

Original Article

NANO TUBE TITANIUM DIOXIDE / TITANIUM ELECTRODE FABRICATION WITH NITROGEN AND SILVER METAL DOPED ANODIZING METHOD: PERFORMANCE TEST OF ORGANIC COMPOUND RHODAMINE B DEGRADATION

MAULIDIYAH¹, MUHAMMAD NURDIN¹, DWIPRAYOGO WIBOWO¹, ASRUL SANI²

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Halu Oleo, Kendari 93232, Indonesia, ²Department of Mathematics, Faculty of Mathematics and Natural Sciences, Universitas Halu Oleo, Kendari 93232, Indonesia
Email: maulid06@yahoo.com

Received: 02 Feb 2015 Revised and Accepted: 28 Feb 2015

ABSTRACT

Objective: The objective of this study was to prepare the titanium dioxide (TiO₂) by using Anodizing method that was subsequently coated with nitrogen (N) and silver metal (Ag) in the TiO₂/Ti matrix.

Methods: The preparation of N-TiO₂/Ti using the sol-gel method was carried out by adding 3 ml of 5M NH₄Cl as the source of nitrogen with a dip-coating technique. Ag@TiO₂/Ti was prepared using an electrodeposition method with 0.1M AgNO₃ solution in 0.5% EDTA as the source of Ag metal dopants for one minute.

Results: Photocurrent response test using the Linear Sweep Voltametry (LSV) showed that the TiO₂/Ti electrode becomes active when irradiated UV light, while the addition of dopants makes nonmetal (N-TiO₂/Ti) and metal (Ag@TiO₂/Ti) active in visible or UV light irradiation. The analysis of Rhodamine B organic compound degradation by using UV-Vis spectrophotometer showed that the TiO₂/Ti electrode was active in UV light irradiation at degradation rate 0.09 min⁻¹, while N-TiO₂/Ti and Ag@TiO₂/Ti were active in visible light irradiation at degradation rate 0.0372 min⁻¹ and 0.0732 min⁻¹, respectively.

Conclusion: The photoelectrocatalytic activity test to degrade organic compound of Rhodamine B showed that N-TiO₂/Ti and Ag@TiO₂/Ti electrode were able to be active in visible light.

Keywords: TiO₂/Ti, Silver (Ag), Nitrogen (N), Rhodamine B, Anodizing, Photoelectrocatalytic.

INTRODUCTION

The rapid increase in the number of textile industries nowadays has contributed to the large increase in industrial waste generated worldwide [1]. One of the organic compounds commonly used in the textile industry is Rhodamine B [2]. The use of this dye has been banned in Europe since 1984 as the compound belongs to a strong carcinogen. If it accumulates in the water, it will become toxic and harmful to the environment. The Indonesian government itself, through the decree of the Environment Ministry, No. KEP.42/MENLH/10/1996, October 29, 1996, has set for both the rules and the parameters of industrial waste water pollution, which is considered to be harmful to the environment.

Many efforts have been made to address the problem of pollution, for example, by conventional approach such as biological process that uses microorganisms and other approaches like the use of activated carbon. However, the conventional treatment of waste water shows to be less effective because the structure of the organic compounds in the effluent contains one or more relatively stable benzene rings [3].

One of the alternative approaches being developed to degrade a variety of organic waste in pollution management, especially for industrial waste, is a photocatalytic process. Some advantages of this process are that organic pollutants can be degraded into harmless compounds such as water and CO₂ and then the use of chemicals and energy becomes more efficient. The photocatalytic technology with a TiO₂ semiconductor photocatalyst is one way to address liquid waste problem. Photocatalytic process can be carried out at room temperature and the energy requirement is much less [4].

Various modifications and methods to increase the activity of TiO₂ photocatalyst have been studied. Mahoney *et al.* have modified TiO₂ material with the approach to use a molecule template (surfactants) and add an alkali metal as well as a transition metal or a doped metal [5]. Nurdin M. modified TiO₂ by adding with transition metals

such as Cu which increases the photoelectrocatalytic activity [6]. Ruslan *et al.* did the preparation of N-doped TiO₂ by a hydrothermal process and this has succeeded to reduce the energy gap which makes the catalyst active in visible light [7].

TiO₂ photocatalytic performance can be improved electrochemically by combining the photocatalytic and electrochemical processes, known as photoelectrocatalysis [8]. Photoelectrocatalytic method is a method of reaction process between photon and voltage. This mechanism is not much different from the photocatalysis but with the addition of an electric field variable in which it can be observed the relationship between the occurring photocatalytic reaction and the resulting current. Photoelectrocatalytic process has been proven to be one of the very effective methods to degrade organic pollutants in water [9]. Zhang *et al.* developed a photoelectrochemical cell system in which the most important part is the preparation of nano-sized TiO₂ films [10].

The addition of dopants (metal and non-metal) can improve the photocatalytic activity in visible light exposure. Several studies have been carried out to try to make metal immobilization in TiO₂, including immobilization of gold [11], iron [12] and silver [13].

For non-metal immobilization, Aditi *et al.* studied for nitrogen immobilization in TiO₂ [14]. Dopant metal ions have a Fermi energy level which is lower than that of TiO₂ so that the excited electrons can be transferred from the conduction band to insert metal particles on the TiO₂ surface, while the holes in the valence band remained in TiO₂ which in turn they increase the photocatalytic activity [15]. Several researchers have applied the modification of this method to the photocatalytic process.

