Cu-TiO$_2$ doped Ti thin-layer photoelectrode for visible-light induced photoelectrocatalytic activities: degradation of methylene orange

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Abstract. Cu-TiO$_2$ doped Ti thin layer was prepared by anodizing and electrodeposition. Characterization electrode using Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX) and activity test using Linear Sweep Voltammetry (LSV) under UV and visible light to degrade methylene orange. The result of electrode surface characterization using EDX showed that the Cu peak at 0.992 keV indicated the precious metal Cu on the TiO$_2$/Ti electrode. The activity test of Cu-TiO$_2$/Ti electrode by Linear Sweep Voltammetry (LSV) showed the electrode activities on the visible light. The TiO$_2$/Ti electrode has activities on the UV light. Degradation test Cu-TiO$_2$/Ti electrode by photoelectrocatalyst against methylene orange showed the percentage of degradation produced was 92.88%.

1. Introduction
Photocatalytic is a process of photoelectrochemistry using semiconductors material. Semiconductors, there was a gap called a bandgap, where between the valence band and the conduction band was loaded. The magnitude of the band gap value at semiconductors (0.5 to 3.0 eV)[1–4], some electrons at semiconductors have enough heat energy to go up the conduction gap. In the process of photocatalysis, there is a chemical transformation process that involves the help of photons[5–7]. A semiconductor that was charged with photon pumped to a higher energy level, which is an excited state (conduction band) by producing a hole ($h^+$). The chemical transformation that occurs in the photocatalytic process is a reduction and oxidation mechanism that can be used in substrate degradation that interacts with the surface of the photocatalyst[8–13]. The photocatalyst process has been developed to treat organic waste problems in the water[14–16].

The use of TiO$_2$ semiconductor material is a promising waste treatment. TiO$_2$ has been widely developed in dealing with waste problems because it has high photocatalytic activity and has significant levels of degradation. TiO$_2$ implementation as a material that can deal with waste is able to reduce organic concentration matter[17], organic waste[18], pesticides[19], phenols[20] and surfactant[21]. TiO$_2$ modifications are a way of eliminating restrictions from using TiO$_2$ to degrade organic pollutants[22–25]. So, currently developed TiO$_2$ photocatalysts that can efficiently use sunlight or light indoors.

The potential approach to the use of TiO$_2$ in areas of light is seen by modifying the chemical structures of the TiO$_2$ photocatalyst. Photocatalytic modification by doping is one of the ways the efficiency of photocatalysts by lowering the ribbon's bandgap energy. Doping is an effective method for changing the physical properties of semiconductor material that will expand its application[26,27]. Metal can be used as doping to trap electrons because of its non-oxidized nature and has a high reduction potential[28].
The formation of a thin layer of metal can be synthesized by electrodeposition[29–31]. This allows for good metal growth because it can be monitored based on variations of electrical power used, spent time depositions and concentrations of a solution. In this study metal, Cu is used as an electron trap on semiconductor TiO$_2$, so it has photocatalyst activity to degrade methylene orange waste that is applied in the sun.

2. Experimental

2.1. Preparation Sample dan Substrate
The size of the Ti plate used is 4 cm x 0.5 cm. The Ti plate was sanded until its surface was clean and shiny then immersed for 2 minutes in a mixture of HF, HNO$_3$, and distilled water[32].

2.2. Formation TiO$_2$/Ti thin Layer by Anodizing Method
The anodizing process uses electrolyte solution NH$_4$F electrolyte solution and glycerol. Ti plate was placed as an anode and Cu plate as a cathode by giving a potential change of 25 volts for 4 hours then calcined at 500º C for 1.5 hours[33].

2.3. Formation Doped Cu-TiO$_2$/Ti Thin Layer by Electrodeposition Method
Copper sulfate (CuSO$_4$.5H$_2$O) is used as an electrodeposition solution as a source of Cu metal dopant. Electrodeposition is carried out for 3 seconds with a potential difference of 1 Volt. Cu-TiO$_2$ plate formed was washed again with aquabides, then dried in a desiccator[34].

2.4. Characterization of Electrodes
Characterization of Cu-TiO$_2$/Ti Electrodes using SEM-EDX to provide data on the surface of the synthesized Ti plates. The electrode activity test used the Linear Sweep Voltammetry (LSV) method. LSV tests are carried out by UV, visible and no-light radiation. using NaNO$_3$,0.1 M as an electrolyte solution and connected to a portable potentiostat.

