

## ENHANCING DSSC PERFORMANCE THROUGH CHLOROPHYLL AND PORPHYRIN DYE INCORPORATION ON TiO<sub>2</sub>-ZnO: Al COMPOSITES

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**Abstract.** This research systematically investigates the impact of porphyrin and chlorophyll dyes on Dye-Sensitized Solar Cells (DSSC) performance, aims to achieve maximum solar cell efficiency. This investigation involved the use of Fluorine-doped Tin Oxide (FTO) coating with TiO<sub>2</sub>-ZnO composite, incorporating Al doping, and introducing variations in the concentration of chlorophyll SP and porphyrin (2:2:0.1 and 2:2:0.2). Synthesis of Al-doped ZnO was carried out via the sol-gel method, which involves mixing and heating at 65°C, followed by degradation at 150°C. TiO<sub>2</sub> and ZnO: Al composites were formed using the sonication method at 45°C for 60 minutes. This study evaluates the impact of dyes on the growth of TiO<sub>2</sub> and ZnO: Al composites and examines their characteristics - including UV-Vis, band gap, current versus voltage curves, DSSC efficiency-using EDX, and FTIR analyses of solar cells. The DSSC efficiency testing utilizes a photon light source from a halogen lamp with an intensity of 328-580 lux. The results showed that DSSC based on TiO<sub>2</sub>-ZnO: Al + chlorophyll produced an efficiency of 13.3%, while porphyrin (2:2:0.1) and (2:2:0.2) produced an efficiency of 8.9% and 13.9%, respectively. In conclusion, this study shows that adding dye to the TiO<sub>2</sub>-ZnO: Al composite significantly improves DSSC performance and shows optimal characteristics. The highest DSSC efficiency of 13.9% underscores the interdependence of absorber layer quality with photovoltaic performance, providing valuable insights for future solar cell design and optimization.

**Keywords:** TiO<sub>2</sub> and ZnO fluorine-doped tin oxide, porphyrin, ZnO with Al doping.

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### Introduction

Solar cells operate on the fundamental principle of photovoltaic, harnessing the ability to convert light into electrical energy. The generation of Dye-Sensitized Solar Cells (DSSC) has significant advances in the field of solar cell materials [1]. DSSC efficiency has demonstrated remarkable progress, achieving levels of 11% [2] and 12.3% [3], particularly when utilizing TiO<sub>2</sub> as the active material in the working electrode.

Recent advancements have shown that employing SM315 porphyrin dye [4] with TiO<sub>2</sub> as the semiconductor can further enhance power conversion efficiency, reaching an impressive 13%. Despite TiO<sub>2</sub>'s efficiency as a photo-catalyst [5-10], its limited surface area poses a challenge, resulting in relatively low adsorption of the photo-catalyst. Additionally, the higher cost of TiO<sub>2</sub>, compared to ZnO, has led researchers to explore ZnO as a viable alternative for the working electrode [11-15]. ZnO, an abundant natural element with an energy gap of 3.37 eV, is a justifiable substitute given its energy characteristics comparable to TiO<sub>2</sub> (3.2 eV) [16].

Various materials, such as Ga, Sn, Mg, Al, and B, have been explored for doping to further optimize ZnO's physical, optical, and electrical properties [17]. Aluminium is a convenient choice for atomic doping [18-22] due to its smaller ionic radius compared to ZnO, which enhances the electrical conductivity of ZnO and presents a cost-effective alternative to other materials [23,24].

Considering these factors, the combination of TiO<sub>2</sub> with ZnO emerges as a necessity for developing components with superior optical and electrical properties for photo-electronic applications [25]. This study introduces innovation by focusing on the composite TiO<sub>2</sub>-ZnO with Al doping [26]. The sol-gel method, involving forming initial compounds (precursors) followed by drying and calcination, is employed for doping ZnO with Al. Additionally, the sonication method, utilizing ultrasonic waves with a frequency of 20 kHz – 10 MHz, is adopted for manufacturing TiO<sub>2</sub>-ZnO: Al composites specifically tailored for solar cell applications.

Since TiO<sub>2</sub> exhibits absorbance primarily in ultraviolet wavelengths, incorporating a sensitizer becomes imperative to extend its absorption spectrum into the visible light range [27]. The objective of this study is to investigate the enhancement of sensitivity and efficiency through the utilization of porphyrin dye and chlorophyll extracted from *Syzygium Paniculatum* (S.P.) as sensitizers. The study aims to comprehensively compare the performance of these two sensitizers in enhancing sensitivity and efficiency.

