https://doi.org/10.48048/tis.2025.8697

Facile Synthesis of Thin Film Cobalt-doped Zinc Oxide Nanorods Photoanode for Efficient Methylene Blue Degradation

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Received: 16 July 2024, Revised: 14 August 2024, Accepted: 21 August 2024, Published: 30 November 2024

Abstract

ZnO nanorod thin films doped with cobalt were successfully synthesized on Indium Thin Oxide (ITO) glass substrates using the chemical bath deposition method to assess their characteristics and methylene blue degradation capabilities. ZnO nanorod thin films doped with cobalt were successfully synthesized on Indium ThinOxide (ITO) glass substrates using the chemical bath deposition method to evaluate their characteristics and methylene blue degradation capabilities. This study compared undoped and Co-doped ZnO on ITO glass substrates for photoelectrocatalytic (PEC) applications. XRD analysis confirmed that all samples exhibited a crystalline hexagonal wurtzite structure, with no additional phases detected in films with 5 % Co doping. The formation of nanorod structures in both undoped and Co-doped ZnO was revealed by SEM images where the presence of Co in the doped ZnO was confirmed through EDX analysis UV-DRS analysis indicated changes in band gap values with the addition of 5 % Co doping, decreasing from 3.09 to 3.07 eV for the ZnO/ITO and Co-ZnO/ITO photoanode. Evaluation of the PEC performance of the photoanodes toward methylene blue in an aqueous solution showed that Co doping enhanced the PEC efficiency of the ZnO/ITO photoanode. The decolourization efficiency of methylene blue reached 93.72 % using Co-ZnO/ITO, which is higher than that of ZnO/ITO at 86.84 %. Furthermore, the kinetic study showed that Co-ZnO/ITO photoanode follows a first-order reaction kinetics model with a reaction rate constant of 0.0085 min^{-1}. The result of our study suggests the potential of Co-ZnO/ITO photoanode in addressing dyecontamination issues effectively.

Keywords: ZnO, Thin film,Photoelectrocatalyst, Methylene blue, Nanorods, Chemical bath deposition

Introduction

The textile industry is classified as a major producer of toxic and hazardous waste, with approximately 95 % of its waste stemming from dyeing, while the remaining 5 % originates from rinsing [1]. The utilization of these dyes necessitates appropriate treatment methods. Methylene blue is one of the most used dyes in the textile industry, particularly for dyeing silk, cotton, and wool. As a cationic dye, its prolonged presence in the environment can adversely affect aquatic organisms. Additionally, exposure to methylene blue can cause symptoms such as vomiting, diarrhea, nausea, and a burning sensation in the eyes [2].

The potential impact of dye waste must be mitigated through appropriate waste treatment before its release into the environment. Various methods for treating dye waste include ozonation [3], adsorption [4], chlorination [5], biological methods [6], and Advanced Oxidation Process (AOP) [7]. Among these, the AOP method is particularly efficient due to its highly reactive species, which degrade pollutants non-selectively and

rapidly. Photocatalysis, a promising technique within the AOP framework, offers advantages such as ease of application, high efficiency, stability, corrosion resistance, low cost, no secondary pollution, non-toxicity, and good reproducibility. It is highly effective in treating dye waste, and several studies have highlighted its efficacy in removing methylene blue dye. However, despite its ease and cost-effectiveness, the high recombination rate of charge carriers in photocatalysis limits its practical application for wastewater treatment. To address this limitation, the photoelectrocatalytic technique is employed, combining photocatalytic and electrochemical processes to achieve a higher degree of degradation of organic dye compounds, ensuring environmental safety [8]. Therefore, an analysis of methylene blue degradation using the photoelectrocatalytic method, facilitated by a semiconductor, was conducted to assess its effectiveness.

Various semiconductor materials are commonly utilized in the photoelectrocatalytic process, with ZnO thin films being a prominent example due to their band gap of approximately 3.37 eV at 300 K. Under UV-visible light irradiation, electron-hole pairs are generated which further form radical species such as •OH and $\bullet O_2^-$ (superoxide) as strong oxidizing agents against organic pollutant molecules [5]. However, the relatively wide band-gap value of ZnO has consequence in lower light absorption efficiency, thereby limiting its photocatalytic performance [4].

