# Natural Dyes Extraction of Curcuma Longa, Tradescantia Spatacea, and Bryophyta Absorption Capability on TiO<sub>2</sub> Nanofiber Thin Layer

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Exploration of plant variations is required to determine the absorbance ability and potential utilization of dye in the development of Dye-Sensitized Solar Cells (DSSC). Extraction of four different plants was carried out to obtain three different types of natural dyes. The curcumin dye was obtained from the extraction of *Curcuma longa*, the chlorophyl dye was obtained from the extraction of *Bryophytes*, the anthocyanin dye was obtained from the extraction of *Brassica oleracea var capitata f. rubra*, and *Tradescantia spathacea*. The research was conducted to determine the absorbance capability of each different type of dye and the image of the thin layer of TiO<sub>2</sub> nanofiber used by DSSC. Extraction is carried out through a drying and pounding process. The powder of each plant was then synthesized using ethanol through a homogenization process for 12 hours. The research utilizes a spectrophotometer UV-Visible to determine the wavelength of the natural dye, as well as a scanning electron microscope (SEM) to determine the size of the titanium dioxide (TiO<sub>2</sub>) thin film nanofiber based on the displayed image. DSSC utilizes TiO<sub>2</sub> nanofiber as a thin layer of semiconductor. The dye absorption peak is in the wavelength range of 350-500 nm and 650-700 nm. Based on the analysis of absorbance results, curcumin dye has the greatest potential to be used in DSSC with the highest absorption ability in all its occurrences at visible light wavelengths.

Keywords: TiO2 Nanofiber; Dye Curcuma Longa; Dye Tradescantia Spathacea; Dye Bryophyta; Absorption Capability

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### I. INTRODUCTION

The discovery of the Dye-Sensitized Solar Cells (DSSC) renewable energy device makes utilization of dyes as active elements a must for further study. These dyes are part of synthetic dyes and natural dyes. During the development of the solar cell industry, the dye has been developed into a free electron-producing material in its application to dyesensitized solar cells [1]. Natural dyes are dyes obtained from nature, especially dyes derived from plants, whether these dyes are obtained directly or indirectly. Each plant has a source of natural dyes (pigments). The potential of the dye in plants is determined by the intensity of the color produced by the plant and depends on the sensitivity of the dye in its function. Anthocyanin natural dyes have the most dominant properties as acid-base indicators because red pigments tend to have fairly high stability [2]. Anthocyanin pigments also have absorbance capabilities and improve photovoltaic performance better than other pigments in DSSC [3].

On the working principle of DSSC, the natural dye sensitizer is excited when electrons interact with the dye. This interaction occurs when sunlight hits the DSSC so that electrons enter the conduction band through a thin mesoporous layer. The number of dye molecules adsorbed on its surface is affected by the porosity and morphology of the  $TiO_2$  layer which provides a very large reaction area for the monolayer dye molecules to harvest incident light [4]. Curcuma longa extract is mostly used in phytotherapy. Curcuma longa is famous for its curcumin content [5]. Dye chlorophyll derived from Bryophyta has a highly significant ratio in terms of absorbance ability but has the same absorption wavelength range as most natural dyes. The wavelength range of chlorophyll dye plays a crucial role in the DSSC photoelectric process. The wavelength range of dye bryophytes is in the wavelength range of visible light to infrared light, which is 300 nm to 700 nm. Each natural dye will show a difference in the absorption wavelength and the absorption ability of the material. It is influenced by the characteristics of natural dyes and the ratio of the solvents used [6], [7].

In previous studies, the difference in solvent volume ratio used in optical dye characterization used solvent volume ratios of 9:1, 7:5, 5:7, and 1:1. The dye used comes from trollflower petals that have been deionized in water and dried at 50°C for 15 minutes. Measurement of optical properties was carried out using UV-Vis Spectra 4802 [3]. Based on the solution used, the dye absorbance ability appears at visible light wavelengths, only the peak of the dye absorption wavelength does not appear significantly, so the absorption peak is not known for sure. In this study, the difference in volume ratio was varied again with a ratio of 1:5, and the variety of plants as natural dye materials used variety of different plants.

