CHARACTERIZATION OF Cu-DOPED TiO2 USING SOLVOTHERMAL METHOD PHOTOANODES

AHMAD TIRMIZI BIN ROSLAN

J20A0408

A reported submitted in fulfilment of the requirements for the degree of Bachelor of Applied Science (Materials Technology) with Honours

FACULTY OF BIOENGINEERING AND TECHNOLOGY

UMK

2024

DECLARATION

I declare that this thesis entitled "title of the thesis" is the result of my own research except as cited in the references.

Signature : ATR

Student's Name: AHMAD TIRMIZI BIN ROSLAN

Date : 28/2/2024

Verified by:

Signature :

Supervisor's Name : DR HIDAYANI BT JAAFAR

Stamp :

Date : 2/3/2024

ACKNOWLEDGEMENT

Assalamualaikum, firstly I would like to thank Allah S.W.T for giving an opportunity and good health to me in aspect mental and physical to finished my Final Year Project (FYP). I would like to thank my supervisor, Dr. Hidayani Binti Jaafar for her encouragement, sharing her advice, knowledge and expertise in this study and also giving me an opportunity to do this research on the topic that was of great importance to me. Her passion in teaching me to do my final year project was the valuable thing and I really appreciate what she has done to me. Her guidance has made me to finish my FYP and I really grateful was having such kind-hearted supervisor like Dr. Hidayani.

I also would like to express my gratitude towards the lab assistance, Ts. Hanisah Izati Binti Adli for letting me to do this research in the Material Science Laboratory. By her provision and guidance in the lab, I can handle experiments correctly to prevent accidents in laboratory. The most appreciation also gives to Mr. Mohd Afifi Bin Shuhaimin and Mr. Muhamad Qamal Bin Othman who helped me a lot regarding the uses of furnace in the material workshop and without them, I cannot finish my FYP.

Also special thanks to my friends. They also have provided me all the needed in order to complete my research and thesis writing. Undoubtedly, none of this could not happen without my family especially my parents who always concern about me and giving me moral support to stay focus in studying.

Finally, I wanna thank me, I wanna thank me for believing in me, I wanna thank me for doing all this hard work, I wanna thank me for having no days off, I wanna thank me for never quitting, and for just being me at all times.

Synthesis and Characterization of Cu Doped TiO2 Composite Photovoltaic Thin Films Using Solvothermal Method: The Effect of Cu Content

ABSTRACT

Dai Synthesized Solar Cells (DSSCs) have emerged as a financially and technically feasible alternative to p-n junction solar systems. Copper type semiconductors and titanium dioxide P are the primary operational components in solar cells. The material composition was assessed using X-ray diffraction (XRD). Cu is an attractive solar absorber of choice because of its high solar absorption and low thermal radiation. This work discusses the solid-state reaction production and characterization of semiconductor particles. UV-visible absorption spectra were analyzed to determine optical characteristics and band gaps. According to XRD analysis, Cu doping causes the lattice constant to move by a specific amount. These data show that the energy band gap lowers as the annealing temperature increases, which can be attributed to the sample's higher crystallinity. Additionally, increasing the weight percentage of Cu-doped TiO2 reduces the band gap. Every photovoltaic parameter was recorded and discussed.

Keywords: Dai-synthesized solar cells, Photovoltaics, Solvothermal reaction, Cu, TiO2, Band gap.

Sintesis Dan Pencirian Filem Nipis Fotovoltaik Komposit Cu doped TiO2 menggunakan kaedah solvoterma: Kesan Kandungan Cu

ABSTRAK

DSSC (Sel Suria Tersintesis Dai) telah muncul sebagai penyelesaian yang berdaya maju dari segi kewangan dan teknikal kepada sistem fotovoltaik simpang p-n. Separa konduktor jenis kuprum dan Titanium diokside P adalah bahan operasi utama yang digunakan dalam sel suria. Untuk penilaian komposisi, bahan telah dicirikan menggunakan pembelauan sinar-X (XRD). Cu ialah penyerap suria pilihan yang menarik kerana penyerapan suria yang kuat dan pancaran haba yang kecil. Kertas kerja ini menerangkan sintesis tindak balas keadaan pepejal dan pencirian zarah semikonduktor. Spektrum penyerapan boleh dilihat UV digunakan untuk menyiasat ciri optik dan jurang jalur. Menurut analisis XRD, doping Cu menyebabkan pemalar kekisi beralih kepada jumlah tertentu. Penemuan ini mendedahkan bahawa jurang jalur tenaga berkurangan dengan peningkatan suhu penyepuhlindapan, yang boleh dikaitkan dengan kehabluran sampel yang lebih baik dan juga peningkatan peratusan berat TiO2 didop Cu juga mengurangkan jurang jalur. Semua parameter fotovoltaik telah direkodkan dan dibincangkan.

Kata kunci: Sel suria tersintesis dai, Fotovoltaik, Tindak balas solvoterma, Cu, TiO2, Jurang jalur.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

C	:	Carbon
Cu	:	Copper
DH2O	:	Distilled water
O	:	Oxygen
TiO2	:	Titanium Dioxide
ITO	:	Indium-Tin-Oxide
XRD	:	X-ray diffraction

LIST OF SYMBOLS

%	:	Percentage
°C	:	Degree Celsius
ρ	:	Density
µm	:	Micrometer
eV	:	Electron Volt
~	:	Approximation
Å	:	Angstrom
nm	:	Nanometer
mA	:	Milliampere
mV	:	Millivolt
a.u.	:	Arbitrary unit

CHAPTER 1

INTRODUCTION

1.1 Background of Study

A cost-effective and technically feasible alternative to p-n junction photovoltaic systems is important to develop DSSCs (dye-sensitized solar cells). Electricity perhaps produced by illuminating natural dyes in electrochemical cells, as discovered in the late 1960s (Sharma et al., 2018).

As a consequence, by increasing the porous of the fine oxide powder electrode, the efficiency was improved, which boosted dye absorption over the electrode, and which lead to light harvesting efficiency (LHE). For this reason, nano-porous titanium dioxide TiO2 electrodes with a 11-roughness factor of around 1000 were discovered, and in 1991, DSSCs with a 7% performance were developed (Yan et al., 2012).

