Experimental Results for Mushroom-based Dye Sensitized Solar Cell

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***Abstract*—This study explores the usage of novel oyster mushroom dyes in dye-sensitized solar cells (DSSCs) as photosensitizer to substitute the costly chemical dyes with a more eco-friendly, natural alternatives. Utilization of oyster mushroom dye as a natural dye for DSSC is due to their large biomass yield and the fact that they can be cultivated in a regulated environment. Dye from pink oyster mushroom was extracted and dried using freeze-drying methods. Characterization involved I-V measurements for electrical properties, UV-Vis spectrophotometry for optical analysis, and testing using solar simulator for current density-voltage (J-V) characterization. Freeze-dried pink mushroom dyes showed optimal properties for DSSCs, with energy bandgaps of between 1.71 and 2.14 eV. The fabricated DSSC performance was determined using a solar simulator, and the fabricated DSSC device exhibited an efficiency of 0.107%.**

Keywords— DSSC, TiO_2, electrical properties, optical properties, J-V characteristics.

I. Introduction

The ability of power plants to meet energy needs may be hampered by climate change and rising electricity consumption, according to research, which presents serious difficulties to global energy production. It is critical to find flexible and dependable renewable energy sources in order to assure sustainable energy production, as studies indicate that non-renewable energy sources may run out by 2040 [1]. The loss of non-renewable resources and the harm that burning coal and other fossil fuels causes to the environment, such as air pollution, soil contamination, and resource scarcity, are the main drivers behind the switch to renewable energy [2], [3]. In addition to promoting sustainable and green energy technologies, solar photovoltaic (PV) technology - which directly convert sunlight into electricity - are drawing attention as a potential solution to the energy crisis and environmental problems [4]. As non-renewable resources become fewer, solar energy is set to become more technologically and economically feasible. The amount of sunlight that the Earth receives per square meter is roughly 1366 W, providing an almost infinite and easily accessible source of energy. Because they use abundant sunshine and need less labor, solar PV offer a substantial advantage over traditional power sources [5].

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According to data from the International Energy Agency, stocks of fossil fuels might continue for as long as 29 years, whereas reserves of coal could remain for about 41 years [6]. The urgent need to find and create flexible renewable energy solutions is highlighted by the prediction made by certain research that the peak use of non-renewable energy sources may only last until 2040 [1].

Solar energy is a viable renewable energy source because of its positive effects on the environment and absence of drawbacks [7]. This is especially important for equatorial nations with substantial solar energy potential, like Malaysia. One hour's worth of energy from the sun can cover Earth's yearly energy needs (1.75×10^7 W), indicating that solar energy may be able to supply some of the world's energy needs. Third-generation solar cells that seek to boost efficiency and reduce production costs include hot carrier cells, polymer solar cells, quantum dot solar cells, dye-sensitized solar cells (DSSCs), heterojunction solar cells, and others [8]. The low cost of energy conversion of DSSCs is drawing interest in photovoltaic technology. They employ inexpensive, non-toxic, naturally derived pigments that are environmentally safe, potentially negating the need for costly chemical synthesis techniques [9]. Because of its low cost, simplicity of construction, and increased photo-conversion efficiency, DSSCs are preferred. A counter electrode, an electrolyte with redox characteristics, and semiconductor photoanodes that are dye-sensitized are essential parts of DSSCs. With titanium dioxide (TiO_2) acting as the semiconductor, the dye's capacity to absorb photons and transform them into electrons is a major factor in DSSC performance. Although their intricate production can be laborious, traditional DSSCs employ coordination of transition metals, primarily osmium and ruthenium complexes—as efficient sensitizers [10].

Knowing that natural dyes are inexpensive and easy to produce, there has been a significant increase in interest in using them as sensitizers in DSSC in recent years [11]. Chemical components that are essential to the growth of all living things make up natural colors. Plant pigments are categorized as flavonoids, carotenoids, anthocyanins, or chlorophylls based on their comparable structures and metabolic background [12]. The synthesize of natural dyes are simple and inexpensive, eco-friendly and have high absorption coefficients. Scientists are still working to find new natural dye sources, even if the effectiveness of these natural dyes is still inadequate for widespread sensible use. These fascinating investigations into the synthesis of DSSCs with dyes derived from biological resources are still ongoing [13].

