

Nickel Oxide (NiO) Thin Film Synthesis via Electrodeposition for Methylene Blue Photodegradation

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Abstract

Nickel oxide (NiO) is an ideal photocatalyst material for methylene blue photodegradation. NiO is known to have high photocatalytic activity, good stability, and non-toxic properties. However, conventional NiO thin film synthesis methods are inefficient because require high temperatures, complex equipment operations, and volatile precursor solutions. Therefore, in this study, NiO was synthesized by the electrodeposition method and then applied for methylene blue photodegradation. NiO thin film's morphological structure and elemental composition percentage were characterized by field emission scanning electron microscopy and energy-dispersive X-ray spectroscopy, respectively. Meanwhile, the crystal structure was characterized using an X-ray diffractometer. Several electrochemical and photodegradation tests were conducted to analyze the performance of the NiO photocatalyst. The results showed NiO was successfully synthesized using the electrodeposition method. The morphology of NiO was a coral-like structure. A sharp diffraction peak with high intensity at 2θ with 43.28° indicates a well-ordered crystalline of NiO. The maximum photocurrent density generated from the photoelectrochemical test was 0.1287 mA/cm^2 . The small charge transfer resistance value (1353.6Ω) confirmed from the electrochemical impedance spectroscopy test indicates low charge transfer resistance. Percent photodegradation of methylene blue was obtained at 65% in 100 min, which indicated good photocatalytic activity.

Keywords: nickel oxide, electrodeposition, methylene blue.

1. Introduction

Contamination of water resources is one of the global problems that has a severe and long-term impact, which can disrupt the viability of organisms [1]. One of the water pollutants is synthetic dye waste which is usually used by various industries such as textiles, paints, paper, plastics, cosmetics, and others [2]. There are various dyes with an estimated annual production of about 1.6 million tons [3]. Methylene blue (MB) is a synthetic dye that is most commonly used as a colorant for paper, wool, silk, and cotton [4]. Untreated disposal of MB from industry can cause various diseases in humans such as vomiting, jaundice, and increased heart rate [5]. Therefore, treatment or removal of MB in wastewater before discharge is important. Several physicochemical and biological treatment methods that have been proposed to

remove MB from effluents including carbon adsorption, flocculation, ozonation, and activated sludge, have not been successful in completely removing dye pollutants and require expensive equipment and may cause secondary pollution [6].

On the other side, the photodegradation method using photocatalyst materials is a potential method that can be used to decompose organic dye waste. This method has been chosen because it is low-cost, environment-friendly, and easier to treat wastewater containing dyes [7–10]. In this method, it only requires light energy (photons) that is irradiated to the surface of the photocatalyst. Photons are then absorbed by the photocatalyst material and produce electrons and holes that form radicals. The radicals formed then react with the MB dye to produce simpler molecules such as H_2O and CO_2 [11].

Previous studies reported that nickel oxide (NiO) is considered a metal oxide semiconductor that can be used as a photocatalyst material. This metal oxide is a p-type semiconductor. The band gap width of NiO is between 3.6 to 4.0 eV [12]. NiO is commonly employed in photodegradation applications because it is known to have high photocatalysis activity properties, good chemical and physical stability, non-toxicity, and relatively low synthesis cost [13].

Nickel oxide can be synthesized using several physical and chemical methods such as pulsed laser deposition, chemical vapor deposition, aerosol-assisted chemical vapor deposition, and spray pyrolysis [14–17]. However, these methods are carried out at high temperatures that require a reactor, use a lot of volatile precursor solutions, and have complex equipment operations making it inefficient for NiO thin film synthesis. The electrodeposition method can be preferred because the synthesis can be carried out at room temperature. In addition, the electrodeposition method can control the morphology and the surface of the thin film [18].