The objective of this study has two folds: (1) to compare data from TiO₂/Ti photoelectrocatalysis using anodizing method (electrochemical), then doped with non-metal (nitrogen (N)) and metal (silver (Ag)) whose role is to improve the degradation of organic pollutants; (2) based on this system, to study the efficiency of the photoelectrocatalytic

method in degrading Rhodamine B organic compound with variations of TiO₂/Ti, N-TiO₂/Ti and Ag@TiO₂/Ti.

MATERIALS AND METHODS

Preparation of Ti (titanium) plate

The preparation of Ti (titanium) plate was done by cutting Ti plate with 99% purity, 0.5 mm thickness and size 4 cm x 2 cm. Next, it was sanded with 1200 CC fine sandpaper until the surface was clean and shiny, and then washed with the detergent solution, water, and distilled water. The purpose of this treatment was to obtain a clean Ti plate from impurities. After dried in air, Ti plate is then immersed (etching) using a mixed solution of HF, HNO₃, and distilled water in the ratio 1:3:6 for two minutes.

This treatment was aimed to remove fat and oxide layer left on the Ti metal surface. The final stage was to rinse Ti plate with distilled water in order to remove residual etching solution on the Ti plate surface and then dried in air [16].

Preparation of TiO₂ layer with anodizing method

The prepared titanium plate was inserted in the probe which was filled with the electrolyte solution in the form of 0.27M NH₄F and distilled water with a 98% glycerol. The electrolyte solution was produced by dissolving 0.99 g of NH₄F using 4 ml of distilled water and 96 ml of 98% glycerol. Anodizing process was done by placing a Ti plate as anode and Cu plate as cathode by using a magnetic stirrer and a potential difference of 25 volts was provided 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 hours with temperature 500 °C to evaporate the residual electrolyte solution remained on the surface of Ti plate and to obtain crystals of TiO₂ anatase which has a better activity than other types of crystals [16].

TiO₂/Ti doping process with nitrogen (N) using sol-gel method

To dope TiO₂ with nitrogen, sol made from Solution 1 in the form of TiO₂ colloidal solution was prepared by using controlled hydrolysis of 4 mL titanium tetra isopropoxide, 0.5 mL acetyl acetone 15 ml of 99% ethanol. Solution 2 was in the form of 15 ml of 99% ethanol and 2 ml of distilled water with the addition of 1 ml of 0.1 M acetic acid. The solution was mixed and refluxed for 3 hours at temperature 50 °C. Then, it was stirred using a magnetic stirrer for 3 hours at temperature 50 °C, followed by the addition of 5 M NH₄Cl to produce TiO₂ sol containing nitrogen.

The resulting sol was evaporated at room temperature for 48 hours to form a gel. Furthermore, the resulting gel was heated in the oven at temperature 80 °C for 30 minutes. The coating process was done by using the dyeing process in the TiO₂-covered areas of the titanium plate. After performing dyeing technique for 10 minutes, then the plate was lifted out smoothly. Finally, it was calcined in furnace for 15 minutes at temperature of 150 °C.

Doping process with silver metal (Ag) using electrodeposition method

Electrodeposition process of TiO₂/Ti electrode was carried out as follows; metal electrodeposition solution used was AgNO₃ as source of Ag metal dopant [17], 0.17 g of AgNO₃ was dissolved in 100 ml of distilled water, with the addition of EDTA 0.5gr in 100 ml, and then both AgNO₃ and EDTA solutions were mixed. Electrodeposition method was performed for one minute with a potential difference of 1.0 volts. Then, the formed Ag@TiO₂ was stored in a desiccator for 24 hours.

Catalyst characterization

Linear sweep Voltammetry (LSV)

LSV was measured with Linear Sweep Voltammetry using 0.1 M NaNO₃ solution, where 0.85 g of NaNO₃ 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 TiO₂/Ti, N-TiO₂/Ti, and Ag@TiO₂/Ti electrode was tested by illuminating the UV and visible light. The LSV results were used to observe the photoelectrocatalytic activity during the testing process.

Ultra violet-visibel (UV-Vis) spektrofotometer

The measurement using a UV-Vis spectrophotometer was intended to determine the performance of TiO₂/Ti, N-TiO₂/Ti and Ag@TiO₂/Ti electrode on Rhodamine B degradation.

Dye degradation test with photoelectrocatalytic system

Determination of the standard curve of Rhodamine B

The method to determine the standard curve of Rhodamine B was using Rhodamine B solution with a concentration of 0.5; 1.0; 2.0 and 3.0 ppm. The solution was made as follows; 0.01 g of 100 ppm Rhodamine B was dissolved in 100 ml distilled water. Then, 100 ppm Rhodamine B was pipetted for each 5 ml; 10 ml; 20 ml and 30 ml and then each was diluted with 0.1M NaNO₃ in 1000 ml of distilled water. Finally, wavelength and absorbance values were determined from each concentration of Rhodamine B by using UV-Vis spectrophotometer.

