

Preparation of ZnO-In₂S₃ Thin Semiconductor Film on Fluorine-Doped Tin Oxide (FTO) for Methyl Orange Degradation

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Abstract:- The synthesis of the ZnO-In₂S₃/FTO semiconductor thin layer was accomplished, aiming to serve as a photocatalyst for degrading methyl orange dyes. ZnO photocatalyst synthesis on FTO was conducted through the current electrodeposition method using a potentiostat device, while the In₂S₃ coating on ZnO/FTO employed the spray pyrolysis method. The characterization of the sample was performed using XRD and SEM-EDX. The X-ray diffraction analysis revealed the presence of ZnO and In₂S₃ in the sample, with average crystal grain sizes of 34.28 nm and 41.24 nm, respectively. SEM characterization depicted the morphology of ZnO crystals resembling nanoflowers, while the pattern of agglomerates was identified as In₂S₃. The EDX data confirmed the presence of Zn, O, In, and S elements. To assess the photocatalytic activity of ZnO-In₂S₃/FTO, degradation tests against methyl orange were carried out using photocatalysis and photoelectrocatalysis methods under UV and tungsten ray irradiation. The results indicated a more significant decrease in methyl orange concentration under tungsten rays compared to UV lighting, observed in both photocatalysis and photoelectrocatalysis processes.

Keywords:- Semiconductors, ZnO-In₂S₃/FTO, photocatalysis, Methyl Orange.

I. INTRODUCTION

The rapid advancement of today's industries has led to the generation of waste, posing significant threats to aquatic environments and public health. The textile industry, in particular, stands out as a major contributor to pollution, producing waste laden with dyes and a mix of organic and inorganic substances. Methyl orange, an azo compound commonly employed in textiles as a coloring agent, can become a source of disease in aquatic environments due to its carcinogenic and mutagenic properties over extended periods [1]. Therefore, the need for effective waste treatment techniques to degrade these compounds is imperative.

One viable approach to addressing aquatic pollution involves harnessing the photocatalytic properties of materials [2]. Zinc oxide (ZnO), chosen for its high photocatalytic activity as a semiconductor, possesses a band gap energy of 3.2 eV, making it active photocatalytically in the UV region [3]. However, utilizing UV light as a radiation source is not only hazardous but also entails high operational costs [4]. Hence, there is a pressing need to modify ZnO to make it compatible with solar energy,

allowing for more cost-effective and safer activation of its properties.

To enhance the photocatalytic efficacy of ZnO, the modification of semiconductor mixtures with varying band gaps can lead to the creation of new materials with smaller band gap energies. Drawing from the concept of semiconductor bandgaps, the use of semiconductors with different band gaps facilitates electron transfer, increasing the separation of hole-electron pairs and minimizing the recombination process [5, 6]. Indium sulfide (In₂S₃), known for its narrow band gap (2.0-2.3 eV), is recognized as a promising photocatalyst with stability and activity in the visible light spectrum [7, 8]. The incorporation of In₂S₃ semiconductors can form a hetero-junction type II with ZnO.

In the research process, thin films of ZnO-In₂S₃/FTO were grown by separately synthesizing each component. ZnO synthesis in Fluorine-doped Tin Oxide (FTO) employed the electrodeposition method, while the In₂S₃ coating on the ZnO/FTO substrate utilized the pyrolysis spray technique. The synthesized ZnO-In₂S₃/FTO films were then applied to degrade methyl orange dyes, demonstrating the potential of this approach in addressing pollution from the textile industry.

II. RESEARCH METHOD

A. Tools and Materials

The tools used in this study were standard laboratory glassware, a Multimeter (Krisbow), Potentiostat (CorrTest CS 150), X-ray diffraction instrument (PanAlytical), SEM-EDX instrument (Phenom Pro X), UV-Vis spectrophotometer (Pharo 300).

The materials used were Zn(CH₃COO)₂ p.a (Merck), KNO₃ p.a (Merck), InCl₃ p.a (Merck), thiourea (CS(NH₂)₂) p.a (Merck), Elektroda Pt, Elektroda Ag/AgCl, FTO glass (Sigma Aldrich, surface resistivity ~7Ω/sa).