In this study, NiO thin films were synthesized using the electrodeposition method. The films were then characterized with field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDS) to analyze the samples morphology and percentage of elemental content, respectively. X-ray diffractometer (XRD) characterization was also performed to study the crystal structure of NiO. Several electrochemical tests were conducted to evaluate the performance of photocatalysis. In addition, the photocatalytic activity was tested using the MB solution.

2. Materials and Method

Materials used in this study were nickel (II) sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) (Merck), potassium hydroxide (KOH) 1 M (Merck), potassium chloride (KCl) 3 M (Merck), sodium sulfate (Na_2SO_4) 0.5 M (Merck), ethanol, aquades, methylene blue (Merck).

Nickel oxide synthesis was carried out by dissolving 0.6570 grams of solid nickel (II) sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) into 25 mL of distilled water. Then, the pH was adjusted to 7.7 by adding 1 M KOH while stirring at 900 rpm on a magnetic stirrer. After that, electrodeposition was carried out on a copper wire using a potentiostat at a voltage of -1.3 V on an Ag/AgCl (KCl 3M) working electrode for 30 minutes. Followed by annealing for 1 hour in a furnace at 300 °C.

2.1 Characterization

Morphological and compositional analysis used FESEM (FEI brand, type: Inspect-S50) instrument equipped with EDS. Identification of NiO crystal structure was accomplished using an XRD (PANalytical Aeris with PIXcel1D-Medipix3 detector, and $\text{CuK}\alpha$ radiation source).

2.2 Electrochemical test

Electrochemical tests included photoelectrochemical (PEC) and electrochemical impedance spectroscopy (EIS) tests conducted in a three-electrode configuration electrochemical cell consisting of the working electrode NiO, reference electrode Ag/AgCl (KCl 3M) and counter electrode platinum (Pt). PEC was measured by linear sweep voltammetry with a voltage range of -500 mV to 2000 mV vs. Ag/AgCl (KCl 3M) with a scan rate of 10 mV/s in an electrolyte solution of 25 mL Na_2SO_4 0.5 M. The EIS test was carried out with a frequency range of 1 Hz to 100.000 kHz and an amplitude of 5 mV in 25 mL KCl 0.5 M electrolyte solution. All tests were performed under solar simulator irradiation.

2.3 Photodegradation test

The photocatalytic activity of the NiO photocatalyst was determined using photodegradation of a 5 ppm MB solution under visible light irradiation (solar simulator). The sample was put into 2.5 mL of a MB solution. The test was conducted for 100 minutes. The absorbance value was measured using a UV-Vis spectrophotometer (GB Cintra 2020). The following formula (1) was used to determine the percentage of MB degradation:

$$\text{Degradation (\%)} = \frac{A_0 - A_t}{A_t} \times 100\% \quad (1)$$

Where A_0 and A_t respectively show the absorbance value of the dye before and after the photodegradation test.

3. Results and Discussion

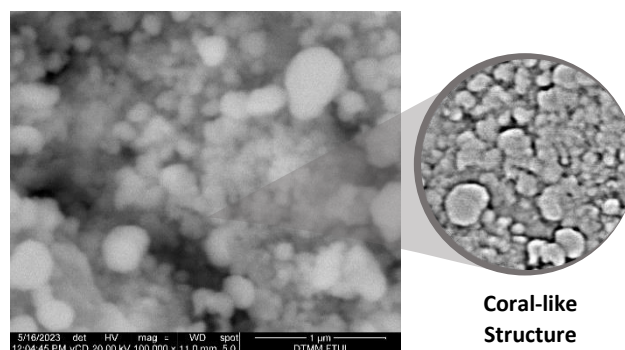
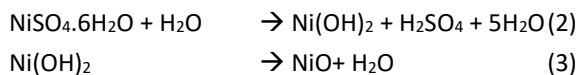


Figure 1. FESEM analysis of coral-like structure morphology of NiO surface.

