

Photoelectrocatalysis Response with Synthetic Mn–N–TiO₂/Ti Electrode for Removal of Rhodamine B Dye

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Abstract—The photoelectrocatalytic (PEC) degradation of rhodamine B (RhB) organic dye using manganese (Mn)-nitrogen (N) doped titanium oxide (TiO₂) electrode was investigated under two applied electrochemical modes such as cyclic voltammetry (CV) and linear-sweep voltammetry (LSV). The synergetic effect between light variation and photocurrent response demonstrated that the TiO₂ thin films were active under the ultraviolet (UV) light illumination with a photocurrent value (I_{pa}) of 2.65 μA ; meanwhile, the Mn–N–TiO₂ was periodically activated under visible (Vis) light illumination with I_{pa} of 3.63 μA . In addition, the photolysis was evaluated to compare the degradation effect under varying light illuminations without catalyst with the PEC system. The good ability of TiO₂ to degrade RhB under UV light was found with a percentage degradation value at 0.5 mg L⁻¹ of 63%. In comparison, the Mn–N–TiO₂ was activated under Vis light with 0.5 mg L⁻¹ of 74.2%.

Keywords: photoelectrocatalysis, photolysis, TiO₂, doped, rhodamine B

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INTRODUCTION

Currently, textile wastewater (TW) has been categorized as hazardous liquid waste because it contains various pollutants, including recalcitrant dyes, and it can cause health complications such as cancer, liver and kidney disorders, etc. [1–3]. In addition, it is a non-biodegradable material that contains azo dyes which cannot be removed easily from the aquatic environment [4, 5], that is, it is toxic to the aquatic ecosystem [6–10].

One of the dyes in TW is rhodamine B (RhB) a synthetic dye commonly used in textile and paper industries [11, 12]. There were cases of economically moti-

vated adulteration where it was illegally used to print clothes and even applied to food ingredients [13, 14]. So, the safety of dye materials should be considered properly for them to be used wisely. Conventional wastewater treatment methods such as filtration, chemical precipitation, ion exchange, membrane technologies, and adsorption have several major drawbacks: a high operating cost, inefficiency at low concentrations, poor selectivity, and could discharge secondary toxic pollutants into the ecosystem, which presents a serious risk to the environment and human health [15, 16].

In recent decades, the photocatalytic method has attracted the attention of researchers being highly effective in dyes degradation by using TiO_2 , ZnO , SnO_2 , SrTiO_3 , Fe_2O_3 , NiO , etc. because it is non-toxic, photoactive, low-cost, easy for preparation, insoluble in water, capable of being used in Vis and near-ultraviolet (UV) lights [17–21]. This paper focuses on titanium dioxide (TiO_2), widely known for its excellent electrochemical properties and used in many applications, making it desirable to be applied in degradation of organic contaminants in the aquatic environment. Application of photo-catalysis does not allow to rapidly degradation organic compounds due to the high electron recombination in the TiO_2 semiconductor [22–25]. This is why, in the present study, photocatalysis was combined with an electrochemically-assisted method to reduce the recombined electron-hole pairs. This method has proven auspicious to degrade organic compounds rapidly and can be used for electro-chemical sensors. Unfortunately, it has the disadvantage of only being active in the UV light (<388 nm), making it difficult to apply at the Vis light.

Recently, an improved TiO_2 modification has moved some researchers to apply it under the Vis light region. The use of non-metal and metal dopants was intended to modify the electrical and optical properties of the TiO_2 semiconductor [26, 27]. The insertion of a dopant can shift the band edge to the Vis region, inducing carrier traps density, oxygen vacancy, or increasing the free carrier, etc., thus enhancing the visible photosensitivity or conductivity [28, 29]. It was reported elsewhere that the N-doped TiO_2 has created a large-scale oxygen vacancy in the crystal lattice [30, 31]. The bandgap studies of N as dopant revealed the N 2p state localization above the O 2p state valence band maximum, which decreased the valence band maximum to lower binding energy [18, 32]. Besides, a metal dopant gives the signal related to the electron trap at the TiO_2 surface lattice site, which indicates an active charge injection from the valence band to the conduction one. The catalytic performance of TiO_2 modified with dopant can improve the surface species to facilitate the active hydroxyl radical species for rapid photodegradation of dye molecules [18].

The electrical current has been frequently used to drive the photoelectrocatalytic (PEC) reactions because it is easily accessible. PEC is energy-saving and recyclable in removing a wide range of pollutants, including amino acids [32], lignin [34–36], organic dyes [37–39], pesticides [40–42], bacteria [43], etc. The PEC system is usually applied in bio-sensor devices, dye-sensitized solar cells, for studies of degradation materials, electrodeposition processes, electrolyte detection. PEC is widely applied in various fields with various designations [44–46]. The utilization of the PEC system for the degradation of organic pollutants using TiO_2 when a bias potential is applied to the working electrode showed that the electron movement

from the negative to the positive polar charge towards the Pt wire, a counter electrode, initiates the reduction reaction. In contrast, the working electrode initiates the oxidation reaction [48, 49]. In addition, it is also demonstrated that usage of Mn and N as dopants for the TiO_2 band changes the optical properties of TiO_2 by using lower energy and reducing recombinations of electron-hole pairs [48]. The purpose of the present study was to discuss the PEC role in the degradation test against RhB dye under photolysis and PEC system by doping TiO_2 thin films with Mn and N to observe the behavior when irradiating with UV and Vis lights.

