

Effect of Solar Energy and Furnace on the Characterization of Purple Cabbage on TiO₂ – Cu₂O Semiconductors Using the Dr Blade – Spin Coating Method as a Renewable Energy

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Abstract. This study reports the synthesis and characterization of TiO₂–Cu₂O-based FTO coatings using diethanolamine, methanol, antimony chloride, and isopropanol precursors. The TiO₂–Cu₂O layers were prepared via the Dr. Blade–Spin Coating method and subjected to calcination at 350°C, 450°C, and 550°C. Structural, morphological, and optical properties were examined using X-ray diffraction (XRD), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX), Fourier-transform infrared spectroscopy (FTIR), and UV–Vis spectrophotometry. XRD analysis revealed decreasing crystal sizes with increasing temperature, ranging from 105.21 nm at 350°C to 64.34 nm at 550°C. SEM-EDX confirmed compositional variations, while UV–Vis analysis demonstrated efficient absorption of purple cabbage dye in the visible region. Results indicate that higher calcination temperatures significantly improve the absorbance, crystal structure, and morphology of the TiO₂–Cu₂O coatings, enhancing their potential performance in solar cell applications. Optimal properties were observed at 450°C and 550°C.

Keywords: TiO₂ – Cu₂O Semiconductor, Purple Cabbage Dye, Synthesis, Calcination, and Thin Films FTO.

1. Introduction

The amount of energy consumed by humans and other living creatures on a daily, weekly, monthly, and yearly basis is fundamental to human survival and global stability. This is recognized by various industries and investors seeking to develop energy sources in the fields of economics, science, technology, defense, and security. Indonesia is a country with abundant natural resources, such as water, coal, biodiesel, geothermal energy, wind, and solar energy, which are renewable energy sources. The World Bank projects that energy consumption would explode, approaching thirty trillion, by 2050, along with a global population of nine billion [1]

The demand for electricity and other energy sources is rising in accordance with the growing economy and increasing world population. Consequently, the government and the business sector remain in their efforts to advance technology and construct power plants that align with economic growth and anticipated electricity consumption [2].

Alternative energy sources refer to non-fossil fuel energy sources, such as those excluding petroleum and coal has been utilized for energy generation to meet human requirements. Unrestrained and excessive consumption of fossil fuels has negatively impacted health due to air pollution and the degradation of the ozone layer. Consequently, we are currently witnessing global warming, which is accelerating the melting of polar ice, elevating sea levels, inducing irregular precipitation, and precipitating dramatic climate change. In the forthcoming decades, fossil fuel sources will be exhausted, impacting the global economy [3,4]. Thus, environmental and human-made sources have been thought of as an alternative to provide energy.

Energy is an important component in human life and various natural processes. Humans need energy to carry out daily activities and maintain biological functions. In this context, energy is obtained from various sources, including food for metabolic processes and renewable resources such as solar energy. In addition to food, alternative energy sources include solar energy, electricity, and hydrocarbon-derived fuels [4]. Energy simply constitutes the capacity to perform labor. Energy may also be sent from one thing to another. This change shows that energy doesn't go away or get destroyed; it just changes from one form to another.

The main sources of energy can be classified into two groups. First one is conventional energy which is obtained from sources that are only available in limited quantities on earth and cannot be regenerated. The energy sources will run out sooner or later and are harmful to the environment. The second sources of energy is renewable energy. Renewable energy is energy generated from natural sources such as the sun, wind, and water and plant. The sources will always be available and do not harm nature [5,6]. Conventional and renewable energy sources can be converted into secondary energy sources, such as electricity. Electricity differs from other energy sources and is called a secondary energy source or energy carrier because it is used to store, transfer, or distribute energy. Primary energy sources are needed to generate electrical energy [3].