The TiO2 nanoparticles (TiO2) and Ag-doped TiO2 nanocomposites (Ag-TiO2) were synthesized using a simple, less time-consuming, and economical sol-gel approach, using titanium tetra isopropoxide (TiO2) and silver nitrate (Ag) as the precursors, respectively. Hydrothermal electrochemical, microwave, sonochemical, and sol-gel procedures are just some of the many ways that TiO2 and modified TiO2 may be manufactured. Sol-gel distinguishes out from other methods because to its simplicity, high degree of surface area control, and conventional crystallite size, phase structure, and form. Dye-sensitized solar cells (DSSCs) use the dye to guide electrons to the semiconductor.

Photoanodes play a crucial role in DSSC because of their ability to keep dye molecules alive and transfer electrons. A high electron transit rate is required to reduce electron-hole recombination and boost modification efficiency. Efforts are now being made to replace the porous TiO2 photoanode with a ZnO photoanode in an effort to improve solar cell quality by increasing the efficiency with which electrons are gathered and transported and by reducing the likelihood of charge recombination (Yan et al., 2012). However, DSSC based on pure ZnO photoanode has a low conversion efficiency (Yan et al., 2012) because ZnO is unstable in acid dyes and has a poor electron injection performance from Ru-based dyes. Photoanodes comprised of two or more component materials have recently attracted attention due to the obvious benefits of combining different materials, such as the high electron transport rate of ZnO and the outstanding electron injection efficiency of TiO2 from Ru-based dyes. While DSSCs have shown similar efficiency in recent years, they still need additional development to address some of the constraints that have been identified with these cells. Here, the photoanode efficiency of solar cells is improved by combining a composite material like Cu-doped TiO2 with sol-gel.

Copper oxide semiconductor materials have great light absorption, are harmless, and are inexpensive to manufacture (Kidowaki et al., 2011). CuO and Cu2O are p-type semiconductors with band gaps of 1.5 eV and 2.0 eV, respectively. These band gaps are near to the optimal energy gap for solar cells and allow for good solar spectrum absorption. Cu2O solar cells' maximum efficiency of 2% was attained by combining a high-temperature annealing process with an expensive vacuum evaporation technique.

1.2 Problem Statement

TiO2 is the ideal material for a broad variety of solar energy conversion and environmental applications because to its inertness to biological and chemical processes, its high oxidizing power, its cheap cost, and its long-term stability against photocorrosion and chemical corrosion. The photocatalytic activity of doped TiO2 containing silver nanoparticles is higher than that of its undoped counterpart. This is because the bandgap of the doped TiO2 is smaller, and the electrons can more easily jump from the valence band to the conduction band. TiO2 may be manufactured using a wide variety of methods, some of which include the sol-gel, hydrothermal, electrochemical, microwave, and sonochemical processes. In contrast to the solid-state method, which involves more work on the part of the researcher, the sol-gel technique, which needs less effort overall and gives better control over the surface area, average crystal size, phase structure, and morphology of the end product, is the method that I like. When compared to the solid-state technology, the annealing temperature for the sol-gel method is lower.

The solvothermal method is simpler and provides more control over surface area, average crystal size, phase structure, and morphology than the solid-state approach. It also has a lower annealing temperature than the solid-state approach.

1.3 Objectives

i. To study the effect Cu content at different weight percentage wt% by using solvothermal method.
ii. To investigate the performance of Cu-doped TiO2 photoanodes using solvothermal method.

1.4 Scope of Study

The aim of the current study is to create a dye-sensitized solar cell (DSSC) using Cu doped TiO2 by synthesized sol-gel method for photoanode (%). Samples will be fully prepared at University Malaysia Kelantan (UMK). At University Malaysia Kelantan (UMK), samples will be characterized X-ray Diffraction, and Ultraviolet visible (UV-Vis) Spectroscopy for structural and optical properties.

1.5 Significances of Study

Titanium dioxide is a metal transition oxide with three primary crystal structures: rutile, brokite, and anatase, and a band gap range of 3.0 - 3.2 eV. Titanium dioxide (TiO2) is a prominent photocatalyst that has been used to make a variety of commercial items such as white pigment in paint manufacturing, cosmetics, and semiconductor material. Because of its wide range of applications, TiO2 modification has been a critical task. These materials were created and then analysed using XRD patterns and UV Vis spectroscopy.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Technologies such as the sol-gel technique (solution method), vapour phase compression, mechanical alloying, and collision with high-energy pellets, plasma, and electrochemical processes are now employed to create and synthesise nanoparticles. All three methods have the ability to manufacture very large amounts of nanomaterial, but the sol-gel method is the one that has seen the most use and has gained the most popularity among commercial enterprises. Nanoparticles of uniform size and quality may now be manufactured in large quantities, thanks to this technology and its special qualities. Alloys may be made by mixing more than one metal (or metal oxide) precursor in a controlled proportion, and the approach can yield multiple nanoparticle kinds simultaneously. Other technologies, like the plasma process and electrochemical methods, allow for the fabrication of single-step alloy products, but the sol-gel approach is well-suited for industrial-scale manufacturing.

Making it possible to produce metal and ceramic nanomaterial at temperatures between 70 and 320 °C, this technology has another benefit over conventional methods: a lower process temperature. In contrast, the other methods need temperatures of 1400-3600 °C to create nanomaterial. An example of a bottom-up synthesis approach is the sol-gel method. The cost-effective sol-gel technology also allows for considerable control over the chemical composition of the product because of the low reaction temperature. Sol-gel technology is used to connect metal oxide thin films in many different contexts. Materials made by the sol-gel technique are used in a wide variety of technologies across many different industries, including optics, electronics, energy, surface engineering, biosensors, and medicines. Sol-gel is a well-established and effective method for producing nanoparticles with a wide range of chemical compositions. The solgel process begins with the production of a homogeneous sol from a precursor and continues with the gel's subs. The sol-gel process is predicated on the generation of a homogeneous sol from a precursor and the subsequent conversion of the sol to a gel.

2.2 Working principle of thin film and Deposition techniques of after working principle.

2.2.1 Working principle of dye synthesized solar cell.

A direct-sequence solar cell (DSSC) consists of four main components: the working electrode, the counter electrode, the sensitizer (dye), and the redox mediator (electrolyte). Working and counter electrodes, each containing a sensitizer and a thin layer of electrolyte, are joined together using hot melt tape to prevent leaking of the electrolyte and form the DSSC. The four fundamental processes in the functioning of a DSSC are the fusion of light, the injection of electrons, the passage of carriers, and the collection of current. To turn light into electricity, the following procedures must be carried out. By absorbing the photon of incoming light, the photosensitizer raises the energy level of the dye from its ground (S+ /S) to its excited (S+ /S*) state.

