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Photoelectrocatalysis Activity TiO_2/Ti electrode doped with N and Ni Deposition for Congo Red Degradation

Muh. Edihar [1,*], Irwan Irwan [2], Andini Lidong [1]

[1] Departement of Chemistry, Faculty of Science Technology and Health, Institut Sains Teknologi dan Kesehatan 'Aisyiyah Kendari, Indonesia

[2] Department of Pharmacy, Faculty of Sciences and Technology, Institut Teknologi Dan Kesehatan Avicenna Kendari, Indonesia

*Email (corresponding author): ediharmuh@gmail.com

Abstract

The TiO_2/Ti electrode was successfully synthesized by combining element N and metal Ni on the TiO_2 matrix to degrade the organic compound Congo Red under UV-visible radiation. The aim of this study is to obtain Ni@N-TiO_2/Ti electrodes and test their performance in degrading Congo Red dye under UV-visible light radiation. The Ni@N-TiO_2/Ti electrode was prepared using the Sol-Gel and electrodeposition methods. The presence of nitrogen in N-TiO_2 is determined by FTIR and detected at a wavelength of 1.064 cm1. The analysis of UV-Vis DRS indicates an energy gap of 3.06 eV for N-TiO. XRD analysis revealed anatase crystal structure formation and nickel's presence in the Ni@N-TiO_2/Ti electrode detected at 2θ 52.8°. The usage characteristics of linear sweep voltammetry indicate that the TiO_2/Ti electrode is active under UV light, while the Ni@N-TiO_2/Ti electrode is active under visible light. An electrode activity test using the multi-pulse amperometry method showed that the photoelectrocatalysis performance of Ni@N-TiO_2/Ti under visible light radiation reached an ideal degradation rate of 36%.

Keywords: *Congo red, electrode, electrodeposition, Ni@N-TiO_2/Ti, sol-gel*

1. Introduction

The high level of industrialization and economic growth worldwide has increased industrial waste production, including hazardous organic compounds. Congo red, a synthetic dye, is an organic compound found in waste from the textile industry. This compound is classified as an azo compound and can seriously threaten water environments if not properly managed. Therefore, research continues to focus on developing effective methods to degrade these organic compounds. One promising approach is through photoelectrocatalysis activity on TiO2/Ti electrodes (1-3).

The TiO_2/Ti electrode is recognized as a very efficient catalyst material for degrading organic compounds with a high level of efficiency (4, 5). The primary advantage of TiO_2/Ti electrodes as catalysts is their ability to oxidize organic compounds into safer products (6), utilizing ultraviolet (UV) light or sunlight as an energy source (7). Furthermore, TiO_2/Ti electrodes have the advantages of chemical stability and corrosion resistance, allowing them to withstand harsh environments for extended periods (8-10).

Enhancing the performance of TiO_2 photocatalysts has become a research focus, motivating several researchers to apply it in the visible region (Vis). The use of non-metal and metal doping materials is intended to enhance the photocatalytic activity of TiO_2. The use of the doping substance causes changes in electronic and optical properties, shifting the catalyst's band gap to the visible region, increasing conductivity, producing more electron-hole pairs,

and enhancing its reactivity towards organic compounds (11-17). As Due et al. (15) and Cheng et al. (11) reported, TiO_2 doping with N reduces the band gap, making the catalyst active in the visible region.

Dopan N can alter the electron energy position inside the TiO_2 catalyst structure. Specifically, the nitrogen atom can produce a localized electron energy level 2p above the oxygen atom's electron energy level 2p (16). This reduces the maximum valence bond energy of the catalyst, affecting its reactive properties and conductivity. The purpose of metal-doped TiO_2 is to enhance the catalyst's photocatalytic activity. Specific metals such as iron (Fe), nickel (Ni), copper (Cu), and others can serve as active centers that aid in the formation of hydroxyl radicals and reduce the rapid recombination of electron-hole pairs formed during photocatalytic reactions (17-20).

This research focuses on the electrochemical synthesis of TiO_2 by depositing metal on the catalyst surface of TiO2/Ti. In this case, metals act as electron traps, inhibiting the recombination of electron-hole pairs and preventing changes in the electronic structure. Various studies have been successfully conducted, such as Lei et al. (21), who managed to create and modify the TiO_2 catalyst surface by attaching copper and silver metals through electrodeposition using $CuSO_4.5H_2O$ and $AgNO_3$ electrolyte solutions under controlled current. Nasirpouri et al. successfully developed catalyst modification by attaching nickel metal using the electrodeposition method. Liang et al. also enhanced photocatalytic activity under visible light radiation by electrodeposition of Ni on the TiO_2 surface.