Dye degradation test of rhodamine B

Dye degradation test of Rhodamine B for each 0.5; 1.0; 2.0 and 3.0 ppm (+0.1M NaNO₃) was carried out by using the Multi Pulse Amperometry (MPA) with a ten-minute duration and a potential difference of 0.5 volts in a state of UV and visible light variation. Every ten-minute span within one hour period the absorbance measurement was performed by using a UV-Vis spectrophotometer to determine the decrease in the dye concentration. The measurements were made for TiO₂/Ti, N-TiO₂/Ti, and Ag@TiO₂/Ti electrodes. These results were plotted; the absorbance against the degradation rate constant of Rhodamine B compound.

RESULTS AND DISCUSSION

Fabrication of TiO₂/Ti thin layer through anodizing method

To produce TiO₂ thin layer on the surface of Ti plate, an anodizing method has been carried out for four hours with a potential difference of 25.0 volts. The most important part in the development of photoelectrochemical cell system is the preparation of nano-sized TiO₂ films [18]. The high voltage in producing TiO₂/Ti thin layer results in a formed structure which tends to look like nodules or particulates. In general, the anodizing process will form a nanomaterial with size between 1 to 100 nm [19].

Anodizing is an electrochemical oxidation process that will result in the addition of a layer film on the top of metal surface. Plate which has been in anodizing was then calcined at temperature 500 °C for 1.5 hours. The calcination process aims to evaporate organic solvents which are trapped in a titanium plate. In addition, Zhang et al. reported that the calcination process is intended to obtain crystals of TiO₂ anatase with a better photocatalytic activity than the other types of crystals for a calcination temperature at about 500 °C [10].

This is due to the crystals of anatase that has a larger surface area and greater active side such that they absorb light better than any kind of rutile crystals. The band gap energy of anatase structure is 3.2 eV which is equivalent to 388 nm. This band gap energy indicates how much energy is required for the transition of electrons from the valence to conduction band.

The appearance of pores and void spaces on the surface of TiO₂ layer is the first step for the formation of nano-tube [20] and the high acidity on the tube base helps the pore in forming tube structure [21]. This technique will result in TiO₂/Ti formation on the surface of Ti plate. Fig. 1 shows visually that the TiO₂ layer produced by anodizing method is quite homogeneous with a good layer thickness.

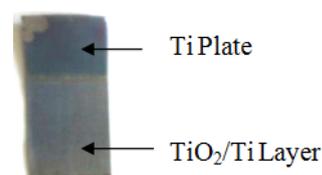


Fig. 1: The results of anodizing process on a Ti plate to produce TiO₂

Doping TiO₂/Ti with nitrogen (N) using sol-gel method

N-TiO₂/Ti material was prepared by using the sol-gel method. Sol-gel method is the most common used to synthesize non-metal or metal TiO₂ doped nanoparticles because the sol-gel method has many advantages, for example, in terms of purity, homogeneity, flexibility, easily controlled, economically. Based on the report of Asahi *et al.* sol-gel approach can produce TiO₂ nanoparticles doped with nitrogen in 1% to 20% concentration [22].

Sol-gel was synthesized by using titanium tetra isopropoxide base material (TTIP) as a matrix, acetyl acetate which acts as chelating ligands will produce an exothermic reaction and makes the yellow solution. To dope with nitrogen, the formed sol was added 5M NH₄Cl as a source of nitrogen atoms. This process aims to reduce the energy (band) gap, in which the nitrogen atom is expected to replace some of the positions of oxygen atoms in the TiO₂ semiconductor [23].

The formed TiO₂ by using the anodizing method was then coated by using a dip-coating technique in the formed sol-gel. The dip-coating method has been widely used in the formation of a thin film layer on the surface because the resulting thin film has good transparency. After the dip-coating process was completed, it was calcined at temperature of 150 °C. Lockman *et al.* has reported the anatase crystalline form which was observed in TiO₂ heating temperature starting from 120 °C and it reaches a perfect form at temperature of 500 °C. [23] This temperature choice aims to bind the N-TiO₂ layer more powerful such that the adhesive force between a N-TiO₂ thin layer and formed TiO₂ layer on Ti plate becomes better and this eliminates the excess of water solvent as well as forms crystalline phase TiO₂ anatase.

This technique is a process in incorporating other atoms (dopants) for the purpose of improving the properties of the material designation, such as increasing the conductivity of semiconductors, gaining semiconductor with only one charge carrier (electron or hole), or getting a semiconductor with a lower energy gap with origin. Doping N-TiO₂ showed a significant photocatalytic activity in various types of reaction under visible light region and it has a good stability [25]. Visually, the result obtained in the N-TiO₂ doping technique is shown in fig. 2.

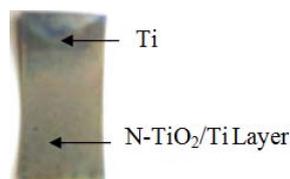


Fig. 2: The surface of TiO₂/Ti which has been immobilized N-TiO₂

Doping TiO₂/Ti with metal silver (Ag) by using the electrodeposition method

Ag doping was done by the electrodeposition method. Ag metal was deposited on the TiO₂/Ti surface which was previously made by

using the anodizing method. Ag metal was used because it can act as a trap electron and it can be expected to reduce the recombination of electrons and holes [26].