The application of natural dyes as DSSC sensitizers was first discussed by the scientific community 20 years ago, but the efficiency of the results has been poor. Efficiency levels below 2% have been found in several studies. A power conversion efficiency (PCE) of 5% has been attained by a subset of them. Because of their wide availability, ecological friendliness, economic feasibility, and biodegradability, natural dyes are good sensitizers for DSSCs. But according to earlier data, nobody has recorded a PCE for natural dyes that was higher than 10%. A sizable fraction of them has PCE values between 3 and 4%. The intrinsic volatility of natural dyes is one of its drawbacks. They also easily agglomerate, making the collection of charges created by photolysis useless. Most of them don't stick to the oxide semiconductor surface well enough. Considering the derivatives of this dye have not attracted much interest, the dearth of research on substitute dyes offers a chance for additional study [14].

Most of the natural dyes utilized in DSSCs come from higher plants, but there are also other, as yet unexplored, sources of pigment, including bacteria, cyanobacteria, microalgae, yeast, and molds [9]. Despite their wide range of colors, mushrooms have not been thoroughly researched as natural dye supplies. Age and tissue damage can both have an impact on their coloring. While mushrooms may contain terpenoids and betalains, including carotenoids, they do not contain anthocyanins or chlorophylls like plants do [15].

Several studies have already increased the effectiveness of solar cells with natural dyes [16]. The effectiveness of DSSC has been found to be impacted by a number of constructional factors. The dye made from anthocyanin pigment was the most successful. Mangosteen pericarp extract (anthocyanin pigment) was utilized by Ma et al. with 1.17% cell efficiency. TiO_2 was used to make pomegranate juice (anthocyanin pigment), with a 1.076% efficiency rate. With TiO_2, improved DSSC efficiency was also shown. TiO_2 has significantly better dye absorption than ZnO. Using a novel mixed dye method that combines shisonin and chlorophyll, Kumara et al. achieved a PCE of 1.31% [17].

In contrast to natural dyes, which have a narrower absorption spectrum, metal complex dyes, such as Ru complexes dye, have a wide absorption spectrum, close correlation between excited and ground states, and stability in the oxidized state all contribute to the exceptional PV behavior. These factors contribute to higher DSSC efficiency [18].

The oyster mushroom, or Pleurotus spp., has a high fiber and protein content, a low-fat content, and a high vitamin and amino acid content. It is prized for its antioxidant and anticancer effects, as well as its nutritional advantages and other health benefits. After Agaricus bisporus, Pleurotus spp. are the most widely grown mushrooms worldwide, with production rising dramatically between 1997 and 2010 [19].

The cap of the pink oyster mushroom (Pleurotus djamor) is pink, either bright or dark, determined by the strain and development circumstances. Pink oyster mushrooms are a good choice for sustainable agriculture because of their quick development and ability to flourish in a range of agricultural waste materials [20].

II. Research Methodology

With a small modification, the protocol previously published in the literature was utilized to isolate and purify the fungal pigments from the oyster mushrooms. The process flow for fabricating the DSSC is summarized in the flowchart in Fig. 1.

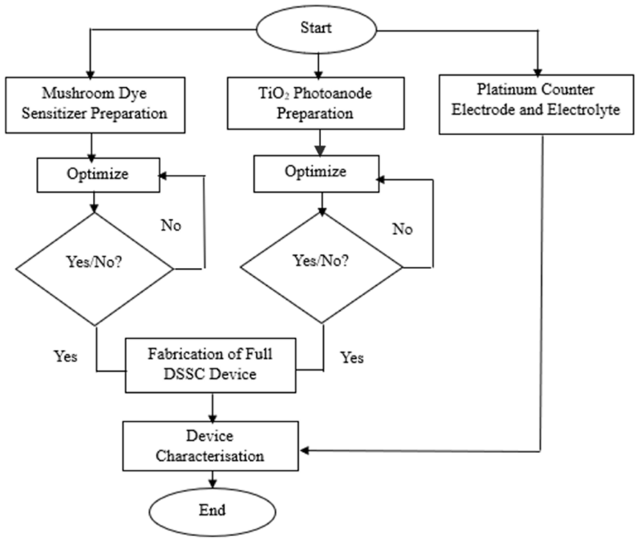

Fig. 1. Flowchart of the DSSC Fabrication.