Doping ZnO with other semiconductor metals can enhance its physicochemical properties [9]. Previous studies showed improved ZnO photocatalytic performance by doping with transition metals such as Fe, Co, Mn, Ni, and Ag [4]. Isai and Shrivastava [10] conducted research utilizing Fe-doped ZnO for the removal of methylene blue and achieved a degradation efficiency of 92 %. Both pure and transition metal-doped ZnO are frequently employed in diverse applications, including solar cell sensors, photoelectronic devices, and photocatalytic or photoelectrode systems.

This research focuses on synthesizing ZnO thin film electrodes by doping them with cobalt using the chemical bath deposition method. The objective is to evaluate the characteristics of the thin film electrode substrate and the efficacy of the dopant in enhancing the performance of ZnO thin films as anodes in the photoelectrocatalytic degradation of methylene blue waste before its release into the environment.

Materials and methods

Materials

The materials used in this study include $Zn(NO_3)_2.6H_2O$, $Co(CH_3CO_2)_2.4H2O$, hexamethylenetetramine, and NaCl were analytical grade and obtained from Merck. Acetone, isopropanol, methylene blue dye, graphite plates, and Indium Tin Oxide (ITO) glass (dimension: 20×20×1.1 mm, sheet resistance 5.4 - 6.8 Ω/sq, and transparency 78.8 %) were obtained from commercial suppliers. All the chemicals were used without further purification.

Synthesis of ZnO/ITO and Co-ZnO/ITO thin film electrodes

The synthesis process for the Co-ZnO/ITO thin film electrode began by mixing 25 mL of $Zn(NO_3)_2.6H_2O$ and 25 mL of hexamethylenetetramine, followed by stirring at 95 °C. For the Co dopant source, an amount of $Co(CH_3CO_2)_2.4H_2O$ was added with a Zn: Cu molar ratio of 5 %. Once a homogeneous solution was obtained, pre-washed ITO glass using isopropanol and acetone subsequently was immersed vertically into the solution with a deposition surface area of 2 × 1.5 cm. During the process, the bath solution was continuously stirred for 6 h to obtain the homogenous thickness of the ZnO thin film and prevent agglomeration. The Cu-ZnO/ITO glass was then dried at room temperature and subsequently calcined at 300 °C for 1 h. For a

comparison purpose, the ZnO/ITO thin film electrode was also synthesized without the addition of Co dopant.

Characterization

The crystal structure and phase analysis of ZnO/ITO and Co-ZnO/ITO were characterized using X-ray Diffraction (Bruker D8 Advance X-Ray Diffraction) with Cu-Kα radiation (λ = 1.5406 Å) at 40 kV and 15 mA over the range of 10 - 90°. Morphological characterization of the ZnO/ITO and Co-ZnO/ITO thin film electrodes was conducted using Scanning Electron Microscopy (JEOL JSM-6510LA at the energy range of 0 - 20 keV at certain magnifications), and surface composition and elemental identification were analyzed using Energy Dispersive X-ray analysis. Band gap values for both samples were determined using UV-Vis Diffuse Reflectance Spectroscopy (Shimadzu UV-2450). Absorbance values in methylene blue samples before and after the photoelectrocatalytic process were measured using UV-Vis spectrophotometry (Shimadzu UV-1280).

Photoelectrodegradation test

The photoelectrodegradation test was conducted on methylene blue samples using the synthesized thin film electrode. The ITO glass deposited by ZnO and Co-ZnO thin film served as the anode, while a graphite electrode (dimensions: 40×20×1 mm) acted as the cathode. These electrodes were positioned parallel to each other with a fixed distance of 2 cm. A solution containing 50 mL of methylene blue at a concentration of 10 ppm, supplemented with 0.1 M NaCl as an electrolyte, was prepared and placed into a sealed cell reactor supplied with an external electrical current (DC) at a voltage of 3 Volts from a power supply. The solution was then exposed to irradiation from a 10-watt UV lamp. The photoelectrocatalytic process was carried out over various time intervals: 40, 80, 120, 160, 200, 240, and 280 min at room temperature. The methylene blue solution was sampled before and after the photoelectrodegradation process and analyzed using a UV-Vis spectrophotometer. Subsequently, these results were analyzed to determine the reaction kinetics order.