A possible source of renewable energy for generating electricity is solar energy extracted from sunshine. The sun is an infinite and sustainable power source. The most advantageous aspect of solar energy development in Indonesia is its significant potential, averaging 4.8 kWh/m²/day [7]. Nuclear physics hypothesis posits that the solar energy incident on earth will remain constant for billions of years, averaging 1,000 watts per square meter. If 25 percent of solar energy is turned into electricity, a maximum of 250 watts per square meter of electrical energy may be generated [8].

Alternative energy sources refer to non-fossil fuel energy sources (such as petroleum and coal) that can be utilized to provide energy for human need. Uncontrolled and excessive fossil fuel usage would adversely affect health because of air pollution and ozone layer damage. Consequently, people are currently witnessing global warming, which is accelerating the melting of polar ice, elevating sea levels, inducing irregular precipitation, and precipitating dramatic climate change. In the forthcoming decades, fossil fuel sources will be exhausted, impacting the global economy [9].

Solar energy, harnessed through photovoltaic cells, is a clean, abundant, and inexhaustible resource for power generation. Its efficiency is enhanced through advances in solar cell and

power electronics manufacturing, with a focus on optimizing nonlinear current-voltage equations to generate maximum energy [10]. In addition, various innovative approaches in solar cell design and materials continue to be developed to improve performance, such as the use of organic and hybrid materials, which offer higher efficiency potential with lower production costs.

Dye-Sensitized Solar Cells (DSSCs) are a type of solar cell that uses dyes to absorb photons. Dye-sensitized solar cells (DSSCs) are good because they are good for the environment and don't cost much, as they may use dyes made from natural materials [9,11]. Dye-sensitized solar cells (DSSCs) have a layered structure that looks like a sandwich. The layers usually contain an operating electrode, a TiO₂ (titanium dioxide) – Cu₂O layer, and an opposing electrode with a catalyst on top. A sequential procedure is used to create every single surface of a dye-sensitized solar cell. The operating photoelectrode and opposing electrode often utilize ITO (indium tin oxide) glass or FTO (fluorine-doped tin oxide) glass as substrates. A dye is put on top of the TiO₂-Cu₂O paste, and then an electrolyte solution is put on top of the dye layer to make the solar cell respond better to sunlight [12–14].

The researcher aims to enhance Indonesia's natural resources by conducting an in-depth analysis utilizing TiO₂ and Cu₂O semiconductors as synthesis materials, alongside purple cabbage as extracts and combinations [11]. The employed techniques include the Dr. Blade/spin coating method, diverse precursor procedures, modifications in calcination, data analysis, influence assessment, and testing methods like UV–Vis, XRD, SEM, along with measurements of current, voltage, and electrical power.

Therefore, this study aims to synthesize and characterize TiO₂–Cu₂O thin films sensitized with purple cabbage dye using the doctor blade–spin coating method and to investigate the effect of calcination temperature on their structural and optical properties.

2. Method

The synthesis of TiO₂-Cu₂O nanocomposite samples started with the procurement of requisite materials. 2.5 grams of TiO₂ powder is mixed into a 100 mL measuring cup and 2 grams of Cu₂O powder and 15 mL of methanol are blended into the vessel containing Cu₂O. Subsequently, the mixing process is conducted with a magnetic stirrer for one hour at a temperature of 100°C and a speed of 100 rpm until the sample attains a gel-like consistency. Once the sample has solidified into a gel, it is transferred to a crucible dish and allowed to dry. After the sample has dried, the TiO₂-Cu₂O sample is calcined in an oven at a temperature of 350°C or 1 hour. Once the TiO₂-Cu₂O sample has been calcined, it is ready to be tested using XRD, SEM-EDX, FTIR, and UV–Vis. The same procedure applied to samples which is exposed to calcination at a perpetual temperature of 450°C and 550°C.

To make the TiO₂ solution, zinc acetate dihydrate (Strem Chemical, 99.998%) was dissolved in isopropanol (Merck, 99.8%), then monoethanolamine (Merck, 99.8%) was added. The mixture was stirred for 60 minutes at 100 °C until it became homogeneous. Titanium tetraisopropoxide (Aldrich, 97%) is initially dissolved in isopropanol and methanol at ambient temperature to prepare the Cu₂O solution. Following a duration of 60 minutes, the solution underwent titration using a combination of acetic acid, methanol, and distilled water. Subsequently, it was agitated for a further 60 minutes at ambient temperature. The TiO₂:Cu₂O

coating procedure on the FTO glass substrate was executed utilizing the spray coating/doctor blade approach.

