Chalcogenide material as high photoelectrochemical performance Se doped TiO$_2$/Ti electrode: Its application for Rhodamine B degradation

M Z Muzakkar$^1$, A A Umar$^2$, I Ilham$^1$, Z Saputra$^1$, L Zulfikar$^1$, M Maulidiyah$^1$, D Wibowo$^3$, R Ruslan$^4$ and M Nurdin$^{1,*}$

$^1$Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Halu Oleo, Jl. HEA Mokodompit Kampus Hijau Bumi Anduonohu, Kendari 93232 – Southeast Sulawesi, Indonesia.
$^2$Institute of Microengineering and Nanoelectronics, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia
$^3$Department of Environmental Engineering, Universitas Muhammadiyah Kendari, Kendari 93127 – Southeast Sulawesi, Indonesia.
$^4$Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Tadulako, Palu 94118 – Central Sulawesi, Indonesia

Email: mnurdin06@yahoo.com

Abstract. The objective of this research is to synthesize the Selenium (Se) doped TiO$_2$/Ti electrode as a novel chalcogenide material by anodizing and dip-coating method. The electrode was applied for Rhodamine B (RhB) degradation test in high-photoelectrocatalytic (PEC) performance. It is found out that the morphology and element containing on Se-TiO$_2$/Ti electrode has honeycomb structure with the element composition of Ti (51.09%), O (36.91%), and Se (12.00%), respectively. In addition, the PEC response test using Linear Sweep Voltammetry (LSV) showed that the optical properties of Se-TiO$_2$/Ti electrode was active under visible light, meanwhile the TiO$_2$/Ti was active under ultraviolet (UV) light. The PEC test using Multi Pulse Amperometry (MPA) technique was exhibited that the 5 ppm RhB corresponded to the degradation of 73.27%.

1. Introduction

In the last decades, the industrial wastewater has been interesting to be studied because of damage and wastewater pollution in the aquatic environment [1, 2]. Wastewater is a water substance disposed after primary used. Actually, the existence of wastewater can be tolerated if it has low concentration and kept to the threshold of industrial wastewater quality standard based on Environment Minister Regulation. One of the types of hazardous textile industry wastes is Rhodamine B (RhB) [3].

RhB dye is a synthetic dye commonly used in textile and paper industry. The danger of RhB contamination causes accumulation in our body, leading to liver cancer, renal enlargement, and physiological disorders [4]. In the aqueous system, it can affect the water pH which disrupting microorganisms in the aqueous environment [5, 6]. A new innovation in handling this problem is needed in order to reduce the impact of environmental pollution [7, 8].
The various methods of wastewater treatments in order to make the environment safe such as filtration, adsorption, oxidation/reduction, coagulation, and microbiology [9]. However, today the people only to localize the contaminants in filter equipment and adsorbent material to resolve the wastewater. It is assumed that the most effective method for wastewater treatments is by reduction-oxidation (redox) process by photocatalytic to reduce organic dyes in aquatic [10-14].

The principle of photocatalytic system uses a catalyst-assisted and photon irradiation for electron excitation in order to redox initiation mechanisms [15, 16]. Titanium dioxide (TiO$_2$) is one of the most used photocatalyst material due to a band gap of 3.22 eV and high stability, non-toxic, good optical properties, eco-friendly, and durability [17-20]. The disadvantages from TiO$_2$ that only active under ultraviolet (UV) light, thereby the limits of performance using sunlight irradiation. It can achieve high performance under sunlight irradiation (visible light) by adding the dopant into TiO$_2$ crystalline to improve the optical properties [21-23].

The modification of TiO$_2$ photocatalyst has been optimized by inserting metals and non-metal dopants. The utilization of Iron (Fe) and Silver (Ag) metals was able to decrease TiO$_2$ band gap energy and increase photocatalyst activity [24, 25]. Unfortunately, the metals dopant used to TiO$_2$ doped was lead for high cost, rare materials, and toxicity [26]. Whereas non-metal dopants was used by using nitrogen (N) has been widely applicable [3]. A novel materials doped in TiO$_2$ using metals chalcogenide group because it is high stability, electropositive element, and photoconductive as a catalyst. Hereby, we study of Selenium (Se) doped TiO$_2$ that the one famous element in chalcogenide group showed the high absorption properties [27]. This is related to the decrease of material band-gap energy and would be activated visible light range optimally.