Results and discussion

Design and characteristics of Co-ZnO/ITO thin film

The synthesis and deposition of ZnO and Co-ZnO on ITO electrodes were conducted using the Chemical Bath Deposition method. The process for synthesizing Co-doped ZnO/ITO thin film electrodes followed similar steps, involving the addition of 5 % $Co(CH_3CO_2)_2{\cdot}4H_2O$ along with HMTA. The mixing process between ZnO and HMTA follows the following Eqs. (1) - (8) [1,11].

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \quad (1)$$

$$(CH_2)_6N_4 + Zn^{2+} \leftrightarrow [Zn(CH_2)_6N_4]^{2+} \quad (2)$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + HO^- \quad (3)$$

$$Zn^{2+} + 4NH_3 \leftrightarrow Zn(NH_3)_4^{2+} \quad (4)$$

$$Zn^{2+} + 4HO^- \leftrightarrow Zn(OH)_4^{2-} \quad (5)$$

$$Zn(NH_3)_4^{2+} + 2OH^- \leftrightarrow ZnO + 4NH_3 + H_2O \quad (6)$$

$$Zn(OH)_4^{2-} \leftrightarrow ZnO + H_2O + 2OH^- \quad (7)$$

$$[Zn(CH_2)_6N_4]^{2+} + 2OH^- \leftrightarrow ZnO + H_2O + (CH_2)_6N_4 \quad (8)$$

The synthesis outcomes reveal the formation of a thin white layer on the ITO surface, confirming the effective deposition of both ZnO and Co-ZnO onto the ITO substrate. The success of the synthesis is further assessed through diverse characterization methods including XRD, SEM-EDX, and UV-DRS.

Characteristics of Co-ZnO/ITO thin film

X-Ray diffraction analysis

The range of 2θ spanning from 10 to 90 degrees was employed to analyze the crystallinity and crystal size of ZnO/ITO and Co-ZnO/ITO. According to the results, the peaks observed in the synthesis of thin film electrodes correspond to a hexagonal wurtzite structure with a P63mc space group, in accordance with ZnO COD Card standard data No. 96-101-1259. The most intense peaks were identified at 31.94 ° (100), 34.60 ° (002), and 36.43 ° (101) for ZnO/ITO, and at 32.21 ° (100), 34.86 ° (002), and 36.68 ° (101) for Co-ZnO/ITO. No additional peaks indicative of CoO, Co_2O_3, Co_3O_4, or impurity phases were detected in the diffractogram of the Cobalt-doped samples [1]. This indicates the successful incorporation of Co metal into ZnO without altering the hexagonal wurtzite structure, as depicted in **Figure 1** [12]. The crystal size of the ZnO/ITO and Co-ZnO/ITO nanostructures was determined using the Debye-Scherrer as in Eq. (9) [13].