EXPERIMENTAL METHODS

Preparation of TiO_2/Ti Thin Films

The initial stage to prepare TiO_2 thin films was carried out by cutting the Ti plate (Shanxi Yuanlian Rare Metals Limited, China) of 4.0×0.5 cm with a thickness of 0.5 mm. After that, it was sanded with soft sandpaper 1200CC and rinsed using a mixed solution (detergent, distilled water, and acetone), aimed to reduce the oil or mineral contents on the Ti surface. Subsequently, it was submerged (etching) by using HF (Merck, Germany), HNO_3 (Merck, Germany), and distilled water (1 : 3 : 6) to reduce the oxide layer and the shape of the pore tube on the Ti surface. Next, it was rinsed using distilled water and dried in a desiccator. TiO_2 thin films on the Ti plate were fabricated using the thermal oxidation process under the annealing process in a furnace at 500°C for 90 minutes. According to Mursalim et al. [49], the annealing process at 500°C can produce anatase TiO_2 as a photoactive surface. As the final step, it was cooled in a desiccator, thus being ready for the Mn and N doping.

TiO_2/Ti Doping with Mn and N Using Sol-Gel Method

The sol-gel process was as in Mursalim et al. [49], by mixing 15 mL of ethanol, 2 mL of distilled water, and 1 mL of 0.5M acetic acid into a reflux flask containing 4 mL of titanium tetra-isopropoxide as TiO_2 precursor, 0.5 mL of acetylacetonate, and 15 mL of ethanol. They were refluxed and sintered for 3 h at 50°C using a magnetic stirrer followed by adding 0.5 mL 0.5 M $\text{CO}(\text{NH}_2)_2$ as a source of N and 2.5 mL of MnCl_2 solution as doped Mn metal. After that, the sol was transferred to a beaker glass and evaporated in an oven to form a sol-gel. Hydrothermal TiO_2/Ti was immobilized in the Mn–N– TiO_2 sol-gel with liquid phase deposition evenly. It was heated at 150°C for 15 min to obtain the high crystallinity of the Mn–N– TiO_2 lattice.

Electrochemical Test

The electrochemical response was examined by CV and LSV techniques using a DY2100 potentiostat

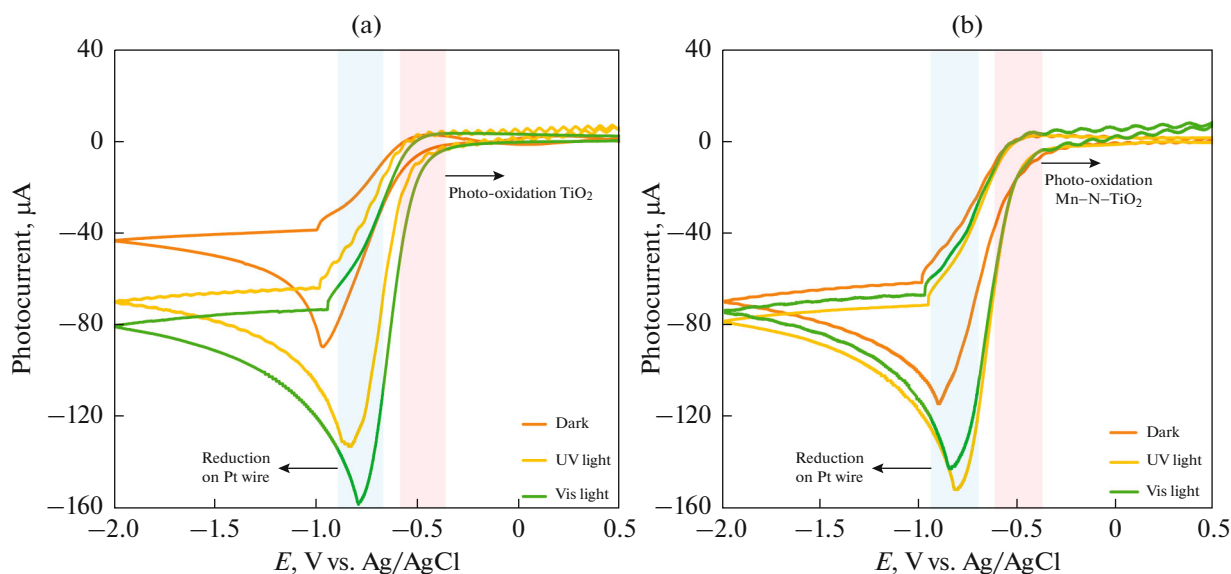


Fig. 1. CV responses of working electrodes: (a) TiO₂/Ti, and (b) Mn–N–TiO₂/Ti.

