



PREPARATION, CHARACTERIZATION AND PHOTOELECTROCATALYTIC ACTIVITY OF Cu@N-TiO₂/Ti THIN FILM ELECTRODE

MUHAMMAD NURDIN*

*Department of Chemistry, Faculty of Mathematics and Natural Sciences,
Universitas Halu Oleo, Kendari 93232, Southeast Sulawesi, Indonesia*

ABSTRACT

This research focused on the preparation and characterization of Cu@N-TiO₂/Ti (N-TiO₂/Ti decorated with Cu) thin film electrode and its activities test in photoelectrocatalytic system. This study investigated the time effect of Copper (Cu) electrodeposition and the concentration of nitrogen (N) in the photocatalytic characteristics of TiO₂. The catalyst has been prepared for activities test on congo red. These results indicated the value of the smallest band gap (3.06 eV) on the N-TiO₂ prepared by sol - gel method (using 1M urea), thin film electrode of N-TiO₂/Ti further decorated with Cu using electrodeposition method with the highest activity was 20 seconds. The thin film electrode of Cu@N-TiO₂/Ti showed excellent activity under visible light illumination, which gave the best photocurrent and capable to degrade congo red better than TiO₂/Ti (12.11%) or N-TiO₂/Ti (34.87%) which was equal to 49.38%. This electrode might be recommended for Chemical Oxygen Demand Sensor.

KEYWORDS: TiO₂, nitrogen, copper, sol-gel, electrodeposition, congo red, Cu@N-TiO₂/Ti



MUHAMMAD NURDIN

Department of Chemistry, Faculty of Mathematics and Natural Sciences,
Universitas Halu Oleo, Kendari 93232, Southeast Sulawesi, Indonesia.

*Corresponding author

INTRODUCTION

The rapid development of industrial technology in both the developed and developing countries are always faced with the problem of environmental pollution such as water pollution impacts on living beings. Liquid waste that produced by industries has the potency to harm people and the environment. Textile industry is one of industries that produce a non biodegradable dyes organic pollutants. The technologies that may be developed to degrade a wide range of liquid waste is photocatalytic process using TiO_2 semiconductor material¹⁻³. TiO_2 photocatalytic process offers a promising technology to completely degrade organic pollutants into carbon dioxide, either in the air or in the water. For air purification, some practical technologies have been achieved and successfully applied. Currently, some air purifiers using TiO_2 photocatalytic technology have been available in the market. Whereas for the purification of water or waste water treatment, this technology still faces several challenges, including the reported efficiency, which was still relatively low⁴⁻⁶. To improve efficiency, many efforts have been made by researchers, such as by modifying the TiO_2 photocatalytic involving dopant of the metal and non-metal. Dopant element was created as a new catalyst matrix, which has a smaller energy gap. This is equivalent to the energy of visible light. Several types of metallic elements that have been used are Fe and Ag⁷, Cu, Ni and La^{8,9}, while the non-metallic elements are N¹⁰⁻¹², C¹³ and S¹⁴. In addition, the works done is to combine the photocatalytic process with electrochemical process, which was then known as photoelectrocatalysis. Photoelectrocatalysis process has been proven to be one of the most effective method in degrading the organic pollutants in water. In general, the photocatalytic process begins with the absorption of photons energy by the semiconductor, which leads to charge separation or photo-excitation in semiconductors. Electron (e^-) will be excited into the conduction band, leaving *holes*/positive hole (h^+) in the valence band. The positive hole is a very strong oxidizing agent if there are organic compounds adsorbed on the TiO_2 surface. Oxidation

efficiency can be improved by application of a bias potential for the electrons flow through an external circuit, so as to prevent the recombination of positive holes and electrons. This is the principle of photoelectrocatalysis^{15,16}. Photocatalyst TiO_2 is commonly used in suspension system. It is not effective enough because it takes a huge amount of TiO_2 . The problem may be overcome by immobilizing photocatalyst on a variety of supporting materials such as fiber, glass, silica and titanium plate^{17,18}. This study was conducted by modifying TiO_2 semiconductor material for the dye degradation through a photoelectrocatalysis process with catalyst of non-metallic TiO_2 doping, which was a nitrogen immobilized on Ti plate to form a composite of N- TiO_2/Ti . It was then decorated with Cu with electrodeposition method. Thus, the expected composite of Cu@N- TiO_2/Ti has high photoelectrocatalysis activity in degrading dyes by utilizing the visible light. It was expected that in the future the sunlight may be utilized as a light source.