Within this context, the study aims to evaluate and characterize the activity of TiO_2/Ti electrodes modified with N doping and Ni deposition in degrading the organic compound Congo Red. This study will examine the influence of parameter variations such as time, concentration, and potential on the efficiency of degrading organic compounds. The research aims to provide a deeper insight into the potential of this technology for addressing environmental pollution caused by hazardous organic compounds and to establish a foundation for developing more efficient and environmentally friendly waste treatment methods.

2. Experimental

2.1. Synthesis of TiO_2 and N-TiO_2

The sol-gel process was carried out as described in the research (23, 24) 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 tetraisopropoxide as the TiO2 precursor, 0.5 mL of acetylacetone, and 15 mL of ethanol. The mixture was refluxed and stirred using a magnetic stirrer for 120 minutes at a temperature of 50°C, then adding 3 mL of $CO(NH_2)_2$ solutions at 1M, 1.50M, and 2M as a nitrogen source.

2.2. Preparation of TiO_2/Ti

The initial stage of preparing a thin TiO_2 layer involves cutting a 2 × 6 cm plate of Ti (Shanxi Yuanlian Rare Metals Limited, China) with a thickness of 0.5 mm. Afterward, the plate is rubbed with a soft 120-grit sandpaper and washed with a mixture solution (detergent, distilled water, and acetone) to reduce the oil or mineral content on the surface of Ti. Next, the plate was immersed in HF (Merck, Germany), HNO_3 (Merck, Germany), and distilled water (1:3:6). Next, the plate was washed with distilled water and dried in a desiccator. A thin layer of TiO_2

on a Ti plate is created using a thermal oxidation process at 500°C for 90 minutes. The plate was cooled in a desiccator, preparing it for the N doping.

2.3. Preparation of N-TiO_2/Ti

The doping of N-TiO_2/Ti hydrothermal was immobilized in the sol-gel N-TiO_2 by evenly coating it on the surface and stirring it using a magnetic stirrer for 30 minutes and subsequently calcined at 500°C for 2 hours. The N-TiO_2/Ti was characterized utilizing a potentiostat with the LSV (Linear Sweep Voltammetry) method.

2.4. Electrodeposition of Nickel

Electrodeposition is carried out in a cylindrical reactor containing a solution of 0.04% $Ni(NO_3)_2.6H_2O$ in 100 mL of EDTA and a 0.1 M $NaNO_3$ electrolyte solution. The N-TiO_2/Ti electrode functions as the cathode, whereas the anode is a Pt wire mesh. Electrodeposition occurs at a current potential of -1.0 V for 10, 15, and 20 seconds. The cathode is dried in a desiccator for 24 hours. The sample was characterized using a potentiostat using the LSV (Linear Sweep Voltammetry) method under dark conditions, under UV-visible radiation (40 Watt tungsten lamp) with an Initial Voltage of -1000 mV, Final Voltage of 1000 mV, Scan Rate of 10 mV/s, and Range of 10 mA.

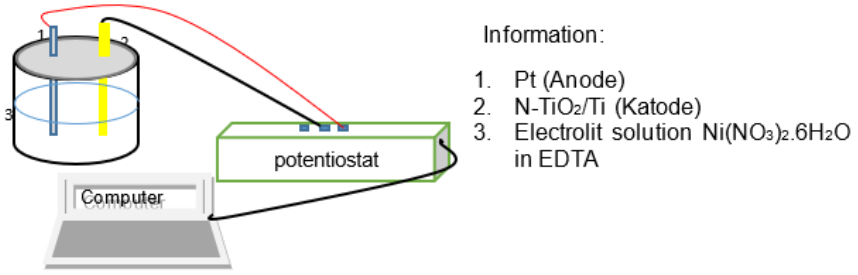

Figure 1. Electrodeposition reactor schematic

2.5. Electrochemical Assessment

Testing photoelectrocatalysis activity using a portable Potentiostat (e-DAQ) with Linear Sweep Voltammetry method. The experiment was conducted in darkness under UV-visible radiation (40-watt tungsten lamp) with an initial voltage of -1000 mV, final voltage of 1000 mV, scan rate of 10 mV/s, and range of 10 mA.

2.6. Photocatalytic Activity Test

The photoelectrocatalysis activity was tested by measuring the decrease in the concentration of congo red solution across the irradiation time. An activity test of photoelectrocatalysis was conducted in a photoelectrochemical reactor using visible light with a bias potential of 500 mV. The analysis used a portable potentiostat (e-DAQ) and multi-pulse amperometry.