The fruiting bodies of the pink mushrooms were crushed using a homogenizer. Next, a 1:30 volume ratio is used to suspend the sodium hydroxide solution and the mushroom mash together. The suspension will be incubated in an 80 W sonicator (Fisher Scientific, USA) for 80 minutes in order to guarantee full extraction. The leftover material will subsequently be separated using centrifugation for 15 minutes at 10,000 rpm. A solution of 7 mol/L HCl was then added into an Erlenmeyer flask to bring the pH of the supernatant down to 1.5. 3 hours were spent for the supernatant to precipitate at room temperature [21]. After 15 minutes of centrifuging at 10,000 rpm, the precipitate will be collected and washed using deionized water to the point its pH become neutral. The raw pigments will next be extracted and dried in a freeze dryer (Delta 1-24 LSC, Germany). Organic solvents including ethanol, chloroform, and ethyl acetate will be utilized to remove the proteins, lipids, and carbohydrates in order to purify the crude pigments. First, the raw pigments will be suspended in a 7 mol/L HCl solution for two hours at 100 °C. After centrifuging the precipitates, distilled water will be used three times to rinse them. Before being dried at room temperature, ethyl acetate, chloroform, and ethanol will be used to wash the insoluble pigment.

Pigments will be suspended for 5 minutes in phosphate-buffered saline (PBS, pH 7.0) and then soaked for 24 hours at 4 °C in a 2.5% (v/v) glutaraldehyde solution. The samples will next go through three PBS washes for five minutes each. The samples are first dehydrated at ethanol concentrations of 30%, 50%, 70%, 80%, 90%, and 100% before the ethanol is gradually replaced with tert-butanol (ethanol: tert-butanol = 1:1, 20 min; ethanol: tert-butanol = 1:3, 20 min; pure tert-butanol, 20 min for further dehydration). After that, the samples will be submerged entirely in tert-butanol and chilled to 20 °C in order to induce crystallization. Using an EMitech K550 sputter coater, the samples will be freeze-dried and gold-sputter coated. The pink oyster mushroom dye was freeze-dried prior to further usage.

The sol-gel manufactured TiO_2 was created by dissolving 10 milliliters of titanium (IV) butoxide in 10 milliliters of ethanol and stirring the mixture for an hour. After that, 5 ml of distilled water was added to the solution gradually, drop by drop. The resultant gel developed quite instantly and was agitated for many minutes. For an hour, the mixture was vigorously agitated to produce a white, colloidal precipitate. The solutions were filtered after 24 hours and then dried for an additional 12 hours at 100 °C in the oven. Following drying, a ball mill will be used to grind the material into a fine powder.

In order to create a uniform TiO_2 paste, theTiO_2 powder synthesized (2 g) was mixed with 100 ml of ethyl alcohol and agitated for 30 minutes. The solution was left in the dark before to use. To produce a single coating layer, ten drops of TiO_2 paste were applied to the cleaned and dried glass substrates at 3,000 rpm. After that, the glass substrate was allowed to dry for ten minutes at 100 °C. The second and third coating layers were applied using the same method. The finished coating was annealed at 500 °C for 30 minutes.

In a petri dish, the FTO/TiO_2 photoanode was sensitized for the entire night using an aqueous mushroom dye solution. Before being used, the previously made and stored powdered mushroom colors will be diluted with deionized water. In this phase, the ideal dilution ratio was applied.

Platinum paste was coated on the the conductive side of uncoated FTO glass to create the experiment's counter electrode (cathode). 50 ml of acetonitrile were mixed with 0.1 g of iodine and 0.5 g of potassium iodide (KI). Before being used, the solution will be shaken for half an hour and then kept in a closed bottle.

The DSSC was attached to a platinum counter electrode and a TiO_2 photoelectrode coated with electrolyte before being put together. Binder clips were used to hold the cathode and anode electrodes attached on the coated surfaces. Before analysis, liquid electrolyte was dropped across the electrodes.

The current-voltage was measured using a 2-point probe in order to analyze the electrical properties. A 99.9% gold (Au) metal contact with a thickness of 60 nm was applied to the TiO_2/oyster mushroom dye photoanode. A thermal evaporator was used to carry out the deposition.