MATERIALS AND METHODS

The materials used are Titanium Tetra Iso Propoxide (TTIP) 97% Aldrich, distilled water, acetylacetonate (Merck), ethanol 99% (Merck), EDTA (Merck), acetic acid (Merck), Urea (Merck), Titanium Plate, NaNO_3 (Merck), HF 40% (Merck), HNO_3 (Merck), and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Merck). The instruments used are Diffuse Reflectance Spectrophotometer (DRS) UV-Vis, FTIR, XRD, portable potentiostat (e -DAQ).

(i) Synthesis of TiO_2 and N- TiO_2

In this study made into two solutions, where the 1st solution in the form of a colloidal solution of TiO_2 prepared by controlled hydrolysis from titanium tetra isopropoxide is taken 4 mL in acetilacetonate by 0.5 mL and 15 mL of ethanol 99%. The 2nd solution is 15 mL of ethanol 99% and 2 mL of distilled water with the addition of 1 mL of glacial acetic acid. Mixture of the solution is reflux for 60 minutes at a temperature of 50°C. Doping TiO_2 with nitrogen, sol was stirred, followed by the

addition of 1, 1.5, and 2 M urea with a volume ratio of TiO₂ sol and urea is 1:0.5. Stirring was continued for 30 minutes to produce optimum N-doped TiO₂. Part of the solution is heated in an oven with a temperature of 80°C for 30 minutes and calcined at 500°C for 2 hours to produce powder of TiO₂ and N-TiO₂, while some other part is used for coated on titanium plate that had been prepared.

(ii) Photoelectrocatalytic Activity Test

a. Preparation of Ti (titanium) Plate

Plate preparation process is done by cutting the titanium plate measuring 4.5 cm x 2 cm, then sanded using sand paper until the surface is clean and shiny then washed using a detergent solution, water, and distilled water. Furthermore, the plate is immersed in a solution of a mixture of HNO₃, HF and distilled water with successive ratio is 3: 1: 6. Then rinsed with distilled water and allowed to dry. Then the Ti plate which has been prepared previously calcined for 2 hours at a temperature of 500°C.

b. Preparation of Working Electrode

Ti plate which has been previously prepared immobilized by TiO₂ and N-TiO₂ sol by means of superimposing on the surface of the plate evenly with dip coating technique. Then the tube is heated in an oven with a temperature of 80°C for 30 minutes and calcined using a furnace at a temperature of 500°C for 2 hours to allow the formation of crystalline anatase is going well and obtained a uniform thin film on the surface of the plate, the coating process was varied as much as 2, 3, 4, and 5 times.

c. Decoration of N-TiO₂/Ti with Cu Transition Metal

Electrolyte solution was prepared by dissolving 0.04 g of CuSO₄.5H₂O in 100 mL of distilled water, and then mixed with a solution of 0.5 g EDTA in 100 mL of distilled water. Piece of N-TiO₂/Ti is placed as a cathode in an electrolyte solution of CuSO₄.5H₂O and EDTA. As anode was used woven wire of Pt. Electrodeposition carried out at -1.0 V. The time of electrodeposition was varied in 10, 15 and 20 seconds. Furthermore, cathode was

dried in a desiccator for 24 hours, so that the resulting thin film electrode is Cu@N-TiO₂/Ti.

(iii) Catalyst Characterization of TiO₂, N-TiO₂ and Cu@N-TiO₂/Ti

Catalyst characterization of TiO₂, N-TiO₂, and Cu@N-TiO₂/Ti done with DRS UV-Vis to determine the energy gap of the crystal of TiO₂ and N-TiO₂, FTIR is to determine the nitrogen bond with oxygen as an indication of the formation of N-TiO₂. SEM is to know the surface morphology of the catalyst of Cu@N-TiO₂/Ti. XRD is to obtain information on the crystal structure of TiO₂, N-TiO₂, and electrode surfaces of Cu@N-TiO₂/Ti. Photoelectrocatalysis activity test was using Linear Sweep Voltametry. The experiments were conducted with and without UV light irradiation and Wolfram (40 watts) using 0.1 M NaNO₃ electrolyte.

(iv) Testing the Photoelectrocatalytic Activity

Photoelectrocatalytic activity test with the LSV method, and then used to degrade the 10 ppm congo red dye in 0.1 M NaNO₃ with a volume of 14 mL. Photoelectrocatalysis activity test was performed on photoelectrocatalytic reactor using visible light and done using the Multi Pulse Amperometry with the duration of 10 minutes and bias potential at 500 mV. The absorbance measurements were taken using Spectrophotometer UV-Vis to observe a decrease in the concentration of the dye.