B. Solution Preparation

The preparation of solutions involved two distinct stages corresponding to the sequential steps in thin layer formation, specifically the deposition of ZnO and In₂S₃. For the ZnO synthesis, the mother liquor consisted of 0.1 M Zn(CH₃COO)₂ and 0.4 M KNO₃ solutions. Each substance was dissolved in distilled water and then diluted in a 50 mL volumetric flask. Subsequently, the solution's pH was adjusted to 8 by adding 1 M NaOH. The solution was then subjected to air bubbling and magnetic stirring at 70°C for

30 minutes before deposition. Regarding the In_2S_3 synthesis, the stock solution comprised 0.1 M InCl_3 and 0.8 M thiourea ($\text{CH}_4\text{N}_2\text{S}$), thoroughly mixed in a 10 mL volumetric flask.

C. Electrode Preparation

The FTO sheet was trimmed to dimensions of 2x1 cm. An area of 1x1 cm was designated for deposition, and the remaining portion was covered with masking tape, serving as the electrodeposition surface. The glass underwent a thorough cleaning process involving nitric acid, acetone, ethanol, and distilled water, with each solvent applied for 15 minutes to eliminate any contaminants and impurities. Subsequently, the FTO glass was weighed before the electrodeposition procedure.

D. ZnO Electrodeposition

The FTO was coated with ZnO through an electrodeposition process conducted in a three-electrode cell, utilizing FTO as the working electrode, Ag/AgCl as the reference electrode, and Pt as the counter electrode. The potential applications were assessed using Linear Sweep Voltammetry (LSV) of the solution, with a potential adjustment ranging from 0 to -3.0 volts. A thin layer of ZnO was deposited using a galvanostat over 1200 seconds. The subsequently coated FTO glass was allowed to air dry and was then weighed.

E. In_2S_3 Deposition

The pyrolysis spray technique was employed to coat ZnO/FTO samples with indium sulfide. In a 10 mL volumetric flask, 0.2218 g of InCl_3 and 0.60896 g of thiourea were combined, and distilled water was added to reach the specified volume. The ZnO/FTO sample designated for spraying was initially positioned on a hotplate at 350°C. Simultaneously, the precursor solution

was loaded into an airbrush, and using a compressor, the solution was uniformly sprayed over the ZnO/FTO sample.

G. Material Characterizations

Characterization by X-ray diffraction (PanAlytical) was carried out to determine qualitatively the formation of ZnO- In_2S_3 layers that had been synthesized. Characterization with SEM-EDX (Phenom pro-X) was carried out to determine the surface morphology and elemental composition.

H. Methyl Orange Liquid Waste Photodegradation Test

The photocatalysis procedure took place within a reactor containing a 15 mL solution of 10 ppm methyl orange. For each session conducted under tungsten ray irradiation, spanning durations of 1, 2, 3, and 4 hours, the absorbance of methyl orange was gauged using a UV-Vis spectrophotometer. A parallel set of samples, identical in size, underwent the same process but with the inclusion of an additional treatment: the application of a 5 V external potential to the cell over 4 hours.

III. RESULTS AND DISCUSSION

A. Electrodeposition

➤ Determination of application current

The objective of assessing the applied current was to establish the minimum current required for the formation of ZnO during the electrodeposition process. This task was executed by employing a scanning potential through the Linear Sweep Voltammetric (LSV) program. The potential utilized for ZnO deposition underwent a linear sweep ranging from 0 to -3 volts at a scan rate of 10 mV per second.