Solar cells that use TiO<sub>2</sub> as the main material have various advantages, namely, the raw materials are very easy to find, the voltage generated is quite large, solar panels produced with TiO<sub>2</sub> materials can be made in various forms, and the application of TiO<sub>2</sub>-based solar cells is very wide. Nanostructures that can be applied to TiO<sub>2</sub> materials can improve the performance of TiO<sub>2</sub>-based solar cell systems. The nanostructure has a characteristic high surface area, so it will increase the amount of dye adsorption which increases the number of photons that can be absorbed. TiO<sub>2</sub> morphological layer will greatly determine the number of dye molecules absorbed by TiO<sub>2</sub>. In this research, TiO<sub>2</sub> was produced from the solgel method using a solution of Titanium Tetra-Isopropoxide (TTIP) in the anatase phase. The anatase phase of the  $TiO_2$ layer was obtained after heating at a temperature of 450°C [8].

The anatase phase was used in this research because the anatase phase is more photoactive than the rutile phase so the anatase active site will be wider. While the brookite phase was not selected in the research because the anatase phase was more stable. In addition, the anatase phase can be produced at a lower temperature than the rutile and brookite phases which require high temperatures to obtain. Therefor, TiO<sub>2</sub> was used to increase the efficacy of DSSC. Based on the latest research, DSSC is considered not yet effective in increasing the voltage compared to silicon solar cells. The addition of natural dye agarose to the TiO<sub>2</sub> layer was able to increase the voltage yield to 0.58 V in DSSC [9]. Natural dyes are recognized as beneficial materials in photoelectric, photochemical, and various other fields, including active coating materials for generating electricity. Recognition of the benefits of natural dyes has led to the exploration of natural dyes from various plant-owned dyes carried out on every part of the plant. DSSC was chosen as one of the potential new energy producers because of its easy materials and manufacture with promising energy conversion results [10]. DSSC utilizing natural dyes will further streamline the required production costs, the combination can also increase the photoelectric ability of solar cells through further studies.

## II. METHOD

#### A. Preparation of Natural Dye Solution

The implementation of the research begins with the preparation of tools and materials to be used. The chemical glass used is ensured to be clean and free from other residues. The beakers used in the study were sterilized in two stages, namely by using distilled water and HCL solution. Sterilization was carried out using an ultra sonic cleaner for 10 minutes at 40°C. Preparation of natural dye extracts from *Curcuma Longa, Tradescantia Spathacea, Bryophyta,* and *Brassica Oleracea Var Capitata F. Rubra.* These materials were extracted and synthesized to obtain natural dyes anthocyanins,



FIG. 1: Schematic electrospinning process by 15 kV [16]

curcumin, and chlorophyll dyes. Extraction of all natural dyes was carried out using the same method for all types of natural dyes. Each natural ingredient is cleaned of residue and unwanted parts in the research. The material is then dried at  $50^{\circ}$ C for 12 hours. The natural ingredients are mashed in a sterile state, then dissolved using an ethanol solution [11]. The ratio of natural ingredients powder with ethanol solution is 1 gram compared to 5 ml of ethanol.

The dye solution was then homogenized using a stirrer with a rotating speed of 3 rpm for 12 hours at room temperature. The homogeneous solution was then synthesized using filter papers with a pore size of 0.45 m to remove the remaining powder and deposits from natural materials.