RESULTS AND DISCUSSION

(i) The Determination of the band gap by DRS UV-VIS

In this study, absorption measurement of TiO₂ and N-TiO₂ that have been prepared, analyzed by DRS UV-Vis in the wavelength range from 200 nm to 800 nm. In Figure 1 it can be seen that TiO₂ and N-TiO₂ with dopant concentration variation has a different profile. Reflectance spectra profile clearly shows that the N-TiO₂ has a visible light absorption area ($\lambda > 400$ nm).

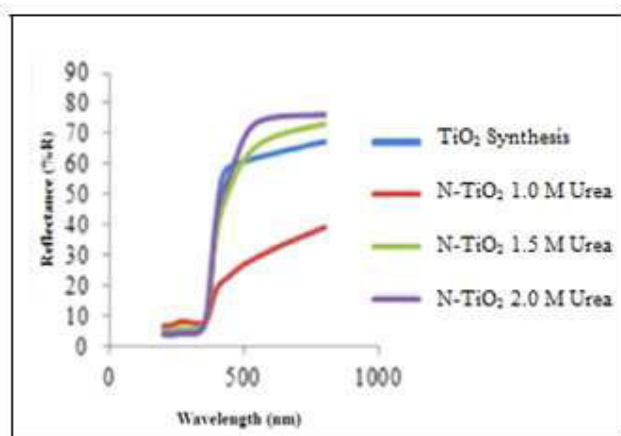


Figure 1
DRS UV-Vis spectra of TiO_2 and $N-TiO_2$

Based on the obtained spectra, the energy-gap is determined by using the equation :

$$F(R) = \frac{K}{S} = \frac{(1-R)^2}{2R}$$

Where: F (R) = Kubelka-Munk factor
K = Coefficient of absorption
S = Coefficient scattering
R = Reflectance value measured

$$F(R) = A(h\nu - E_g)^m$$

Where: A = Constanta proportional
Eg = Energy gap
m = 1 for a direct transition is allowed

Then by plotting F(R) against $h\nu$ and extrapolating the linear region can be determined $h\nu$ value on F(R) = 0, which is nothing but it is the value of the energy gap of the absorbing species. The energy gap of TiO_2 thin film $N-TiO_2$ can be determined by the Kubelka-Munk equation.

Tabel 1
Band Gap values of TiO_2 and $N-TiO_2$

Samples	Band Gap (eV)
TiO_2 Synthesized	3.20
$N-TiO_2$ (1.0M Urea)	3.06
$N-TiO_2$ (1.5M Urea)	3.15
$N-TiO_2$ (2.0M Urea)	3.21

In Table 1, it can be seen that the band gap value between synthesized TiO_2 and $N-TiO_2$ with variations of dopants addition have different values. TiO_2 doped with nitrogen has a value of band gap energy smaller than synthesized TiO_2 . With the decreasing in the value of the band gap, the energy of light is needed to form photohole (conduction band) and photoelectron (valence band) will be smaller, for example, it is just enough by using a visible light source. Moreover, it can also be seen that the higher of the nitrogen

source concentration added in comparison of the same amount to make $N-TiO_2$, it proved that, the higher band gap value will be, although not too significant, so that they can decrease the photocatalytic properties. The optimum band gap value was obtained at the concentration of 1.0 M Urea, that is 3.06 eV.

(ii) Characterization by FTIR

The aim of this measurements by FTIR is to identify indications of the existence of a bond between the Ti-O-, the presence of nitrogen

in TiO_2 matrix of synthetic result. In Figure 2, it can be observed the characteristics of the O-Ti-O bonds appears on the wavenumber region of 400- 1250 cm^{-1} . There is also a peak absorption at 3300-2500 cm^{-1} which is the characteristic of OH stretching vibration and 1625-1650 cm^{-1} indicating the peak of OH bending vibrations originating from the solvent trapped in the crystal structure of TiO_2 , or titanol group and 1000-1300 cm^{-1} is a peak of absorption for the C-O stretching vibration resulted from imperfect combustion.