3. Result and Discussion

3.1 Test Results of Thin Films XRD TiO₂ 550° C, TiO₂ : Al 550° C and TiO₂ : Al / Cu₂O 550° C.

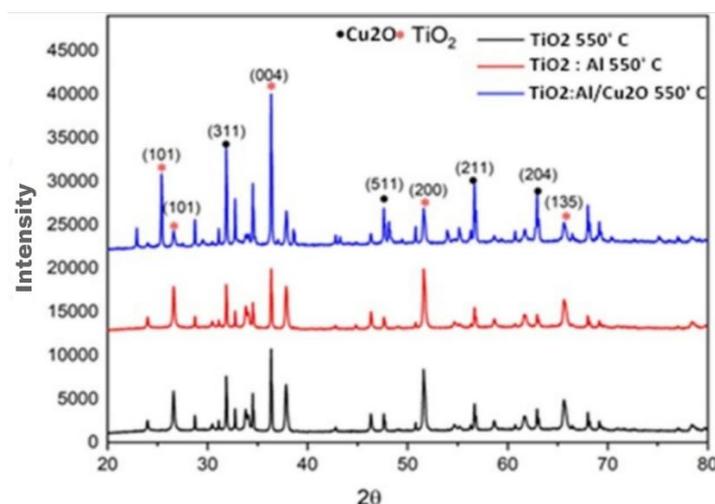


Fig. 1. Test Results of Thin Films XRD TiO₂ 550° C, TiO₂ : Al 550° C and TiO₂ : Al / Cu₂O 550° C

The XRD pattern shows that the main diffraction peak (1), shown by the blue line (h.k.l) (101) on TiO₂: Al/Cu₂O at 550°C, has an intensity of 31000 (au) with an angular range of 25–30°C. Peak (2) (h.k.l.) (101) exhibits an intensity of 25000 (au) at an angle of 22.5–30°C. Peak (3) (h.k.l.) (311) exhibits an intensity of 35000 (au) within an angular range of 32.5–35°C, whereas Peak (4) (h.k.l.) (004) demonstrates an intensity of 40000 (au) within an angular range of 37.5–40°C.

The peak 1, shown by the red line (h.k.l.) (101) on TiO₂: Al at 550°C, has an intensity of 17500 (au) and is located at an angular range of 27.5–30°C. Furthermore, peak (2) (h.k.l.) (311) reaches an intensity of 17500 (au) with an angular range of 32.5–35°C. Peak (3) (h.k.l.) (004) has an intensity of 20000 (au) with an angular range of 37.5–40°C.

Previous research described that the intensity measured at 2 degrees is in the range of 720 (au) with an angle of 20–25 degrees, resulting in a low peak and small crystallite size (15). Meanwhile, in the research conducted, the intensity is 40000 (au) and the angle is 37.5–40 degrees. The graph shows that peak 1 (black) (h.k.l.) (101) for TiO₂ at 550°C, has an intensity of 5000 (au) with an angular range of 27.5–30°C. The peak (2) (h.k.l) (311) has an intensity of 7500 (au) at the angle of 32.5–35°C. Peak (3) (h.k.l.) (004) has an intensity of 10000 (au) with an angular range of 37.3–40°C. Of the three graphs above, the highest is TiO₂: Al/Cu₂O with an intensity of 40000 (au) and an angle of 37.5–40° C.

3.2 Thin films TiO₂: Al/Cu₂O 550° C, TiO₂: Al 450° C, and TiO₂ 350° C.

The results of the thin films on TiO₂: Al/Cu₂O 550°C, TiO₂: Al 450°C, and TiO₂ 350°C are shown in Table 1 below.

