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Fotoelectrocatalytic Degradation of Organic Compound Congo Red Using TiO_2/Ti Electrode

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Abstract: In this study, we synthesized photobilized TiO_2 on a Ti plate and tested its photoelectrocatalytic activity towards Congo Red. The background of this research is to develop an effective and environmentally friendly water treatment method. The main method used was the sol-gel synthesis of TiO_2 prepared from titanium tetra isopropoxide as a complexing agent, followed by photobilization on a Ti plate. Material characterization was conducted using XRD technique, portable Potentiostat (e-DAQ), and UV-Vis DRS (Diffuse Reflectance Spectrophotometric) spectroscopy. The results of this research showed that the TiO_2 synthesis produced Anatase crystal structure with particle size of 13–16 nm and a band gap of 3.20 eV. Furthermore, the photoelectrocatalysis test demonstrated that TiO_2/Ti exhibited activity in degrading Congo Red. The main conclusion of this study is that the synthesis of TiO_2/Ti using the Sol-Gel method and immobilization on a Ti plate can enhance the photodegradation efficiency towards Congo Red. This finding has significant implications in the development of more effective and environmentally friendly water treatment technologies.

Keywords: Photodegradation, TiO_2/Ti, Sol-Gel, Ti plat, congo red

1. Introduction

In this context, photoelectrochemical catalysts, particularly TiO_2/Ti, have shown great potential in degrading recalcitrant organic compounds through photocatalysis. TiO_2 is the most commonly used semiconductor in photocatalytic reactions due to its stability, resistance to photocorrosion, and unique photocatalytic properties. The integrity of TiO_2 can be enhanced by attaching it to a titanium (Ti) substrate to improve its catalytic efficiency and photocatalytic stability (Chakhtouna et al., 2021).

Several synthesis methods have been developed to obtain photobilized TiO_2 on Ti plates with desired structures and properties. However, there are still doubts and differing opinions regarding the optimal synthesis method to achieve a catalyst with the best performance in dye degradation. Therefore, the main objective of this research is to synthesize TiO_2/Ti using a specific method and evaluate its photoelectrocatalytic activity towards Congo Red.

In this study, we will introduce the synthesis method used to produce TiO_2/Ti, as well as the material characterization involving XRD and UV-Vis spectroscopy techniques. Furthermore, we will test the photoelectrocatalytic activity of TiO_2/Ti towards Congo Red using a photocatalytic reaction. It is expected that the results of this research will provide a better understanding of effective TiO_2/Ti synthesis and its potential application in water treatment and organic contaminant reduction.

In summary, this research aims to synthesize TiO_2/Ti and evaluate its photoelectrocatalytic activity towards Congo Red. The study is expected to offer new insights into the development of efficient photoelectrochemical catalysts for dye degradation in water, which, in turn, will contribute to environmental protection and improved water purification.

2. Methods

The materials used in this research were Titanium Tetra Iso Propoxide (TTIP) 97% (Aldrich), deionized water, acetone 98% (Merck), ethanol 99% (Merck), EDTA (Merck), acetic acid (Merck), (Merck), Titanium (Ti) plate, detergent, $NaNO_3$ 0.1 M (Merck), deionized water, HF 40% (Merck), concentrated HNO_3 (Merck), $Ni(NO_3)_2 \cdot 6H_2O$ 0.04%, and Congo Red.

The synthesis of TiO_2 was carried out by preparing two solutions, where the first solution was a TiO2 colloid solution prepared through controlled hydrolysis. 4 mL of titanium tetra isopropoxide was added to a mixture of 0.5 mL acetylacetone and 15 mL of ethanol 99%, then refluxed for 30 minutes. The second solution was prepared by mixing 15 mL of ethanol 99% and 2 mL of deionized water, then adding 1 mL of 0.1 M acetic acid. The mixture was refluxed for 120 minutes at 50°C (Noman et al., 2019).

The preparation of photobilized TiO_2 on a Ti plate involved cutting a titanium plate into a size of 2 x 6 cm, followed by sanding it with sandpaper until the surface became clean and shiny, and then washed with a mixture of detergent, water, and deionized water. Next, the plate was immersed in a mixture of HNO_3, HF, and deionized water with sequential ratios of 3:1:6, and then calcined at 500°C for 2 hours. The prepared Ti plate was photobilized with TiO_2 sol by evenly applying the sol onto the plate's surface while stirring with a magnetic stirrer for 30 minutes. The plate was then left to dry and calcined at 500°C for 2 hours. The coating process was repeated 2, 3, 4, and 5 times.