In another hand, we optimized the high performance by combining the photocatalyst and electrochemical as PEC system has been proved an effective method for degrading the organic pollutants in water. The Se-TiO$_2$/Ti composite preparation was applied in PEC system and characterization of a high-performance electrode for RhB dyes degradation has studied in this paper.

2. Experimental Methods

2.1. Apparatus and chemical
The material used were titanium (Ti) plate (1 mm thickness, purity 99.98%, was purchased from Shanxi Yuanlian Rare Metals Limited (China), hydrofluoric acid (HF) (Merck, Germany), nitric acid (HNO$_3$) (Merck, Germany), glycerol (C$_3$H$_8$O$_3$) (Sigma-Aldrich), ammonium fluoride (NH$_4$F) (Sigma-Aldrich), selenious acid (H$_2$O$_2$Se) 98.1% (Shanghai Runwu Chemical Technology Co., Ltd.), ethylene glycol (C$_2$H$_4$O$_2$) (Sigma-Aldrich), sodium nitrate (NaNO$_3$) (Sigma-Aldrich), titanium tetraisopropoxide (C$_4$H$_8$O$_4$Ti) (Sigma-Aldrich), and distilled water.

2.2. Titanium (Ti) plate preparation and anodization method
Ti plate was prepared by cutting to 4 cm × 0.5 cm then sanded using a fine sandpaper (1200 cc) to obtain clean and shiny surface. It was then washed by using detergent, distilled water, and dried in ambient temperature. Subsequently, the Ti plate was immersed (etching) using mixture of HF, HNO$_3$, and distilled water in ratio 1.0: 3.0: 6.0 for 2.0 min. The final step, Ti plate is rinsed with distilled water to remove the residual etching solution on Ti plate surface and dried in ambient temperature.

The anodization process was conducted using Ti plate was inserted in probe glass containing the electrolyte solution of glycerol: distilled water (24: 1) and 0.27 M NH$_4$F as corrosion agent. Anodizing was conducted by placing Ti plate as anode and Cu plate as cathode using 25 volts potential, then connected to power supply. Anodizing process was carried out for 4 hours and calcinated for 1.5 hours at 500°C to evaporate the remaining electrolyte solution on Ti plate surface and to obtain the TiO$_2$ nanotube arrays (TiO$_2$-NTAs) [22].
2.3. Preparation of Se-TiO$_2$/Ti sol-gel
Preparation of Se-TiO$_2$/Ti sol-gel consists of 2 stages. The first, sol Se-TiO$_2$ was prepared by mixing 2 solution types: Solution A was prepared by dissolving 0.43 grams of H$_2$O$_3$Se 98.1% into 15.0 mL C$_2$H$_6$O$_2$, then stirring until dissolved. Solution B by dissolving of 4.0 mL C$_{12}$H$_{28}$O$_4$Ti into 15.0 mL of C$_2$H$_6$O$_2$. The solution mixture was refluxed for 5.0 hours at 60°C with stirring by magnetic stirrer to obtain a sol Se-TiO$_2$. It is heated to remove the solvent at a temperature of 80°C for 1 hour to produce a Se-TiO$_2$ sol-gel. The coating process was carried out by dip-coating method on TiO$_2$/Ti immersed into Se-TiO$_2$ sol-gel for 10 min and calcined at 200°C for 15 minutes to obtain the Se-TiO$_2$/Ti electrode.

2.4. Characterizations

2.4.1. Diffuse Reflectance Spectrophotometry UV-Visible (DRS UV-Vis). DRS UV-Vis Measurements was conducted to determine the absorption wavelength of catalyst in wavelength range from 200 to 800 nm. Based on obtained spectra, band gap energy of Se-TiO$_2$/Ti composites can be calculated.