#### B. Preparation of TiO<sub>2</sub> Nanofibers Thin Films

A thin layer of TiO<sub>2</sub> nanofiber is a semiconductor layer that conducts as an electron acceptor. Furtemore, in Dye-Sensitized Solar Cells (DSSC) TiO<sub>2</sub> applied as the working electrode [12]. Modification of the surface structure of the TiO<sub>2</sub> layer into the fiber structure in this study was carried out based on the electrospinning technique by considering the success rate of electrospinning in producing nanofibers [13]. Electrospinning is a versatile and feasible technique for producing ultra-thin fibers [14]. A photosensitizer attached to the anode attached to an n-type semiconductor can absorb light in the blue spectrum range and a photosensitizer attached to a p-type semiconductor at the cathode must absorb red light and transmit positive holes to the semiconductor. So the spectrum of usable light greatly expands what needs to be significantly improved. The expansion of the photosensitizer capture area is carried out by reducing the size of the semiconductor morphology. Electrospinning nanofiber produces a stratified morphology with a very small size, so that the electron harvesting area is significantly increased [15]. Electrospinning used in this research is an electrospinning device that is made and designed based on research needs. The electrospinning device has also been previously tested and validated.

The main ingredient of  $TiO_2$  (titanium dioxide) nanofiber thin film was synthesized from a mixture of  $Ti\{OCH(CH_3)_2\}_4$ (titanium tetra isopropoxide) solution, acetic acid, ethanol, and polyvinyl pyrrolidone. the proportion of each ingredient in the  $TiO_2$  synthesis solution was 0.5 ml: 2 ml: 5 ml: 2.5 grams. The homogenization of the solution was carried out for 24 hours. Thin film deposition was carried out on fluorine-doped tin oxide (FTO) substrate with a flow rate of 3.0 ml/hour and annealing process was carried out at 450°C for 3 hours.

#### C. Characterization of Optical Properties and Size of TiO<sub>2</sub> Nonofibers Thin Films

Characterization of the optical properties of natural dyes was carried out using a Lambda 25 ultraviolet-visible (UV-Vis) spectrophotometer. The Lambda 25 UV-Vis spectrophotometer uses the double beam method and is capable of scanning wavelengths from 190 nm to 1100 nm. Tests were carried out to determine the absorption wavelength region and the absorption ability of each material. The results obtained from this measurement are a graph of the wavelength of the absorption area of the material and the intensity of the absorbance of the material. The region scanned in this measurement is between 300-700 nm. In this study, the comparison of the absorption value and the dye absorption ability in the wavelength range in the scan area becomes a reference for the comparison of the analysis of the ability and potential of dye as an electricity producer in DSSC.

TiO<sub>2</sub> nanofiber thin films were characterized using a scanning electron microscope (SEM). SEM characterization was carried out with 1500x magnification at 10 m scale. Characterization of TiO<sub>2</sub> was carried out to observe the size of the TiO<sub>2</sub> nanofiber which became the acceptor of the dye as an electron donor. The results of SEM images for morphological characterization of TiO<sub>2</sub> are image size of TiO<sub>2</sub> nanofibers.

#### **III. RESULTS AND DISCUSSION**

The natural organic dye extracted in this study was curcumin dye obtained from the extraction of *Curcuma Longa*, anthocyanin dye derived from the extraction of *Tradescantia Spathacea* and *Brassica Oleracea Var Capitata F. Rubra*, as well as chlorophyll dye obtained from the extraction of *Bryophyte* plants. The use of dyes derived from natural materials has attracted the attention of many studies. Considering that natural dyes are a new alternative that allows them to be used in the production of renewable energy with lower costs and abundant material resources.

Determination of the optical properties of dye materials is generally classified as the material's response to an electromagnetic reaction, and in more detail the response will occur in the visible light range. The optical properties of the material are divided into several properties, namely the nature of absorbance (absorb), reflection properties (reflecting), and transmission [17]. The discussion of research on the characterization of optical properties and analysis of the extraction of natural materials as natural dye solutions is limited to the absorbance properties of natural dyes only. The occurrence of light absorbance is when electrons that are excited from the valence band then move through the band gap and forward



FIG. 2: Graph of Ultra Violet Visible (UV-Vis) test results; a) Comparison of the absorption peak length of *Brassica F. Rubra*, *Tradescantia Spathacea*, *Bryophyta*, and *Curcuma Longa*; b) Comparison of the peak length of *Tradescantia Spathacea*, *Bryophyta*, and *Curcuma Longa* dye absorption peaks.