## Experimental

### Materials

This study utilized TiO<sub>2</sub>, ZnO, AlCl<sub>3</sub>, Al-doped ZnO, methanol, ethanol, NaOH, distilled water, iodine, KI, ethylene glycol (EG), carbon, chlorophyll from S.P. and porphyrin produced by HACH, Germany (Hach Method 8143 Range: 2–210 µg/L Cu).

### *Al-doped ZnO synthesis process via the sol-gel method*

The materials used included ZnO, methanol as a solvent, NaOH as a ligand, hexane for washing, and aluminium trichloride (AlCl<sub>3</sub>) as a dopant compound. One hundred grams of ZnO and 80 mL of methanol were heated on a hotplate with a stirrer at 60°C for 15 minutes, resulting in percussion. Separately, one hundred grams of AlCl<sub>3</sub> and 50 grams of NaOH were dissolved in 200 mL methanol and heated on a hotplate with a stirrer at 60°C for 15 minutes. The heating percussion was carried out using a three-neck flask by slowly dripping the NaOH + AlCl<sub>3</sub> + MeOH solution. Stirring continued at 65°C for 180 minutes until the solution turned white. The solution was then allowed to stand for 48 hours until a white precipitate formed. The resultant mixture was washed with 10 mL hexane and 10 mL methanol to produce ZnO, which was then dried in an oven at 150°C for 8 hours, producing ZnO powder [28-30].

### *Mixing TiO<sub>2</sub>, ZnO: Al, and chlorophyll dye using the sonication method*

The materials used were nano TiO<sub>2</sub>, Al-doped ZnO, ethanol as a solvent, and distilled water. The process involved mixing with several variations and operating conditions at a temperature of 45°C, 70% amplitude on-off for 20 minutes, as follows [31,32].

TiO<sub>2</sub> powder (20 g), distilled water (15 mL), and (EG) (15 mL) were sonicated for 20 minutes until TiO<sub>2</sub> was entirely dispersed. An addition of 20 g of ZnO: Al was re-sonicated for 20 minutes,

and 10 mL of chlorophyll was added and sonicated again for 20 minutes (TiO<sub>2</sub>-ZnO: Al + chlorophyll composite).

TiO<sub>2</sub> powder (20 g), distilled water (15 mL), and EG (15 mL) were sonicated for 20 minutes until TiO<sub>2</sub> was entirely dispersed. An addition of 20 g of ZnO: Al was re-sonicated for 20 minutes, 1 mg of porphyrin was added and sonicated again for 20 minutes (TiO<sub>2</sub>-ZnO: Al + porphyrin 2: 2: 0.1 composite).

TiO<sub>2</sub> powder (20 g), distilled water (15 mL), and EG (15 mL) were sonicated for 20 minutes until TiO<sub>2</sub> was entirely dispersed. An addition of 20 g ZnO: Al was re-sonicated for 20 minutes, and 2 mg of chlorophyll was added and sonicated again for 20 minutes (TiO<sub>2</sub>-ZnO: Al + porphyrin 2: 2: 0.2 composite).

### *FTO coating with TiO<sub>2</sub>-ZnO composite doped with Al and dye using a spray gun for solar cell materials*

The FTO was cleaned using ethanol, and the process of deposition of the initiator layer (seed layer) on top of the FTO substrate was performed. The seed layer solution consists of TiO<sub>2</sub>, ZnO: Al + dye. Layer deposition was performed using a pressurized gun spray technique at 3.2 kg/cm<sup>2</sup>. The heating process was gradual, starting at 150°C and increasing to 250°C, aimed at facilitating the formation of the TiO<sub>2</sub>-ZnO: Al seed layer (photo-anode) crystals.

### Instrument

Characterization was conducted using the Bruker Quantax X-Flash for Energy Dispersive X-ray Spectroscopy (EDX) testing and the Perkin Elmer Spectrum Two FT-IR Spectrometer for Fourier Transform Infrared (FTIR) analysis. Sample composition was determined *via* energy-dispersive X-ray (EDX) testing, which involves using X-rays to analyze the elemental composition of materials. The purpose of EDX testing is to determine the composition of a sample by providing information about the elements present. These analyses were conducted at an accelerating voltage of 10 kV and a magnification of 1.300 × with an analysis time of 5 minutes.

The FTIR (Fourier-transform infrared spectroscopy) test was carried out on dyes to determine chemical bonds in natural dyes. In this case, testing was performed explicitly on dyes to identify and analyse chemical bonds found in natural dyes. Experiments were conducted on spectra collected through the total attenuation reflectance (ATR) method, ranging from 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> and resolution of 4 cm<sup>-1</sup>.