2.4.2. Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX). SEM-EDX measurement was conducted to investigate Se-TiO$_2$/Ti composite surface morphology which formed by anodizing and dip-coating methods. SEM equipped with EDX, elemental composition of composite can be determined to validate doping process of Se on TiO$_2$/Ti plate has been successful.

2.4.3. Linear Sweep Voltammetry (LSV). LSV method was carried out by using electrolyte solution of 0.1 M NaNO$_3$. The potential response was obtained by using -1.0 Volt to 1.0 Volt and scan rate of 1.0x$10^{-4}$ V/s. The TiO$_2$/Ti and Se-TiO$_2$/Ti electrodes were tested by light variations i.e. UV and visible lights irradiation to determine their performance in different light irradiation.

2.5. Degradation test by photoelectron chemical system
The PEC test was carried out by using 5.0 mg L$^{-1}$ RhB solution in 0.1 M NaNO$_3$ as electrolyte solution. Degradation was conducted by Multi Pulse Amperometry (MPA) method by three electrodes (working electrode (TiO$_2$/Ti and Se-TiO$_2$/Ti)); Counter electrode (Pt); Reference electrode (Ag/AgCl)) in a PEC reactor with potential bias of 0.5 Volt under UV and visible lights irradiation. The illustration three electrodes were connected with potentiostat (DY2100B-Digi-Ivy.Inc) can be seen in figure 1.

![Figure 1. Schematic of PEC system (1) probe, (2) Pt counter electrode, (3) working electrode TiO$_2$/Ti and Se-TiO$_2$/Ti, (4) Ag/AgCl reference electrode, (5) UV light source, (6) magnetic bar, (7) magnetic stirrer](image-url)
3. Results and Discussion

3.1. Fabrication of Se-TiO$_2$/Ti as Working Electrode

The TiO$_2$-NTAs was fabricated on Ti plate by anodic oxidation in the electrolyte solution of C$_2$H$_6$O$_2$ and 0.27 M NH$_4$F at the potential bias of 25 Volts for 4 hours. The utilization of C$_2$H$_6$O$_2$ as oxidation control for stability electron transfer in aqueous solution, and provider the -OH group to a high oxidation process [26]. The glycerol solution after used should be replaced to obtain the TiO$_2$-NTAs crystalline.

Meanwhile, the NH$_4$F solution was applied to form honeycomb (nanotubes) on Ti plate because it will react with fluorine ions (F$^-$) and contribute to the controlling formation to form the TiF$_6^{2-}$ as template agent. The high surface area of TiO$_2$-NTAs was fabricated to examine photocatalyst performance will be more effective in a degradation process. Then, anodized TiO$_2$/Ti electrode was calcined at 500°C for 90 minutes to remove residues of organic compound and electrolyte solution on the plate surface as well as TiO$_2$ anatase crystals form has better photocatalytic activity than other crystalline phases. The anatase phase of TiO$_2$ has a larger surface area and active side lead to the photons absorbing effectiveness was increasing. The successful preparation of a selenious doped TiO$_2$/Ti composite using dip-coating method in Se-TiO$_2$ sol-gel can be seen in Figure 2b of a yellow thin layer on the TiO$_2$/Ti surface.

![Figure 2. TiO$_2$/Ti thin film prepared by anodizing method (a) and Se-TiO$_2$/Ti thin film prepared by dip coating method (b)](image)

3.2. Characterizations Catalyst

3.2.1. DRS UV-Vis. Figure 3 show that the $(\alpha E_{bg})^2$ versus $E_{bg}$ for a indirect band-gap transition, where $\alpha$ is the absorption coefficient and $E_{bg}$ is the photon energy. The value of $E_{bg}$ extrapolated to $a = 0$ gives an absorption energy, which corresponds to a band-gap energy. The band-gap value of 3.20 eV TiO$_2$/Ti was reported by Maulidiyah et al. in the literature that the pure anatase nanoparticles [12]. The band-gap energy was decreased for 2.9 eV with inserted by Se dopant on TiO$_2$/Ti. According to Steng et al. that addition of Se can decrease the band-gap energy of TiO$_2$ because it can be inserted onto TiO$_2$ lattice and shift the absorbance of Se-TiO$_2$/Ti composite to the visible region because Se has narrow band gap of 2.0 eV [27,28].