Electrodeposition of Ag metal on TiO₂/Ti surface was performed by using 0.1% AgNO₃ electrolyte in EDTA solution which served to bind the metal and control the number of Ag metal attached to the formed TiO₂ [26]. Electrodeposition process was done by connecting the TiO₂/Ti electrodes (cathode) with a negative current source, while the Cu plate (anode) was connected to the positive current source with the potential current of 1.0 volts for one minute. With the electrodeposition process, The Ag metal attached to the TiO₂ surface which has been formed through anodizing process, see fig. 3.

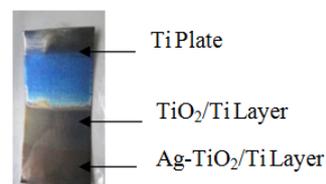


Fig. 3: Immobilized TiO₂/Ti surface with Ag metal

The Construction of a photoelectrocatalytic reactor

The obtained electrodes were then used in the photoelectrocatalytic reactor. The technique to provide a reactor was using UV and visible light in a box size of 60 cm x 30 cm where inside the box was covered by aluminum foil. The scheme of photoelectrocatalytic reactor can be seen in fig. 4.



Fig. 4: A Photoelectrocatalytic reactor

Determination of the electrode activity

The photocurrent is the observed current when the electrode is irradiated by UV or visible light. This current is also the measurement of the transfer rate among semiconductor/electrolyte surfaces. Thus, it can be also used to measure the rate of OH radical formation on the catalytic surface. In this study, the measurement of the photocurrent as a potential function was performed by using Linear Sweep Voltammetry (LSV) technique in an electrolyte solution of 0.1 M NaNO₃ connected to portable potentiostat.

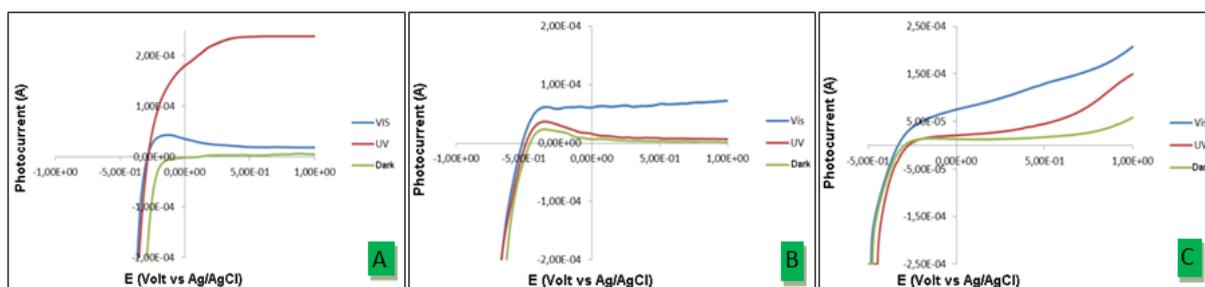


Fig. 5: Linear Sweep Voltammetry (LSV) Graph; (A) TiO₂/Ti electrode, (B) N-TiO₂ electrode, and (C) Ag@TiO₂/Ti electrode

Fig. 5 (A), LSV of produced TiO_2/Ti electrode has the highest activity when it was irradiated by UV light. This is consistent with the theory that TiO_2 has photoelectrocatalytic activity when it is irradiated by UV light, which is active at a wavelength of ≤ 388 nm and at Energy gap (E_g) of 3.2 eV. The TiO_2 matrix without dopants did not respond in the dark and it gave a response to the light current when irradiated with visible light as the energy obtained from the visible light is smaller to activate TiO_2/Ti .

Fig. 5. (B) shows LSV of produced N-TiO_2 by the photoelectrocatalytic activity. When illuminated the UV light, photocurrent response observed was near zero while it has a good intensity when the electrode was irradiated in visible light. Activity of $\text{N-TiO}_2/\text{Ti}$ electrode shows the visible light irradiation which proved that doping N in TiO_2 has a good activity and able to be photoelectrocatalytic in visible light irradiation.

Fig. 5. (C) shows that LSV of produced Ag@TiO_2 indicates a good activity when it was irradiated with visible light and the resulting response proved that the $\text{Ag@TiO}_2/\text{Ti}$ electrode was able to work with visible light irradiation. When the electrons moved from the valence to conduction band, they were trapped by Ag metal which is enable to minimize the recombination between electrons and holes such that the energy used with the visible light irradiation is much smaller. Likewise the UV light irradiation on the Ag@TiO_2 , electrons are able to move from the valence to conduction band so that it has photoelectrocatalytic activity, however, it showed that UV light irradiation is lower than the visible light irradiation.

Degradation test of organic compound Rhodamine B using TiO_2/Ti , $\text{N-TiO}_2/\text{Ti}$ and $\text{Ag@TiO}_2/\text{Ti}$ electrodes

Determination of organic compound Rhodamine B using UV-Vis spectrophotometer

Colorful compounds can be measured by UV-Vis spectrophotometer as it has chromophore group that gives color to the compound. This is due to that each molecule is able to absorb light in accordance with the required wavelength and energy to undergo an electron transition from the ground state to an excited state. The maximum wavelength of Rhodamine B was obtained by 554 nm.