to the conduction band. This phenomenon will result in the emergence of free electrons in the conduction band and the creation of holes in the valence band [17]. The measurement of the absorbance spectrum or the absorption wavelength of the optical properties possessed by each dye is limited to a wavelength of 300 nm to 700 nm. The wavelength range is the region of visible light to infrared light. Based on the measurements that have been made, the results are obtained as shown in Fig. 2 as follows:

Figure 2 shows that the method of preparation of natural materials and dye extraction using the same proportion will produce different absorbance values for each material. Based on Fig. 2a, it is known that the anthocyanin dye absorption peak obtained from *Brassica oleracea var capitata f. rubra* appears in the range of ultra violet (UV) light and visible light, which is between 300 nm to 400 nm. The graph on the absorption results of Brassica dye shown different character because the volume ratio used is different from the character of the

dye, so the Brassica dye solution was too concentrated. While *Tradescantia Spathacea* anthocyanin dye, *Bryophyta* chlorophyll dye and curcumin dye have the same absorption wavelength region, namely the peak absorption area of visible light in the range of 350 nm to 500 nm. In contrast to Curcuma Longa, based on Fig. 2b the chlorophyll dye of *Bryophyta* and anthocyanin dye from tradescantia Spathacea has a second absorption wavelength peak in the infrared wavelength range in the range of 650 nm to 700 nm.

The potential of curcumin dye in generating electricity based on the characterization of the solution is very high compared to other dye solutions. with the same solution ratio curcumin has an absorbance unit value of 2.1 a.u. In addition to the high absorbance value, curcumin dye also has a larger ratio of absorption area. This can be seen from the area under the orange graph. In addition, in other studies, the application of curcumin dye from Curcuma Longa on DSSC has enormous potential. Based on the results, it is known that the power conversion efficiency of DSSC utilizing dye Curcuma Longareaches 0.86% [18]. Dye chlorophyll and anthocyanins also produce a fairly good potency in the visible light region. However, based on their light absorbance characteristics, the two dyes tend to have narrower absorption capabilities than curcumin dyes. This will cause a decrease in the ability of the dye to generate electrons as a power source, compared to curcumin dye. While the anthocyanin dye from Brassica oleracea var capitata f. rubra could not be observed because Brassica did not show a good characterization of the solution comparisons made in this research. Very high absorbance graph values appear in the visible light wavelength range, but are observed to be very low and tend to be undetectable in the 400 nm - 700 nm wavelength range. So it was concluded that the dye Brassica Oleracea Var Capitata F. Rubra has no potential to be used as a potential electron donor dye for use in DSSC.

On the other hand, at the wavelength of the infrared absorption region, curcumin dye displays a very low ability compared to anthocyanin dyes and chlorophyll dyes. In the infrared light wavelength range, chlorophyll dye has a higher potential for generating electricity as shown in Figure 1.b. The different absorption peak heights in each natural dye indicate the dye's ability to absorb the received light. The comparison of the absorbance values of each natural dye is shown in Table I. Table I shows the comparison of the peak absorption wavelength data possessed by each dye. Based on these data, curcumin dye has the best absorption in the visible light wavelength range (350-500 nm) with an absorbance peak that occurs at a wavelength of 447 nm. Meanwhile, the absorption peak of chlorophyll dye and Tradescantia Spathacea anthocyanin dye each occurred in the visible light wavelength range with an absorption peak at 419 nm. The second absorption peak for chlorophyll dye and anthocyanin dye occurred in the wavelength range of ultra-infrared light (650 700 nm) with an absorbance peak at a wavelength of 674 nm. The presence of the second absorption peak on the chlorophyll dye and the anthocyanin dye causes the dye to carry out a good photoelectric process due to the wide range of wavelengths possessed by the two dyes. Based on the results of dye absorbance



FIG. 3: Image SEM of Characterization TiO2 Nanofibers Thin Layer Size.

characterization in the visible light and infrared wavelength ranges, in general, the absorbance capability of the dyes used can increase the efficiency of DSSC power conversion. The absorbance ability of the dye can increase the production of excited electrons, thus enabling the performance of  $TiO_2$  to increase in its conduction band [19].