2.7. Characterization of Ni@N-TiO_2/Ti electrode

The electrode morphology was characterized using X-ray diffraction (XRD) with a Shimadzu 6000 instrument at 2θ=20-80° using Cu-Kα = 1.54060. The morphology of nanocomposites and atomic composition were characterized using a Scanning Electron Microscope-Energy Dispersive X-ray, SEM (HITACHI SU3500). Photoelectrocatalytic

activity was tested by measuring the Congo Red solution concentration decrease during irradiation. Photoelectrocatalysis testing is conducted in a photoelectrochemical reactor under visible light irradiation with a bias potential of 500 mV. The analysis used a portable potentiostat (e-DAQ) using the multi-pulse amperometry method.

3. Results and Discussion

3.1. Characterization of Ni@N-TiO_2/Ti by UV-Vis DRS

Characterization using Diffuse Reflectance UV-Vis DRS was conducted to determine the band gap energy of TiO_2 and N-TiO_2. Figure 2, indicates that the band gap energy of TiO_2 is 3.2 eV. The obtained spectrum data is consistent with previous research (25, 26), with an optimal wavelength of 387 nm corresponding to the UV region. This indicates that the synthesis of TiO_2 from TTIP precursor using the sol-gel method has been successfully carried out. The predetermined band gap energy indicates that TiO_2 material exhibits semiconductor properties, making it suitable for various photocatalytic applications in the UV light range.

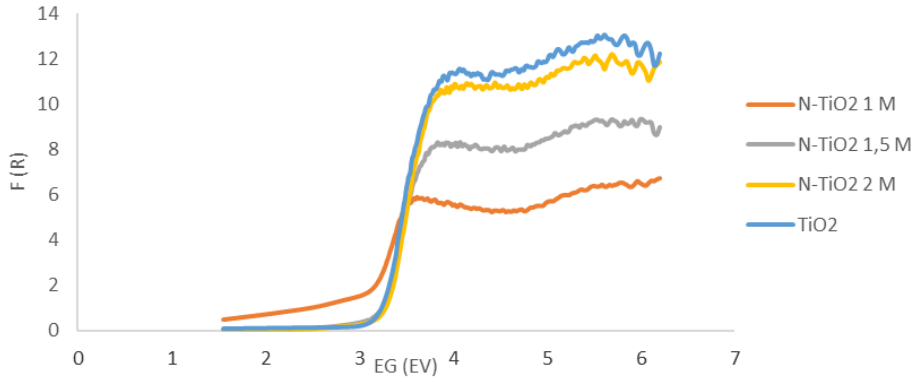

Figure 2. Graph of band gap in N-TiO_2

3.2. Some Common Mistakes

Table 1 illustrates how the energy band gap of TiO_2 decreases with N doping. As the band gap energy decreases, the required light energy to excite an electron from the valence band to the conduction band decreases due to the reduced distance between the valence and conduction bands. The decrease in band gap energy demonstrates that TiO_2 with added nitrogen can enhance the absorption region. The optimal absorption is expected to shift towards the visible area by adding nitrogen. The N-TiO_2 1 M has a band gap energy of 3.06 eV, corresponding to a wavelength of 405 nm. This provides information that N-TiO_2 1M is active in the visible region. The average crystal size of TiO_2 NPs was 13-16 nm. The peak at an angle of $2\theta = 25$ is the peak of anatase (7, 17). It indicates that the production of TiO_2 on the surface of a Ti plate has been successfully achieved.

Table 1. Band gap data of TiO_2 and N-TiO_2

Sample	Band Gap / Eg (eV)	Wavelength / λ (nm)
TiO_2	3.20	387
N-TiO_2 1 M	3.06	405
N-TiO_2 1.5 M	3.15	395
N-TiO_2 2 M	3.21	386

3.3. Determination of Optimal Electrode

Photon current response is the observed response of an electrode when irradiated with appropriate light and subjected to a current, which also serves as a measure of the rate of electron transfer occurring at the electrode surface. The coating was applied five times in this study. Figure 3(a). shows that the Ni@N-TiO_2/Ti catalyst can absorb visible light radiation, although to a much lesser extent than the electrode irradiated with UV light. The optimal electrode on Ni@TiO_2/Ti is shown when decorating Nickel metal for 15 seconds in Figure 3:(b). The presence of Ni on the N-TiO_2/Ti electrode is believed to prevent electron-hole recombination and enhance catalytic activity for visible light absorption despite its small quantity.