The TiO_2/Ti electrode that was created was characterized using a portable potentiostat (e-DAQ) with the Linear Sweep Voltammetry (LSV) method. Experiments were conducted in the dark, under UV light exposure, and under visible light exposure (using a 40-watt tungsten lamp) using a 0.1 M $NaNO_3$ electrolyte solution. The LSV parameters were set as follows: Initial Voltage: -1000 mV, Final voltage: 1000mV, Scan Rate: 10 mV/s, Range: 10 mA (Muzakkar et al., 2021; Nurdin, Maulidiyah, et al., 2021; Nurdin, Nuhung, et al., 2021).

The characterization of photobilized TiO_2 on the Ti plate was done using UV-Vis DRS (Diffuse Reflectance Spectrophotometric) (Zhang et al., 2020a), portable potentiostat (e-DAQ), and X-Ray Diffraction (XRD) techniques. The photoelectrocatalytic activity was tested by measuring the decrease in Congo Red solution concentration over irradiation time. The photoelectrocatalysis tests were performed in a photoelectrochemical reactor under visible light irradiation with a potential bias of 500 mV. The analysis was carried out using a portable potentiostat (e-DAQ) with the multi-pulse amperometry method.

3. Results and Discussion

3.1. Synthesis of TiO_2

TiO_2 Synthesis in this research was conducted using the sol-gel method. This method was chosen because it is simpler and allows for better control over the formation of the sol, including variations in pH, concentration, and desired crystal shape with nanoparticle size. The TiO_2 sol was prepared from precursor materials, Titanium Tetra Iso Propoxide (TTIP), ethanol, and acetylacetone, under controlled conditions, and refluxed for 30 minutes at 50°C (Noman et al., 2019).

Acetylacetone functions as a chelating ligand, which is expected to slow down the hydrolysis rate of TTIP in ethanol solvent, leading to the formation of Ti(OH)n monomer complexes. The formed sol consists of precursor molecules that undergo condensation polymerization, forming interconnected chains at specific points to create macromolecules that trap the solvent within.

Stage 1. Hydrolysis reaction:

$Ti(OC_3H_7)4 + 4H_2O \rightarrow Ti(OH)_4 + 4C_3H_7OH$ ……(1)

Stage 2. Condensation polymerization reaction:

$nTi(OH)_4 + nTi(OH)_4 \rightarrow [(OH)_3TiOTi(OH)_3]n + H_2O$ ……..(2)

3.2. Immobilization of TiO_2 on a Ti Plate

TiO_2 immobilization is performed by dipping the Ti plate substrate into a TiO_2 colloid. The choice of Ti plate is due to its conductive and heat-resistant properties. As shown in Figure 13, this coating process is repeated 2, 3, 4, and 5 times to achieve a uniform and photoactive TiO_2 thin layer. Subsequently, the coated Ti plate is calcined at 500°C with the aim of promoting the growth of anatase crystal and bonding the thin TiO_2 layer to the stronger Ti plate. Therefore, in this research, calcination is conducted at 500°C, which is considered an optimal condition for the growth of TiO_2 on the Ti plate (Gowthambabu et al., 2021a).