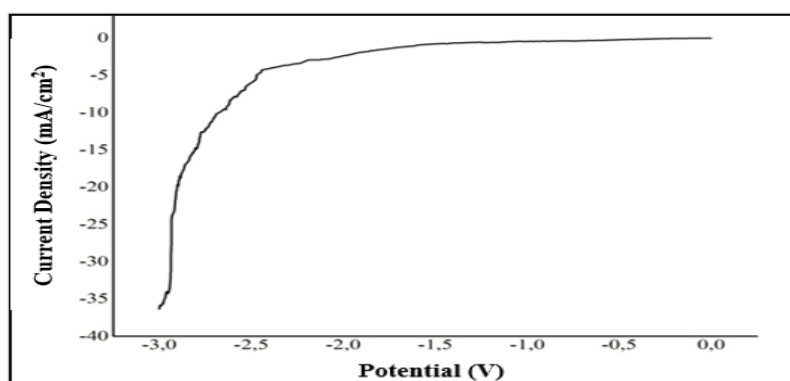
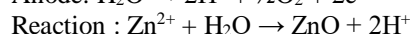
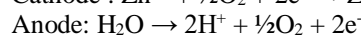
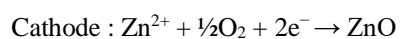


Fig. 1: ZnO's Linear Sweep Voltammogram

Referring to Figure 1, a substantial decline in current density was observed at a potential of -2.2 V, indicating an application current of -5.0 mA. This decline signifies the initiation of ZnO deposition on the FTO glass. The current diminishes over time due to the reduction of ions in the solution [9]. The current value derived from the voltammogram was subsequently established as the deposition current for ZnO. Employing this method, the electrolysis process for material deposition was carried out over 1200 seconds, during which zinc oxide was deposited at the cathode.

➤ ZnO electrodeposition on FTO glass

In the ZnO electrodeposition process a 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2$ solution was used as a source of Zn^{2+} , KNO_3 as an electrolyte, and NaOH as an adjusting pH. Zinc oxide could be precipitated along with a reduction of oxygen at the cathode and water oxidation at the anode. Redox reactions that occur:



According to the reaction mentioned earlier, the formation of zinc oxide on FTO glass is possible. Additionally, the inclusion of NaOH aimed to regulate the solution's pH to an alkaline level of pH 8. The ZnO

deposited on FTO was subsequently subjected to calcination at 450°C for 2 hours, resulting in the acquisition of 2.8 mg of ZnO deposits.

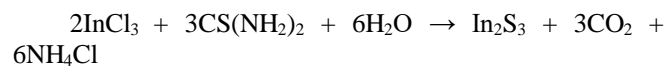


Fig. 2: ZnO/FTO electrodes produced in the electrodeposition process

B. In₂S₃ Deposition on ZnO/FTO

The deposition of In₂S₃ involved spraying a solution onto the heated ZnO/FTO glass substrate. The solution was prepared using InCl₃ as the source of indium and thiourea (CS(NH₂)₂) as the source of sulfur ions. Before spraying, the substrate was heated on a hotplate until it reached a temperature of 350°C. Subsequently, the solution was sprayed onto the substrate using a pressurized gas stream (compressor). The particles from the spray adhered to the

substrate, forming a thin layer. The overall reactions in the formation of In₂S₃ are as follows:



In₂S₃ that was successfully deposited was characterized by the color of yellow deposits on the ZnO/FTO semiconductor layer. Based on Figure 3, the weight of In₂S₃ deposited on the ZnO/FTO semiconductor layer was 3.3 mg with 2.29 mm in thickness.



Fig. 3: In₂S₃ deposited on ZnO/FTO substrates

C. Characterization of Material by X-Ray Diffraction

Qualitative characterization was performed using X-ray diffraction (XRD) to identify the presence of ZnO and In₂S₃ on fluorine-doped thin oxide (FTO) glass. The diffractogram, representing the relationship between the

scattering angle (2θ) and intensity (I), was analyzed for characteristic peaks. The XRD analysis utilized a Cu source with a wavelength (λ) of 1.54098 Å, operating at a voltage of 400 kV, a current of 300 mA, and an angular range (2θ) in the graph spanning from 20° to 90°.