### DSSC fabrication

Cells were arranged to form a sandwich structure consisting of a working electrode (FTO covered with TiO<sub>2</sub>-ZnO and aluminium doped and immersed in a dye solution), electrolyte, and counter electrode. The electrolyte was prepared by dissolving 8.3 g of KI and 1.26 g of I<sub>2</sub> into 100 mL of Polyethylene Glycol (PEG). The counter electrode was produced by coating grafit on top of the FTO until it was evenly distributed over the entire surface. The FTO glass containing TiO<sub>2</sub>-ZnO: Al + dye was then glued to the counter electrode and coated with carbon using a clamp (paper clip). The electrolyte-solution was injected through the gap between the two FTO glass plates. The DSSC test used a halogen lamp as the photon light source with an intensity ranging from 328 to 580 lux, an active area of 1 cm<sup>2</sup>, and the anode was sensitized for 15 minutes.

### Determination of Band Gap Energy

To calculate the band gap energy value in TiO<sub>2</sub>-ZnO: Al + chlorophyll and TiO<sub>2</sub>-ZnO: Al + porphyrin composite, the Tauc Plot method [33] was carried out in several calculation steps until band gap energy was obtained. The process begins with the use of the Tauc's relation formula is as follows in Eq.(1).

$$ah\nu = B (h\nu - E_g)^\gamma \quad (1)$$

where:  $a$  - 2.302  $A$ ;

$h\nu$  -  $(hc)/\lambda$  or  $E_g$ ;

$A$  - the absorbance (arbitrary units, au);

$B$  - a constant;

$E_g$  - the band gap (eV);

$h$  - Planck's constant,  $6,626 \times 10^{-34}$  J.s or  $4.14125 \times 10^{-15}$  eV.s (where  $1 \text{ eV} = 1.6 \times 10^{-19}$  J);

$\nu$  - a frequency (equivalent to  $\frac{c}{\lambda}$ ; where  $c$  is  $3 \times 10^8$  m/s and  $\lambda$  = wavelength obtained in nm);

$\gamma$  -  $\frac{1}{2}$  for direct type semiconductors;

$\lambda$  - the wavelength (nm).

### Current and voltage measurement

Current and voltage measurements were taken to determine photovoltaic parameters:  $I_{sc}$  and  $V_{sc}$ . The Fill Factor ( $FF$ ) was calculated according to the following Eqs.(2,3) [34-37].

$$FF = \frac{I_{max} \times V_{max}}{I_{sc} \times V_{sc}} \quad (2)$$

$$\eta = \frac{FF \times I_{sc} \times V_{sc}}{P_{in}} \times 100\% \quad (3)$$

where:  $V_{max}$  - the maximum voltage (mV);

$V_{sc}$  - the open-circuit voltage (mV);

$I_{max}$  - the maximum current ( $\mu\text{A cm}^{-2}$ );

$I_{sc}$  - the short-circuit current ( $\mu\text{A cm}^{-2}$ );

$P_{max}$  - the total power ( $\text{W/cm}^2$ );

$P_{in}$  - the power of the halogen lamp ( $\text{W/cm}^2$ ,  $479 \times 10^{-7} \text{ W/cm}^2$  to  $846.9 \times 10^{-7} \text{ W/cm}^2$ ).

### Results and discussion

#### Absorbance measurements were conducted using an ultraviolet-visible (UV-Vis) spectrometer

The optical properties of the composites were characterized by generating absorbance data with the UV-Vis spectrometer. Calculations to determine the band gap energy ( $E_g$ ) were performed using the Tauc Plot method. The characterization of TiO<sub>2</sub> composites with Al-doped ZnO was carried out over a wavelength range of 300–800 nm, spanning from ultraviolet to visible light.

Figure 1 illustrates the variations in absorbance at different wavelengths. The TiO<sub>2</sub> composite with Al-doped ZnO exhibits the highest absorbance at a wavelength of 530 nm, with a value of 1.44 a.u. The same composite shows the lowest absorbance at the same wavelength, with a value of 1.0175 a.u.