3.2.2. Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX)

Characterization by SEM was conducted to the analysis surface morphology of TiO$_2$/Ti and Se-TiO$_2$/Ti composites. The difference in surface morphology between TiO$_2$/Ti and Se-TiO$_2$/Ti composites as shown that the success of Se doped TiO$_2$/Ti electrode. Figure 4a can be seen the surface of TiO$_2$/Ti electrode is honeycomb-shaped. The fabricate of TiO$_2$ honeycomb on the Ti plate surface was the initial stage to nanotubes tubular formation with a pore size of 500 nm. The formation of porous materials makes the semiconductor has a large surface area lead to as a photocatalyst will be more effective in degradation process. Figure 4b shows that the presence of agglomerates structure of 5-10 $\mu$m doped on TiO$_2$-NTAs. These results showed that the Se was successfully doped on TiO$_2$/Ti plate.
It was expected to give a double effect in optimizing TiO$_2$ performance in the visible region. The double effect to decrease of TiO$_2$ band gap energy due to its creation the new energy levels between valence and conduction bands of TiO$_2$, as well as triggering the formation of a new trapping site which can recombine the electron-hole. This phenomenon of recombination rate of photogenerated electron/hole (e$^-$/h$^+$) pair can be minimized.

Characterization by EDX was conducted to determine the type of elements as well as the sample quantity. Figure 5 shows the EDX spectra of Se-TiO$_2$/Ti composite that sample was containing the three elements i.e titanium (Ti), oxygen (O), and selenium (Se). This results exhibited the doping process has been successfull with quantitatively data showed percentages of Ti, O, and Se are 51.09; 36.91; and
12.0 respectively. Based on composition of Se-TiO$_2$/Ti composite, can be proposed for empirical formula that is Ti$_7$O$_{15}$Se.

![EDX spectra of Se-TiO$_2$/Ti composite](image)

**Figure 5.** EDX spectra of Se-TiO$_2$/Ti composite

**Table 1.** Elements Composition of Se-TiO$_2$/Ti composite

| Elements | % Mass |
|----------|-------|
| Ti       | 51.09 |
| O        | 36.91 |
| Se       | 12.00 |

**Total** 100.00

**Table 2.** Empirical formula proposed of Se-TiO$_2$/Ti composite

| Elements | % Mass | × 100 | Mol | Coefficient |
|----------|-------|-------|-----|-------------|
| Ti       | 51.09 | 5109  | 106.73324 | 7.02        |
| O        | 36.91 | 3691  | 230.69615 | 15.17       |
| Se       | 12.00 | 1200  | 15.197568 | 1.00        |

3.2.3. **Photocurrent Response**

The PEC activity was studied by LSV method in 0.1 M NaNO$_3$ electrolyte solution using a potentiostat. The working electrodes are Se-TiO$_2$/Ti and TiO$_2$/Ti, platinum (Pt) electrode as counter electrode, and Ag/AgCl electrode as reference electrode. The working electrode performance is compared to variation of UV, visible and dark condition by PEC system. Voltamogram shows the intensity of redox reaction occurring at working electrode surfaces. Oxidation has occurred and reducing agents formed on catalyst surface due to photon induction with the appropriate energy. Photoelectrochemical activity of TiO$_2$/Ti and Se-TiO$_2$/Ti electrodes can be seen in figure 6.
Figure 6 showed that without illumination (dark condition) the TiO$_2$/Ti electrode does not exhibit PEC activity because there is not photogenerated of electron-hole pairs on the surface. Meanwhile, the irradiation by using UV and visible irradiation were indicated that the high activity PEC performance. Figure 6a show that the TiO$_2$/Ti electrode has high activity on UV light irradiation compared with visible light. This condition that the TiO$_2$ anatase was activated by UV light radiation with wavelengths from 365 nm to 388 nm [29]. Whereas irradiation by visible light exhibits a small activity because the visible energy does not suitable to the photogenerated of electron-hole. Figure 6b shows that the activity of Se-TiO$_2$/Ti electrode exhibit a new optical properties. The Se-TiO$_2$/Ti electrode has high activity on visible light irradiation compared with UV light. These results indicated that the Se doped has succeeded to decrease the TiO$_2$ band-gap energy.