Nickel oxide was obtained through electrodeposition and thermal treatment methods. In the electrodeposition process, a nickel hydroxide ($\text{Ni}(\text{OH})_2$) deposit was formed, characterized by a green color that coats the surface of the substrate [19]. To convert $\text{Ni}(\text{OH})_2$ into NiO , a heating process was carried out at $300\text{ }^\circ\text{C}$ for 1 hour. The reaction is as follows.



During the annealing process, the decomposition of $\text{Ni}(\text{OH})_2$ into NiO occurs [20].

2.1 Morphology, composition, and structure analysis

Figure 1 shows the surface morphology of the NiO film with heterogeneous structure and particle size. The morphology of the deposited NiO has angular and rounded particle shapes that agglomerate on the substrate surface. Such particles form a coral-like structure when observed [21]. The morphological structure of NiO reported in this study was different from previous reports such as spherical lobes, nanoflakes, granular porous, and grain structure [20,22–24]. The difference in morphological structure was observed due to the use of different synthesis methods with different treatment variations.

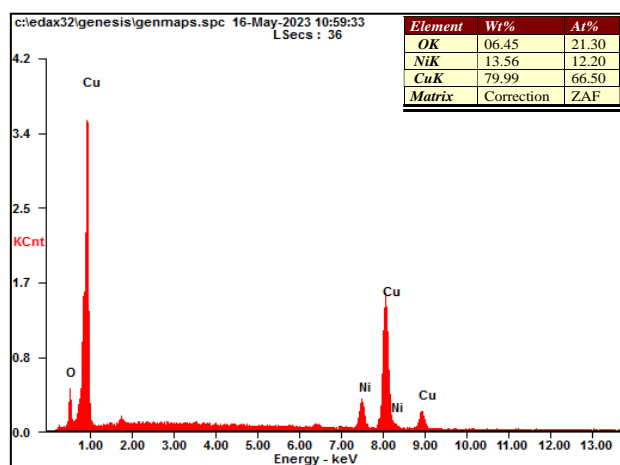


Figure 2. EDS analysis results of NiO deposit on copper wire substrate.

EDS analysis was used to determine the percentage composition of the elements in the film samples. Figure 2 presents the results of the EDS analysis of the samples. The graph shows the peak intensity, weight percentage, and atomic percentage of the elements contained in the sample. It can be seen that the percentage of copper (Cu) substrate is higher than nickel (Ni) and oxygen (O) which indicates the formation of a thin NiO layer on the substrate surface.

Figure 3 shows the XRD pattern of single-phase NiO appearing peak at $2\theta = 43, 28^\circ$, by the ICDD standard data card # 01-078-0423 [25]. The strong and sharp diffraction peak indicates good crystallinity [26]. In addition, diffraction peaks of Cu substrate appeared at $\theta = 50.41^\circ$ and 74.28° according to ICDD data 01-085-1326 [27]. These results confirm the successfully synthesized NiO and also confirm the results of the EDX analysis of the formation of the NiO layer on the copper substrate.