In this case, the electron transition has occurred in which it is involved the π electrons conjugating along the chromophore group of heterocyclic Rhodamine B compound by absorbing energy and this becomes an evidence. This compound shows a red color because of the transition in the visible light region. A calibration curve was obtained by plotting the concentration versus the absorbance and the equation is as follows.

$$y = 0,2018x + 0,0011 \dots\dots\dots (1)$$

Degradation test for organic dye rhodamine B using TiO_2/Ti , $\text{N-TiO}_2/\text{Ti}$ and $\text{Ag@TiO}_2/\text{Ti}$ electrodes

The photoelectrocatalytic system is a combination of electrochemical process with photocatalyst, where the TiO_2/Ti , $\text{N-TiO}_2/\text{Ti}$ and $\text{Ag@TiO}_2/\text{Ti}$ electrodes work if they are subjected to UV or visible light in which this can give a pair of electrons and positive holes (h^+). The positive hole can initiate the oxidation reaction at the electrode surface, while the electrons flow through the back contact to the counter electrode and they are transferred to the electron catcher being present in the solution. The electron flow can be observed as a current proportional to the light and the amount of organic matter content of Rhodamine B in solution.

The electron-hole separation will increase the provision of positive bias potential on the working electrode immersed in solution, as a result of the formation of the electrical field near the interface, so that the surface of the working electrode is anodic. In this situation the recombination of electrons and holes by transferring to the solution through the auxiliary electrode is cathodic [8]. With this way, the potential difference can increase the efficiency of separation charge so that the formation of OH radicals that accelerate the process of organic compound degradation of Rhodamine B becomes higher.

Testing the degradation of organic compound Rhodamine B was performed using Rhodamine B concentration of 0.5 ppm, 1 ppm, 2 ppm and 3 ppm, with treatment as photolysis and also photoelectrocatalysis. Photolytic method is a method used to degrade a compound by using only radiation, as shown in fig. 6.

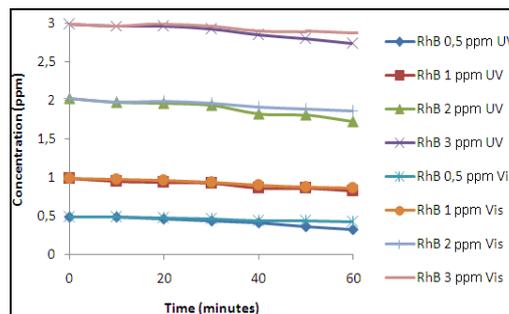


Fig. 6: Graph of Rhodamine B photolysis when irradiated by UV and visible light

Fig. 6 shows that the concentrations of Rhodamine B when irradiated in UV and visible light photolytically decreases slowly, due to the oxidation reaction and the broken bond of Rhodamine B. According to Wilhelm and Stephan when Rhodamine B is illuminated by UV or visible light and the oxidation reactions occurs on its organic compound, the bond break in Rhodamine B occurs [28].

Photocatalyst is a catalyst that works with the help of light (photons). With the photocatalytic method the concentration of Rhodamine B decreases as shown in fig. 7. In this case, the TiO_2 semiconductor is a photocatalyst that absorbs photon energy in the UV region.

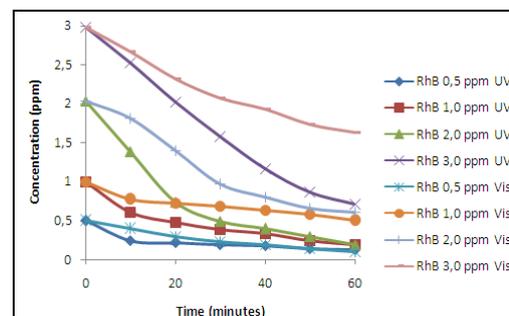


Fig. 7: Graph of the decrease of the rhodamine B concentration in TiO_2/Ti photocatalysis

Compared to the photoelectrocatalytic method of TiO_2/Ti , the potential difference of 0.5 volts on the various types of concentration and light showed that the activity in degrading organic compound of Rhodamine B using a portable potentiostat is faster than that using TiO_2 photocatalyst. Fig. 8 shows a significant decrease in the concentration of Rhodamine B by using TiO_2/Ti catalyst.

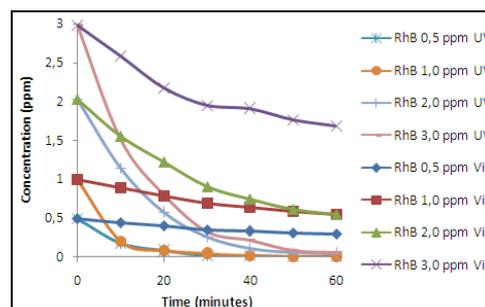


Fig. 8: Graph of the decrease of Rhodamine B concentration in photoelectrocatalysis by using a TiO_2/Ti catalyst

It is clearly shown in fig. 6, fig. 7 and fig. 8 that there was a difference of degradation rate obtained from the photolytic, photocatalytic and photoelectrocatalytic process. Photolytic process had the lowest degradation activity compared to other two processes where Rhodamine B was illuminated with photons that may break the bond of the Rhodamine B compound. The photocatalytic process has shown a good degradation activity although it is not as good as the photoelectrocatalytic process. This is because this photoelectrocatalytic process sometimes suffers from the electron-hole recombination so that the active species can be reduced and results in a low degradation activity. Photoelectrocatalytic process is basically not much different from the photocatalytic process. In the photoelectrocatalytic process, electrons (electric current) were applied such that this prevents the electron-hole recombination when illuminated with light. The results showed that the molecular degradation of Rhodamine B dye can be more efficient by using the photoelectrocatalytic method compared to both photolytic and photocatalytic method.