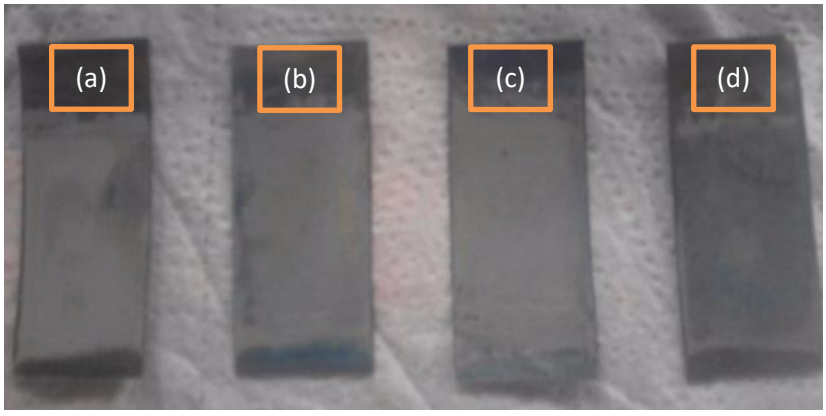

Figure 1. a. Coating 2x ; b. Coating 3x; c. Coating 4x; d. Coating 5x

3.3. Characterization of TiO_2/Ti

3.3.1. Diffuse Reflectance UV-Vis DRS

The characterization using Diffuse Reflectance UV-Vis DRS was conducted to determine the band gap energy of the synthesized TiO_2. Figure 2 shows that the band gap energy of TiO_2 is 3.2 eV, with an optimum wavelength of 387 nm, which corresponds to the ultraviolet (UV) region. The obtained spectrum data is consistent with previous research indicating the successful synthesis of TiO_2 from the TTIP precursor using the sol-gel method (Macwan et al., 2011; Zhang et al., 2020b). The determined band gap energy indicates that the

TiO_2 material exhibits semiconducting properties, making it suitable for various photocatalytic applications in the UV light range.

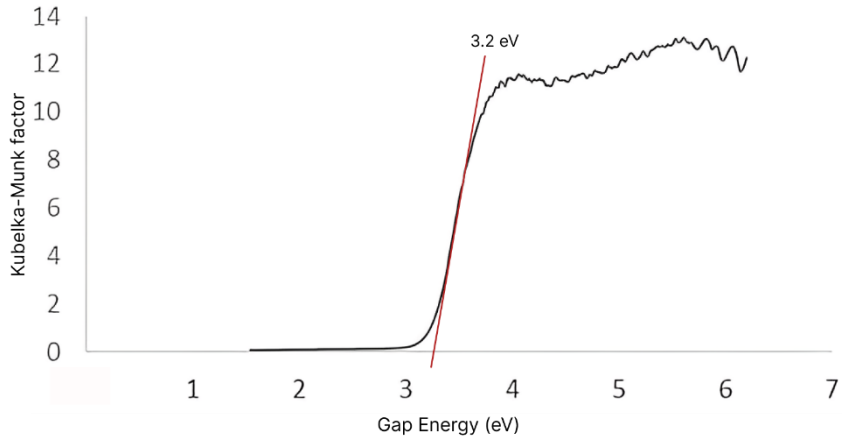

Figure 2. Kubelka-Munk factor Spectrum for TiO_2

3.3.2. Potentiostat (e-DAQ) with the Linear Sweep Voltammetry (LSV) Method

Figure 3 shows the immobilization of TiO2 on a Ti plate, with a significant difference in current between the dark and UV-illuminated conditions. Under UV illumination, the TiO_2/Ti composite exhibits a higher photocurrent response compared to the dark condition. This demonstrates that the conductive Ti plate has been successfully coated with TiO_2, indicating its photoactive behavior towards UV light. The highest photocurrent response in TiO_2 immobilization is observed in the second layer, which serves as the optimal TiO2/Ti electrode. This spectrum is consistent with previous reports (Muzakkar et al., 2021; Nurdin, Maulidiyah, et al., 2021; Nurdin, Nuhung, et al., 2021).

Photocurrent measurements reveal that as the number of layers increases, the photocurrent response to light decreases. This is attributed to the growing thickness of the TiO_2 layers on the Ti plate, causing the generated electrons under UV light irradiation to be confined to the surface of the catalyst, unable to move towards the bulk semiconductor and only remain on the catalyst's surface. Consequently, the bulk semiconductor cannot transfer electrons to the counter electrode as a cathode. Additionally, the thickness of the thin TiO_2 layer grown on the Ti plate results in limited penetration of UV light to the inner layers of the TiO_2 film.