Dyes typically have an absorbance of 1.72 eV per photon at 700 nm. In addition, excited electrons with nanosecond lifetimes migrate into the conduction band when UV light is absorbed by a nanoporous TiO2 electrode positioned below the excited state of the dye (Sharma et al., 2018). The dye will oxidize as a result. These implanted electrons go via the gaps between nanoparticles of transparent conducting oxide TiO2 to reach the rear contact. Electrons have to go through a circuit to get to the counter electrode. The number of electrons in the negative electrode is lower than in the positive electrode. In the process of dye restoration, the dye takes electrons from the redox mediator, leading to dye oxidation. After being oxidized, the mediator is reduced as it makes its way toward the counter electrode.

2.2.2 Deposition techniques of after working principle.

Sol-gel deposition is one of the easiest and most adaptable processes for making thin films. The approach with the same name serves as the foundation for this deposition process. An excellent way for creating porous, glass-like materials, ceramics, nanoparticles, or nanocomposites is the sol-gel method. Sol-gel reactions have attracted a lot of scientific interest because they can produce a variety of inorganic networks from metal alkoxide solutions. To create gel, a substance that has a continuous solid skeleton encasing a continuous liquid phase, all of these reactions need to the formation of a sol, consecutive gelation, and solvent removal.

Besides, the liquid precursors are the aforementioned alkoxides. Different materials can be created because of the complete process, depending on factors such as the type of precursor, temperature, water: alkoxide molar ratio, pH, nature and concentration of the catalyst, or the inclusion of other chemicals. Materials made from sol-gel have important applications in a variety of fields, including chemistry, materials science, optics, electronics, biology, and biomedicine.

2.2.3 Application

TiO2 nanoparticles, which are more efficient than other metal oxide semiconductors, are used as working electrodes in dye-sensitized solar cells. In contrast, the best solar efficiency for TiO2 is just 11.5 percent. TiO2's biological and chemical inertness, considerable oxidizing power, cost-effectiveness, and long-term durability against photocorrosion and chemical corrosion make it the most suitable material for widespread solar energy conversion and environmental applications. Silver-doped titania compounds have been created for use in photo electrochemistry and as an antibacterial. Doped TiO2 with silver nanoparticles has more photocatalytic activity than its undoped counterpart. The counter electrode significantly improves electron transmission, which is a big deal for DSSC. Candidate perfection would need strong catalytic activity toward the reduction of tri-iodide ions together with being chemically inert, stable, and corrosion-free. Graphite and carbon nanotubes are only two examples of the carbonaceous materials utilized as counter electrodes.

Table 1: Compares the Solvothermal method and Solid-state method.

Material	Solvothermal method	Solid state method
Advantage	- Solvothermal conditions enable fine control over the size, form, and morphology of synthetic materials. This control is critical for adapting the qualities of the finished product to specific applications. - The high-temperature and high-pressure conditions used in solvothermal synthesis frequently result in materials with exceptional purity and homogeneity.	- They are less fragile than hard disks since they don't contain any moving parts. - There are no mechanical delays for them. - They are extremely portable due to their light weight and compact dimensions.
Disadvantage	- Solvothermal synthesis may be limited in its usefulness for particular materials or delicate chemicals due to the high temperatures and pressures involved. - Solvothermal processes require complex and costly equipment.	- Teed for high temperatures - The potential for heterogeneity

2.3 Synthesis of TiO_2 and CuO

2.3.1 Synthesis of TiO_2

Due to their distinctive optical and electrical characteristics, titanium dioxide (TiO_2) semiconductor nanoparticles are one of the most significant and promising types of photocatalysts used in photocatalysis. In photocatalysis, their characteristics, which are influenced by the preparation process, are crucial. An overview of the many techniques used or previously utilised to create titanium dioxide nanoparticles has been undertaken in this chapter. The solvothermal method is one of the many techniques that can be used to make TiO_2, and it is also one of the most popular. The use of solvothermal synthesised photoanodes will be the focus of this work.

2.3.2 Synthesis of CuO

The market for high CuO in sector has increased in the simplified of processes such as precipitation, thermal oxidation, hydrolysis, and electrochemical as well as the development of more advanced and high-tech methods such as microemulsion system, so-gel, solvothermal and microwave hydrothermal process. All methods strive to alter the qualities of the material by modifying its crystalline structure, composition, particle size, shape, and stability. The qualities of the material can be adjusted by changing the raw material utilised in a specific process (Kazmi & Hameed, 2016).

2.3.3 Properties of CuO

CuO is a secondary copper mineral, a rare earth metal, and the most durable monoclinic form of oxidized copper. A volcanic sublimate discovered in the oxidized zone of hydrothermal copper deposits. CuO is a semiconductor that is p-type. CuO has piqued the interest of researchers since it is the most basic member of the copper compound family and possesses a range of potential important physical features such as high temperature superconducting, electron correlation phenomena, and spin dynamics (Kidowaki et al., 2011). Copper oxide is generally inexpensive, easily combined with polarized liquids such as water and polymers and has physical and chemical characteristic that are fairly constant. Highly ionic nanoparticulate metal oxides, such as CuO, maybe hugely valuable antibacterial agents due to the large surface areas and unique crystal structures.

CuO, a light sensitive p-type semiconductor with a low band gap of 1.2-1.7 eV, has piqued the curiosity of many academics who want to investigate its possible applications in 21 industry (Razali et al., 2012). CuO nanostructures are widely used in photothermal, photoconductive, and gas sensor applications. Copper oxide-based materials have received a lot of attention due to their distinctive features, which are valuable in disciplines like optics, optoelectronics, and catalysts. CuO has been used in solar cell development and photoelectrochemical cells. CuO has been utilized as a hole transfer layer and barrier layer in dyesensitized solar cells, as an active layer in several kinds of solar cells, and as a passivation layer in sun-selective surfaces. For its strong solar absorbance and moderate thermal emittance, it would create an excellent preferential absorbing layer (Dissertation, 2010).

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

The materials that will be used in this experiment are ITO (Indium doped Tin Oxide), natural dye (anthocyanin), Ethanol, $TiO2$ powder (99.99%), CuO powder (99.99%), acetic acid, distilled water, ethylene glycol, triiodide solution, multimeter, hot plate, binder clips, and alligator clips, spatula, filter paper, forest, beaker, cylinder 250 ml and microwave.