3.3. Degradation Test by Photolytic, Photocatalytic, and Photoelectrocatalytic
The RhB compound was degraded by 3 different processes i.e. photolytic, photocatalytic and photoelectrocatalytic. Thoose methods were performed with variations of UV and visible irradiation for 60 minutes. The utilization of methods variety was intended to study the effect of catalyst degradation
and the light irradiation. The effect of dopant to improve in visible light performance range and effect of PEC system applied in the degradation process. The 5.0 mg L\(^{-1}\) RhB was degraded by using TiO\(_2\)/Ti and Se-TiO\(_2\)/Ti electrodes.

![Comparison of percent degradation by photolytic, photocatalytic and photoelectrocatalytic](image)

**Figure 7.** Comparison of percent degradation by photolytic, photocatalytic and photoelectrocatalytic

Photolytic is a degradation method using a light source to attack RhB organic compound to initiate the mineralization process. Based on Figure 7 shows that degradation by the photolytic method is less effective because the reduced concentration is very small [3]. The high degradation performed by photolytic was exhibited using UV light irradiation with percent degradation of 20.74%. This occurs that the photon induction was difficult to remove RhB bonds with higher energy of UV light. Subsequently, the photocatalytic is a degradation process using catalyst and photons that occurs when UV light irradiated to the TiO\(_2\) semiconductor the electron excitation from the valence to conduction bands. This phenomenon forms photogenerated e-/h\(^+\) pairs in the semiconductor. The photocatalytic performance was conducted by TiO\(_2\)/Ti as a working electrode under UV and visible lights irradiation. The data showed that the high photocatalytic performance was able to degrade 5.0 mg L\(^{-1}\) RhB using TiO\(_2\)/Ti under UV light with percent degradation of 49.31%.

The PEC is a combination of photocatalytic and electrochemical processes. The electrochemical application systems become the basis of the difference between both. The external potential was applied in PEC system due to the external circuits formation which occurs passed by the photogenerated electrons. The electrons will be transferred to the counter electrode for minimizing the recombination electron [7,8]. Based on Figure 7 the PEC was able to degrade the RhB by using Se-TiO\(_2\)/Ti electrode under visible light with percent degradation of 73.27%.