Table 1. Thin film wavelength, crystal size, and percentage

Temperature	Wavelength (nm)	Crystal size (nm)	Percentage (%)
TiO ₂ : Al/Cu ₂ O 550°C	457.435 nm	45.75 nm	47%
TiO ₂ : Al 450°C	427.727 nm	42.77 nm	43%
TiO ₂ : 350°C	374.429 nm	37.54 nm	37%

Table 1 presents the study's findings, indicating that the TiO₂: Al/Cu₂O thin film, processed at 550°C, exhibits a wavelength of 457.435 nm, a crystal size of 45.75 nm, and a percentage of 47%. The TiO₂: Al at 450°C has a wavelength of 427.727 nm, a crystal size of 42.77 nm, and a percentage of 43%. The TiO₂ at 350°C has a wavelength of 374.429 nm, a crystal size of 37.54 nm, and a percentage of 37%.

3.3 SEM-EDX Thin Film Test Results TiO₂ 350° C

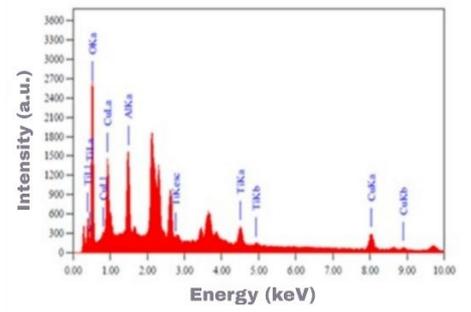


Fig. 2. SEM EDX chart

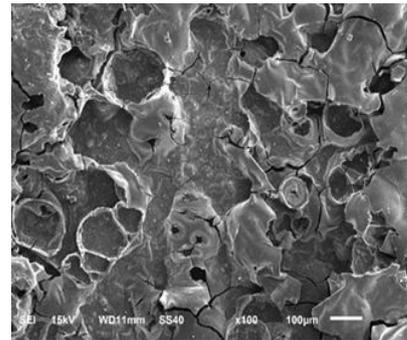


Fig. 3. SEM EDX morphology

Table 2. Mass composition and atomic composition of TiO₂ samples

Element	Mass Composition (%)	Atomic Composition (%)
C	2.02	3.89
O	49.07	71.07
Na	0.72	0.73
Mg	0.13	0.12
Al	0.45	0.38
Si	-	-
K	1.53	0.91
Ca	6.55	3.79
Ti	39.41	19.06
Zn	0.13	0.05

The result of analysis is described below:

1. The intensity, peak (h.k.l.), and energy (keV) are measured on EDX.
2. The SEM morphology images of the structure and pores showed differences because the shapes of the morphological clumps were not yet perfect. This means that the surface morphology is still relatively porous and the crystal grains are not fully developed.
3. In composition, there are differences in mass and atomic values, which can improve efficiency of some results such as elements, mass composition, and atomic composition.

The findings of the thin film test in Figure 2 described that peak (1) exhibits an intensity of 28,000 a.u. at an energy ranging from 0 to 0.5 keV. At peak (2) (ZnLa - NaKA - ZnLb), the intensity is 68,000 (au) with the energy level of 0.5–1.0 keV, while at peak (3) (Si Ka), the intensity is 16,000 (au) at an energy ranging from 2.0 to 2.5 keV.

Figure 3 shows that the formation of pores is still sparse and has not yet merged due to the sample properties, which have imperfect bonds. On the other hand, there is a periodic separation of pore morphology. The size formed in the morphology is SEI, 15 kV, WD, 11 mm x 5000, and 5 μm .

The mass composition and atomic composition of the TiO_2 sample demonstrated that oxygen constituted the biggest proportion at 49.07%, while magnesium and zinc represented the smallest proportion at 0.13% each. The analysis revealed that the largest element was oxygen (O), comprising 49.07% by mass and 71.07% by atomic composition, whereas zinc (Zn) was the least abundant, accounting for 0.13% by mass and 0.05% by atomic composition.

