectrocatalysis performance characterized by Linear Sweep Voltammetry (LSV) and Cyclic Voltammetry (CV). The characterization result shows a band gap of FeTiO3 is 2.94 eV. XRD data showed that FeTiO3 formed at 20 were 35.1° (110), 49.9° (024), and 61.2° (214). The morphology of FeTiO3/Ti and FeTiO3/TiO2/Ti using SEM shows that the formation of FeTiO3 thin layer signifies the Liquid Phase Deposition method effectively in the coating process. Photoelectrochemical (PEC) test showed that FeTiO3/TiO2/Ti electrode was highly oxidation responsive under visible light compared to the FeTiO3/Ti electrodes i.e. 7.87×10−4 A and 9.87×10−5 A. Degradation test of FeTiO3/Ti and FeTiO3/TiO2/Ti electrodes on titan yellow showed that the percentages of degradation with photoelectrocatalysis at 0.5 mg/L were 41% and 43%, respectively.

1. Introduction
The management and disposal of wastewater needed attention for increasing the awareness and the main concern for public health in a modern era [1,2]. The wastewater treatment has categorized in physical, chemical, and biological processes to improve an excellent method of eliminating aspects in wastewater pollutants [3,4]. The handling efficiency and low-cost factors are one of ways to solve the wastewater pollutants [5,6]. Chemical processes are a way of dealing with environmental pollution using semiconductor materials such as TiO2, ZnO, Fe2O3, etc [7,8].

The pollution control requires the development of new infrastructure technology as a degradation instrument in overcoming the level of wastewater pollution in the environment. Therefore, it is needed a material to support the realization of the instrument design. In recent decades, environmentally friendly materials have been developed such as TiO2. It has various benefits such as environmental protection, water purification, sensors, and photovoltaic [9,10]. The utilization of TiO2 based on the photocatalyst process as categorized of a very strong oxidizing agent when exposed to ultra violet (UV) light with a wavelength of 365-385 nm [11,12]. UV light irradiation will experience separation of electrons in the conduction band and the valence band to form a hole (h+) [13,14]. In the valence band will produce a hydroxyl radical (•OH) an oxidizing agent to overcome the wastewater [15,16].

In the last decade, TiO2 photocatalyst study still has various constraints namely the recombination of electrons and holes which decrease the performance of TiO2 semiconductors [17,18]. Recent development performed by Nurdin et al. using the TiO2 semiconductor by merging photocatalysis and
electrochemical methods into photoelectrocatalysts that have the advantages for degrading of organic pollutants into harmless compounds such as H₂O and CO₂. It is more efficiently in the use of chemicals and energy consumption [19,20].

The current TiO₂ photoelectrocatalyst method becomes an advantage in the development of TiO₂ as a degradation agent of organic matter and Chemical Oxygen Demand (COD) sensors [15,21]. However, the disadvantage of TiO₂ is only active by using UV light irradiation because of the relatively large value of TiO₂ energy gap (Eg) of 3.2 eV for the anatase phase, whereas UV rays entering the Earth only about 3-5% and low yield efficiency (<10%). One of attempts to activate TiO₂ in visible light which have been performed in some researches is by adding dopants (both metals and nonmetals) [9]. Researchers have done by immobilizing metal elements in TiO₂, including gold (Au), iron (Fe), and silver (Ag) show the success of activating TiO₂ in visible light to enhance the photoelectrocatalytic performance [9,21].

Research for non-metallic immobilization, which have been carried out among others are Nitrogen (N), Carbon (C), Sulphur (S) have been shown to effectively shift TiO₂ optical absorption to lower energy levels [13]. The function of dopant addition is to modify TiO₂ crystals so it can change the electronic structure, optical properties, and high stability [10].

A recent study by Yu et al. has performed Fe-TiO₂ nanotube doping and its application in photocatalysis that the Fe doping is best used because the radius of Fe³⁺ (0.64Å) ion is almost the same as the radius of Ti⁴⁺ (0.68Å) ion. Fe³⁺ ions will more easily substitute Ti³⁺ ions in TiO₂ crystals [22]. Raghavender et al. reported that Fe³⁺ doping on TiO₂ with Fe(NO₃)₃ composition tends to form ilmenite, which can overcome environmental pollution by using visible light with band gap value of 2.58-2.9 eV [23]. The iron element (Fe) in ilmenite with structure of TiO₂ perovskite for upgrading the titanium lattice, then yield rutile-type TiO₂ that can be active in visible light with Eg <3.0 eV [22].