4. **Conclusions**

The TiO\(_2\)/Ti electrode was prepared by anodizing Ti plate method to form TiO\(_2\)-NTAs electrode, followed by dip-coating in sol-gel Se-TiO\(_2\) to obtain the Se-TiO\(_2\)/Ti electrode. The photocurrent response of Se-TiO\(_2\)/Ti electrode was able to visible light, while the TiO\(_2\)/Ti electrode can be activated under UV light. The high PEC system showed that the Se-TiO\(_2\)/Ti electrode can be degraded RhB with percent degradation of 73.27%.
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References
[1] Sari AA, Kurniawan HH, Nurdin M, and Abimanyu H 2015 Energy Procedia 68 254-262
[2] Dahnum D, Tasum SO, Triawhyuni E, Nurdin M, and Abimanyu H 2015 Energy Procedia 68 107-116
[3] Maulidiyah, Nurdin M, Wibowo D, and Sani A 2015 Int. J. Pharma. Pharmaceu. Sci. 7(6) 141-146
[4] Wibowo D, Ruslan, Maulidiyah, and Nurdin M 2017 IOP Conf. Series: Mater. Sci. Eng. 267 012007
[5] Wibowo D, Maulidiyah, Ruslan, Azis T, and Nurdin M 2018 Anal. Bioanal. Electrochem. 10(4) 465-477
[6] Maulidiyah, Tribawono DS, Wibowo D, and Nurdin M 2016 Anal. Bioanal. Electrochem. 8(6) 761-776
[7] Nurdin M, Azis T, Maulidiyah, Aladin A, Hafid NA, Salim LOA, and Wibowo D 2018 IOP Conf. Series: Mater. Sci. Eng. 367 012048
[8] Maulidiyah M, Wijawan IBP, Wibowo D, Aladin A, Hamzah B, and Nurdin M 2018 IOP Conf. Series: Mater. Sci. Eng. 367 012060
[9] Maulidiyah, Wibowo D, Hikmawati, Salamba R, and Nurdin M 2015 Orient. J. Chem. 31(4) 2337-2342
[10] Nurdin M, Ramadhan LOAN, Darmawati, Maulidiyah, and Wibowo D 2017 J. Coat. Technol. Res. 15(2) 395–402
[11] Maulidiyah, Natsir M, Fitrianingsih F, Arham Z, Wibowo D, and Nurdin M 2017 Orient. J. Chem. 33(6) 3101-3106
[12] Maulidiyah, Ritonga H, Faiqoh CE, Wibowo D, and Nurdin M 2015 Biosci. Biotechnol. Res. Asia 12 985-1989
[13] Maulidiyah, Azis T, Nurwahidah AT, Wibowo D, and Nurdin M 2017 Environ. Nanotechnol. Monit. & Manag. 8 109-111
[14] Nurdin M, Muzakkar MZ, Maulidiyah M, Nurjannah M, and Wibowo D 2016 J. Mater. Environ. Sci. 7 3334-3343
[15] Natsir M, Tuwo MA, Suyuti N, Hafid H, Ansharullah A, Sutrizal LO, Maulidiyah M, and Nurdin M 2018 Asian J. Chem. 30(7) 1590-1592
[16] Natsir M, Maulidiyah M, Ansharullah A, Arham Z, Wibowo D, and Nurdin M 2018 Int. Res. J. Pharmacy 9(6)
[17] Arham Z, Nurdin M, and Buchari B 2016 Int. J. ChemTech Res. 9(11) 113-120
[18] Ruslan, Mirzan M, Nurdin M, and Wahab AW 2016 Int. J. Appl. Chem. 12(3) 399-409
[19] Nurdin M, Zaeni A, Rammang ET, Maulidiyah M, and Wibowo D 2017 Anal. Bioanal. Electrochem. 9(3) 480-494
[20] Maulidiyah M, Wibowo D, Herlin H, Andrini ML, Ruslan, and Nurdin M 2017 Asian J. Chem. 29(11) 2504-2508
[21] Nurdin M, Zaeni A, Maulidiyah, Natsir M, Bampe A, and Wibowo D 2016 Orient. J. Chem 32 2713-2721
[22] Hikmawati, Watoni AH, Wibowo D, Maulidiyah, and Nurdin M 2017 IOP Conf. Series: Mater. Sci. Eng. 267 012005
[23] Mursalin LOAM, Ruslan, Safitri RA, Azis T, Maulidiyah, Wibowo D, and Nurdin M 2017 IOP Conf. Series: Mater. Sci. Eng. 267 012006
[24] Nurdin M, Yanti NA, Suciani, Watoni AH, Maulidiyah, Aladin A, and Wibowo D 2018 Asian J. Chem. 30(6) 1387-1392
[25] Maulidiyah M, Wibowo D, Herlin H, Andrini ML, Ruslan, and Nurdin M 2017 Asian J. Chem.
29(11) 2504-2508

[26] Nurhidayani, Muzakkar MZ, Maulidiyah, Wibowo D, and Nurdin M 2017 *IOP Conf. Series: Mater. Sci. Eng.* 267 012035

[27] Chou J, Yang S, and Wang Y 2003 *Mater. Chem. Phys.* 78(3) 666-669

[28] Stengl V, Bakardjjeva S, and Bludska J 2011 *J. Mater. Sci.* 46 3523–3536

[29] Wunderlich W, Oekermann T, Miao L, Hue NT, Tanemura S, and Tanemura M 2004 *J. Ceramic Process Res.* 4 342-347