Finally, XRD thin film results are Cu_2O : Al 350°C, Cu_2O : Al 450°C, and Cu_2O : Al 550°C. The highest results were found in Cu_2O : Al 550°C with a peak intensity of 7500 (au) and an angle of 25°–30°, and the lowest were identified at Cu_2O : Al at 450°C with an admittance peak of 5300 (au) and an angle of 25°–27.7°. The result can be described in the Figure 4.

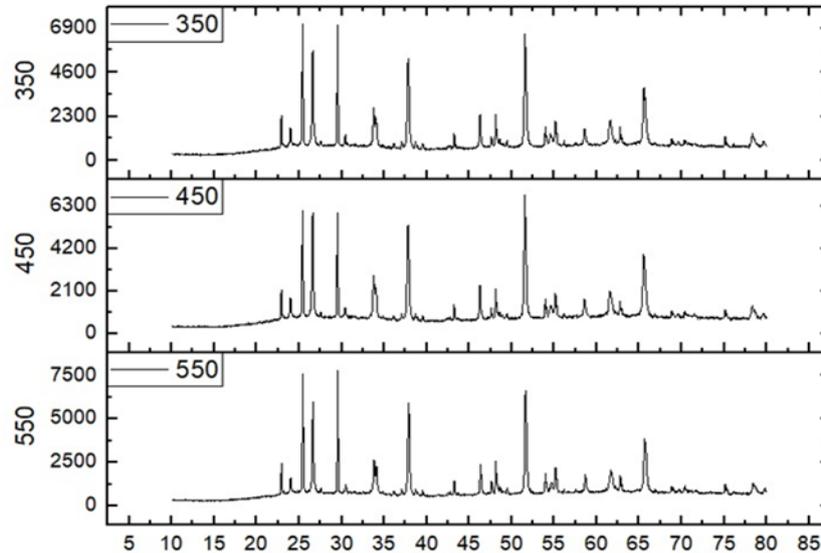


Fig. 4. XRD Thin Film Results Cu₂O: Al 350° C; Cu₂O: Al 450° C; and Cu₂O: Al 550° C

4. Conclusion

From the results of XRD thin film testing of TiO₂ at 550°C, TiO₂:Al at 550°C, and TiO₂:Al/Cu₂O at 550°C, it was found that the highest intensity appeared in the TiO₂:Al/Cu₂O sample with an intensity of 40.000 (au) and an angle of 37.5–40°, while the lowest was observed in TiO₂ at 550°C with an intensity of 10,000 (au) and a peak angle of 37.3–40°. The TiO₂:Al/Cu₂O thin film at 550°C also showed the highest wavelength, crystal size, and percentage, with a wavelength of 457.435 nm, a crystal size of 45.75 nm, and a percentage of 47%. Meanwhile, the lowest values were found in TiO₂ at 350°C, with a wavelength of 374.429 nm, a crystal size of 37.54 nm, and a percentage of 37%. Based on SEM test results of the TiO₂ thin film at 350°C, the highest intensity and energy were detected at peak 2 (ZnLa–NaKA–ZnLb) with an intensity of 68000 (au) and energy range of 0.5–1.0 keV, while the lowest were found at peak 3 (Si Ka) with an intensity of 16000 (au) and energy range of 2.0–2.5 keV. Furthermore, the EDX test on the TiO₂ thin film at 350°C showed that the highest mass and atomic compositions were from the O element, with a mass composition of 49.07% and an atomic composition of 71.07%, while the lowest compositions were found in the Zn element, with a mass composition of 0.13% and an atomic composition of 0.05%.

In the process of fabricating TiO₂ and Cu₂O composite semiconductor materials and their mixtures, it is crucial to determine the precise amount of each component used to minimize errors during sol-gel formation and calcination. Proper laboratory safety procedures must always be followed, and researchers should comply with institutional safety regulations to prevent accidents or adverse effects. These findings demonstrate that calcination temperature significantly influences the crystallinity, morphology, and optical absorption of TiO₂–Cu₂O thin films. The results suggest that the synthesized materials have potential for application in dye-

sensitized solar cells using natural dye sensitizers.