Based on the previous literature, in this research has fabricated Fe-doped TiO₂ working electrode with of Fe(NO₃)₃ as a Fe dopant to form ilmenite (FeTiO₃)/Ti with a sol-gel method to degrade Titan Yellow (TY) test compound. The focus of this research to assess the performance of FeTiO₃/Ti electrodes which would be compared with the FeTiO₃/Ti electrode to study the efficiency level in degrading TY compound presents in water. The TY organic compound has chosen because it is one of the harmful triazine dyes that irritate human skin when contained in water because of contains one or some relatively stable benzene rings [24].

2. Experimental Method

2.1. Fabrication of TiO₂/Ti by anodizing

The Ti (titanium) plate was performed by cutting Ti plate with 99% purity and 0.5 mm thickness with a size of 4 cm × 0.5 cm then sanded using fine sandpaper size of 1200CC until the surface was clean and shiny then washed by using a detergent solution, water, and distilled water (D.I. H₂O). After being air-dried, the Ti plate was etched using a mixture solution of HF, HNO₃, and D.I. H₂O with a ratio of 1: 3: 6 for 2 minutes.

The Ti plate was inserted into the probe which has contained electrolyte solution of 0.27 M NH₄F and D.I. H₂O in 98% glycerol. The anodizing process was performed by placing Ti plate as anode and Cu plate as a cathode and providing bias potential of 25 Volts connected to the power supply. Anodizing process performed for 4 hours and calcined for 1.5 hours at a temperature of 500°C to evaporate the remaining electrolyte solution on Ti plate and to obtain TiO₂ anatase crystals which have high-photodegradation activity.

2.2. Synthesis of FeTiO₃ by sol-gel method

The FeTiO₃ sol-gel was made with mixing two solutions in a reflux method. Solution 1 was prepared in colloidal solution of TiO₂ using controlled hydrolysis of 4 mL TTIP in 0.5 mL of acetyl acetone and 15 mL of 99% ethanol. Solution 2 was prepared by 15 mL of 99% ethanol and 2 mL of D.I. H₂O by adding 1 mL of 0.1 M acetic acid. Then two solutions was mixed and stirred using a magnetic stirrer for 3 h at 50°C and added Fe(NO₃)₃ to produce FeTiO₃ sol. The resulting solvent was evaporated at room
temperature for 48 hours to form a gel and heated to 80°C in the oven for 30 minutes. Ti and TiO\textsubscript{2}/Ti anodizing plates were immobilized with sol-gel by coating the FeTiO\textsubscript{3} sol-gel on the Ti and TiO\textsubscript{2} plate using Liquid Phase Deposition (LPD) method then sintered at 150°C for 15 minutes to obtain FeTiO\textsubscript{3}/Ti and FeTiO\textsubscript{3}.TiO\textsubscript{2}/Ti electrodes.

2.3. Photoelectrocatalytic degradation test
Determination of TY standard curve with a concentration of 0.5; 2.0; 4.0; and 5.0 ppm dissolved with 0.1 M NaNO\textsubscript{3} as an electrolyte solution. The wavelength was determined and absorbance value using UV-Vis spectrophotometer. TY dye degradation tests of 0.5 ppm (+ 0.1 M NaNO\textsubscript{3}) were performed using a Multi Pulse Amperometry (MPA) method with a duration of 10 min and a potential difference of 0.5 Volt under variations of UV and visible lights. For 10 minutes the absorbance was determined to obtain decrease of concentration. Measurements were variated against FeTiO\textsubscript{3}/Ti and FeTiO\textsubscript{3}.TiO\textsubscript{2}/Ti electrodes.

3. Results and Discussion
3.1. Fabrication of TiO\textsubscript{2}/Ti by anodizing
Preparation of TiO\textsubscript{2}/Ti nanotubes by electrochemical oxidation was performed by using copper (Cu) metal at cathode and Ti metal at the anode for 4 hours with a bias potential of 25.0 Volt. The function of high voltage in the fabricating TiO\textsubscript{2}/Ti thin film is to form nodules or particulates on Ti metal. The anodizing process will form nanomaterials with sizes between 1-100 nm [3]. The reaction process in anodizing methods containing F\textsuperscript{-} ions can be seen in Figure 1.