(Digi-Ivy) to observe the oxidation response from the working electrode (TiO₂/Ti and Mn–N–TiO₂/Ti) under UV and Vis light illuminations. The CV test was evaluated from a potential of -1.5 to 1 V, with a scan rate of 10^{-4} V/s. The LSV test was examined from a potential of -1.0 to 1.0 V, with a scan rate of 10^{-4} V/s.

Photoelectrocatalytic Performance

Before the PEC degradation test of RhB organic dye, we determine the linearity curve by varying concentrations of 0.5 , 1.0 , 2.0 , and 3.0 mg L⁻¹ to obtain the linearity equation, which later can plot against the absorbance of samples. Then, the PEC degradation test was carried out using the multipulse amperometry with a potential bias of 0.5 V and the duration time of 60 min. Every 10 min, the RhB absorption was evaluated using a UV-Vis spectrophotometer to observe the decrease of RhB dye against working electrodes performance.

RESULTS AND DISCUSSION

Electrochemical Performance

In this study, the photoelectrochemical responses were observed and characterized by CV and LSV modes which represent redox and photocurrent properties. The working electrodes of TiO₂/Ti and Mn–N–TiO₂/Ti were evaluated at varying illuminations of UV and Vis lights by using the 1.0 M NaNO₃ as an electrolyte solution to determine the CV response, that is, to determine the reversible reaction occurring in an electrode due to the transfer electron charge flowing in the system.

Figure 1 shows that the CV responses of two electrodes. There was a high reduction response because of the absence of resistance in the transfer rate of electrons to the Pt wire. The downward curve (blue transparent) characterizes as a reduction response of the Pt wire, while the upward one is the oxidation response on the working electrode (red transparent). Figure 1a exhibits that the TiO₂ has low oxidizing activity when irradiated with Vis light, but under dark conditions and the photocurrent response of photo-oxidation close to zero, the values are 1.89 and 0.3 μA, meanwhile under the UV light irradiation, the photo-oxidation value is 2.65 μA. This evidences that TiO₂ is activated under the UV light, even though the photo-oxidation values of both UV and Vis are almost close. It is concluded that the synthesized TiO₂/Ti has a wavelength range up to 388 – 390 nm so that the gap range under a valence band to a conduction band is quite near. Figure 1b characterizes the Mn–N–TiO₂/Ti electrode active under the Vis illumination and its inactivity under UV and dark conditions. The photo-oxidation instability occurs due to the uneven distribution of Mn and N dopants on the TiO₂/Ti surface.

In Fig. 1b, the photocurrent oxidation value at the Vis illumination is 3.63 μA, while under UV and dark conditions, the values are 2.46 and 2.27 μA, respectively. When inducing an electron from a potentiostat, it happens that the electron is excited to the conduction band quite quickly and is proportional to the reduction response. So, it is supposed that the electrolyte plays a role in the electron transfer in the system bulk; a similar number of ions formed per molecule and concentration used is also worth mentioning.

The LSV mode is an electroanalytic measurement to examine analyte performance between working