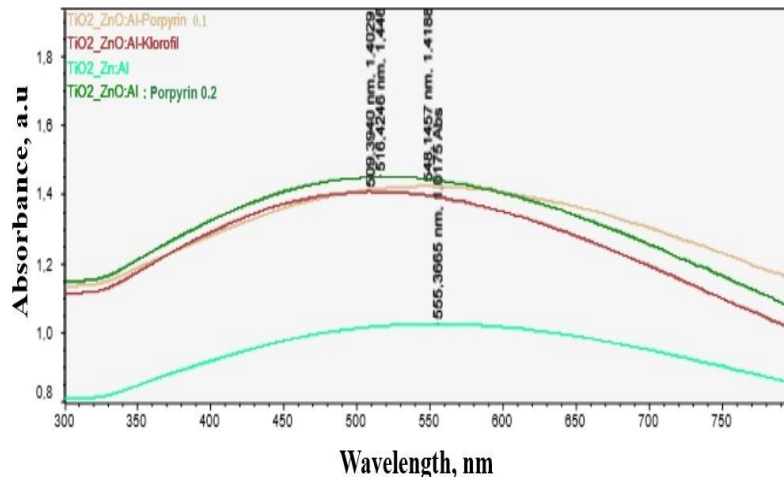


Figure 1. Graph showing the relationship between wavelength and absorbance for various composite variations.

Variations in composites containing dyes from chlorophyll and porphyrin exhibit absorbance values close to those of the TiO<sub>2</sub> composite with Al-doped ZnO. Absorbance decreases at wavelengths below 500 nm and above 550 nm. These changes indicate differing optical absorption properties in each sample, which affect the band gap energy values.

### Band Gap Energy

The energy difference between the valence band and the conduction band in a semiconductor material. It determines the wavelength of light the material can absorb. By plotting  $(\alpha E_g)^2$  against  $E_g$ , a linear relationship is expected for direct band-gap materials. The intercept on the energy axis ( $E_g$  axis) can be used to determine the band-gap energy.

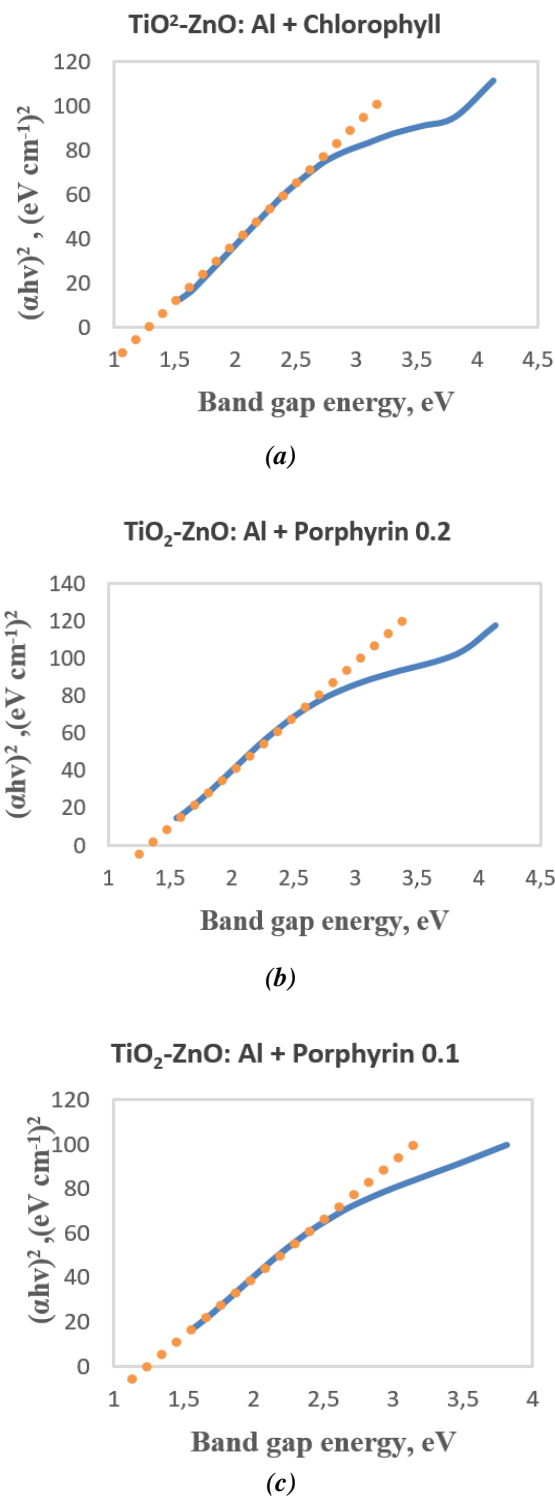
Figure 2 illustrates that the largest band gap energy ( $E_g$ ) occurs in the TiO<sub>2</sub> composite with Al-doped ZnO and Porphyrin 0.2, which is 1.25 eV. Conversely, the smallest band gap is found in the TiO<sub>2</sub> composite with Al-doped ZnO and Porphyrin 0.1 dye, measuring 1.1 eV. The data indicate that Al doping effectively reduces the band gap energy of TiO<sub>2</sub>, which originally was 3.2 eV [38], and ZnO, originally 3.7 eV [39]. Furthermore, the band gap of Al-doped ZnO itself is recorded at 3.24 eV [40]. This reduction is more pronounced when ZnO: Al is composited with TiO<sub>2</sub>. Importantly, a decrease in the band gap enhances light absorption, thereby improving the performance of solar cells. Based on these findings, this alternative material TiO<sub>2</sub> with Al-doped ZnO and porphyrin dye shows to be promising.