3.2. FeTiO\textsubscript{3} doped TiO\textsubscript{2}/Ti electrode
The sol-gel method is a method for synthesizing non-metallic or metal-doped TiO\textsubscript{2} nanoparticles. This method has many advantages in terms of purity, homogeneity, flexibility, easily controlled stoichiometry, easily processing and compositions which are controlled quickly, economically, simply and accurately [10].

The basic composition in the preparation of FeTiO\textsubscript{3} sol-gel used was (TTIP) compound in sol-gel method for dopant ion distributor medium or matrix and forming a nanoparticle, acetyl acetone acting as a chelating ligand which will produce an exothermic reaction and make the yellow solution [10]. The creation of FeTiO\textsubscript{3} sol by adding Fe(NO\textsubscript{3})\textsubscript{3} compounds may increase the activity of photocatalysis which acts as trap of electron photoregeneration and hole so it can suppress the occurrence of electron-hole recombination. The modification of TiO\textsubscript{2} using FeTiO\textsubscript{3} doping can produce high photocatalytic activity under visible light. Visually the results obtained in FeTiO\textsubscript{3}/Ti and FeTiO\textsubscript{3}.TiO\textsubscript{2}/Ti doping techniques are shown in Figure 2.
3.3. Characterizations

3.3.1. Bandgap FeTiO$_3$

The UV-Vis Diffuse Reflectance Spectrophotometer (UV-Vis DRS) is used to determine the energy gap \( (E_g) \) produced by semiconductor from the synthesized FeTiO$_3$ solid. \( E_g \) values of the resulting semiconductor can affect the performance of the semiconductor in exciting electrons from the valence band to conduction band region [2]. This condition is depending on the bandwidth gap width generated by the semiconductor. Small \( E_g \) values will make it easier for electrons to move from the valence band to the conduction band so that the flow of electrons will get easier.

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E_g (eV) = \frac{1239.8}{\frac{\lambda}{nm}}
\]

The \( E_g \) value was plotted in the equation above to obtain the wavelength area of FeTiO$_3$ performance and it has been obtained the wavelength at 423.13 nm [15].

3.3.2. X-ray Diffraction (XRD)

Measurements using XRD aims to obtain crystal structure information of FeTiO$_3$/Ti and FeTiO$_3$.TiO$_2$/Ti working electrodes. The appearance of XRD diffractogram peaks of 35.1° (110), 49.9° (024) and 61.2° (214) indicates the FeTiO$_3$ has coated on the substrate. It has been compared with the JCPDS standard No. 29-0733, and 76-1821. The peak of 42.5° (400) shows the Fe$_3$O$_4$ magnetic corresponding to JCPDS No. 19-0629.

The a-anatase crystal in TiO$_2$ at 2 theta 25° (101) does not absence to indicate that the possibility of rutile crystals is formed. The presence of Fe dopant in TiO$_2$ crystal that possibility of rutile crystals formed. The Ti element as conducting substrate has appeared at 2 theta 37.5°, 39°, dan 52°. The diffractogram peaks between FeTiO$_3$/Ti and FeTiO$_3$.TiO$_2$/Ti plate crystal are shown in Figure 4.

Figure 2. The results of electrodes; (A) FeTiO$_3$/Ti, and (B) FeTiO$_3$.TiO$_2$/Ti

Figure 3. The bandgap of FeTiO$_3$
Figure 4. The diffractogram of FeTiO$_3$/Ti and FeTiO$_3$.TiO$_2$/Ti electrodes

3.3.3. Scanning Electron Microscopy (SEM)

The result of characterization using SEM aims to look at the morphology on the surface of the electrode that has been coated with FeTiO$_3$ sol-gel. The result of SEM characterization can be seen in Figure 5.