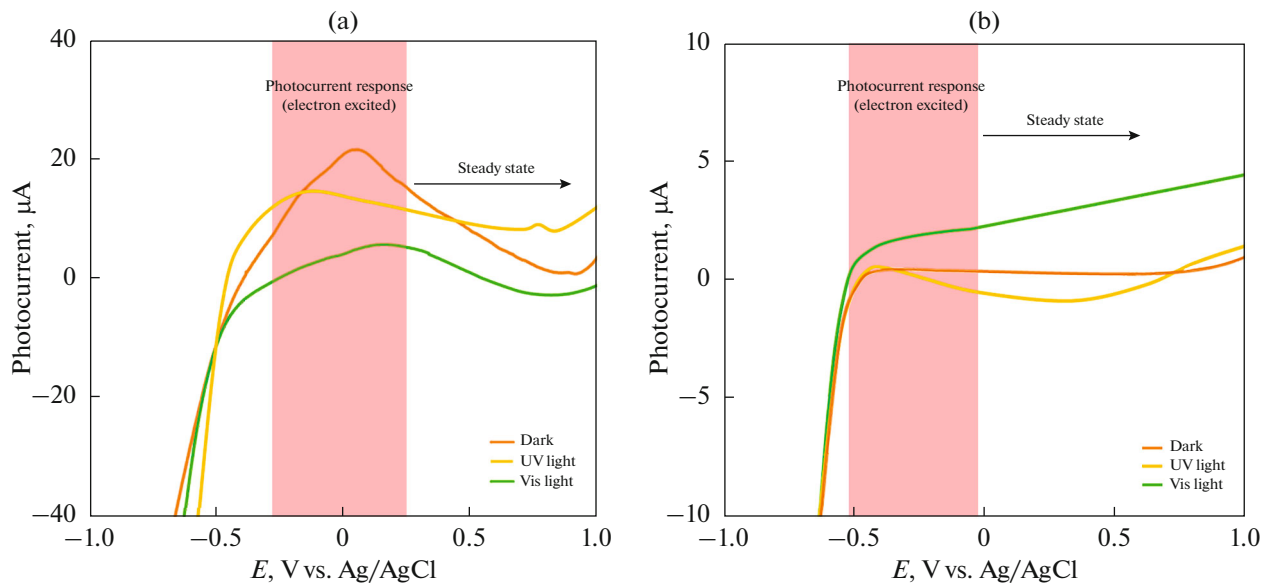


Fig. 2. LSV voltammograms of working electrodes: (a) TiO_2/Ti , and (b) $\text{Mn-N-TiO}_2/\text{Ti}$.

electrodes based on photocurrent and potential. Based on LSV, the TiO_2 electrode performance showed the initial photocurrent response by varying the light illumination such as UV and Vis lights. In addition, LSV also describes the ability of the electrode response under light exposure in its ability to degrade organic compound pollutants. In this study, the LSV test was carried out with three electrodes: TiO_2/Ti and $\text{Mn-N-TiO}_2/\text{Ti}$ as working electrodes, a platinum wire as counter electrode, and Ag/AgCl as reference electrode. The working electrodes were measured simultaneously by varying UV and Vis light illuminations using a 0.1M NaNO_3 electrolyte solution to increase the electron transfer, thereby together they started a redox reaction on the electrode surface. In addition, a potentiostat also provides electron induction to reduce recombination of electrons to the holes, increasing the redox reaction and the rate of the OH radical formation on the electrode surface.

Figure 2 depicts that both electrodes have provided the photocurrent activity by varying the light illumination. In addition, the dark condition was also tested and provided a weaker electron transfer rate under steady-state conditions. Figure 2a shows the LSV voltammogram of the TiO_2/Ti electrode with good activity performance under UV illumination during the steady-state condition, while the visible and dark areas show fairly good photocurrent activity in the initial response, which gradually decreased during the steady-state. It is due to the initial electron induction from the potentiostat that there is a rapid movement of electrons towards the conduction band, while the UV radiation provides good photocurrent stability because it is active at a wavelength ≤ 388 nm, with an energy gap of 3.2 eV which is equivalent with the UV wavelength

[18]. The high energy induction of the UV illumination has a high impact on the rapid excitation of electrons from a valence band to a conduction band. However during the steady state condition, the electrons also readily recombine in the valence band [32].

Figure 2b exhibits an LSV graph of $\text{Mn-N-TiO}_2/\text{Ti}$, with its good activity under the Vis illumination. The Vis light response gradually increased on the working electrode towards the steady-state condition. This phenomenon occurs due to adding of Mn and N dopants on the TiO_2/Ti layer, and it demonstrated better performance under Vis wavelengths up to 400 nm in an effort to degrade organic pollutant with the Vis light. However, both UV and dark conditions had a fairly low photocurrent response.

In this study, the utilization of the PEC system aims at facilitating the electron movement to a Pt wire to start a reduction reaction, as well as an electrode that works to start an oxidation reaction (Fig. 3). This condition is supported by the presence of Mn and N as dopants for TiO_2 band, which leads to a change in the optical properties of TiO_2 , use of low energy, and reduced recombination of electron hole pairs.

The efficiency of PEC in degradation of organic pollutants in water bodies is through mineralization to CO_2 and H_2O , without producing toxic and detrimental intermediates. It is because the sample is only inside a glass tube during the PEC degradation, and after the mineralization process, it is safe in nature. The RhB in a glass tube could be oxidized by hydroxyl radicals ($\cdot\text{OH}$), oxygen peroxide radicals ($\text{RhB}\cdot\text{O}_2^-$), and photogenerated holes (h^+) into CO_2 and soluble degradation products [28].