References

- [1] Holechek JL, Geli HME, Sawalhah MN, Valdez R. A Global Assessment: Can Renewable Energy Replace Fossil Fuels by 2050? Sustainability (Switzerland). 2022 Apr 1;14(8).
- [2] Strielkowski W, Civín L, Tarkhanova E, Tvaronavičienė M, Petrenko Y. Renewable energy in the sustainable development of electrical power sector: A review. Energies. 2021 Dec 7;14(24):8240.
- [3] Gaulin N, Le Billon P. Climate change and fossil fuel production cuts: assessing global supply-side constraints and policy implications. Climate Policy. 2020 Sep 13;20(8):888-901.
- [4] Ang TZ, Salem M, Kamarol M, Das HS, Nazari MA, Prabaharan N. A comprehensive study of renewable energy sources: Classifications, challenges and suggestions. Vol. 43, Energy Strategy Reviews. Elsevier Ltd; 2022.
- [5] Mammadov NS, Ganiyeva NA, Aliyeva GA. Role of renewable energy sources in the world. Journal of Renewable Energy, Electrical, and Computer Engineering. 2022 Sep 30;2(2):63-7.
- [6] Bakierska M, Chojnacka A, Świętosławski M, Natkański P, Gajewska M, Rutkowska M, et al. Multifunctional carbon aerogels derived by sol-gel process of natural polysaccharides of different botanical origin. Materials. 2017 Nov 21;10(11).
- [7] Alsharif MH, Younes MK, Kim J. Time series ARIMA model for prediction of daily and monthly average global solar radiation: The case study of Seoul, South Korea. Symmetry. 2019 Feb 15;11(2):240.
- [8] MacKay DJ. Solar energy in the context of energy use, energy transportation and energy storage. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences. 2013 Aug 13;371(1996).
- [9] Jacobs M. Global fossil fuel economy: Historical trajectories and future challenges. In: Affordable and clean energy 2021 Jan 24 (pp. 709-719). Cham: Springer International Publishing.
- [10] Ali AO, Elgohr AT, El-Mahdy MH, Zohir HM, Emam AZ, Mostafa MG, et al. Advancements in photovoltaic technology: A comprehensive review of recent advances and future prospects. Vol. 26, Energy Conversion and Management: X. Elsevier Ltd; 2025.
- [11] Rokhmat M, Wibowo E, Sutisna S, Khairurrijal K, Abdullah M. Development of a Low-Cost TiO₂/CuO/Cu Solar Cell by using Combined Spraying and Electroplating Method. Journal of Mathematical and Fundamental Sciences. 2018 Mar;50(1):92-101.
- [12] Ananthi N, Subathra MS, Emmanuel SC, Kumar NM. Preparation and characterization of two dye-sensitized solar cells using *Acalypha Godseffia* and *Epipremnum Aureum* dyes as sensitizers. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. 2020 Jul 2;42(13):1662-73.
- [13] Zulkiflee NS, Hussin R, Halim J, Ibrahim MI, Zainal MZ, Nizam S, et al. Characterization of TiO₂, ZnO, and TiO₂/ZnO thin films prepared by sol-gel method. 2016 Jun 1;11:7633-7.
- [14] Calogero G, Di Marco G. Top sensitizers for highly efficient dye-sensitized solar cells. Radiation Effects and Defects in Solids. 2022 Dec 2;177(11-12):1260-70.
- [15] Siregar N, Motlan, Panggabean JH, Sirait M, Rajagukguk J, Gultom NS, Sabir FK. Fabrication of Dye-Sensitized Solar Cells (DSSC) Using Mg-Doped ZnO as Photoanode and Extract of Rose Myrtle (*Rhodomyrtus tomentosa*) as Natural Dye. International Journal of Photoenergy. 2021;2021(1):4033692.