$$D = \frac{0.9\,\lambda}{\beta_{1/2}\cos\theta} \quad (9)$$

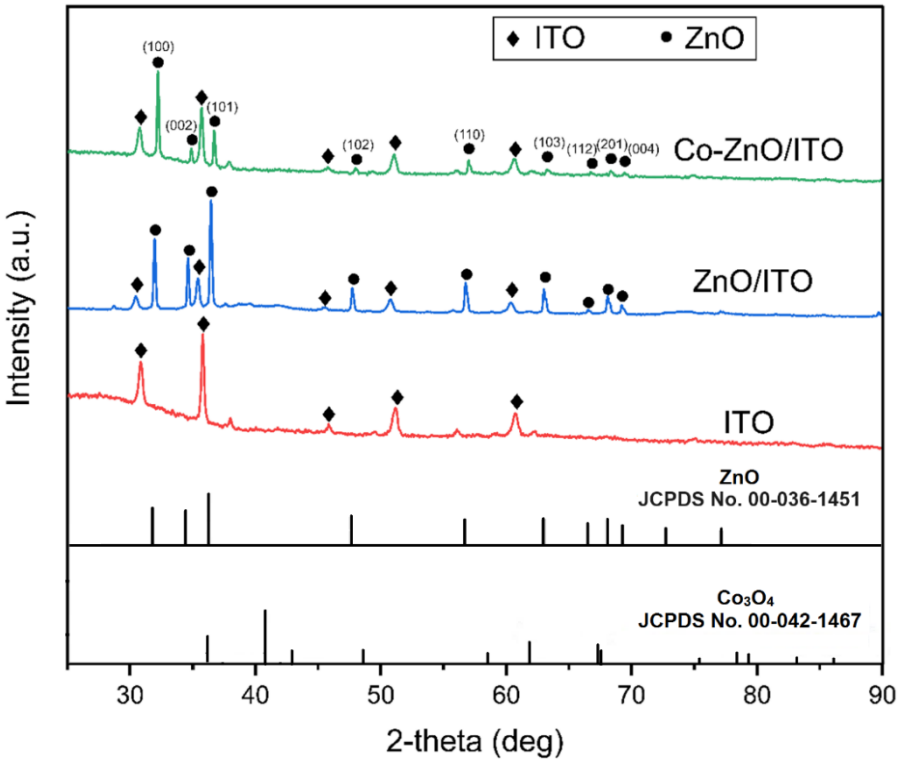

Figure 1 XRD diffractogram of ITO, ZnO/ITO, and Co-ZnO/ITO.

The crystal sizes measured for ZnO/ITO and Co-ZnO/ITO were 58.599 and 74.907 nm, respectively. These findings suggest that incorporating Co during synthesis as a doping agent can increase the crystal size of ZnO nanostructures, indicating improved crystallinity in the presence of Co metal doping crystal sizes measured for ZnO/ITO and Co-ZnO/ITO were 58.599 and 74.907 nm, respectively. These findings suggest that incorporating Co during synthesis as a doping agent can increase the crystal size of ZnO nanostructures, indicating improved crystallinity in the presence of Co metal doping [10,14]. Moreover, the calculation on lattice parameters resulted in the c/a value ratio for ZnO/ITO being 1.602, whereas for Co-ZnO/ITO it was 1.604. These results indicate that the c/a ratios do not significantly differ from the expected value for the

hexagonal wurtzite structure, which is reported to be 1.633 [15]. These results could be associated to oxygen formation occuring in interstitial sites and zinc vacancies (*v*Zn).

SEM-EDX analysis

The morphological analysis derived from the synthesis results is presented in **Figure 2**. These results indicate the formation of nanorods in both ZnO/ITO and Co-ZnO/ITO samples. The morphology of ZnO nanostructures on ITO substrates is highly influenced by experimental conditions, particularly the concentration of Zn^{2+} ions, which can alter the reaction rates of hydroxylation and dehydration during the growth process of ZnO on the substrate, thereby facilitating the formation of ZnO nanostructures.