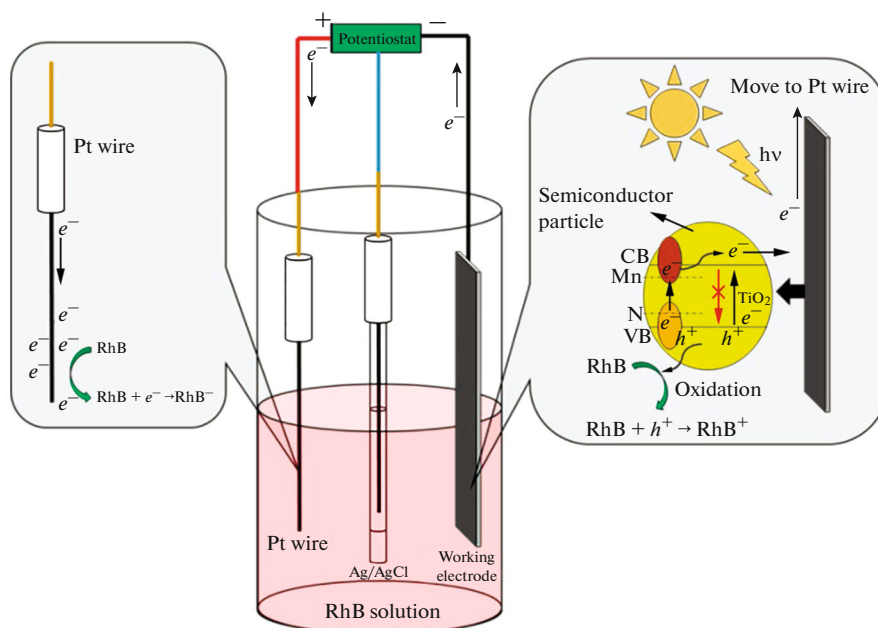


Fig. 3. Presentation of PEC system for RhB dye degradation.

Photoelectrodegradation Test against RhB Dye

First, the wavelength was determined and the regression equation applied in order to measure the decrease in the RhB concentration from the photoelectrodegradation assay. The RhB wavelength was determined using 0.5 mg L^{-1} , then it was analyzed with a UV-Vis spectrophotometer. After scanning from 380–780 nm, a maximum wavelength of 554 nm was obtained. The same result was also reported elsewhere [50] that the RhB wavelength was in the adsorption range at 552–554 nm, which characterizes the electron transition involving π electrons conjugating together with the chromophore groups of heterocyclic RhB compound by absorbing energy [51]. The red colour of RhB organic dye is due to the electron conjugation in the visible area, so it can be measured using a UV-Vis spectro-photometer. After that, the regression equation was evaluated with a concentration variations of 0.5 (0.086 A), 1.0 (0.160 A), 2.0 (0.302 A), and 3.0 mg L^{-1} (0.420 A), so that the linear equation is obtained of $y = 0.134x + 0.024$, $R^2 = 0.997$.

The RhB organic dye degradation test was carried out via multi-pulse amperometry [14, 31]. Every 10 minutes, the evaluated the absorbance of RhB with a UV-Vis spectrophotometer to determine the decrease in the RhB concentration, which tested under PEC for 60 minutes. This study has tested the effectiveness of the photolysis and PEC processes. During photolysis, the decomposition of organic compounds is only exposed to light. Meanwhile, PEC induces the electron energy (electric current) to initiate redox reactions at both electrode poles (anodic-cathodic). In addition, PEC is a combination of pho-

tocatalytic and electrochemical processes involving light, catalyst, and electron transfer (Fig. 3). Based on Fig. 4a, the photolysis test of RhB degradation by exposing to UV and Vis lights without the addition of a catalyst shows a minimal decrease at various concentrations in testing up to 60 minutes. Generally, the function of catalyst is to initiate the formation of OH radicals on the TiO₂ surface from the excitation of electrons process. Uniquely, photolysis also degrades RhB dye although with a low performance under UV and Vis lights, with a percentages of the RhB degradation with a concentration of 0.5 mg L^{-1} of 25.80% (exposed to UV) and 0.5 mg L^{-1} of 22.58% (exposed to Vis), as can be seen in Fig. 4b.

The PEC process was carried out by providing an external bias potential of +0.5 volts from the potentiostat. Based on Maulidiyah et al. [32], the used a low bias potential to provoke the movement of electrons on the surface of the electrode. The addition of electrons (electric current) will also prevent the electron-hole recombination due to the transfer of electrons to the Pt wire, which triggers a reduction reaction (Fig. 3). This phenomenon will occur in forming a more active site on the catalyst to be effective in the degradation process. Figure 5 shows that PEC degradation of RhB using the TiO₂/Ti electrode is better under the UV light compared to the performance of photolysis with the maximum degradation value obtained at a concentration of 0.5 mg L^{-1} of 63%, while in the 3.0 mg L^{-1} of 28.03% under the UV light illumination.