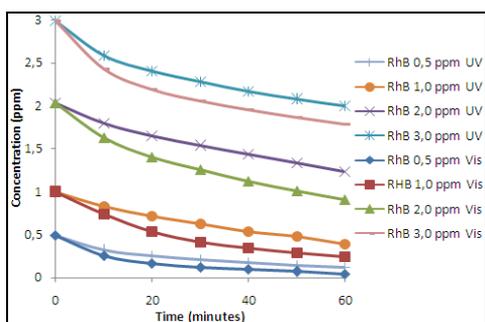


Fig. 9: Graph of Rhodamine B degradation using the N-TiO₂/Ti catalyst

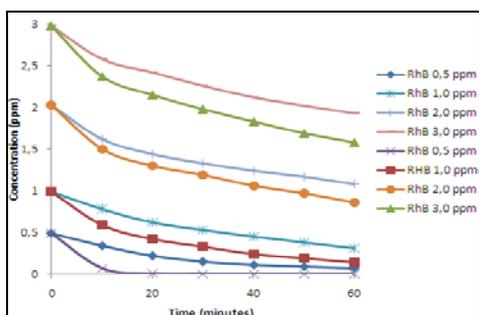


Fig. 10: Graph of Rhodamine B degradation using an Ag@TiO₂/Ti catalyst

Degradation by using N-TiO₂/Ti electrodes has a good activity in degrading Rhodamine B compound. The decrease of the

concentration indicates that N-TiO₂/Ti is able to work actively in the visible light irradiation, see fig. 9. This shows that N-TiO₂/Ti can reduce the band gap energy so that the light energy needed to create the electrons experiencing a transition state from the valence band to the conduction band becomes small due to the relatively small distance between the valence band and the conduction band.

Degradation using Ag@TiO₂/Ti electrode produces a good activation in degrading the Rhodamine B compound in visible light irradiation. Fig. 10 proves that Ag@TiO₂ is able to work well in visible light as silver can trap photogenerated electrons from the semiconductor and allows holes to form hydroxyl radicals which produce degrading reaction of organic species [29].

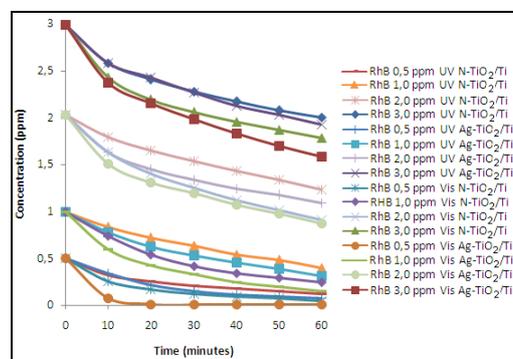


Fig. 11: Graph of Rhodamine B Comparison using of N-TiO₂/Ti and Ag@TiO₂/Ti catalysts

Fig. 11 shows that the results of the Rhodamine B degradation using Ag@TiO₂/Ti electrodes is more active than those using N-TiO₂/Ti in degrading Rhodamine B at visible light irradiation. In this case, Ag@TiO₂/Ti prevented the of electron recombination while N-TiO₂/Ti reduced only the band gap of TiO₂/Ti.

In addition, the preparation of Ag@TiO₂/Ti with the electrodeposition method is much thinner than that with the N-TiO₂/Ti technique. This was shown by the decrease of the Rhodamine B concentration. According to Ibhaddon *et al.* doping technique produces a good photocatalytic activity, homogeneous and transparent flat layer as well as a smaller particle size [30].

Kinetic reaction of photoelectrocatalysis degradation of Rhodamine B using TiO₂/Ti, N-TiO₂/Ti dan Ag@TiO₂/Ti electrodes

By the Langmuir-Hinshelwood equation, the reaction rate constant can be determined by plotting $\ln(c_t/c_0)$ against irradiation time (t) which gives a straight line with a slope k . This is the concentration curve with respect to time for conditions N-TiO₂/Ti and Ag@TiO₂/Ti photoelectrocatalysis in various concentrations. From the curve the value of the degradation rate constant (K_d) is obtained as shown in table 1.

Table 1: Rhodamine B degradation rate constants for each variation of concentration with respect to irradiation of UV and visible light of TiO₂/Ti, N-TiO₂/Ti and Ag@TiO₂/Ti in photoelectrocatalysis

Concentration (ppm)	K_d UV TiO ₂ /Ti (M ⁻¹ min ⁻¹)	K_d Vis TiO ₂ /Ti (M ⁻¹ min ⁻¹)	K_d UV N-TiO ₂ /Ti (M ⁻¹ min ⁻¹)	K_d Vis N-TiO ₂ /Ti (M ⁻¹ min ⁻¹)	K_d UV Ag@TiO ₂ /Ti (M ⁻¹ min ⁻¹)	K_d Vis Ag@TiO ₂ /Ti (M ⁻¹ min ⁻¹)
0.4970	0.0839	0.0088	0.0223	0.0372	0.0331	0.0732
0.9945	0.0900	0.0102	0.0149	0.0233	0.0186	0.0307
2.0393	0.0714	0.0227	0.0080	0.0128	0.0096	0.0130
2.9945	0.0675	0.0094	0.0062	0.0078	0.0069	0.0098
Mean (\bar{x})	0.0782	0.0127	0.0128	0.0202	0.0170	0.0316
Standard deviation (Sd)	0.0050	0.0028	0.0033	0.0057	0.0050	0.0119