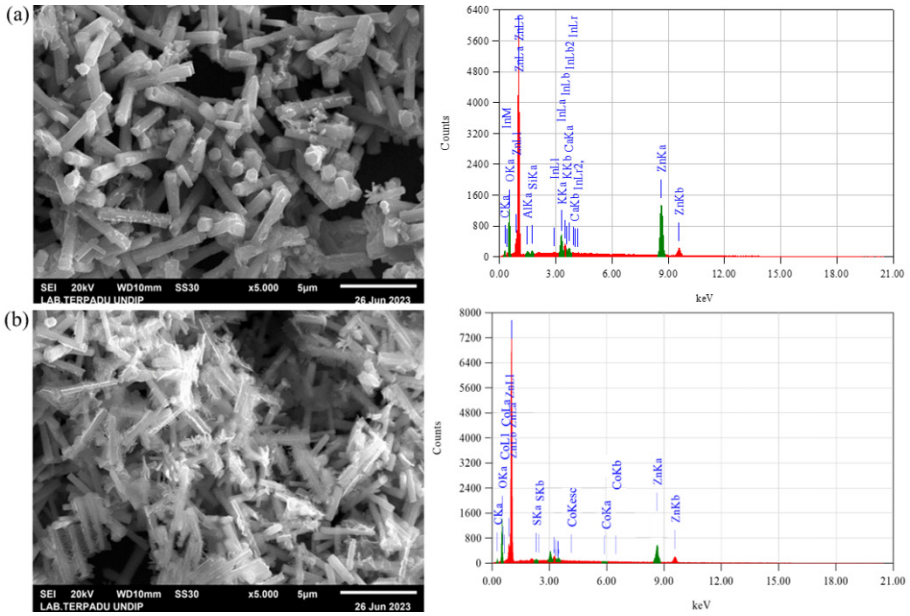

Figure 2 SEM images in 5000× magnification (left) and EDX spectra (right) of (a) ZnO/ITO and (b) Co-ZnO/ITO.

The composition analysis of the composite, including elements Zn, O, Co, In, and Si confirmed the incorporation of Co metal into Co-ZnO/ITO thin film electrodes using EDX. The findings in **Figure 2** and **Table 1** clearly indicate the successful doping of Co into the ZnO structure, verifying the presence of Co within the electrode [11].

Table 1 The percentage of Zn O, Co, Si, and In elements contained in the thin film electrodes.

Element	ZnO/ITO	Co-ZnO/ITO
Zn	28.04 %	19.43 %
O	44.13 %	54.32 %
Co	-	0.12 %
Si	0.64 %	2.21 %
In	1.91 %	4.74 %

UV – diffuse reflectance spectroscopy (UV-DRS) analysis

Band gap analysis was conducted to evaluate the optical characteristics of the ZnO/ITO nanostructures and assess the influence of Co doping on ZnO/ITO. The calculation of the band gap value was derived from measurements using the Tauc plot method, as outlined in Eq. (10) [16].

$$\alpha h\upsilon = \mathrm{c}\,(h\upsilon - E_g)^{1/2} \quad (10)$$

where E_g is the energy band gap, c is the energy constant, and α is the absorption coefficient calculated by the following Eq. (11) [17].

$$\alpha = 2.303\,\frac{A}{t} \quad (11)$$

where A is the absorbance and t is the thickness of the ZnO film.

The band gap values are explained by extrapolating the equation $(\alpha h\nu)^2$ versus the hν plot on the horizontal axis. **Figure 3** shows these plots for both ZnO/ITO and 5 % cobalt-doped ZnO/ITO, showing a decrease in the band gap of Co-doped ZnO/ITO compared to undoped ZnO/ITO. This reduction in band gap is attributed to the interaction exchange between localized sp-d and d electron configurations, where Co^{2+} ions replace Zn^{2+} ions, thereby narrowing the band gap in ZnO/ITO [18]. The band gap value of ZnO/ITO is 3.09 eV, while for Co-doped ZnO/ITO, it is 3.07 eV. Previous studies conducted by Kaphle, Reed, Apblett and Hari [14] reported larger band gap values for ZnO (3.18 eV) and Co-doped ZnO (3.34 eV). These findings indicate that the addition of a dopant can reduce the band gap value in ZnO thin films, which is consistent with the results of this study. This band gap value for ZnO/ITO is lower than that of bulk ZnO, typically around 3.3 eV, potentially due to internal defects such as oxygen

vacancies, zinc vacancies, and Zn and O interstitials [19]. The variability in band gap values in Co-doped samples may be attributed to the concentration of the dopant, the thickness of the thin film, and the specific deposition and annealing conditions during the preparation of the doped ZnO samples.