2.5. Testing of Degradation Activity
The first step is to determine the wavelength of the methylene orange using Uv-vis. The second step is to make a standard methylene orange curve with a concentration of 0.5; 1.0; 2.0 and 3.0 ppm. The degradation activity test of TiO$_2$ / Ti and Cu-TiO$_2$ / Ti electrodes on methylene orange dye were carried out by the Multi Pulse Amperometry (MPA) method with a duration of 10 minutes and a potential difference of 0.5 Volts in the variation of UV and visible lights. Absorbance measurement uses a UV-Vis spectrophotometer to determine the decrease in dye concentration.
3. Result and Discussion

3.1. Anodizing of TiO$_2$

TiO$_2$ synthesis by anodizing is done to convert the surface of the Ti plate by forming an oxide layer. The formation of TiO$_2$ on the Ti plate was carried out for 4 hours given a 25 Volt potential current using NH$_4$F electrolyte solution (Figure 1). The electrolytic solution is used as a link between the cathode and anode so that the surface undergoes an oxidation reaction and an oxide layer is formed.[35–38]. After anodizing calcined at 500°C for 1.5 hours so that the organic solvents trapped in the titanium plate evaporate.

![Figure 1. Anodizing TiO$_2$/Ti Plate](image)

3.2. Electrodeposition of Cu on TiO$_2$/Ti

The electrodeposition process begins with the manufacture of copper sulfate solution as an electrolyte solution. Copper sulfate is used as a source of Cu metal. TiO$_2$/Ti is connected with a negative current source as a cathode and the Cu plate is used as an anode which is connected to a positive current source, then given a potential current of 1.0 Volt with time variations of 1, 2 and 3 seconds. The results of pasting the Cu metal on the surface of TiO$_2$ that have been formed by the electrodeposition process for 3 seconds can be seen in (Figure 2).

![Figure 2. Cu-TiO$_2}$/Tielectrode by electrodeposition](image)

3.3. Characterization of Electrodes

3.3.1. Scanning Electron Microscope (SEM)

The surface of TiO$_2$ that has been formed was observed using SEM with a magnification of 20 μm which did not show nanotubes. In the(Figure 3B) a cross-section of TiO$_2$ allows the formation of nanotubes which are marked by lines such as tube shapes.
Figure 3. (a) Surface morphology of the TiO$_2$/Ti electrode, and (b) Transverse surface of TiO$_2$

3.3.2. Energy-Dispersive X-ray spectroscopy (EDX)

Figure 4 shows the presence of agglomerate particles on the surface of the electrode indicating the presence of Cu metal formed, supported by Figure 4B, namely the energy and intensity of the elements on the electrode surface. The spectra contained in EDX seen the presence of Cu peaks at 0.992 keV with a composition of 12.6% indicating the successful formation of Cu metal on the electrodes.

Table 1. Energy and composition of the elements

| Element | KeV  | Composition (%) |
|---------|------|-----------------|
| Cu      | 0.992| 12.6            |
| Ti      | 0.452| 44.5            |
| O       | 0.525| 42.9            |

3.3.3. Linear Sweep Voltammetry (LSV)

The measurement used LSV technique has the same principle as the potentiometric method which includes the relationship between the current generated and the relative electrode[2,34]. The electrode test was conducted to determine the effect of Cu dopant on the photoelectrolysis system. So, in this study used the measurement of light current as a potential function using the LSV technique in which sodium nitrate 0.1 M as an electrolyte solution is connected to a portable potentiostat. The activity of electrodes by visible light irradiation proves that Cu doping on TiO$_2$ has good activity and is capable of photoelectrocatalysis.
The determination of the maximum wavelength of methylene orange is done using a UV-Vis spectrophotometer. Orange methylene absorbance curve with a maximum peak at a wavelength of 465 nm with an absorbance of 0.142. The calibration curve is obtained by plotting the concentration with absorbance to produce a straight line equation: $y = 0.019x + 0.062$, with a linearity value ($R^2 = 0.96$).

3.4. Degradation Test against Color Methylene Orange

The determination of the maximum wavelength of methylene orange is done using a UV-Vis spectrophotometer. Orange methylene absorbance curve with a maximum peak at a wavelength of 465 nm with an absorbance of 0.142. The calibration curve is obtained by plotting the concentration with absorbance to produce a straight line equation: $y = 0.019x + 0.062$, with a linearity value ($R^2 = 0.96$).
The degradation process of organic compounds will be far more efficient than the photolysis and photocatalysis methods. In the photoelectrocatalysis process, there is the addition of electrons (electric currents) which will prevent the electron-hole recombination process when light illuminations are carried out. The doped Cu will trap electrons and make recombination smaller so that it can trap electron photogeneration from the semiconductor and allow holes to form hydroxyl radicals that produce the degradation reaction of organic species. Figure 7A and Figure 7B show the TiO$_2$/Ti electrodes can reduce the concentration of methylene orange. The maximum performance of TiO$_2$/Ti electrodes is at a concentration of 0.5 ppm with 80% degradation. Doped electrodes (Figure 8B) show maximum activity in visible light with a 92.88% degradation order.

4. Conclusion
The research of Cu doped on TiO$_2$/Ti electrodes has been successfully carried out. The oxide layer on the Ti plate can be formed by the anodizing process. Cu doping is carried out by electrodeposition using copper sulfate as a precursor. Electrode characterization results showed the success of Cu formation using SEM-EDX with a Cu composition of 12.6%. The result of methylene orange degradation by Cu-TiO$_2$/Ti electrodes was 92.88%.
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