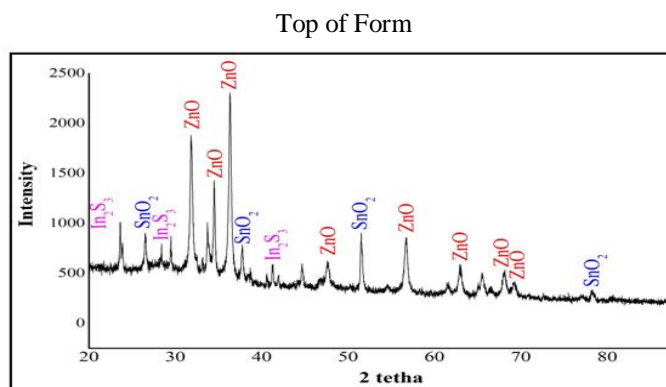


Fig. 4: Diffractogram of ZnO-In₂S₃/FTO synthesized

The standard used for ZnO refers to Match numbers 96–101–1259, In_2S_3 refers to Match 96–151–8188, and SnO_2 refers to Match numbers 96–152–6638. The XRD results were analyzed using the Origin application and compared with data in Match so that we could know the size of the crystal grains, as well as the constituent compounds formed from ZnO- In_2S_3 in the FTO synthesis.

The presence of ZnO compounds was indicated as a peak of 2θ : 31.84°; 34.50; 57.16° that almost coincides with

the standard peak of ZnO at 2θ at 31.77°; 34.55°; 57.32° with a difference of 0.07; 0.05 and 0.16. The ZnO crystal resulted in zincite. The presence of In_2S_3 was seen at the peak of 2θ : 23.63°; 28.41; 41.21° that are matches with a standard peak of In_2S_3 at 2θ at 23.62°; 28.38°; 41.00° with a difference of 0.01; 0.03 and 0.21. This shows that ZnO was present as the product pyrolysis spray method as thin-layer electrodes.

Table 1: FWHM value and ZnO- In_2S_3 crystal grain size

| Material | No. series Match | 2θ (°) | θ (°) | D (nm) | FWHM |
|-------------------------|------------------|---------------|--------------|--------|--------|
| ZnO | 96-101 -1259 | 31.84 | 15.92 | 25.71 | 0.3676 |
| | | 34.50 | 17.25 | 39.86 | 0.2005 |
| | | 57.16 | 28.58 | 37.27 | 0.2005 |
| In_2S_3 | 96-151 -8188 | 23.63 | 11.81 | 50.50 | 0.1671 |
| | | 28.41 | 14.20 | 50.99 | 0.1668 |
| | | 47.61 | 47.61 | 23.80 | 0.4010 |

Table 1 presents data on the polycrystalline size and Full Width at Half Maximum (FWHM) values obtained from the X-ray diffraction analysis of the ZnO- In_2S_3 /FTO thin layer. It is established that a smaller FWHM value corresponds to increased crystallinity, aligning with the Debye-Scherrer equation, which indicates an inverse relationship between FWHM value and crystal size. A smaller FWHM value indicates better quality, as it signifies a sufficiently large polycrystalline size. Conversely, a greater FWHM value suggests a less homogeneous crystal lattice and irregular crystal structure. The average crystal size is 34.28 nm for ZnO and 41.24 nm for In_2S_3 . Top of Form

➤ ZnO- In_2S_3 Material Morphology

Characterization with SEM aims to determine the surface morphology of ZnO- In_2S_3 . SEM results in Figure 4 show morphology of the deposit appears in crystal beads with irregular and not uniform. Particle misalignment was caused by crystal clustering that could occur due to homogenization during the synthesis process. The presence of ZnO was indicated by the morphology in the form of nanoflowers [10], while morphology seen as agglomerates was indicated as indium sulfide (In_2S_3). ZnO- In_2S_3 surface morphology image on FTO glass could be seen as follows:

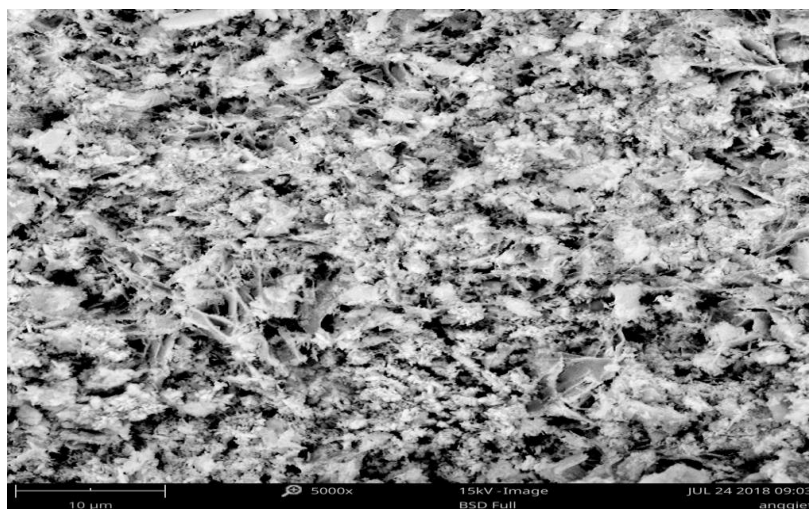


Fig. 5: Results of SEM ZnO- In_2S_3 /FTO thin film

EDX surface analysis was carried out to determine the elemental composition constituting In_2S_3 and ZnO on FTO glass. The result shows that the Energy-Dispersive spectrum

is presented in the form of a graph below, where the horizontal axis is dispersive energy and the vertical axis is the intensity of the enumeration of its constituent atoms.

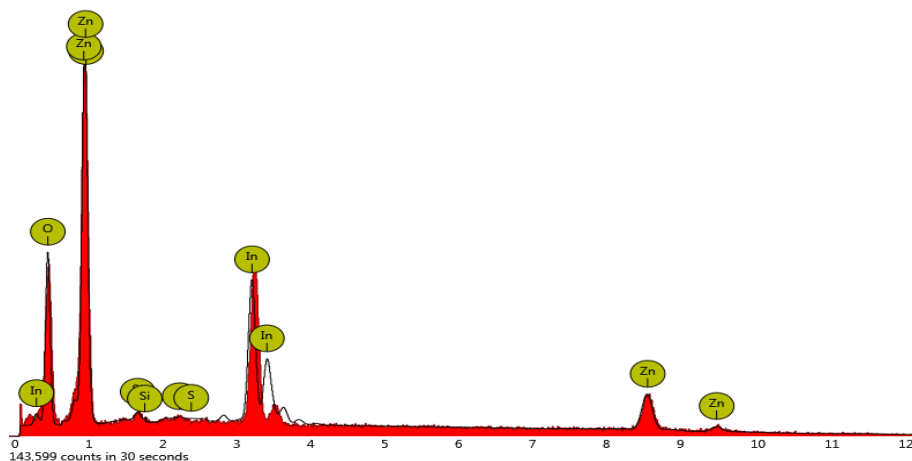


Fig. 6: EDX spectra of ZnO-In₂S₃ thin film

The composition of each element contained in the product is presented below which describes the sample composition.

Table 2: The results of EDX analysis of semiconductor ZnO-In₂S₃

| No. | Element | Relative Mass |
|-----|--------------|---------------|
| 1 | Zinc (Zn) | 27.8% |
| 2 | Oxygen (O) | 26.1% |
| 3 | Indium (In) | 25.1% |
| 4 | Sulphur (S) | 20.7% |
| 5 | Silicon (Si) | 0.3% |
| | Total | 100% |

D. Evaluation in Photocatalysis and Photoelectrochalysis of Methyl Orange

In this experimental procedure, a degradation test was conducted to assess the photocatalytic and photoelectrocatalytic efficacy of the synthesized ZnO-In₂S₃/FTO thin layer against methyl orange (MO) dyes. UV and tungsten lamps, each with a power of 15 W, were employed as light sources. Subsequently, the concentration of methyl orange after treatment was analyzed using a UV-Vis spectrophotometer, and the degradation percentage was calculated based on the obtained data.

Top of Form

➤ *Maximum Wavelength Measurement and Calibration Curve of Methyl Orange Solution*

Before testing, the methyl orange sample was measured in its maximum wavelength using a UV-Vis spectrophotometer that was scanned in the wavelength region of 300-800 nm. The maximum wavelength value indicates the wavelength at which a substance provides the highest absorption. The maximum wavelength was obtained from the curve of wavelength vs. absorbance. Spectra results in maximum absorption of methyl orange sample at 463 nm.