As shown in table 1, the value of degradation rate constant gets smaller as the concentration of Rhodamine B dye solution increases, which indicates that the photoelectrocatalytic process becomes faster in the dye solution with a lower concentration. This is due to that using the same number of catalysts can result in the same number of the active-

surface sides. Consequently, Rhodamine B dye solution with lower concentrations can be entirely absorbed on the electrode surface in which the photoelectrocatalytic process can become more efficiently. Meanwhile, with the higher concentrations of Rhodamine B, the degradation rate constant becomes decreased. According to Tian *et al.* the decrease of

degradation rate constant is affected by the active site of the catalyst in generating O₂ and OH radicals, in degrading the tested compound and in absorbing the UV or visible light of the tested compound, which thereby reduces the effectiveness of degradation [31]. There is an ascertain crystallinity effect which is formed variably and this affects on the degradation rate constant due to the limited surface area of the catalyst. The value of TiO₂/Ti degradation rate constant tends to be good in UV light irradiation whereas in visible light irradiation it becomes less active, due to the effectiveness of TiO₂ to receive energy from UV light in order to move electrons from the valence band to conduction band so that the formed hole and electron species can degrade organic compounds. The Ag@TiO₂/Ti formation tends to be higher than that the active N-TiO₂/Ti in visible light irradiation. This is because of the Ag thin layer formation on the TiO₂/Ti surface so that it is capable to trap the photogenerated electrons from semiconductor and allows holes to form the hydroxyl radical and transfers electron more rapidly that produces degradation reactions of organic species, meanwhile the formed N-TiO₂/Ti layer with dip-coating method from sol gel may be due to slow electron transfer from the semiconductor layer surface to the bulk, causing a slowdown because the layer is not homogeneous and losses sol-gel coating when inserted to the test probe.

CONCLUSION

By using the anodizing method, the formation of TiO₂ nano tube layer on the surface of Ti plate which was subsequently coated with nitrogen (N) and silver (Ag) produces the activities of photocurrent response of N-TiO₂/Ti and Ag@TiO₂/Ti electrode which were able to be active in visible light, while the TiO₂/Ti electrode is capable to be active in UV light. The results of photoelectrocatalysis activity test to degrade organic compound of Rhodamine B showed that the degradation rate constants of TiO₂/Ti electrode when irradiated were 0.0227 min⁻¹ in visible light and 0.09 min⁻¹ in UV light which were active in UV light irradiation. Meanwhile, N-TiO₂/Ti and Ag@TiO₂/Ti have a good activity to degrade the organic compound of Rhodamine B when irradiated; for N-TiO₂/Ti, the degradation rate constants were 0.0372 min⁻¹ if irradiated by visible light and 0.0223 min⁻¹ by UV rays and for Ag@TiO₂/Ti the degradation rate constants were 0.0732 min⁻¹ if irradiated by visible light and 0.0331 min⁻¹ by UV light.

ACKNOWLEDGEMENT

We acknowledge the financial support of the Ditlitabmas-Dikti-Ministry of Research, Technology and Higher Education, the Republic of Indonesia.