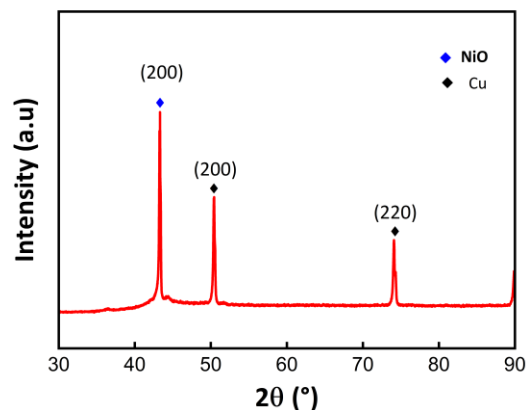


Figure 3. XRD diffraction pattern of NiO deposit on copper wire substrate

2.2 Electrochemical analysis

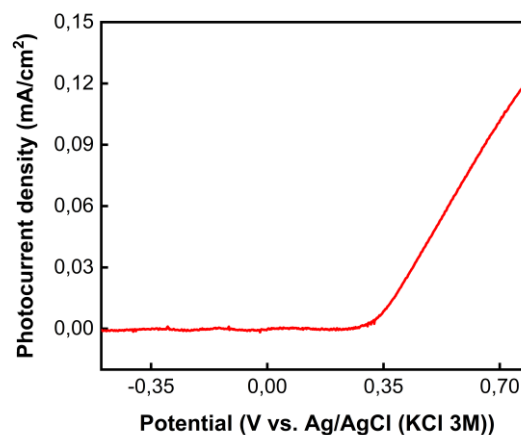


Figure 4. The relationship curve of voltage to photocurrent density ($V-i$) was measured in the voltage range -0.5 V to 0.75 V vs. Ag/AgCl with a scan rate at 10 mV/s in $0.5\text{ M Na}_2\text{SO}_4$ solution.

A PEC test was used to study the photoelectrochemical response of NiO . In the PEC test, the photocatalyst material was irradiated with light which induced photochemical reactions on the surface. Figure 4 shows the relationship of voltage to photocurrent density. From the analysis, the onset potential occurs at 0.25 V vs. Ag/AgCl ($\text{KCl } 3\text{M}$), where at this potential the current starts to increase

significantly, signaling the photocatalysis activity begins. The maximum photocurrent density achieved in this study was 0.1278 mA/cm^2 at 0.75 V vs. Ag/AgCl (KCl 3M).

Impedance measurements were performed on NiO thin films to evaluate the charge transfer using EIS. A Nyquist plot was generated from these impedance measurements, which illustrates the value of the electron transfer resistance (R_{ct}) of the sample. The diameter of the half-circle in the Nyquist plot represents how large the transfer resistance value is at the interface and can be used to describe the interfacial properties of the electrode [28]. The results of the study showed that the R_{ct} value of the sample was 1353.6Ω which indicates a low charge resistance. This charge resistance correlates with the rate of electron transfer at the electrode-electrolyte interface. The lower R_{ct} value indicates that the charge can be transferred more easily between the electrode and the electrolyte. Hence, these results imply a good capability in the process of electrochemical reactions. In the case of photocatalysis, a low R_{ct} value indicates a high efficiency in conducting charge during the photocatalysis reaction, which in turn may affect the photodegradation yield of MB.

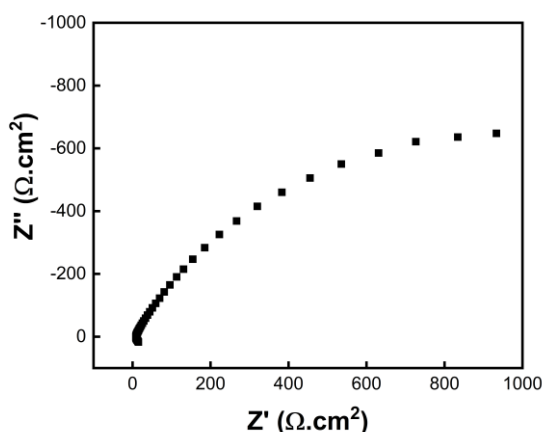


Figure 5. Nyquist plot of NiO photocatalyst under visible light irradiation. EIS spectra were recorded in 0.5 M KCl in the 1 Hz to 100kHz frequency range.

2.3 Photodegradation performance

The photocatalytic activity of NiO material could be determined by testing the photodegradation of MB solution under visible light irradiation. Based on the spectrum in Fig. 6 (a), the maximum absorbance of MB is by the typical absorption peak of MB at a wavelength of 664 nm . The change in concentration of the MB solution was known from the decreasing absorbance value as the period of irradiation increased.