3.2 Preparation of CuO-TiO2

Titanium dioxide powder (TiO2) (99.9%) and Copper Oxide (CuO) (99.9 % purity) will be used as raw materials. Three TiO2-CuO powders of varying compositions were created using wt% CuO values of 1%, 3%, and 5%. A 1% sample was prepared by combining 3g (grammes) of TiO2 powder with 1g CuO and 99ml dH2O, followed by 50ml acetic acid and 100ml ethanol in a beaker. Meanwhile, the second sample, which is 3%, is prepared by combining 3g (grammes) of TiO2 powder with 3g CuO and 97ml dH2O, then adding 50ml acetic acid and 100ml ethanol and placing in a beaker. The final 5% sample is prepared by combining 3g (grammes) of TiO2 powder with 5g CuO and 95ml dH2O, followed by 50ml acetic acid and 100ml ethanol in a beaker. The samples were then swirled for an hour on a hot plate. Then, place the sample in the microwave for 90 seconds. After that, wash all of the samples with distilled water (dH2O). The sample should then be filtered and placed in an oven set to 90°C for 24 hours. Finally, the sample is piled using a mortar and filtered before being characterized with XRD and UV-Vis techniques.

3.3 Characterization techniques of CuO-TiO2 Powder

3.3.1 XRD

We'll hit the change button in Desktop/XRD Commander (XRD Commander). Before hitting the adjusted button, the kV and mA should be adjusted to 40 and 30, respectively, using the toggle switch. As a result, the kV and mA would rise to 40 kV and 30 mA, respectively. After opening the shutter, the mirror will be given fifteen minutes to acclimatise. XRD Commander will close its shutter. The internal light, which is the green switch under the emergency button on the left side of the instrument, will be switched on and two of the diffractometer's doors will be opened.

After positioning the sample in the middle of the stage, the hoover will be turned on to hold it there. The sample will be raised to the knife edge and the knife edge will be lowered to 0.000mm. As the sample closes, the flame is utilised to monitor the distance between the knife edge and the material. Make sure the knife edge does not move from 0.000mm. The knife edge would then be elevated to 1.200mm in a clockwise micrometre. Verify that both handle ends fit into the openings by closing the doors. The X-Ray shutter or window will not open as a safety precaution if the doors are not fully closed. The analysis won't start until every door has been correctly shut.

3.3.2 UV-Vis

The sample will be deposited onto a suitable, clear substrate for UV-Vis characterization sample preparation. The studies will be conducted out using a blank sample of the transparent substrate. The interior of the UV-Vis chamber will be inspected to check that the appropriate sample container (liquid or solid) is present. If the equipment is not shut off, the appropriate sample holder will be located in the cabinet above it. The UV-Vis feature is activated by pushing the button on the device's front. The machine will not function until the wavering green light on the button becomes solid green. The UV-Vis sensor will be linked to the gadget, which will be turned on. To open the Cary Win UV programme, double-click the Scan button on the desktop. The experimental settings will be established after selecting the Setup button. By clicking the Carry Tab, you may adjust the Wavelength range settings if necessary and set the Scan controls to an appropriate speed.

To choose zero/baseline adjustment, go to the Baseline Tab and then click the OK button. A popup will appear stating that the baseline is invalid; then click OK. Then, on the left side of the screen, click the Baseline Button, which prompts you to insert the blank substrate into the holder. Once that is completed, click the OK button. The machine will baseline, and you will get a second pop-up directing you to block the sample beam with cardboard.

Next, the OK button will be pressed. After completing the baseline process, remove the cardboard from the sample chamber and hit the Zero button on the right side. When zero is reached, the blank sample will be removed and inserted into the sample. When you click the Start button in the top centre of the screen, the data will be saved to the appropriate file folder. At this point, the OK button will be hit and the scan will begin. When the scan is complete, a popup window will emerge, allowing you to scan another finished sample.

A new sample will be used in its stead, and the sample name in the pop-up window will also be modified. The Finish button will not be selected; instead, the OK button will be. Turning off the UV-Vis requires hitting the OFF button. The sample and user data will be entered into the red logbook, and the machine will be turned off. A composite film based on the best characterisation outcome will be created.

3.4 Device fabrication

3.4.1 Titanium Dioxide (TiO2) thin film preparation (3 glass)

Firstly, identify the conducting side of indium tin oxide (ITO)-coated of glass by using digital multimeter to measure resistance. Next, add a small amount of TiO2 paste on the ITO surface and quickly spread by pushing down and across with a microscope slide before the paste dries. Slowly heat the TiO2 thin film on the hot plate from room temperature until 70 °C for 5 minutes. Then, transfer TiO2 thin film into oven at 500 °C for 30 min ramp time for annealing.

3.4.2 Preparation of a CuO-TiO2 dye thin film

To make a dye thin film, the CuO-TiO2 film will be steeped in dye solution for an entire night at room temperature in a dark atmosphere. Following a gentle washing with distilled water to extract the dye solids and ethanol to remove the water, the dye-CuO-TiO2 thin films will be cleaned. Using a cotton swab, the dye solution outside the thin film will be removed. For five minutes, the dye-CuO-TiO2 thin films will be gradually heated on the hot plate to 70°C.

3.4.3 Fabrication of Completed Device

Binder clips will be used to join and clamp the two glasses of dye-CuO-TiO2 and carbon thin films with coated surfaces. On the opposing sides of the plate, a drop of triiodide solution would be applied. Using a cotton swab, remove extra triiodide solution from the glass's edge and backside. Two alligator clips will be used to secure the multi-meter to each plate, and it will be used to measure the voltage and current of the device under test in both light and dark conditions (varying distances from light source).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Structural Properties of Cu doped TiO2 Powder

This chapter will go over the composition and characteristics of Cu dopedvTiO2 following doping and XRD spectrum analysis. Next, in preparation for employment as a thin film in the manufacture of DSSCs, the absorption spectra of Cu doped with TiO2 was investigated. The absorption spectrum of the UV-Vis findings is used to study natural dyes. Lastly, the topic of photovoltaic parameters was covered.