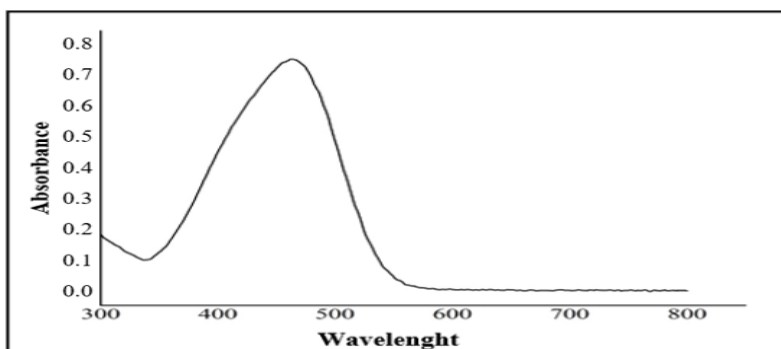


Fig. 7: Spectra of methyl orange of 10 ppm

The next step was making a calibration curve. A calibration curve was made by measuring the absorbance value of several standard concentrations of methyl orange. Results show the graph as linear correlation as shown in Figure 8. The calibration curve of the methyl orange solution

shows a straight line with a square correlation coefficient (R^2) of 0.9966, validating the straight line equation of $y = 0.0719x - 0.0083$. From this equation, the final concentration of methyl orange from the degradation process could be calculated by interpolation method.

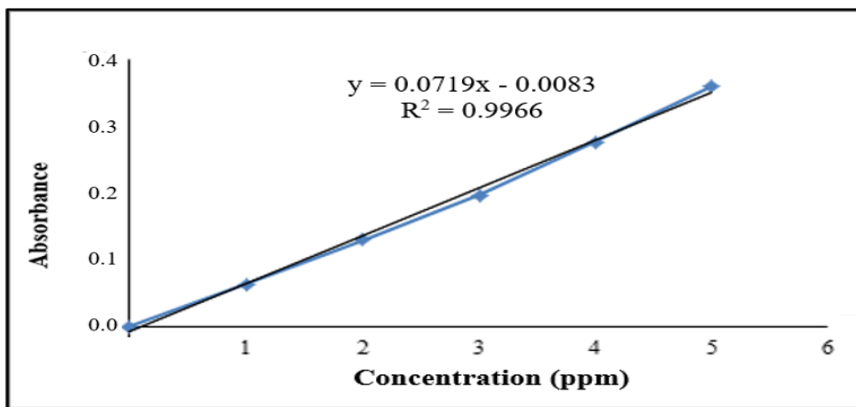


Fig. 8: Calibration curve for methyl orange solution

➤ Effectiveness of Methyl Orange Degradation Process

A degradation investigation was conducted in a reactor, submerging a semiconductor containing ZnO-In₂S₃/FTO in a solution of methyl orange dyes and stirring at 250 rpm. The concentration of methyl orange dyes utilized for this study was 10 ppm, with a volume of 15 mL. Subsequently, the cell was exposed to UV-C and tungsten light within an enclosed space. The degradation process was performed at different

irradiation durations of 1, 2, 3, and 4 hours for photocatalytic degradation and 4 hours for photoelectrocatalytic degradation. Additionally, a control procedure without irradiation was conducted over 4 hours. The degraded methyl orange solution was then assessed for absorbance using a UV-Vis spectrophotometer and compared with a standard methyl orange solution before treatment.