Absorption peak profiles generated from TiO_2 and N-doped TiO_2 by various concentrations, it is found that there are some differences in the absorption peak which is in the area of 470 cm^{-1} . Shifting of this analytical signal can indicate other bonds besides O-Ti-O have been formed, which is expected due to the presence of Ti bond with N. Peak absorption of N-doped TiO_2 has intensity with a higher tendency concomitant with the increasing of the rising addition numbers of dopants.

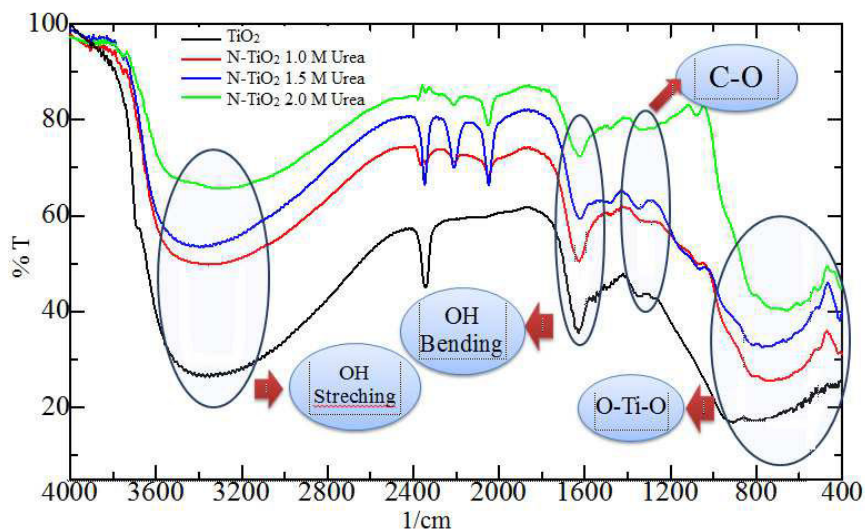


Figure 2
FTIR spectra of TiO_2 and N- TiO_2

(iii) Characterization by using LSV

Measurement by Linear Sweep Voltammetry (LSV) method uses the same principle with the potentiometric method which emphasizes the relationship between the current generated by the electrode potential relative. Photocurrent response is a response of electrode observed when it is irradiated by the right light and given the voltage of current form, where this current is also a measure of the charge transfer rate of semiconductor/electrolyte interfacial, so it can

be used as a measure of the rate of OH radical formation on the catalysts surface.

a. Optimum Coating Measurement

The aim of this measurement is to determine the amount of the sol coating of TiO_2 and N- TiO_2 on titanium plate which had the highest activity. Figure 3 shows the comparison of the results of LSV measurements of TiO_2/Ti and N- TiO_2/Ti with various coatings to the test solution of 0.1 M NaNO_3 electrolyte.

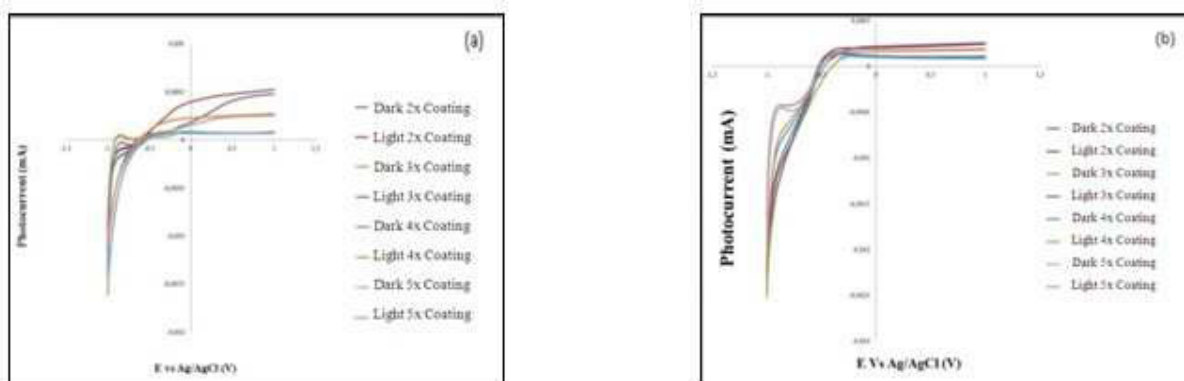


Figure 3
Responses of LSV: (a) TiO_2/Ti , (b) $\text{N-TiO}_2/\text{Ti}$

The response measurement of LSV of TiO_2/Ti electrode with a variety of coatings can be seen in Figure 3 and from the results of the measurements it can be seen that the TiO_2/Ti electrode prepared by immobilization on Ti plate with dip coating TiO_2 method showed that 2 times of coating has greater photocatalytic activity compared with the electrode with 1, 3, 4, and 5 times of coating which were evaluated from the high currents generated during UV light irradiation is given as the source of photons. It can be concluded that 2 times of coating is the most optimum

time to produce TiO_2 with the highest activity. $\text{N-TiO}_2/\text{Ti}$ electrode itself has a high photocatalytic activity given by electrode as much as 3 times of coating.