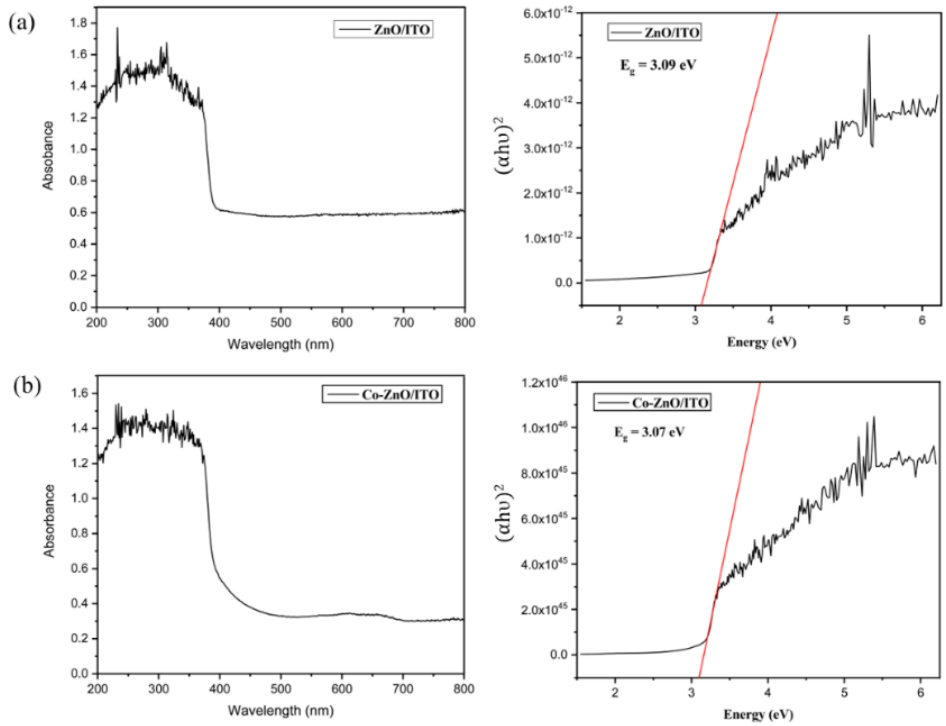

Figure 3 Tauc plot graph for band gap values of thin layer electrodes (a) ZnO/ITO (b) co-ZnO/ITO.

Photoelectrocatalytic test on methylene blue samples

The synthesized thin-layer electrode samples underwent a photodegradation test using methylene blue to assess their capability in degrading organic dyes. This photoelectrodegradation process involved varying the duration of photoelectrocatalysis, which is critical for the electrochemical oxidation reaction occurring on the electrode surface under UV light exposure. This reaction generates hydroxyl radicals that enhance the degradation process [20].

In this investigation, both synthesized samples were employed as anodes, while graphite electrodes served as the cathode, and methylene blue samples were evaluated using a UV-Vis spectrophotometer at a wavelength of 665 nm [18]. The findings indicated that Co-ZnO/ITO exhibited better degradation efficacy compared to ZnO/ITO, achieving yields of 93.15 and 86.84 %, respectively. Pedanekar *et al.* [21] conducted an evaluation study on the electrophotocatalytic degradation of methylene blue using Bi_2WO_6/FTO, achieving a maximum degradation efficiency of 90 %. This result is lower than the degradation efficiency reported in the present study, highlighting the effectiveness and advantages of the material synthesized herein. These results were also graphically represented in **Figure 4**(**a**) to illustrate the relationship between time and decolorization efficiency. The degradation mechanism of methylene blue is elucidated through Eqs. (12) - (21) [22].

$$\text{ZnO: Co} + h\nu_{(E > Eg)} \rightarrow h^+_{VB} + e^-_{CB} \quad (12)$$

$$(h_{vb}^+) + H_2O_{(ad)} \rightarrow OH\bullet_{(ad)} + H^+ \quad (13)$$

$$(h_{vb}^+) + OH^-_{(ad)} \rightarrow OH\bullet_{(ad)} \quad (14)$$

$$O_2 + e^- \rightarrow O_2^{\bullet -} \quad (15)$$

$$O_2 + H^+ \rightarrow HO_2^\bullet \quad (16)$$

$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \quad (17)$$

$$HO_2^\bullet + O_2^{\bullet -} \rightarrow OH_2^{\bullet -} + O_2 \quad (18)$$

$HO_2^{\bullet} + H^+ \rightarrow H_2O_2$ (19)

$H_2O_2 + e^-_{CB} \rightarrow OH^{\bullet} + OH^-$ (20)

$H_2O_2 + O_2^{\bullet-} \rightarrow OH^{\bullet} + OH^- + O_2$ (21)