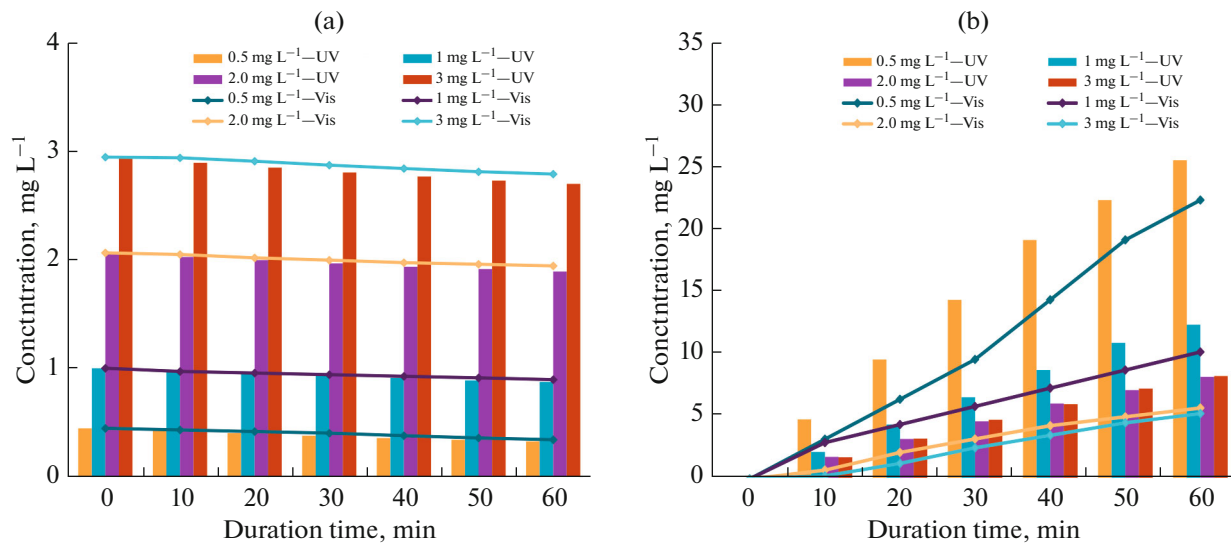


Fig. 4. Data on RhB photolysis: (a) data on decreased concentrations, and (b) percentage of degradation.

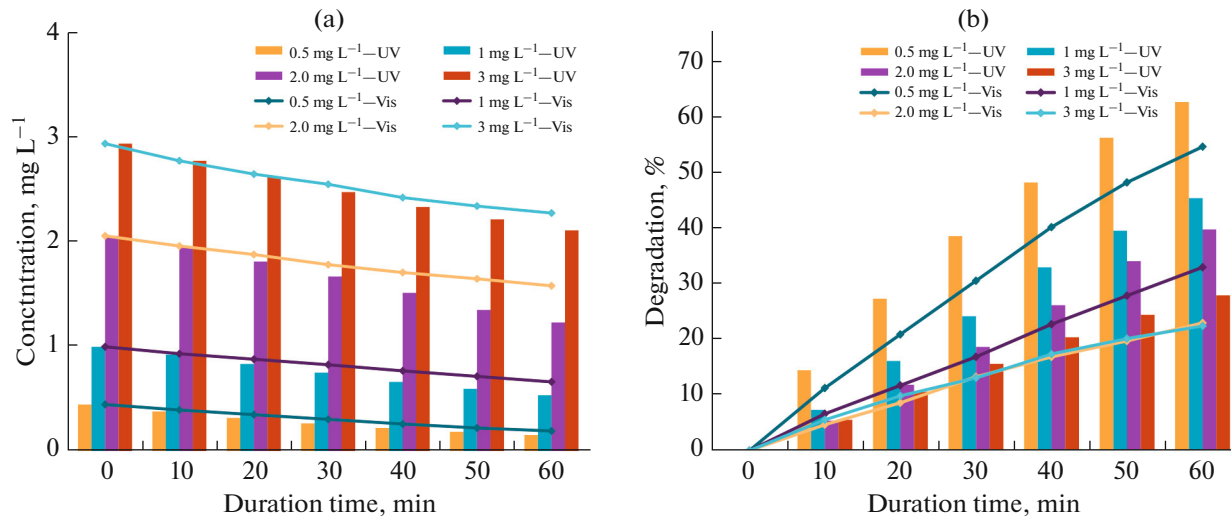


Fig. 5. PEC degradation of RhB using TiO₂/Ti electrode: (a) data on decreased concentrations, and (b) percentage of degradation.

In addition, to improve the performance of TiO₂ in the visible area, metal and non-metal dopants were used to change the optical properties of the working electrode surface. The PEC test on the Mn-N-TiO₂/Ti electrode was carried out in the same manner as the PEC TiO₂/Ti test. Figure 6 shows the good performance of the Mn-N-TiO₂/Ti electrode in degrading RhB under the Vis light illumination when compared to that under the UV light. The maximum degradation value was obtained at a concentration of 0.5 mg L⁻¹ of 74.2%, while at 3.0 mg L⁻¹, it was 58.08% under the Vis light illumination. The presence of dopants on the TiO₂/Ti surface serves to narrow the bandgap energy so that it only requires low energy to excite electrons from a valence band to a conduction

band. The presence of semiconductor heterojunctions is a way of tuning the photoanode towards the Vis light activation. It was demonstrated that the heterojunction of Mn-N-TiO₂ is an effective way of limiting rapid recombination of charge carriers in PEC by promoting effective electrons transfer to the Pt wire to initiate reduction reaction [32]. The usage of double doping can shift the optical properties of TiO₂ to increase the supply in the 2*n* or 2*p* orbitals [18]. The PEC application plays an important role in the system performance because it uses 3 electrodes, where the Pt wire initiates the reduction reaction, while the working electrode—an oxidation reaction so that the mineralization performance of RhB compounds increases faster. The heterojunction of Mn-N-TiO₂/Ti refers