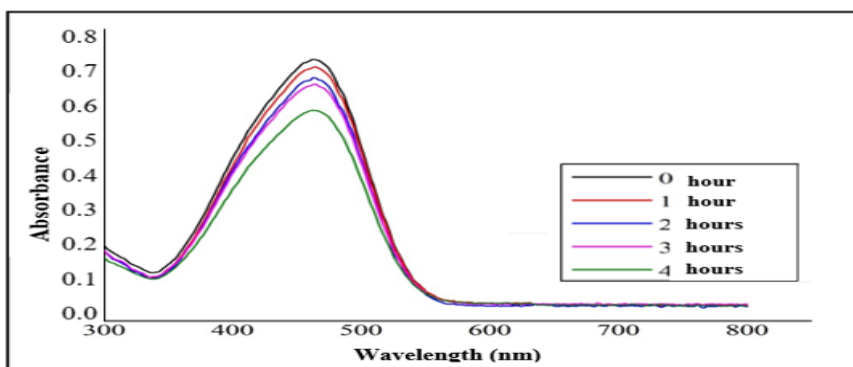


Fig. 9: UV-Vis scanning of mo sample after photocatalytic UV-C irradiation

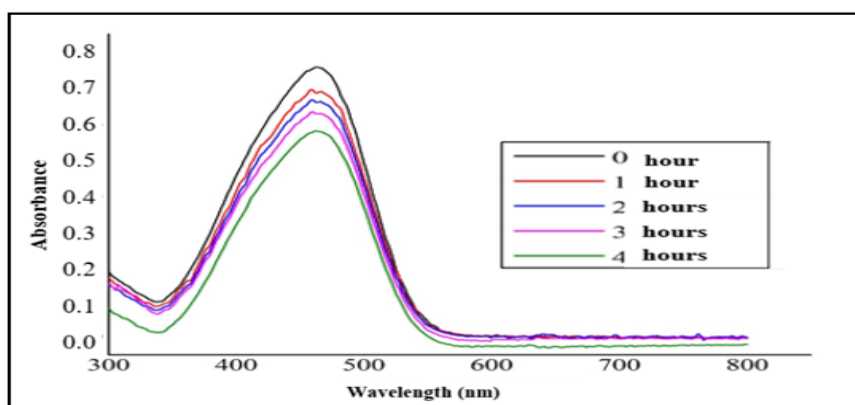


Fig. 10: UV-Vis scanning of the mo sample after photocatalytic by Tungsten irradiation

The findings from this study suggest that the ZnO-In₂S₃/FTO thin layer demonstrates the capability to degrade methyl orange dyes. The results indicate that as the duration of irradiation prolongs, the absorbance decreases, leading to an elevated percentage of degradation. This outcome is attributed to the increased number of photons in the system, enhancing the effectiveness of the degradation process.

The photocatalysis effect is sensitized by the irradiation of the semiconductor material, prompting excited electrons in the valence band to move to the conduction band, creating holes and electrons. These holes then oxidize OH⁻ to [•]OH radicals, while electrons reduce O₂ to generate superoxide radicals ([•]O₂⁻), facilitating the degradation of methyl orange.

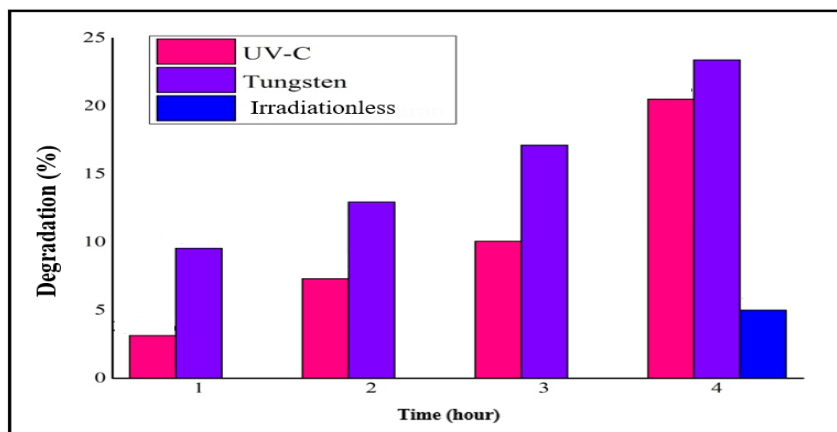


Fig. 11: Comparison of percentage of methyl orange degradation in three modes

Based on the diagram (figure 11), it was known that there was a significant difference between the degradation of methyl orange with and without light. Meanwhile, the percentage of MO degradation in the use of UV-C had a lower activity compared to the use of tungsten light. This shows that the results of ZnO-In₂S₃/FTO synthesis had a small band gap because it works optimally using visible light.