The Jasco/V-670 UV–Vis-NIR Spectrophotometer was utilized to evaluate the optical properties of the pigments present in mushrooms. The absorption coefficient (α) was computed using the film's optical transmittance spectra and the information on film thickness. It measures the distance a light beam with a certain wavelength or energy may travel through a thin film before being absorbed by it. Equations (1) through (3) were applied in order to ascertain Lambert's Law of the thin film. The dye solution was created by diluting the powdered mushroom color in five different ratios: 1:6, 1:8, 1:10, 1:12, and 1:14. The absorption characteristics of the oyster mushroom pigment solution within the ranges of wavelengths were measured using a spectrophotometer. The solar simulator is used to characterize electrical parameters such as efficiency (η), current density-voltage (J-V), open-circuit voltage (V_{oc}), and short circuit current (J_{sc}), and fill factor (*FF*). These tests are essential for uses in solar cells because they demonstrate the performance of the manufactured solar cell. In a well-lit setting, the *J-V* measurement for the solar cell was performed.

III. Results and Discussions

A. Optical and Electrical Properties Characterisation

A Perkin Elmer (LAMBDA 750) UV-Vis-NIR Spectrophotometer was used to measure the transmittance and absorbance of the pink freeze-dried oyster mushroom (PFOM) dyes over a wavelength range of 300–800 nm. The UV-Vis-NIR absorption spectra were measured for various dilution ratios (1:6, 1:8, 1:10, 1:12, and 1:14).

Fig. 2 shows that all samples exhibited a consistent increase in transmittance with rising wavelength. PFOM demonstrated high transmittance (above 85%). It is observed that the 1:10 dilution ratio yielded the maximum transmittance (>80%), followed by the other dilution ratios. High optical transmittance (>85%) in the visible range (450-800 nm) is crucial for efficient energy transfer in solar cells, aligning with the solar spectrum [22]. Increased dye concentration leads to greater light absorption, which can alter the transmittance spectrum. However, high dye concentrations may cause self-quenching, where close proximity of dye molecules reduces electron injection efficiency and energy transfer. Dye aggregation at high concentrations can impact the dye layer's uniformity and negatively impact the optical properties and performance of the DSSCs [23]. Optimal dye concentration is essential for aligning absorption peaks with the solar spectrum, thereby improving solar cell efficiency.

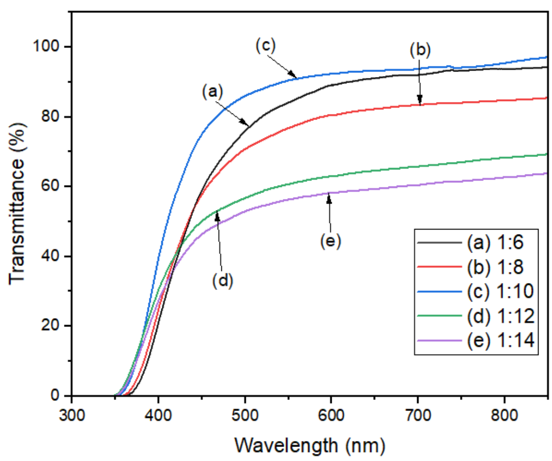

Fig. 2. UV-Vis transmittance spectra for PFOM dye.

The optical characteristics of the pigments found in mushrooms were assessed by the use of a Jasco/V-670 UV-Vis-NIR Spectrophotometer. Using the film's optical transmittance spectra and the information on film thickness, the absorption coefficient (α), which measures the distance a light beam of a certain wavelength or energy can pass through a thin film of prior to being absorbed by it, was computed. The Lambert's Law of a thin film was obtained using Equation 1 [24]:

$$\alpha = 1/t \ln(1/T) \quad (1)$$

where T is the film's transmittance and t is its thickness. The distance from the conduction band and the stretched phase in the valence band is measured in a unit called the optical band gap. Equation 2 determines the optical band gaps (E_g) for dye using the Tauc connection [25].

$$(\alpha h\nu)^{\gamma} = A(E_g - h\nu) \quad (2)$$

where α is the absorption coefficient, A is the Tauc parameter, and $h\nu$ is the photon energy. The intersection of the photon energy axis with the slope of the Tauc determines the optical gap [26]. Equation 3 was used to determine the oyster mushroom particles' band gap, which is obtained from Equation 2 where λ is the sample absorbance value, c is the speed of light (3 x 10^8 m/s), h is the Planck's constant (6.626 x 10^{-34} J/s), and E_g is the band gap energy.