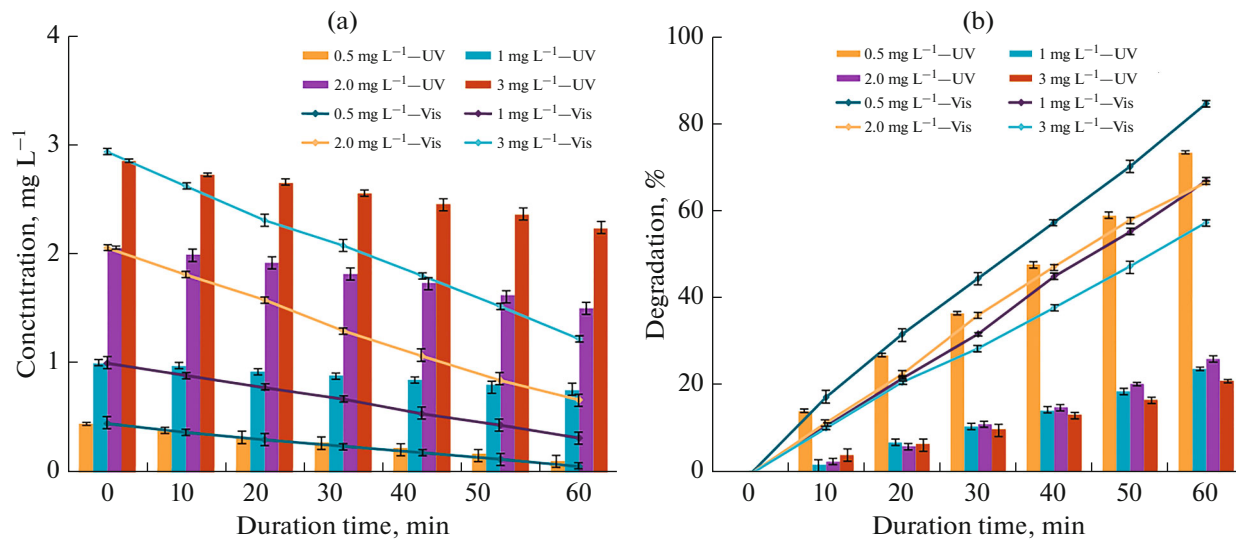


Fig. 6. PEC degradation of RhB using Mn–N–TiO₂/Ti electrode: (a) data on decreased concentrations, and (b) percentage of degradation.

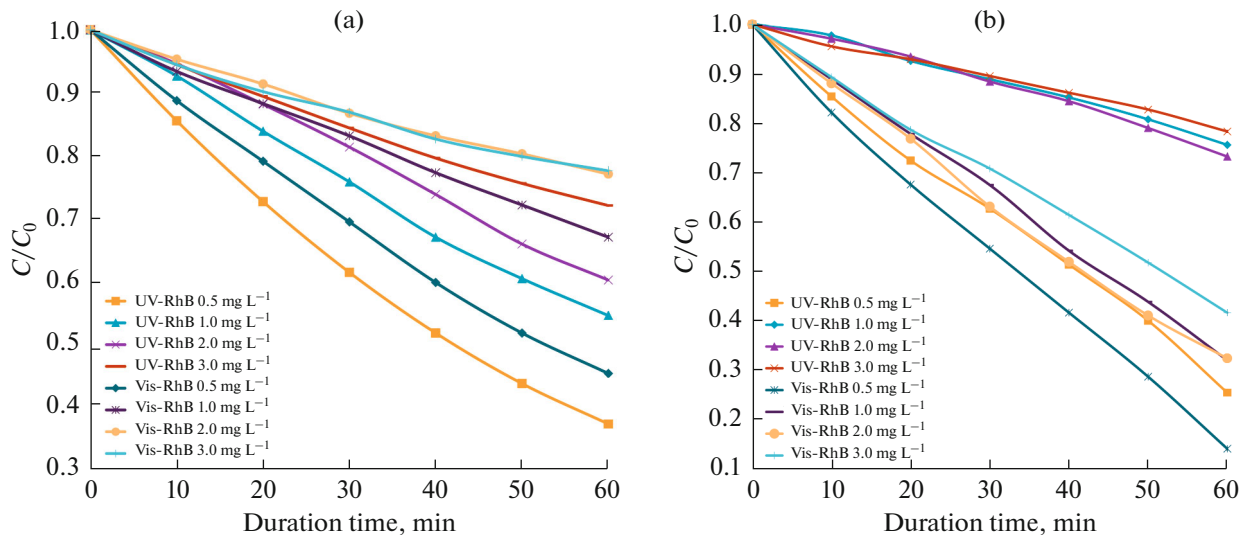


Fig. 7. The rate of decrease in concentration (C/C_0) under PEC degradation of RhB dye, (a) PEC-TiO₂/Ti electrode, and (b) PEC-Mn–N–TiO₂/Ti electrode.