When the anode surface is exposed to UV light equal to or exceeding the band gap energy, electron-hole pairs (e^-/h^+) are generated. Electrons (eCB^-) move to the empty conduction band, leaving holes (hVB^+) in the valence band. With maintained charge separation, electrons and holes migrate to the catalyst surface, participating in redox reactions with adsorbed species. Electrons (e^-) drive reduction reactions, while holes (h^+) catalyze oxidation reactions on the semiconductor surface. Holes in the valence band may react with surface-bound H_2O or OH, producing hydroxyl radicals, while electrons in the conduction band react with oxygen, forming superoxide radical anions ($O_2\bullet^-$). These radicals subsequently react with hydrogen ions to generate hydroperoxyl ($HO_2\bullet$), H_2O_2, and OH•. Hydroxyl radicals (OH•) and superoxide radical anions ($O_2\bullet^-$) play pivotal roles in the photocatalytic oxidation process responsible for degrading methylene blue dye [23].

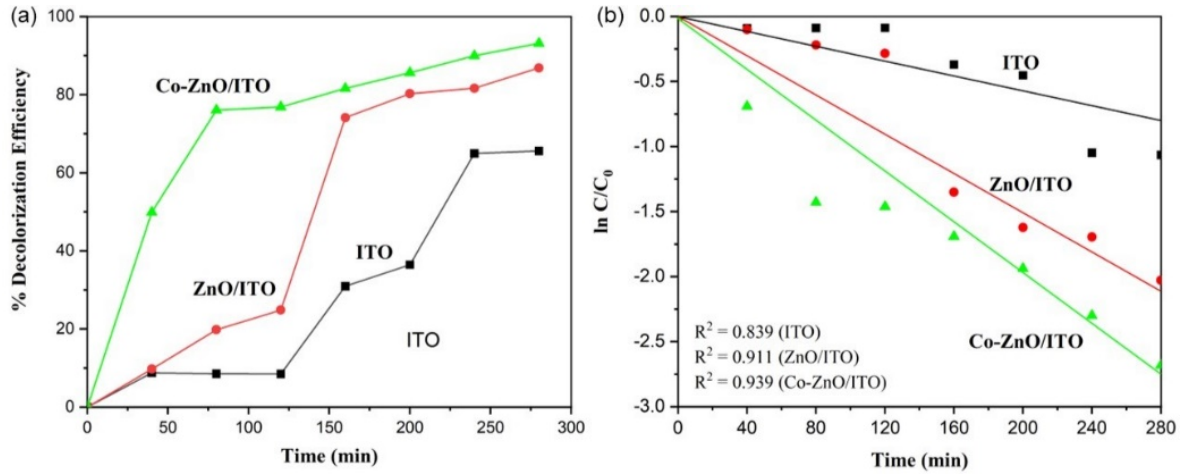

Figure 4 Graph of (a) decolorization efficiency and (b) first reaction order kinetics of thin film electrodes.

From the results of photoelectrocatalysis, the kinetic of the methylene blue degradation was studied based on the Langmuir-Hinshelwood (L-H) model, as expressed by Eq. (22) [24].

$$Degradation\ rate\ (r) = -\frac{dC}{dt} = \frac{K_r K_{dye} C}{1 + K_{dye} C} \quad (22)$$

where dC/dt is the degradation rate ($mgL^{-1}min^{-1}$) and C for the concentration of methylene blue concentration (mgL^{-1}) at degradation time (t). The rate constant and coefficient of adsorption coefficient of methylene blue by the catalyst surface are denoted as K_r and K_{dye}, respectively.

The reaction order of the photoelectrodegradation of methylene blue was determined based on the value of the squared correlation coefficient (R^2), where an R^2 value close to 1 indicates that the kinetics model is in accordance with the experiment. Calculation of first-order kinetics according to Eq. (23), which is done from the data of initial concentration (C_0), final concentration (C_t), and $\ln(C_t/C_0)$ [25].

$$\ln\left(\frac{C_t}{C_0}\right) = -K_r K_{dye} t = -K_{app} t \quad (23)$$

The calculation reveals that using Co-ZnO/ITO as an anode follows a first-order reaction kinetics model with an R^2 coefficient of 0.939, indicating a close fit to

the model, as presented in **Figure 4**(**b**). From the graph, the reaction rate constant is determined to be 0.0085 min^{-1}. This high constant value underscores the rapidity of the reaction. The increased reaction rate indicates accelerated production of radical ions, which in turn enhances the degradation efficiency of methylene blue during the photoelectrocatalytic process [26].