Figure 5. Morphology on electrodes, (A) FeTiO$_3$/Ti, (B) FeTiO$_3$.TiO$_2$/Ti

Figure 5A the morphology of FeTiO$_3$/Ti electrode indicated that the sol-gel method has the thin layer formed and evenly distributed. Based on literature that allows the formation of tubes in Ti metals during etching process using HF, HNO$_3$, and D.I. H$_2$O solvents. The formed tube improves the adhesion of sol-gel onto Ti metal surface. Figure 5B shows a high regular array of crystals in random type. The coated by the sol-gel method on the FeTiO$_3$.TiO$_2$/Ti electrode exhibits uniform results with an excellent crystalline order. The role of TiO$_2$/Ti as a template is excellent for the sol-gel coating process and provides a small probability of covering the surface of TiO$_2$/Ti nanotubes [25]. According to Liu et al. the design of TiO$_2$ electrode by anodizing method acts as a sol-gel adhesive agent to improve the electronic properties of the material [26]. These results show that the LPD technique is very effective in the FeTiO$_3$ coating process on the substrate surface.

3.4. Photocatalyst Test

Measurements using the LSV method to measure the proportional of photocurrent to the potential difference function. The photocurrent is current that can be observed when the electrode is irradiated by UV and visible light. This current is also a measure of the charge transfer rate between semiconductors/electrolytes which can be used as a measure of •OH formation rate on the surface of catalyst. Figure 6A and 6B the LSV data shows that the activity of good photocurrent response when it
is irradiated visible light. The electrons move from the valence band (VB) to the conduction band (CB), so the electrons are trapped by the Fe metal, thus minimizing the occurrence of electron and hole recombination [27]. Visible light irradiated required the lower energy, that the electrons can move from VB to the CB.

Figure 6. Photoelectrochemical graph, (A) LSV of FeTiO$_3$/Ti electrode, (B) LSV of FeTiO$_3$.TiO$_2$/Ti electrode, (C) CV of FeTiO$_3$/Ti electrode, and (D) CV FeTiO$_3$.TiO$_2$/Ti electrode

The CV test is an electrochemical analysis method based on the measurement of the electric current value as a function of potential flow which is given back and forth on the electrochemical cells. Test using CV connected to a potentiostat and connected to a computer with bias potential setting of 0.5 volt and scanrate of 0.05, the movement of potential bias was from -2 volts to 0.5 volts and sensitivity of 1.0 $\times$ 10$^{-3}$ A/V. Performed by test variation to see the peak current differences during the redox reaction. Determination of photocurrent for each electrode by CV technique (Figure 6C and 6D) indicates that the high oxidation process based photocurrent response be greater using FeTiO$_3$.TiO$_2$/Ti electrode.

3.5. Photoelectrocatalytic Degradation

Determining the maximum wavelength of TY dye solution at 0.5 ppm was characterized using a UV-Vis spectrophotometer. The results of the absorbance spectrum of the test dye solution are shown in Figure 7.
Figure 7. The wavelength of Titan yellow organic compound

The calibration curve was obtained by plotting concentration with absorbance so that the equation of straight line is \( y = 0.2003x + 0.0092 \). Photocatalysis is a catalyst that can work with the aid of light (photons). The occurrence of TY concentration decreases in photocatalysis method is shown in Figure 8A and 8B.

Figure 8. Comparison graph of photocatalytic and photoelectrocatalytic performance (A) Photocatalytic degradation, (B) % degradation of photocatalytic, (C) Photoelectrocatalytic degradation, (D) % degradation of photoelectrocatalytic

The process of photoelectrocatalysis (Figure 8C and 8D) will form many active spaces on the catalyst, theoretically the degradation process will run well. This method using FeTiO\(_3\)/Ti and FeTiO\(_3\).TiO\(_2\)/Ti working electrodes illuminated UV and visible lights produce pairs of electrons and holes. The hole will initiate the oxidation reaction on the electrode surface, while the electrons are flown through the back contact to counter electrode and transferred to the existing electron capturer in the solution [5].
4. Conclusion
The photoelectrochemical response test of FeTiO$_3$/Ti and FeTiO$_3$.TiO$_2$/Ti electrodes showed that the photocurrent values of visible light irradiance on each electrode were $9.87 \times 10^{-5}$ A and $7.87 \times 10^{-4}$ A, respectively. The photoelectrocatalytic activity test to degrade TY organic compound showed that the percent of degradation under visible light at 0.5 ppm were 41% and 43%, respectively.