b. Measurement of copper (Cu) transition metal decoration activity

Figure 4 is the photocurrent measurement data by using a LSV method in the determination of the optimum electrode with Cu metal decoration at various time by using UV light and visible light sources.

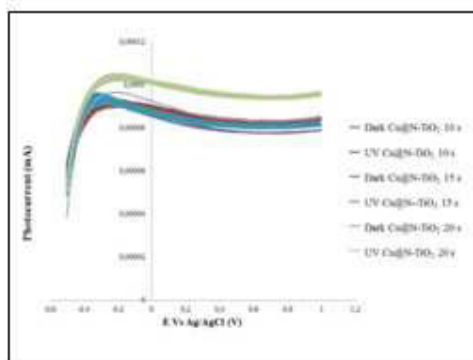


Figure 4
Responses of LSV $\text{Cu@N-TiO}_2/\text{Ti}$ to UV light

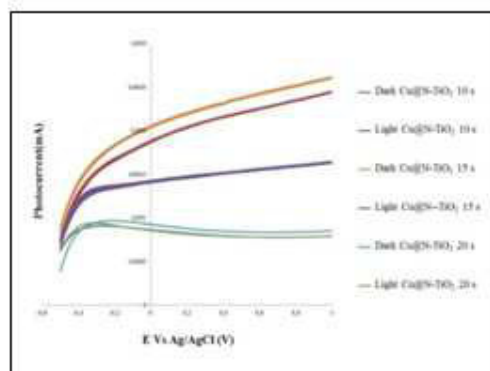


Figure 5
Responses of LSV Cu@N-TiO₂/Ti to visible light

Based on the Cu@N-TiO₂/Ti electrode voltammograms in Figure 4 and 5, it can be seen that in the dark, the light response currents observed approaching zero value while at the time the electrode is irradiated with UV and visible light, the anodic light current response is higher with a potential increase given. This happens because in the dark, conductivity of Cu@N-TiO₂/Ti catalysts is very small. The response of anodic is getting higher when electrode irradiated with UV and visible light indicating Cu@N-TiO₂/Ti electrode can produce pairs of electrons and holes, means responsive to UV or visible light. Electrode has the highest activity in Cu@N-TiO₂/Ti irradiated using UV light and visible which it shown at time decorating for 20 seconds.

(iv) Characterization by XRD

Characterization by XRD performed to obtain information of TiO₂ and N-TiO₂ crystal structure of synthesis results and crystal structure on the surface of Cu@N-TiO₂/Ti electrode. Materials of TiO₂ and N-TiO₂ analyzed is not the result of calcination gel coated on Ti substrate plate, but get the same heat treatment with the Ti plate coated on the substrate. Figure 6 is the result of the XRD analysis of TiO₂ and N-TiO₂ catalysts and crystalline structure on the surface of Cu@N-TiO₂/Ti electrode. In the picture looks peaks that can provide identity information form crystalline TiO₂, N-TiO₂ and Cu@N-TiO₂/Ti electrode prepared in this study. The results of XRD analysis showed the presence of peaks 2θ = 25.3° which is the peak of anatase and the absence of peaks 2θ = 27.4° which marks the rutile crystal types, so it can be concluded that the crystals formed are crystalline anatase type.

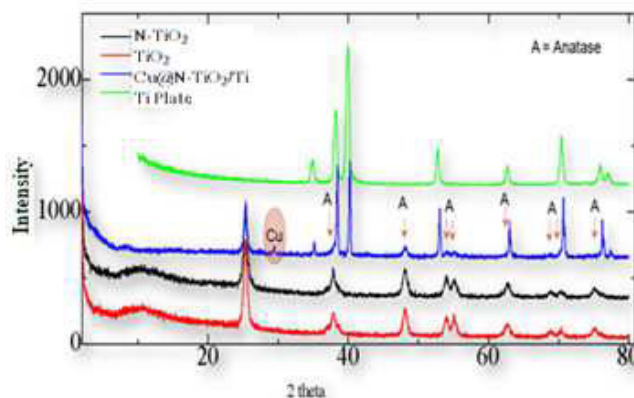


Figure 6
XRD analysis pattern on TiO₂, N-TiO₂ and Cu@N-TiO₂/Ti electrodes

If viewed from XRD spectrum, the presence of a new peak in the small intensity at the Cu@-N-TiO₂/Ti electrode ie at $2\theta = 29.40^\circ$ predicted as the peak of Cu¹⁹ in the form of Cu₂O.