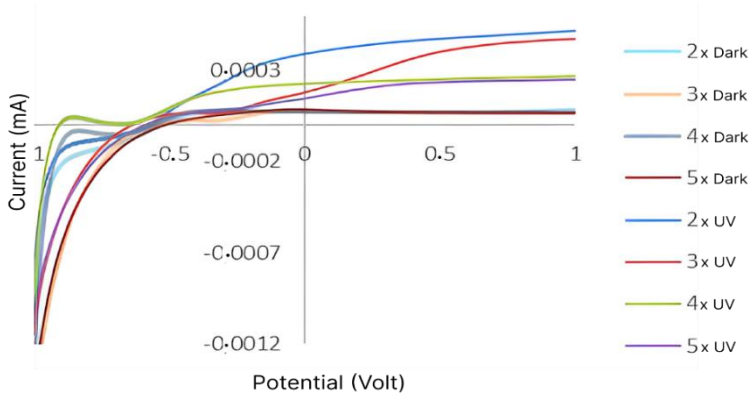

Figure 3. Linear Sweep Voltammetry (LSV) Graph TiO_2/Ti Electrodes

3.3.3. XRD Characterization

Characterization using X-ray Diffraction (XRD) was conducted to observe the structure and size of the solid TiO_2 crystals formed. Figure 1 shows the XRD diffraction patterns of the synthesized titanium dioxide nanoparticles, and peak details are listed in Table 1. The experimental XRD pattern matches with the JCPDS card number 21-1272 (anatase TiO_2) and XRD patterns of TiO_2 nanoparticles reported in other literature (Wang et al., 2020a). The peaks at 2θ angles of 25° and 48° confirm the presence of the anatase structure of TiO_2 (Nurdin, Nuhung, et al., 2021). The strong diffraction peaks at 25° and 48° indicate the presence of TiO_2 in the anatase phase (Nurdin, Maulidiyah, et al., 2021). No spurious diffraction peaks were found in the sample. The peaks at 2θ angles of 25.29° and 48.03° further confirm the anatase structure. The intensity of the XRD peaks from the sample reflects that the formed nanoparticles are crystalline, and the broad diffraction peaks suggest a very small crystallite size.Overall, the XRD analysis confirms the successful formation of anatase TiO_2 nanoparticles and provides valuable information about their crystalline structure and size.

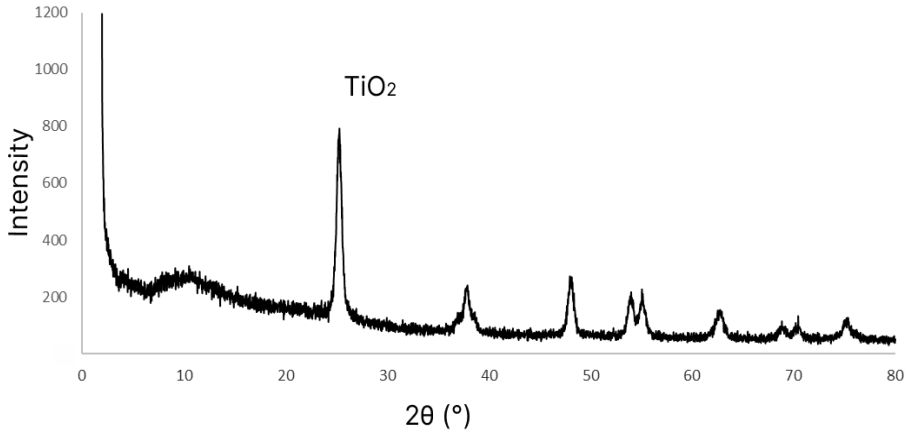

Figure 4. Diffractogram XRD of TiO_2/Ti

The average crystalline size of TiO_2 NPs was calculated from the XRD pattern using the Debye Scherer formula

$D = k\lambda/\beta\cos\theta$ ……(3)

Where D is an average crystalline size, K is a dimensionless shape factor with a value close to unity, λ is the wavelength of the X-ray, β is the full width half the maximum intensity (FWHM) and θ is the Bragg angle (Kibasomba et al., 2018).

Table 1 sows average crystalline size of TiO_2 NPs was found in the range of 13–16 nm. Adanya puncak 2θ = 25 merupakan puncak dari anatase and provides information that the fabrication of TiO_2 on the surface of the Ti plate has been successfully carried out (Gowthambabu et al., 2021b; Wang et al., 2020b).