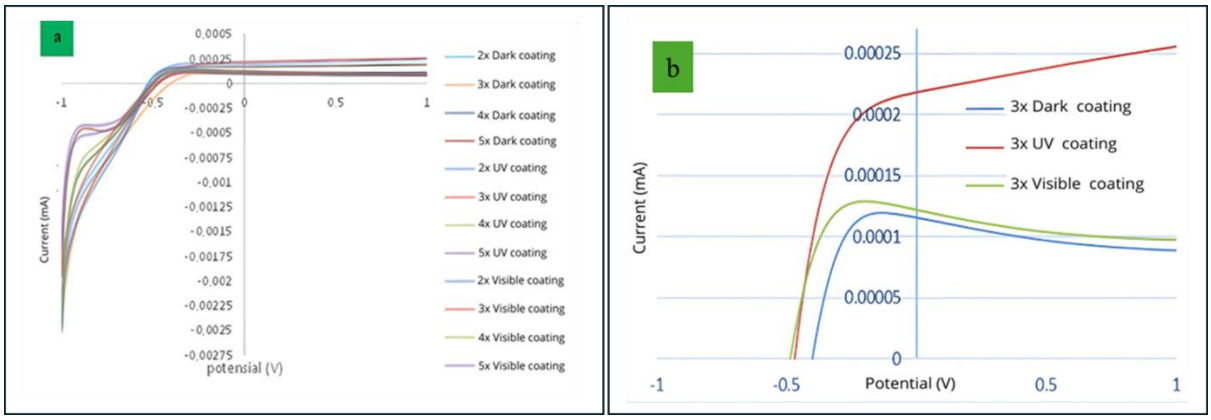

Figure 3. Photocurrent of; (a) Light Current Response of N-TiO_2/Ti; (b) Light Current

3.4. Response of N-TiO_2/Ti 3x Coating

3.4.1. SEM of Ni@N-TiO_2/Ti

The SEM measurement results for **Figure 4.** indicate the surface morphology of the catalyst with an average diameter of 67 nm for anatase crystal structure. SEM **Figure 5b.** shows particles covering the Ti plate and no nano-sized pores, unlike SEM image 5a. The suspected solid covering the surface of the Ti plate is believed to be solid N-TiO_2 resulting from immobilization.

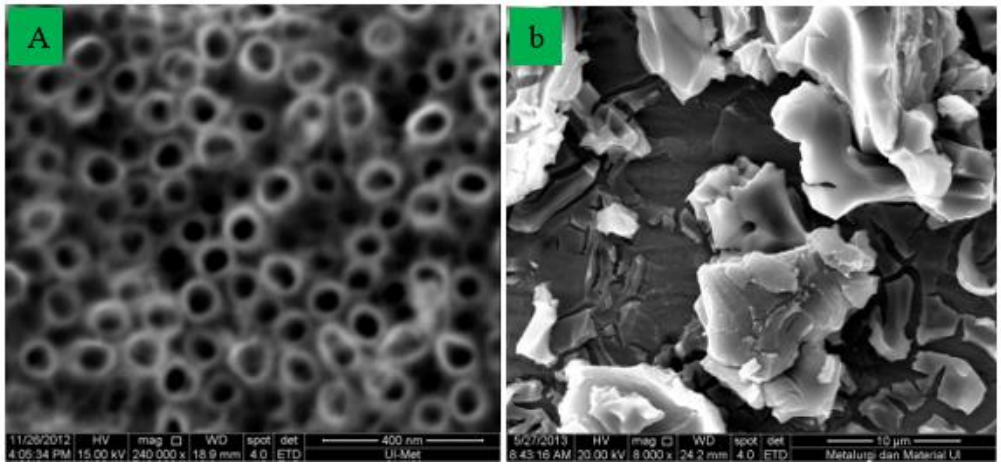

Figure 4. SEM; (a) N-TiO_2/Ti *Nanotube* 240.000x; (b) Ni@N-TiO_2/Ti 8.000x

3.4.2. XRD of Ni@N-TiO_2/Ti

Measurements using X-ray diffraction (XRD) were used to obtain information on the TiO_2 crystal structure. The difference in porosity between TiO_2, N-TiO_2, and Ni@N-TiO_2 crystals is shown in Figure 5. According to JCPDS No. 21-1272 (29–31), the peak intensity at angle 2θ, namely 25.30° (101), 27.25° (110), is characteristic of TiO_2 anatase and rutile. Temperatures as high as 500°C and a duration of 120 minutes caused the crystals to break, even though they were pretty small. Ni-TiO_2 (JCPDS no. 04-012-0745) (32, 33). This indicates the proper crystallization of Ni nanoparticles in the anatase TiO_2 structure.