Characterization of methylene blue at optimum conditions

Following the photoelectrocatalytic process under optimal conditions, methylene blue samples require analysis using a UV-Vis spectrophotometer to determine if decolorization has occurred. The objective is to detect spectral changes before and after treatment. **Figure 5** presents the UV-Vis spectra of methylene blue samples before and after application under optimal conditions. The figure demonstrates a notable decrease in absorbance at the maximum wavelength of methylene blue (665 nm) following the photoelectrocatalytic process using ITO, ZnO/ITO thin-layer electrodes, or Co-ZnO/ITO. Both types of thin-layer electrodes exhibited decreased absorbance values, with Co-ZnO/ITO demonstrating a more pronounced reduction than ZnO/ITO and ITO alone. This decrease in absorbance signifies a significant reduction in methylene blue concentration, aligning with Beer's Lambert Law, which states that absorbance is linearly proportional to concentration [27,28].

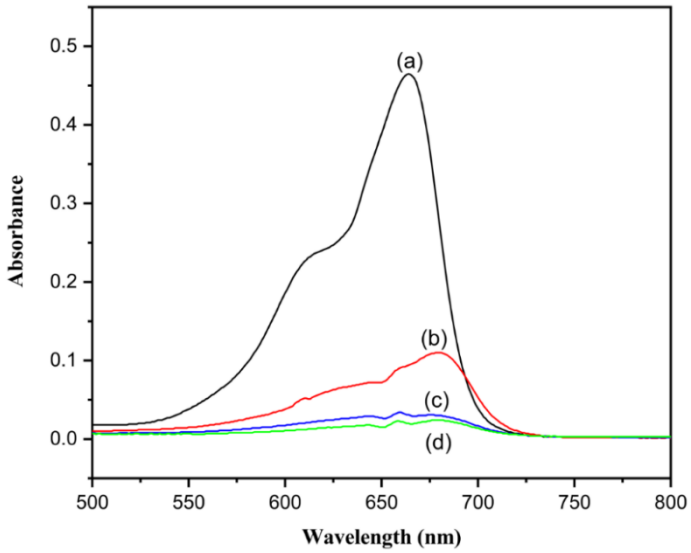

Figure 5 UV-Vis spectrum (a) of methylene blue before application to thin film electrodes. methylene blue after being applied to thin film electrodes via photoelectrocatalyst (b) ITO, (c) ZnO/ITO, and (d) Co-ZnO/ITO. the contact process or protoelectrocatalysis was carried out for 280 min.

Conclusions

The synthesis of ZnO/ITO and Co-ZnO/ITO thin film electrodes was successfully achieved through the chemical bath deposition method, utilizing zinc nitrate hexahydrate and cobalt acetate tetrahydrate precursors for the photoelectrocatalytic degradation of methylene blue. XRD analysis indicates that the addition of Co as a dopant increases the crystal size (crystallinity) of ZnO without altering its hexagonal wurtzite structure. Morphological analysis using EDX confirms the presence of Co metal in the nanorod structure of the thin film electrodes synthesized. The band gap value, determined through Tauc plot analysis, demonstrates a redshift indicating a decreased band gap due to Co doping in the ZnO thin films. In the photoelectrodegradation test using methylene blue dye,

Co-doped ZnO/ITO exhibited better dye degradation performance than ZnO/ITO alone, achieving degradation yields of 93.15 and 86.84 % within 280 min, respectively.

Acknowledgements

The authors gratefully acknowledge the financial support provided by the Ministry of Education, Culture, Research, and Technology, the Republic of Indonesia, Directorate General of Higher Education, Research, and Technology via World-Class Research (Number: 207 02/UN7.6/PP/2022).

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