(v) Photoelectrocatalytic Activity Test

Based on the data of LSV photocatalyst that has been prepared, the properties of its photocatalyst are tested in degrading organic matter, i.e diazo dyes of congo red. Photocatalytic degradation reaction in a thin film of TiO₂ is heterogeneous reactions, where the degradation process occur, the pollutant must migrate from the solution to the surface of the catalyst. Therefore, the scoping of TiO₂ active surface will affect the rate of degradation. Here congo red will break down into CO₂ and H₂O, started with the formation of photohole that will produce a strong oxidizer and highly reactive toward organic compounds, i.e hydroxyl radical (*OH). The lower of initial concentration of congo red used, the less of congo red is adsorbed onto the surface of TiO₂ catalyst and the less it will be degraded. While the degradation rate will be faster if the initial concentration of congo red used is greater,

because of the higher concentration of congo red used, the more congo red adsorbed onto the surface of TiO₂ catalyst and the more it will be degraded. However, the use of the initial concentration of congo red solution which is too large will result in the reduced intensity of the photons that reach the surface of TiO₂ catalyst. This is due to the high initial concentration of congo red indicates the high number of congo red molecules as well, so most of the visible light can be absorbed by the congo red molecules. Therefore, the investigation of the initial concentration of congo red is important to do, so it will be known the optimum concentration of congo red where the active surface of TiO₂ works maximum. Standards solution of congo red used were 2, 4, 6, 8, and 10 ppm in 0.1 M NaNO₃. From those standards solution, maximum wavelength can be determined to be used for testing this degradation. The maximum wavelength of congo red solution is based on measurements of 492 nm. The optimum concentration seen from the TiO₂ ability to degrade congo red. The following (Figure 7) is the result of degradation of congo red using 10 ppm photoelectrocatalyst using tungsten lamp (visible light).

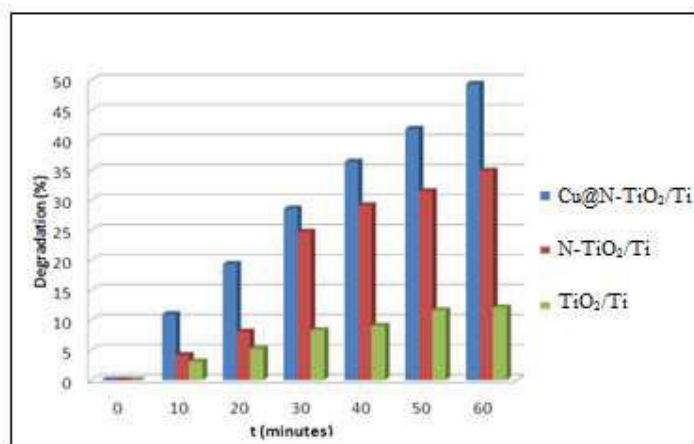


Figure 7
Degradation of Congo red using photoelectrocatalytic method

From the test results Figure 7, it shows that the Cu@-N-TiO₂/Ti can degrade congo red better than TiO₂/Ti (12.11%) or N-TiO₂/Ti (34.87%) which is equal to 49.38%. This is because Cu@-N-TiO₂/Ti are more active in the visible light area. From these data, TiO₂/Ti still provides degradation value, because tungsten lights used still have a little fraction of light with a wavelength of about 390 nm (UV light fraction) which activates TiO₂/Ti that can degrade congo red even with small amounts.

CONCLUSION

Preparation of thin film electrode by TiO₂ and N-TiO₂ on Ti plate then decorated by Cu transition metal using electrodeposition method was successfully fabricated. Activity of TiO₂/Ti, N-TiO₂/Ti and Cu@-N-TiO₂/Ti photoelectrocatalytic in degrading congo red in the visible light area obtained of 12.11%, 34.87% and 49.38%, respectively. The future work will be optimized the performance of the electrode for Chemical Oxygen Demand Sensor.

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