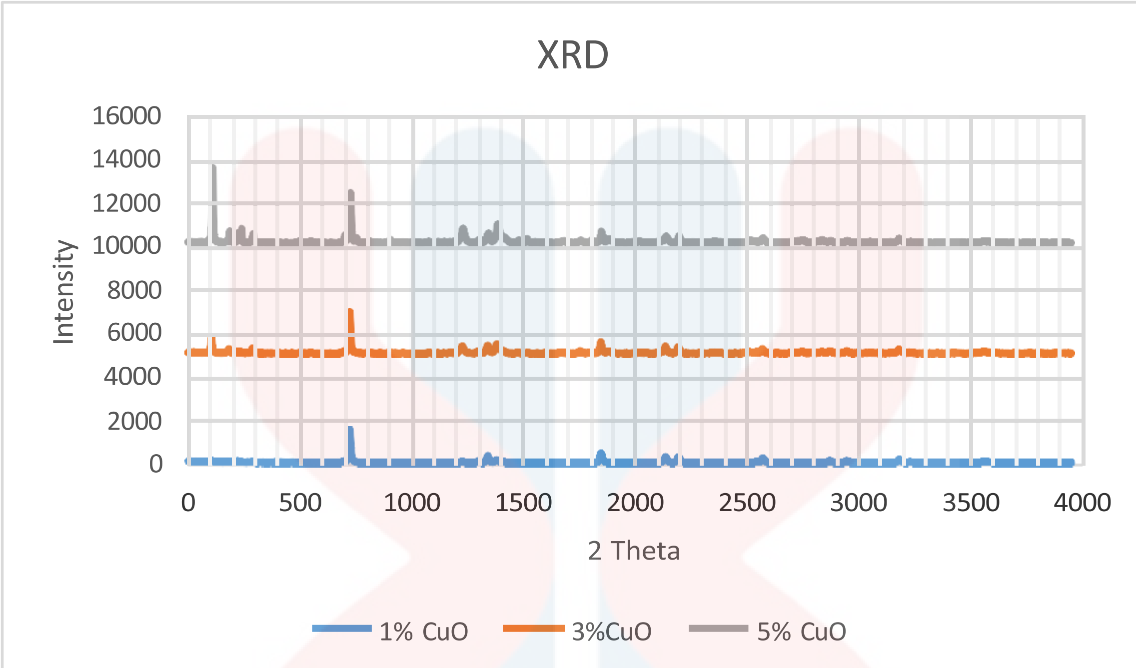

Figure 4.1: The XRD spectrum of Cu doped TiO2 powders

Figure 4.1 shows the XRD spectra of TiO2 doped with Cu powder after fabricated using solvothermal method with different wt%. The diffraction peak is reflected to tetragonal anatase crystal phase TiO2. According to (Scarpelli et al., 2018) this value corresponds exactly to the standard data (JCPDS Card No.21-1272) (Scarpelli et al., 2018). Due to very low Cu content, any crystalline phase containing Cu cannot be observed by XRD in the first 1wt% Cu doped TiO2. However, a new peak emerged in composite architecture proving the presence of Cu, especially at high weight percentages of Cu. A new peak is observed at 3wt% and 5wt% in the CuO-TiO2 composite because it has a high weight percentage corresponding to Cu. Based on this configuration, no impurities can be observed.

The crystalline size (D) of Cu doped TiO2 were calculated from the broadening of the diffraction line using Debye Scherrer's formula i.e. $D = 0.9\lambda / \beta\cos\theta$, where λ is the wavelength of the X-rays, β is the full width at the half maximum intensity (FWHM) (Tenkyong et al., 2015). The calculated crystallite size for Cu doped TiO2 were shown in the Table 4.1,

Table 4.1: Lattice parameter, average crystallite size and d – spacing of Cu doped TiO2

Sampel	Average crystallite size (nm)	Cell volume Å 3	a (Å)	c (Å)
1wt% Cu doped TiO2	485.89	136.93	3.7892	9.537
3wt% Cu doped TiO2	359.03	136.93	3.7892	9.537
5wt% Cu doped TiO2	340.58	136.93	3.7892	9.537

From Table 4.1 it can be concluded that doping Cu increases the crystal size. These doping modifications prevent particles agglomeration, forming well defined crystalline powder with high surface area. It demonstrates that the addition of Cu restrained the growth of TiO2 crystallites (Trang et al., 2019). However, as mentioned by (Ursu et al., 2018), the surface area of a particle and the recombination of photogenerated electron-hole pairs can be affected by particle size. Increased surface area leads to more adsorption of reactants and less light absorption. The quantum confinement effect causes the band gap of Cu doped TiO2 to grow with decreasing particle size. Quantum confinement is a phenomenon. This occurs when the particle's size is too tiny to match the electron's wavelength. Nanocrystals' quantum confinement creates novel optical and electrical features, potentially improving photovoltaic solar cell performance. The particle size of Cu doped TiO2 affected the wavelength of the light source used for the photovoltaic process.

4.2 Absorption Spectra of Natural Dye

A UV Vis spectrophotometer was used to analyse Cu doped TiO2. In optics, the band gap (Eg) of a CuO thin film was estimated using the absorption spectrum and equation.

$$(\alpha h\nu) = A(Eg- h\nu)n \qquad \text{Equation 4.1}$$

After undergo sintering temperature, the result in Figure 4.2 and Table 4.2 showed photon energy and absorbance of the Cu doped TiO2.