$$E_g = hc/\lambda \quad (3)$$

The graph in Fig. 3 is used to calculate the energy gap for the samples. The energy bandgap value was obtained by extending the straight, thin portion of the curve to intercept the energy axis at the visible wavelength range of 300 to 800 nm, which is shown in Table 1. The anticipated bandgap energy for the PFOM at each of the five different dilution ratios was also displayed in Table 1. According to the results, the ideal bandgap for solar cell application is found in all PFOM dye dilutions with bandgap energies between 1.71 eV and 2.14 eV. For dye sensitizers, the optimal band gap is approximately 1.7 to 2.2 eV [27].

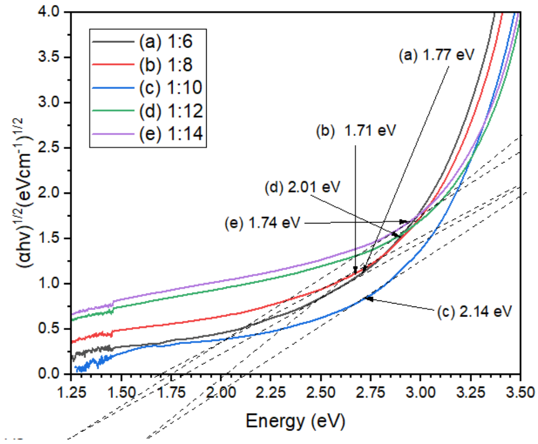

Fig. 3. UV Tauc Plot for PFOM dye.

TABLE I. ENERGY BAND GAPS (EV) READING OF THE PFOM SAMPLES

Dilution Ratio	Bandgap Energy (eV)
1:6	1.77
1:8	1.71
1:10	2.14
1:12	2.01
1:14	1.74

Lower excitation energy electrons can transform into free electrons in a conduction band as energy bandgaps expand, enhancing the electric solar system's efficiency (by roughly 3% for 1 eV). PV device performance is directly impacted by the semiconducting material's bandgap utilized. A photovoltaic effect cannot be produced by a band gap that is too large, and the lattice will heat up due to surplus photon energy in a band gap that is too narrow [28]. To prevent electron recombination processes and maintain a relatively stable ground and excited state, the mediator layer of a DSSC must recycle its photosensitizer quickly. A PV cell that produces electricity from standard air mass (AM) 1.5 sunlight requires a sensitizer that is excellent in absorbing all light with a wavelength exceeding a threshold of approximately 900 nm. This corresponds to a semiconductor with a bandgap of 1.4 eV. The efficiency with which the molecules absorb incident photons, convert photons into electron-hole pairs, and perform separation and collection are among the many parameters that affect the overall performance of the cell [28]. The TiO_2 photoanode's current-voltage (I-V) measurements are shown in Fig. 4.

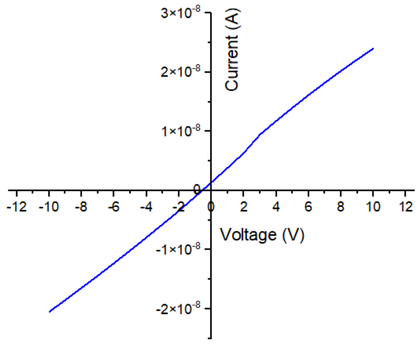

Fig. 4. I-V measurement plots of TiO_2 photoanode after being immersed in PFOM dye.

B. *Current density-voltage (J-V) Characterisation*

The current density-voltage (J-V) characteristics of fabricated DSSC was characterized using Newport Oriel Sol3A solar simulator under AM 1.5 sun condition (100 mW/cm^2, 25 ºC). Based on the result that the solar simulator generated (see Fig. 5), the fabricated FTO/TiO_2-PFOM/electrolyte/Pt with sample size of 1×1 cm^2 indicated the V_{oc} of 0.499 V, I_{sc} of 1.987×10^{-5} A and J_{sc} of 0.397 mA/cm^2. The results of the solar simulator were used to assess the performance of fabricated device. The fill factor, FF, is 0.538, and the cell's overall power conversion efficiency, η, is 0.107%. Further analysis can be found in [29].