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6. References

[1] Nurdin M, Wibowo W, Supriono, Febrian M B, Surahman H, Krisnandi Y K, Gunlazuardi J 2009 *Makara, Sains*, 13 1.
[2] Nurdin M 2014 *Int. J. Pharm. Bio. Sci.* 5 360.
[3] Nurdin M, Maulidiyah 2014 *Int. J. Sci. Technol. Res.* 3 122.
[4] Sari A A, Kurniawan H H, Nurdin M, Abimanyu H 2015 *Energy Procedia* 68 254.
[5] Maulidiyah, Ritonga H, Salamba R, Wibowo D, Nurdin M 2015 *Int. J. ChemTech Res.* 8 645.
[6] Dahnum D, Tasum O S, Triwahyuni E, Nurdin M, Abimanyu H 2015 *Energy Procedia* 68 107.
[7] Maulidiyah, Nurdin M, Erasmus, Wibowo D, Natsir M, Ritonga H, Watoni A H 2015 *Int. J. ChemTech Res.* 8 416.
[8] Maulidiyah, Nurdin M, Widianingsih E, Azis T, Wibowo D 2015 *ARPJ N. Eng. & Appl. Sci.* 10 6250.
[9] Maulidiyah, Nurdin M, Wibowo D, Sani A 2015 *Int. J. Pharma. Pharmaceut. Sci.* 7 141.
[10] Nurdin M, Muzakkar M Z, Maulidiyah M, Nurjannah M, Wibowo D 2016. *J. Mater Environ. Sci.* 7 3334.
[11] Nurdin M, Maulidiyah, Watoni A H, Abdillah N, Wibowo D 2016 *Int. J. ChemTech Res.* 9 483.
[12] Nurdin M, Zaeni A, Maulidiyah, Natsir M, Bampe A, Wibowo D 2016 *Orient. J. Chem.* 32 2713.
[13] Maulidiyah, Wibowo D, Hikmawati, Salamba R, Nurdin M 2015 *Orient. J. Chem.* 31 2337.
[14] Nurdin M, Ramadhan L O A N, Darmawati, Maulidiyah, Wibowo D 2017. *J. Coatings Technol. & Res.* DOI: 10.1007/s11998-017-9976-8.
[15] Ruslan, Mirzan M, Nurdin M, Wahab A W 2016 *Int. J. Appl. Chem.* 12 399.
[16] Maulidiyah, Tribawono D S, Wibowo D, Nurdin M 2016 *Anal. Bioanal. Electrochem.* 8 761.
[17] Maulidiyah, Ritonga H, Faiqoh C E, Wibowo D, Nurdin M 2015 *Biosci. Biotechnol. Res. Asia* 12 1985.
[18] Arham Z, Nurdin M, Buchari B 2016 *Int. J. ChemTech Res.*, 9 113.
[19] Mursalim L O A M, Ruslan, Safitri R A, Azis T, Maulidiyah, Wibowo D, Nurdin M 2017 *IOP Conference Series: Materials Science and Engineering* xx xx.
[20] Nurhidayani, Muzakar M Z, Maulidiyah, Wibowo D, Nurdin M 2017 *IOP Conference Series: Materials Science and Engineering* xx xx.
[21] Wibowo D, Ruslan, Maulidiyah, Nurdin M 2017 *IOP Conference Series: Materials Science and Engineering* xx xx.
[22] Yu J, Wu Z, Gong C, Xiao W, Sun L, Lin C 2016 *Nanomaterials* 6 107.
[23] Raghavender A T, Hong N H, Lee K J, Jung M H, Skoko Z, Vasilevskiy M, Cerquira M F, Samantilleke A P 2013 *J. Magnesium Materials* 331 129.
[24] Maulidiyah, Imran, Muntu W, Nurdin M 2016 *Int. J. Appl. Chem.* 12 347.
[25] Roy P, Berger S, Schmuki P 2011 *J. Chem.* 50 2904.
[26] Liu Y, Wang L, Wang H, Xiong M, Yang T, Zakharova G S 2016 *Sensors and Actuators B: Chem.* 236 529.
[27] Weber U, Weinmann M, Natter H, Bahre D 2015 *J. Appl. Electrochem.* 45 591.