The NiO photocatalyst showed the best percent degradation on MB solution in an irradiation time of 100

minutes. Figure 6 (b) shows the percent of MB photodegradation against irradiation time. The percent degradation of MB in the presence of NiO photocatalyst was 65% . This value is quite large compared to the results reported by Weldekritos *et al.*, which are only about 43% in the same test time. Weldekritos *et al.*, used the chemical precipitation method with calcination at $450 \text{ }^\circ\text{C}$ for 3 hours to synthesize NiO. Photodegradation testing was carried out under ultraviolet (UV) light irradiation [29].

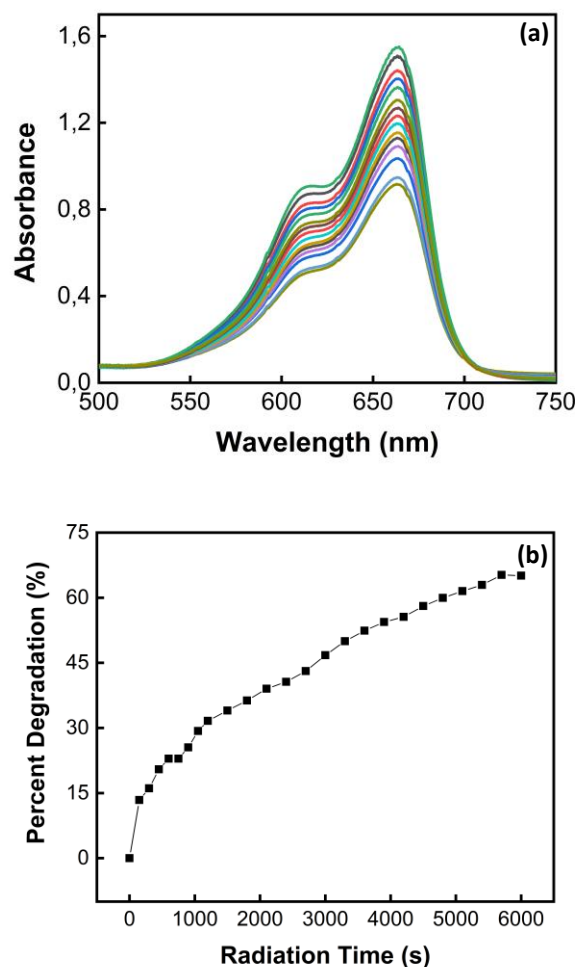
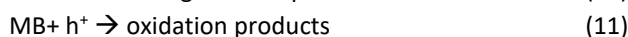
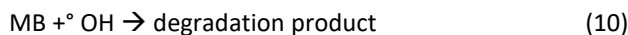
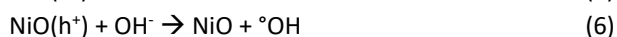
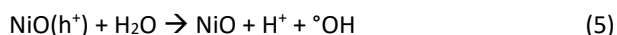


Figure 6. (a) UV-Vis absorption spectra for methylene blue photodegradation using NiO photocatalyst (b) methylene blue degradation efficiency using NiO photocatalyst.

Photocatalytic activity NiO can occur when NiO thin films are exposed to solar simulator light with energy above the band gap energy (3.4 eV). Electrons from the valence band (VB) are excited to the conduction band (CB), while holes (h^+) are formed in VB [30]. The generated electrons and holes react with oxygen or water adsorbed on the NiO surface, producing oxygen (O_2^\ominus) and hydroxyl (OH^\ominus) radicals [31]. The formed radicals oxidize MB and

convert it into a simpler molecule, namely H₂O, and CO₂. The complete mechanism is as follows [31]:



4. Conclusion

The NiO synthesized by the electrodeposition method exhibits potential application for MB photodegradation. The photocurrent density produced in the PEC test is 0.1278 mA/cm² at 0.75V vs. Ag/AgCl (KCl 3M) which indicates a fairly good photocatalysis performance. The low *R_{ct}* value of 1353.6 Ω shows a high efficiency in the charge transfer at the photocatalyst interface. The percent degradation achieved from the pristine NiO thin film was 65% in the test period of 100 minutes.

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