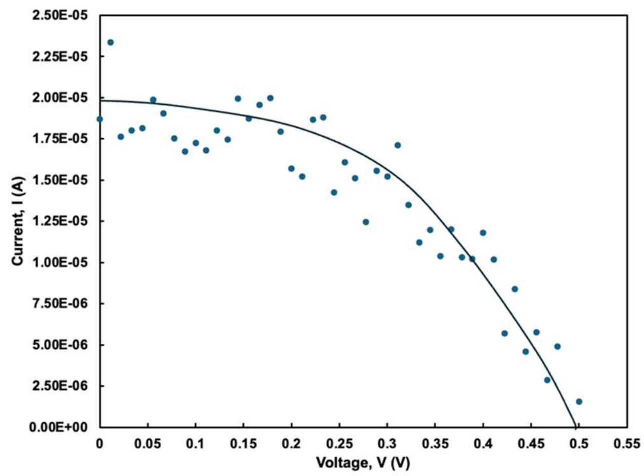

Fig. 5. J-V Characteristics for FTO/TiO_2-PFOM/electrolyte/Pt.

Poor light absorption capabilities in the visible range and a subpar electron injection method could be the cause of the manufactured device's low efficiency. Low DSSC effectiveness of natural dyes is usually caused by the low energy of the dye excited state, fast dye molecule recombination, and the presence of compounds in the extracts that encourage cellular recombination processes [30].

The low extinction coefficient value and lack of or diminished bonding to the TiO_2 are the causes of the lower conversion efficiency. Therefore, improved absorption in the solar cell's visible region and efficient electron transport are responsible for the better efficiency of the device. The two important factors that determine the cell's efficiency are the J_{sc} and V_{oc} [11].

Meanwhile, in other previous study, a crude extract of carotenoids and fucoxanthin from *Sargassum wightii*, a marine brown algae has been investigated as a DSSC sensitizer. Instead of using TiO_2, this instance employed nanocrystalline zinc oxide (ZnO) as a semiconductor, and immersion in the extract was used to achieve sensitization. An efficiency of 0.07% was achieved with this configuration. It may be beneficial to genetically modify bacteria to produce pigments with improved chemical characteristics. As an example, the bacteria E. coli BL21 was genetically modified to overproduce the carotenoid and express the lycopene biosynthesis pathway. The following is the photoelectrochemical behavior: 0.057% PCE, 0.686 mA/cm^2 for J_{sc}, and 0.289 V for V_{oc} [31].

Despite the fact that there are many fungal alternatives that could serve as a source of possible pigments, the industry faces several obstacles that prevent these resources from being commercialized. One of the obstacles is the market's sustained viability for fungal-based pigments. Three crucial elements—pigment yield, purity, and stability—are the main determinants of fungal pigment sustainability. The major challenge with natural pigments is their stability when various kinds of environmental conditions are present, such as food matrices, pH, light, moisture, and temperature. They also have a shorter lifespan due to molecular instability under various conditions, which may restrict their use as commercial pigments [32]. The biggest obstacle to employing natural colorants is the absence of process homogeneity. Since they are natural additions, it can be difficult to standardize color because the source ingredients can differ significantly [15]. Although fungi have many potential uses, little is known about how resistant they are to extreme environments. Fungi are more likely to break down fungal biomass and eliminate useful enzymes when they are exposed to or placed in an unfavorable fungal environment [32].

IV. Conclusions

This study presented a new natural color for DSSC that was taken from the pink oyster mushroom species. The PFOM with a ratio of 1:10 had demonstrated the best characteristics to be used as photosensitizer for DSSC application through UV-Vis, IV and J-V characterization. These characteristics included a bandgap energy of between 1.71 and 2.14 eV (within the optimal bandgap range for solar cells) and possess the efficiency of 0.107%. This research presents a significant opportunity to develop clean and cost-effective energy resources. The use of fungal dyes is particularly promising due to their non-toxic nature, as well as their ease and low cost of cultivation and extraction. Even though DSSC technology has advanced significantly, more tuning is required to increase its effectiveness and economic viability in the future. The dye itself can be improvised with the molecular engineering is the process of modifying a dye's molecular structure to maximize its capacity to absorb light, inject electrons, and transport charges. Another method is by co-sensitization which combining several dyes with complimentary spectra of absorption for determining the increase the use of the solar spectrum.

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