Absorption peak anomaly occurred in experiments conducted on *Brassica* anthocyanin dye. In this type of anthocyanin dye, the absorption peak cannot be detected correctly by the Lambda 25 UV-Visible Spectrophotometer. This is because the solution is too concentrated and the dye absorption exceeds the ability of the Lambda 25 UV-Visible Spectrophotometer. What can be concluded from the dye test *Tradescantia Spatachea* anthocyanin is a dye that has absorption occurs in the ultra violet ray region, namely the dye absorption occurs in the 327-384 nm wavelength region and does not have a second absorption peak wavelength. This is corroborated by similar studies that have been carried out, the wavelength range of UV-Vis absorption obtained from Brassica extraction is in the absorption range around the wavelength of 310 nm to 330 nm [20].

The growth of  $\text{TiO}_2$  nanofiber fibers is intended to determine the size of the  $\text{TiO}_2$  nanofiber used as a thin layer of Dye-Sensitized Solar Cell (DSSC) as an electron acceptor. The smaller the fiber size and the more fibers produced from the electrospinning process, the larger the electron acceptor cross-sectional area. So that the electrons caught will be more and more and the electricity generated from the DSSC will be even greater. Fig. 3 shows the size of the nanofibers produced in the study.

The size of the TiO<sub>2</sub> nanofiber fiber is influenced by the

Natural Dye First Absorbance Wavelength Range		Anthocyanin (Brassica)	Curcumin (Curcuma Longa)	Chlorophyll (Bryophyta)	Curcumin (Tradescantia)
		327-384 nm	350-500 nm	350-500 nm	350-500 nm
First Peak Absorbance	Wavelength Absorbance	356 nm 6 a.u	447 nm 2.106 a.u	419 nm 1.608 a.u	419 nm 0.826 a.u
Natural Dye		Anthocyanin (Brassica)	Curcumin (Curcuma Longa)	Chlorophyll (Bryophyta)	Anthocyanin (Tradescantia)
Second Absorbance Wavelength Range		-	-	650-700 nm	650-700 nm
Second Peak Absorbance	Wavelength Absorbance	-	-	674 nm 0.787 a.u	674 nm 0.372 a.u

TABLE I: Dye Absorption Wavelength Peak

speed of the electrospinning pump and the homogeneity of the solution. A solution that is too viscous or liquid will have a very significant impact on the resulting size of the thin film. Based on Fig. 3, it can be observed that the size of the  $\text{TiO}_2$ fiber in this study is in the range of 0.667 m - 2.774 m. The instability of the TiO<sub>2</sub> fiber size in this study was caused by the rotational speed of the syringe needle in the electrospinning process. The characterization results indicate that the solution used to produce a thin layer of TiO<sub>2</sub> nanofibers has produced a fairly good fiber and can be used as a semiconductor layer for testing the electrical results of DSSC.

#### **IV. SUMMARY**

Research on natural dyes curcumin dye, chlorophyll dye, and anthocyanin dye showed that there were differences in the absorption wavelength of each dye. Based on the optical properties testing using the Lambda 25 UV-Visible Spectrophotometer, apart from the difference in absorption wavelength, differences in the absorption level of natural dyes can also be observed. Chlorophyll dye and anthocyanin dye were observed to be able to absorb light waves in the visible light wavelength range, which is in the range of 350-500 nm. In addition to the visible light range, chlorophyll dye and anthocyanin dye are also capable of absorbing light in the ultrainfrared wavelength range (650-700 nm). Dye curcumin is only able to absorb light in the visible light region. The difference of all dyes observed is in the level of absorption ability of natural dyes. Based on the measurements made, it was observed that the ability of curcumin dye to absorb light was better than the absorption ability of other natural dyes. The SEM image of TiO<sub>2</sub> grown in this research shows that the morphology of TiO<sub>2</sub> nanofibers can reach a size of 0.667 m. The results of these images provide satisfactory results in the process of growing a thin layer of TiO<sub>2</sub> in the anatase phase.

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