Table 1. XRD Data of TiO_2 Nanoparticles

No	k	λ	Center 2θ	θ	Cos θ	FWHM	Size (nm)
1	0.9	1.5406	25.298	12.649	0.975	0.588	13.825
2	0.9	1.5406	37.830	18.915	0.946	0.660	12.723
3	0.9	1.5406	48.039	24.019	0.913	0.589	14.761
3	0.9	1.5406	53.958	26.979	0.891	0.700	12.724
4	0.9	1.5406	55.035	27.517	0.886	0.550	16.286

3.4. Photocatalytic degradation test

3.4.1. Maximum Wavelength of Congo Red

The determination of the maximum wavelength aims to identify the maximum absorption of a substance. This is because each molecule is capable of absorbing light at specific wavelengths and energies required for electron transitions from the ground state to the excited state. Therefore, an investigation to determine the maximum wavelength of Congo Red is necessary.

Figure 5 shows that the maximum wavelength of Congo Red is at 492 nm. This spectrum is consistent with previous research and provides information that the measurement of the maximum wavelength has been successfully carried out (Nurdin, Maulidiyah, et al., 2021).

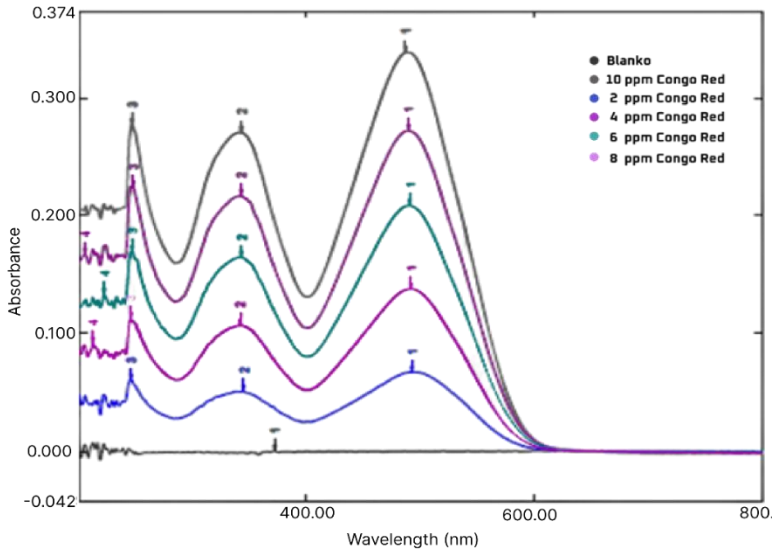

Figure 5. UV-Vis Spectrum of Congo Red

3.4.2. Degradasi Congo Red

Figure 5 shows the maximum degradation strength of the TiO_2/Ti electrode obtained at a percentage of 12% under visible light, demonstrating suboptimal results. This is due to the electrode exhibiting a very low light current response activity. To maximize the photodegradation activity of TiO_2/Ti, further research is required by referring to previous studies (Muzakkar et al., 2021; Nurdin, Maulidiyah, et al., 2021; Nurdin, Nuhung, et al., 2021).

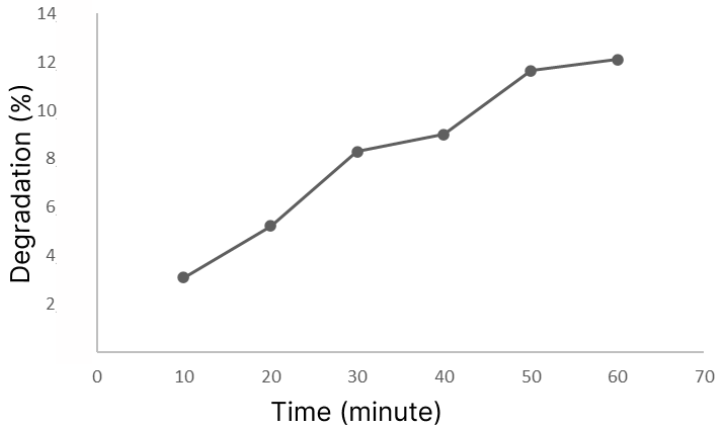

Figure 6. Photocatalytic Reactive Degradation (%) of TiO_2/Ti

Conclusions

TiO_2 immobilization on Ti plates was performed using the dip coating method. Characterization of TiO_2/Ti showed an energy gap of 3.2 eV, and the formed crystal structure was of the anatase type. LSV (Linear Sweep Voltammetry) analysis revealed that the TiO_2/Ti electrode was active under UV light. The TiO_2/Ti electrode exhibited excellent photoelectrocatalysis performance in the UV light region, with a degradation efficiency of 12%.

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Conflicts of Interest

The authors declare no conflict of interest

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