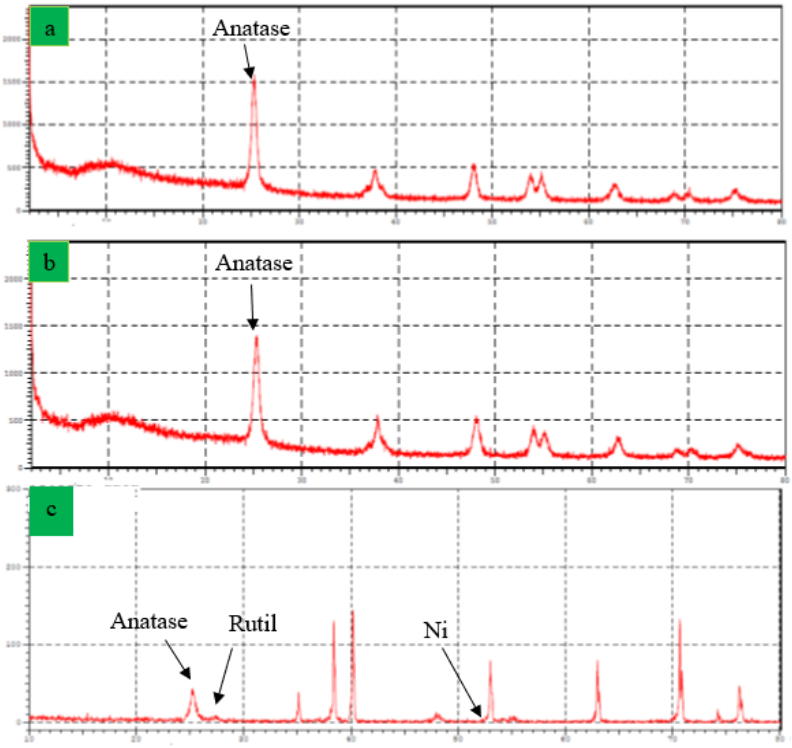

Figure 5. XRD of , (a) TiO_2 , (b) N-TiO_2, (c) Ni@N-TiO_2

3.4.3. Test Activity of Ni@N-TiO_2/Ti

To determine the degradation capability of the Ni@N-TiO_2/Ti catalyst in degrading congo red, photoelectrocatalysis activity testing was conducted using a 40-watt tungsten lamp as a visible light source. From the analysis of Figure 6. N-TiO_2/Ti decorated with Ni exhibits higher activity compared to N-TiO2/Ti and TiO2/Ti. This demonstrates that the presence of Ni metal attached to the surface of the N-TiO2/Ti catalyst can enhance the photodegradation activity. The presence of nickel metal on the catalyst surface is believed to act as an electron trap, preventing recombination between electrons and holes. As a result, the reduction of water by holes produces a more significant amount of hydroxyl radicals compared to N-TiO_2/Ti and TiO_2/Ti catalysts without nickel metal decoration. The results of the photoelectrocatalysis activity test showed suboptimal performance, with a degradation rate of 36% for the Ni@N-TiO_2/Ti catalyst. The suboptimal performance of the catalyst is due to the fact that N-doped TiO_2 can only make the catalyst respond to visible light with deficient activity.

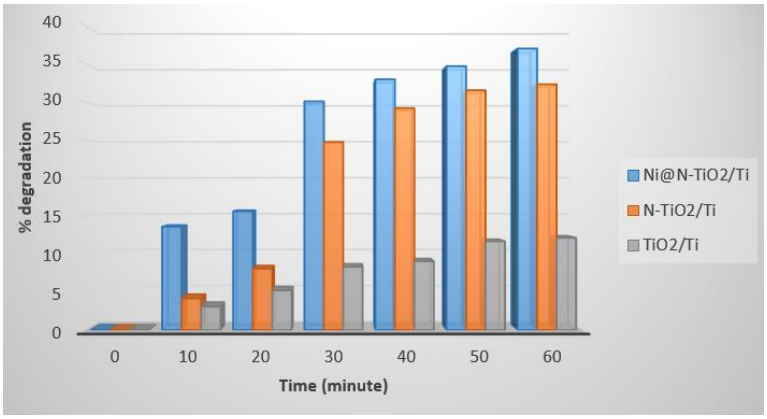

Figure 6. Activity of Ni@N-TiO_2/Ti

Conclusions

The conclusion drawn from this research is that the synthesis of N-Doped TiO_2 can be achieved by the sol-gel method by adding $CO(NH_2)_2$ as the N source. The N-TiO_2 formed is immobilized on a Ti plate using the dip coating method and subsequently decorated with Ni metal using the electrodeposition method. The photoelectrocatalytic activity test showed that the synthesized Ni@N-TiO_2 catalyst is more active compared to N-TiO_2 and TiO_2, with a degradation percentage of 36%.

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