CONFLICT OF INTERESTS

Declared None

REFERENCES

- Daghrir R, Drogui P, Robert D. Photoelectrocatalytic technologies for environmental applications. *J Photochem Photobiol: A* 2012;238:41-52.
- Merck Index. Chemistry Constant Companion, Now with a New Addition. Ed 14th. 1410, 1411, Merck & Co Inc, Whitehouse Station; 2006.
- Safni, Maizatisna, Zulfarman, Sakai T. Degradasi zat warna naphtol blue black secara sonolisis dan fotolisis dengan penambahan TiO₂-Anatase. *J Kris Kim* 2007;1:1.
- Guaraldo TT, Pulcinelli SH, Zanoni MVB. Influence of particle size on the photoactivity of Ti/TiO₂ thin film electrodes, and enhanced photoelectrocatalytic degradation of indigo carmine dye. *J Photochem Photobiol: A* 2011;217:259-66.
- Mahoney L, Koodali RT. Modified TiO₂ material with the approach to use a molecule template (surfactants). *Materials* 2014;7:2697-746.
- Nurdin M. Preparation, Characterization and Photoelectrocatalytic activity of Cu@N-TiO₂/Ti Thin Film Electrode. *Int J Pharma Bio Sci* 2014;5:360-9.
- Ruslan Abd, Wahid Wahab, Nafie NL, Nurdin M. Synthesis and characterization of electrodes N-TiO₂/Ti for chemical oxygen demand sensor with visible light response flow. *Int J Sci Technol Res* 2013;2:220-4.
- Nurdin M, Wibowo W, Supriyono, Febrian MB, Surahman H, Krisnandi YK, *et al.* Pengembangan metode baru penentuan chemical oxygen demand (COD) Berbasis sel fotoelektrokimia: Karakterisasi elektroda kerja lapis tipis TiO₂/ITO. *J Makara Sains* 2009;13:1-8.
- Ye S, Shen S, Ye L, Song X, Luo S. Enhancement of the photoelectrocatalytic activity of TiO₂/ACF for ethylene removal by Ag nanoparticles synthesized by γ -radiolysis. *Mater Sci Semicond Process* 2014;27:397-403.
- Zhang J, Zhou B, Zheng Q, Li J, Bai J, Liu Y, Cai W. Photoelectrocatalytic COD determination method using highly ordered TiO₂ nanotube array. *Water Res* 2009;43:1986-92.
- Yogi C, Kojima K, Wada N, Tokumoto H, Takai T, Mizoguchi, *et al.* Photocatalytic degradation of methylene blue by TiO₂ Film and Au particles-TiO₂ composite film. *Thin Solid Films* 2008;516:5881-4.
- Wang DB, Yu F, Zhou C, Wang W, Liu. Synthesis and characterization of anatase TiO₂ nano tubes and their use in dye-sensitized solar cells. *Materials Chem Phys* 2008;113:602-6.
- Whang H, Huang M, Hseih, J Chen. Laser induced silver nanoparticles on Titanium di oxide for photocatalytic degradation of methylene blue. *Int J Mol Sci* 2009;10:4707-18.
- Aditi R, Gandhe, Julio, B Fernandes. A simple method to synthesize N-doped rutile titania with enhanced photocatalytic activity in sunlight. *J Solid State Chem* 2005;178:2953-7.
- Zaleska A. Doped-TiO₂: A Review. *Recent Pat Eng* 2008;2(3):157-64.
- Nurdin M, Maulidiyah. Fabrication of TiO₂/Ti Nanotube electrode by anodizing method and its application on photoelectrocatalytic system. *Int J Sci Technol Res* 2014;3:122-6.
- Konjari RS, Jacob AA, Jayanthi S, Ramalingam C, Ethiraj SA. Investigation of biogenic silver nanoparticles green synthesized from carica papaya. *Int J Pharm Pharm Sci* 2015;7(3):107-10.
- Quan X, Ruan X, Zhao H, Chen S, Zhao Y. Photoelectrocatalytic degradation of pentachlorophenol in aqueous solution using a TiO₂ nanotube film electrode. *Environ Pollution* 2007;147:409-14.
- Ou H-H, Lo S-L. Review of titania nanotubes synthesized via the hydrothermal treatment: Fabrication, modification, and application. *Sep Purif Technol* 2007;58:179-91.
- Bai J, Zhou B, Li L, Liu Y, Zheng Q, Shao J, *et al.* The formation mechanism of titania nanotube arrays in hydrofluoric acid electrolyte. *J Mater Sci* 2008;43:1880-4.
- El ruby Mohamed A, Rohani S. Modified TiO₂ nanotube arrays (TNTAs): progressive strategies towards visible light response photoanode, a review. *Energy Environ Sci* 2011;4:1065-86.
- Asahi R, Morikawa T, Ohwaki T, Aoki K, Taga Y. Visible-Light photocatalysis in nitrogen-doped titanium oxides. *Sci* 2001;293:269-71.
- Sun L, Cai J, Wu Q, Huang P, Su Y, Lin C. N-doped TiO₂ nanotube array photoelectrode for visible-light-induced photoelectrochemical and photoelectrocatalytic activities. *Electrochim Acta* 2013;108:525-31.
- Lockman Z, Ismail S, Sreekantan S, Schmidt-Mende L, MacManus-Driscoll JL. The rapid growth of 3 μ m long titania nanotubes by anodization of titanium in a neutral electrochemical bath. *Erschienen: Nanotechnol* 2010;2:1-6.
- Zhao K, Wu Z, Tang R, Jiang Y. Preparation of highly visible-light photocatalytic active N-Doped TiO₂ microcuboids. *J Korean Chem Soc* 2013;57:489-92.
- Cheng B, Le Y, Yu J. Preparation and enhanced photocatalytic activity of Ag@TiO₂ core-shell nanocomposite nanowires. *J Hazard Mater* 2010;177:971-7.
- Zhao X, Guo L, Qu J. Photoelectrocatalytic oxidation of Cu-EDTA complex and electrodeposition recovery of Cu in a continuous tubular photoelectrochemical reactor. *Chem Eng J* 2014;239:53-9.
- Wilhelm P, Stephan D. Photodegradation of rhodamine B in Aqueous solution via SiO₂@TiO₂ nano-spheres. *J Photochem Photobiol A: Chem* 2007;185:19-25.
- Leng WH, Zhu WC, Ni J, Zhang Z, Zhang JQ, Cao CN. Photoelectrocatalytic destruction of organics using TiO₂ as photoanode with simultaneous production of H₂O₂ at the cathode. *Appl Catal: A* 2006;300:24-5.
- Ibhadon AO, Fitzpatrick P. Heterogeneous photocatalysis: recent advances and applications. *Catalysts* 2013;3:189-218.
- Tian M, Wu G, Adams B, Wen J, Chen A. Kinetics of Photoelectrocatalytic Degradation of Nitrophenols on Nanostructured TiO₂ Electrodes. *J Phys Chem C* 2008;112:825-31.