to the interface formed when two semiconductors of an unequal band gap combine so that a band alignment results. The PEC semiconductor heterostructure has been extensively applied towards photoelectrochemical water splitting applications where higher PEC efficiencies have been recorded than the single or pristine semiconductors [32].

This notable enhancement of the decolorization rate under PEC degradation could be explained by a synergistic effect of the combined processes. During photoexcitation of a semiconductor under UV irradiation, the application of an electrical current stabilizes the photogenerated charge carriers due to the effective

separation of the electron-hole pairs by the potential of the applied voltage (Fig. 3). The inhibition of the recombination process prolongs the life of redox mediators on the photo-electrode surface, which results in the enhanced degradation efficiency of the dye chromophore TiO₂ thin films modified with Mn and N for an efficient PEC decolorization of methylene blue [10].

As shown in Fig. 7, the decomposition efficiencies with TiO₂/Ti and Mn–N–TiO₂/Ti electrodes are in 0.5 mg L⁻¹ of 63% (exposed to the UV light) (Fig. 7a) and 74.2% (exposed to the Vis light) (Fig. 7b). Obviously, the PEC efficiency decreased sharply at a con-

Table 1. The rate constants of PEC degradation using RhB for each variation of concentrations and UV and Vis illuminations from the working electrode

Concentration, mg L ⁻¹	K_d UV TiO ₂ /Ti, mg L ⁻¹ min ⁻¹	K_d Vis TiO ₂ /Ti, mg L ⁻¹ min ⁻¹	K_d UV Mn–N–TiO ₂ /Ti, mg L ⁻¹ min ⁻¹	K_d Vis Mn–N–TiO ₂ /Ti, mg L ⁻¹ min ⁻¹
0.5	0.0162	0.0112	0.0179	0.0229
1.0	0.0085	0.0053	0.0051	0.0145
2.0	0.0065	0.0044	0.0042	0.0137
3.0	0.0047	0.0046	0.0040	0.0123
Average	0.0090	0.0064	0.0078	0.0159
STD	0.0051	0.0032	0.0068	0.0048
Count	4	4	4	4
Std Error	0.0025	0.0016	0.0034	0.0024

concentration of 0.5 mg L⁻¹ because the use of low concentrations did not mask the active sites on the electrodes, and a large difference in the PEC performance was mainly due to the adsorption capacity of the samples by the surface morphology of the electrodes. However, both used electrodes played an important role in the advancement of PEC, with differences in light exposure. The kinetics for the decolorization of RhB was evaluated using a first-order kinetic model or the Langmuir–Hinshelwood (L–H) equation. This equation helps to determine the reaction rate constant by plotting $\ln C/C_0$ against irradiation time (t). The degradation rate constants (K_d) are presented in Table 1.

According to Table 1, the rate constant for RhB degradation will be smaller with increasing solution concentrations. This indicates that the PEC process runs well at low concentrations in the sample solution. Using the same catalyst size, the active site of the surface will also be the same so that a low concentration of RhB will be completely adsorbed on the electrode surface resulting in a more efficient PEC process. According to Maulidiyah et al. [33], a decrease in the degradation rate constant is influenced by the active site on the catalyst. This condition will occur with the produced O₂ and OH radicals in degrading RhB test compound when illuminated with UV or Vis lights. Table 1 shows the Mn–N–TiO₂/Ti degradation rate constant value meaning good performance under the Vis light, whereas under the UV light illumination, it is also quite good. It is due to adding metal and non-metal dopants that can separate electrons and holes for a long time. In addition, it can act as traps for electron holes, also allowing the holes to form hydroxyl radicals results in degradation reactions of organic species.

CONCLUSIONS

During this study, the PEC degradation of the RhB organic dye towards TiO₂/Ti and Mn–N–TiO₂/Ti electrodes was examined, showing good performance

on the electrochemical response with a variation of the light-exposed: TiO₂/Ti responded under the UV light and Mn–N–TiO₂/Ti—under the Vis light illumination. Then, the PEC degradation against RhB shows good ability of TiO₂ to degrade RhB under UV light, with the percentage degradation value of 63% at 0.5 mg L⁻¹, while Mn–N–TiO₂ was active under the Vis light, with 74.2% at 0.5 mg L⁻¹. The TiO₂ thin films have been fast developed due to their various merits of easy recycling of organic pollutants in the aquatic environment under the UV and Vis illuminations.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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