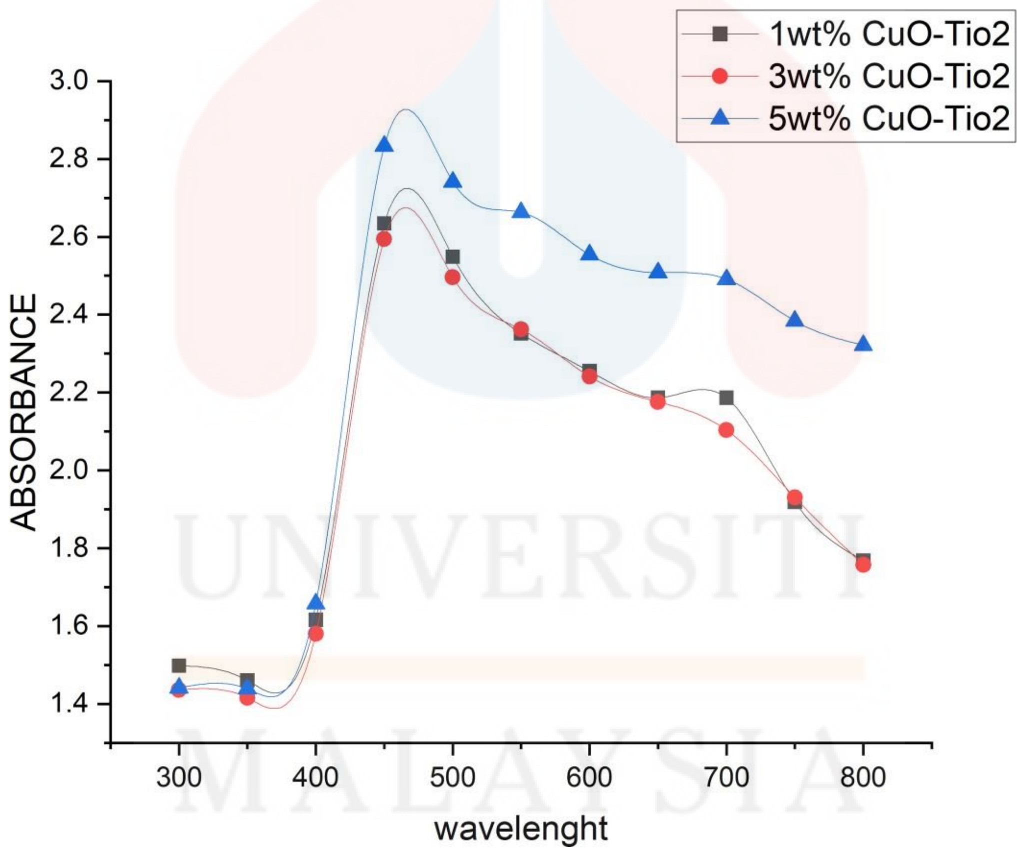

Figure 4.2: UV-Vis spectra of various Cu doped TiO2 thin films

The optical absorbance of Cu doped TiO2 films in the UV region varies according on CuO content. TiO2 has an energy band gap of 3.2 (hv) = A(Eg-hv) according to (Ludin et al., 2014).

According to Ludin et al. (2014), eV absorbs light primarily in the UV band (250-400 nm). From the spectrum, the annelaing temperature at 90˚C with 5wt% Cu doped TiO_2 content has the maximum light absorption, followed by samples with 1wt% and 3wt% Cu doped TiO_2 The sample with 1% Cu doped TiO_2 concentration, on the other hand, has the lowest light absorption.

Table 4.2: Absorbance and photon energy of CuO doped with TiO_2

ENERGY HV	1wt% Cu doped TiO2	3wt% Cu doped TiO2	5wt% Cu doped TiO2
4.133333333	3.096113	2.96787593	2.978842
3.542857143	2.587644	2.507838	2.549123
3.1	2.504693	2.44914725	2.569317
2.755555556	3.629684	3.5738536	3.903479
2.48	3.160754	3.09496932	3.399239
2.254545455	2.650864	2.66348956	3.00202
2.066666667	2.330062	2.31605133	2.63919
1.907692308	2.085491	2.07555588	2.392012
1.771428571	1.936843	1.86286086	2.206418
1.653333333	1.586395	1.59588496	1.970673
1.55	1.37	1.36	1.79

Table 4.2 displays the Tauc plot analysis including estimating the absorption coefficient (α) using the formula $\alpha = 2.303 / d * A$, where d is the thickness of the sample and A is the absorption. Photon energy (hv) is determined using the formula $h\nu = hc / \lambda$, where h is Planck's constant, c is the speed of light, and λ is the wavelength. A tauc plot is created by plotting $\alpha h\nu$ vs $h\nu$ for each material.

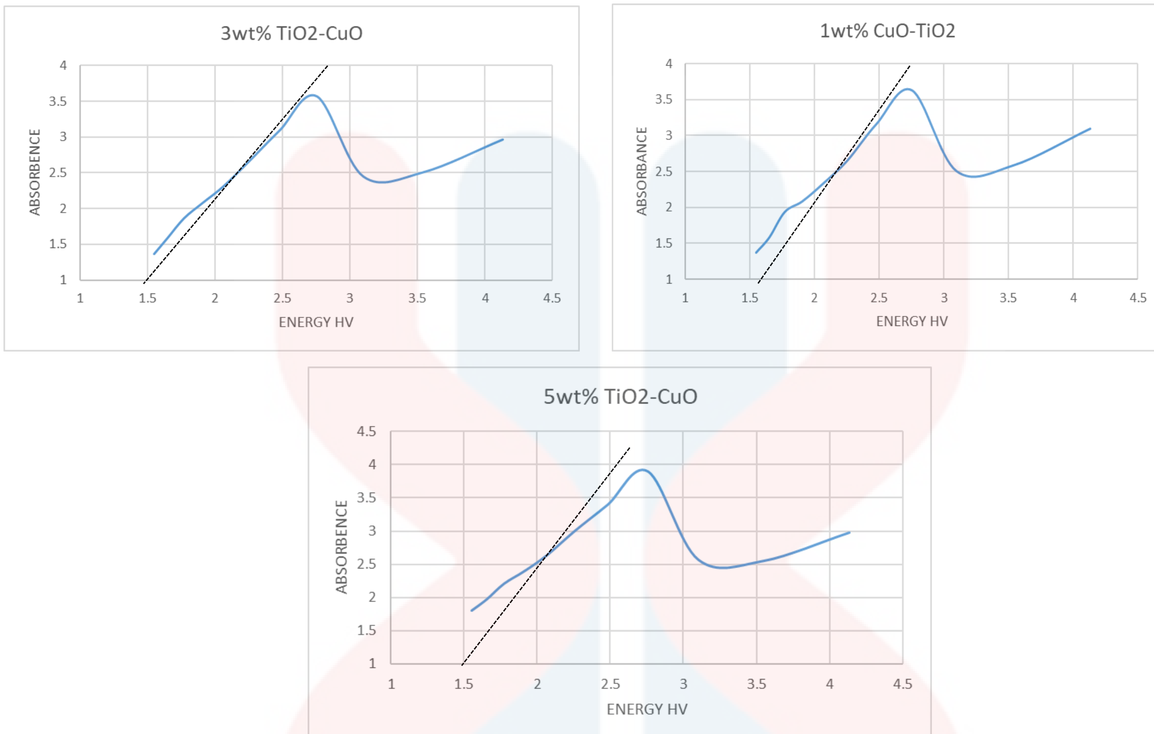

Figure 4.3: Absorbance and photon energy of Cu doped TiO2

Figure 4.3 depicts the trend of 3wt% Cu doped TiO2 energy (Hv) measured at 1.5 eV. This is because it can reveal the energy level at which CuO-TiO2 exhibits substantial absorption properties. The peak is located at (√(α·hv)) 3.09496932. This peak exhibits a strong absorption or transition at the level of the energy flow at 1.5 eV.