A photoelectrocatalytic test was performed by adding an external bias potential of +0.5 V. Degradation was carried out for 4 hours using UV light and Tungsten. The test results in higher performance compared to the photocatalytic one. This was because, in the photoelectrocatalysis process, more radicals were formed. After all, the recombination of electron-hole pairs could be minimized. So that the chromophore contained in methyl orange could be broken down by these radicals and had an impact on decreasing performance.

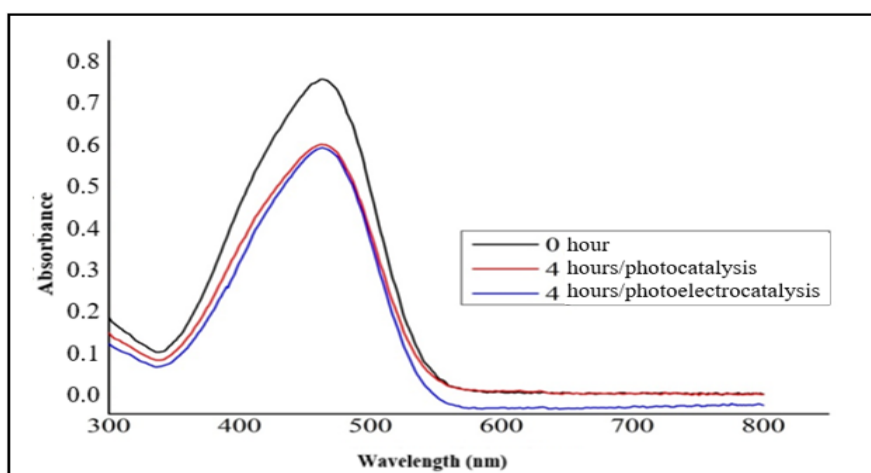


Fig. 12: Comparison of photocatalysis and photoelectrocatalysis of methyl orange sample under UV-C irradiation

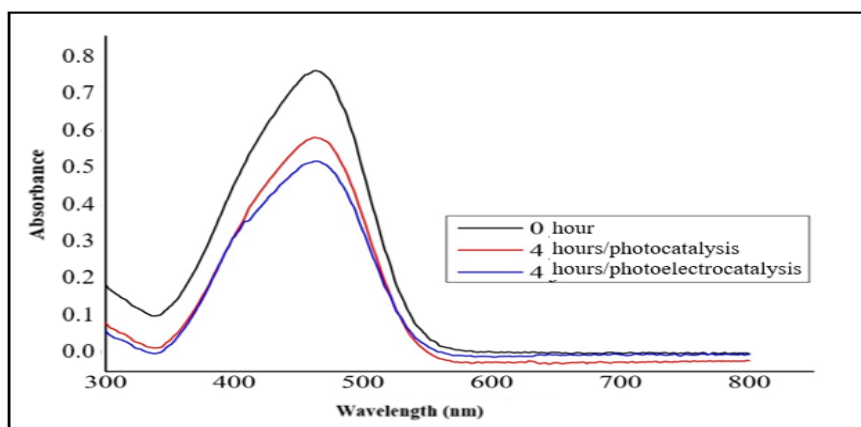


Fig. 13: Comparison of photocatalysis and photoelectrocatalysis of methyl orange under Tungsten light irradiation

IV. CONCLUSION

The synthesis of the ZnO-In₂S₃/FTO thin layer electrode was achieved through a two-step process. ZnO was deposited using the electrodeposition method with an applied current of -5.0 mA, while In₂S₃ was introduced through the spray pyrolysis method. The ZnO crystal grains exhibited an average size of 34.28 nm, while the In₂S₃ grains measured 41.24 nm. Notably, the degradation of the sample showed a more significant reduction in the concentration of methyl orange under tungsten light compared to UV light in both photocatalysis and photoelectrocatalysis processes.

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