Next, the 5wt% Cu doped TiO2 content provides the highest light absorption and the lowest band gap energy of 1.55 eV. According to Nandi Yanto et al. (2020), increasing crystal size significantly affects the rate of photodegradation of organic substances. According to (library, 2021), a semiconductor's band gap is expressed as the absorption peak in nanometres. Absorption (A.U.) Crystal semiconductors have conductive valence electrons due to their chemical structure at specific temperatures (library, 2021).

The study found that Cu doped TiO2 has a high optical absorption coefficient, allowing for easy activation by visible light. (Tang et al., 2019). Because of contaminants. Increasing the number of free electrons will improve conduction even further. Doping with additional elements can enhance photovoltaic characteristics by narrowing the band gap and facilitating electron transitions from the valence to conduction bands.

4.3 Modified of working Photoanode for DSSCs application

The photovoltaic parameters were illustrated in Table 4.3. The fill factor (FF) is defined as follows:

$$P_{max} = I_{max} \times V_{max}$$ Equation 4.2

$$Jsc = Isc/Asc$$ Equation

$$FF = Pmax/Voc \times Isc$$ Equation 4

Where Imax is the maximum photocurrent and Vmax is the maximum photovoltage. Isc denotes the short-circuit photocurrent, whereas Voc denotes the open-circuit photovoltage.

Meanwhile for Energy conversion efficiency (η) is defined as:

$$\eta = (Isc \times Voc \times FF)/Pin$$ Equation 5

Table 4.3: Photovoltaic parameters for the dye-sensitized solar cells (DSSCs) using CuO-TiO2 as thin film.

Sampel	Current density, Jsc (mA/cm2)	Open circuit potential Voc (mV)	Fill factor, FF (%)	η Efficiency (%)
1wt% Cu doped TiO2	0.897	48.015	2.489	10.7
3wt% Cu doped TiO2	0.962	62.02	2.911	16.8
5wt% Cu doped TiO2	1.005	67.257	3.021	20.4

The 1wt% Cu doped TiO2 sample may yield JSC = 1.005 mA/cm2, VOC = 48.015 mV, FF = 2.489, and = 10.7%, as Table 4.3 demonstrates. Afterwards, the 3wt% and 5wt% Cu doped TiO2 samples showed great conversion efficiency and produced good photovoltaic output, with JSC and VOC values of 0.962 and 1.005 mA/cm2, 67.247 mV, and 16.8, 20.4, respectively. As the weight percentage (wt%) increases, the electrical characteristics of VOC, JSC, FF, and η all show a fairly noticeable rise, as seen in the table.

Compared to silicon, which has an indirectly transition band structure, Cu appears to have a directly transition band structure that is more advantageous for optical absorption. Cu is a potential material since it may increase the active zone's absorption, raising the Jsc (Kazmi & Hameed, 2016). This work looks at how weight percentage changes affect photovoltaic solar cells' characteristics, which are determined by how much sun protection reaches the cell's surface.

This study investigates how solar cell characteristics are affected by the quantity of sun protection that reaches the surface of a photovoltaic solar cell, which determines the cell's performance. The open circuit voltage (Voc) increases linearly with weight, reaching a maximum of 67.257 mV on the 5wt% Cu sample. As demonstrated in Table 4.3, 3wt% and 5wt% doped powders outperform 1wt% doped powders in terms of electrical characteristics due to their greater crystal size, which results in higher absorption and a smaller band gap. The quantity of dye molecules adsorbed on TiO2 surfaces, the number of photons absorbed by the dye molecules for effective electron harvesting and decreased electron-hole pair recombination's, and other factors determine the efficacy of DSSC applications (T. Raguram & K.S. Rajni, 2022).

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

The purpose of this study is to investigate the performance and appropriate amount of Cu doped TiO2 powder. This study successfully produced Cu doped TiO2 powder utilizing solid-state procedures to achieve the desired size, morphology, and form, which can influence its optical and structural properties. The XRD patterns of Cu-doped TiO2 with varying weight percentages are same, however the lattice properties varied slightly, according to data analysis. This discrepancy indicates that the doping operation was successful, as the crystallinity of TiO2 is reduced when doped with Cu. According to this study, crystal size increases as Cu concentration increases.

UV-Vis spectroscopy demonstrated substantial absorption between 250 and 400 nm, and based on the UV-Vis analysis spectra of Cu-doped TiO2 powders, the band gap values for Cu-doped TiO2 decreased with increasing Cu concentration. Doping with additional elements can improve photovoltaic properties by decreasing the band gap and facilitating electron transitions from the valence to the conduction band.

5.2 Recommendations

Some recommendations for further research will be offered. First, to create a better solar device, nanomaterial powder must be used to improve the surface area and hence the photovoltaic efficiency. Furthermore, energy dispersive X-ray Spectroscopy (EDX or EDS) can be employed to produce more precise results in determining the existence of elemental components. To minimize the cell's internal resistance, reduce the thickness of the photoanode layer and the space between the electrodes. Finally, apply various deposition processes to increase solar cell efficiency.

REFERENCES

K, Sharma. "(PDF) Dye-Sensitized Solar Cells: Fundamentals and Current Status." *ResearchGate*, www.researchgate.net/publication/329256389_Dye-Sensitized_Solar_Cells_Fundamentals_and_Current_Status.

Yan, Lu-Ting, et al. "Photoanode of Dye-Sensitized Solar Cells Based on a ZnO/TiO_2Composite Film." *International Journal of Photoenergy*, vol. 2012, 2012, pp. 1–4, downloads.hindawi.com/journals/ijp/2012/613969.pdf, https://doi.org/10.1155/2012/613969.

Jilani, Asim, et al. "Advance Deposition Techniques for Thin Film and Coating." Modern Technologies for Creating the Thin-Film Systems and Coatings, 8 Mar. 2017, https://doi.org/10.5772/65702.

Raguram, T., and K.S. Rajni. "Synthesis and Characterisation of Cu - Doped TiO2 Nanoparticles for DSSC and Photocatalytic Applications." *International Journal of Hydrogen Energy*, vol. 47, no. 7, Jan. 2022, pp. 4674–4689, https://doi.org/10.1016/j.ijhydene.2021.11.113. Accessed 17 May 2022.

Lee, Taesoo D., and Abasifreke U. Ebong. "A Review of Thin Film Solar Cell Technologies and Challenges." *Renewable and Sustainable Energy Reviews*, vol. 70, no. C, 2017, pp. 1286econpapers.repec.org/article/eeerensus/v_3a70_3ay_3a2017_3ai_3ac_3ap_3a1286-1297.htm.

Adamu, Abdullahi, et al. "Investigation of Cu/TiO2 Synthesis Methods and Conditions for CO2 Photocatalytic Reduction via Conversion of Bicarbonate/Carbonate to Formate." *Journal of CO2 Utilization*, vol. 70, 1 Apr. 2023, pp. 102428–102428, https://doi.org/10.1016/j.jcou.2023.102428. Accessed 30 Apr. 2023.

Mitronika, M., et al. "Modification of the Optical Properties and Nano-Crystallinity of Anatase TiO2nanoparticles Thin Film Using Low Pressure O2 Plasma Treatment." *Thin Solid Films*, vol. 709, Sept. 2020, p. 138212, https://doi.org/10.1016/j.tsf.2020.138212. Accessed 23 Mar. 2022.

Li, et al. "Review and Perspective of Materials for Flexible Solar Cells." *Materials Reports: Energy*, vol. 1, no. 1, 1 Feb. 2021, p. 100001, Xie, yi,. “Solvothermal Synthesis - an Overview | ScienceDirect Topics.” *Www.sciencedirect.com*, www.sciencedirect.com/topics/materials-science/solvothermal-synthesis#:~:text=Solvothermal%20synthesis%20is%20defined%20as. Accessed 2021.

Sigma Aldrich. “IR Spectrum Table & Chart.” *Merck*, vol. 1, no. 1, 2023, www.sigmaaldrich.com/MX/en/technical-documents/technical-article/genomics/cloning-and-expression/blue-white-screening.

Hendi, Awatif A., et al. “Dye-Sensitized Solar Cells Constructed Using Titanium Oxide Nanoparticles and Green Dyes as Photosensitizers.” *Journal of King Saud University - Science*, vol. 35, no. 3, 1 Apr. 2023, p. 102555, www.sciencedirect.com/science/article/pii/S1018364723000174?via%3Dihub, https://doi.org/10.1016/j.jksus.2023.102555.

Agus Supriyanto, et al. “Effect of Sintering on Transparent TiO2 18NR-T Type Thin Films as the Working Electrode for Transparent Solar Cells.” *IOP Conference Series: Materials Science and Engineering*, vol. 333, 1 Mar. 2018, pp. 012028–012028, https://doi.org/10.1088/1757-899x/333/1/012028.

Scarpelli, Francesca, et al. *Mesoporous TiO2 Thin Films: State of the Art*. *Www.intechopen.com*, IntechOpen, 27 June 2018, www.intechopen.com/chapters/59572.

Ludin, Norasikin A., et al. “Review on the Development of Natural Dye Photosensitizer for Dye-Sensitized Solar Cells.” *Renewable and Sustainable Energy Reviews*, vol. 31, no. C, 2014, pp. 386–396, ideas.repec.org/a/eee/rensus/v31y2014icp386-396.html.

Tenzin Tenkyong, et al. “Investigation of Sol-Gel Processed CuO/SiO2 Nanocomposite as a Potential Photoanode Material.” *Materials Science Poland*, vol. 33, no. 4, 1 Dec. 2015, pp. 826–834, https://doi.org/10.1515/msp-2015-0097.

Trang, T. N. Q., et al. “A High-Efficiency Photoelectrochemistry of Cu2O/TiO2 Nanotubes Based Composite for Hydrogen Evolution under Sunlight.” *Composites Part B: Engineering*, vol. 174, 1 Oct. 2019, p. 106969, www.sciencedirect.com/science/article/abs/pii/S1359836818331238, https://doi.org/10.1016/j.compositesb.2019.106969.

APPENDIX A

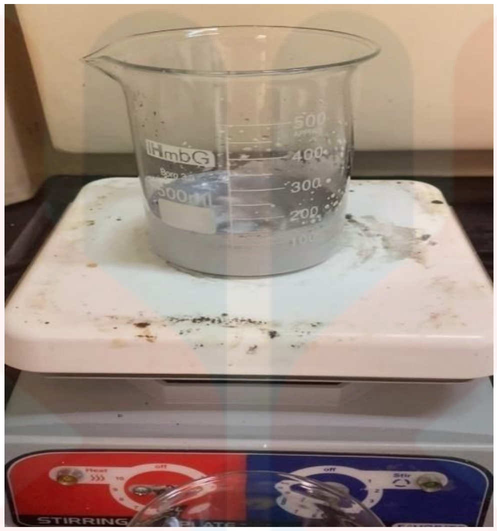

Figure A.1: The sample is spun for an hour on a hot plate.

Figure A.2: Samples must be refined to obtain Cu-doped TiO_2 powder.

APPENDIX B

Figure B.1: Sample place in an oven set to 90 °C.

Figure B.2: The sample piled using a mortar.

APPENDIX C

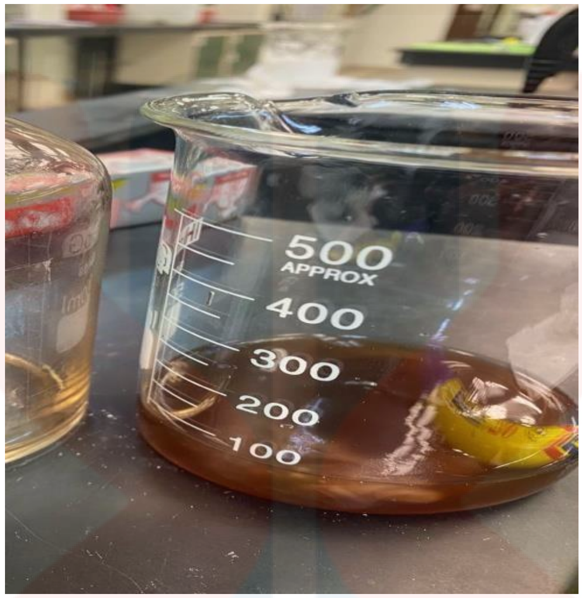

Figure C.1: The dye solution.

Figure C.2: The evaluation for electrical properties of DSSC.