Aluminium (Al) doping offers benefits because Al acts as an electron acceptor, reducing the recombination rate of electron-hole pairs. Furthermore, Al doping enhances the absorption spectrum from 400–800 nm, facilitating charge transfer from the interior to the surface of the TiO<sub>2</sub> [41]. Doping TiO<sub>2</sub> with anionic species such as Al introduces a type of anion doping, where the combination of the doped anion's p orbitals (*e.g.*, from N or Si) with the O<sub>2p</sub> orbitals of TiO<sub>2</sub> elevates the valence band and lowers the band gap of the photo-catalyst.

### FTIR characteristics

FTIR is a test to determine the functional groups formed in the DSSC layer. Figures S1-3 (in Supplementary material) show the results of the FTIR test of TiO<sub>2</sub>-ZnO: Al with chlorophyll dye porphyrin (2:2:0.1) and porphyrin (2:2:0.2), respectively. The test results show several functional groups at specific wave

numbers with wave crests formed. There is an absorption spectrum indicating the presence of anthocyanins with a range of 3200–3400 cm<sup>-1</sup>, namely 3347 cm<sup>-1</sup> (chlorophyll), 3267 cm<sup>-1</sup> (porphyrin 2:2:0.1), and 3341 cm<sup>-1</sup> (porphyrin 2:2:0.2) [42].



**Figure 2. Determination of band gap energy of TiO<sub>2</sub>-ZnO: Al Composites with Chlorophyll (a), Porphyrin 0.1 (b), Porphyrin 0.2 (c).**

Some of the functional groups that occur can be seen in Table 1.

Absorption occurred with vigorous intensity, indicating the presence of the OH group at wave numbers  $3383.26\text{ cm}^{-1}$  ( $\text{TiO}_2\text{-ZnO}$ : Al with dye chlorophyll),  $3458.48\text{ cm}^{-1}$  ( $\text{TiO}_2\text{-ZnO}$  composites: Al and porphyrin (2: 2: 0.1)), and  $3371.68\text{ cm}^{-1}$  ( $\text{TiO}_2\text{-ZnO}$  composites: Al and porphyrin (2: 2: 0.2)). The spectrum results also show moderate intensity absorption at a wave number of  $1413.9\text{ cm}^{-1}$  ( $\text{TiO}_2\text{-ZnO}$ : Al with dye chlorophyll),  $1398.44\text{ cm}^{-1}$  ( $\text{TiO}_2\text{-ZnO}$  composites: Al and porphyrin (2: 2: 0.1)), and  $1398.44\text{ cm}^{-1}$  ( $\text{TiO}_2\text{-ZnO}$  composites: Al and porphyrin (2: 2: 0.2)), corresponding to C-H bonds. These functional groups align with those found in the anthocyanins framework.

Figures 3-5 depict the FTIR spectra of  $\text{TiO}_2$  and Al-doped ZnO. The formation of hetero-junctions is observed in the  $400\text{--}4000\text{ cm}^{-1}$  wave-number range, allowing the identification of various chemical and functional groups within the compounds. Ti-O-Ti bonds reveal the formation of  $\text{TiO}_2$ . Calcination at  $250^\circ\text{C}$  causes the transmission or absorption band to sharpen at  $400\text{--}900\text{ cm}^{-1}$ , indicating the  $\text{TiO}_2$  anatase phase.

The second-highest peak occurred at  $3850\text{ cm}^{-1}$  (chlorophyll),  $3759\text{ cm}^{-1}$  (porphyrin 2:2:01), and  $3711\text{ cm}^{-1}$  (porphyrin 2:2:02), corresponding to the O-H stretch of alcohol [40]. In the  $1184\text{ cm}^{-1}$  band (chlorophyll),  $1194\text{ cm}^{-1}$  (porphyrin 2:2:01), and  $1198\text{ cm}^{-1}$  (porphyrin 2:2:02), the bending of the Ti-O-Ti mode was observed. Transmission bands at  $1481\text{ cm}^{-1}$  (chlorophyll),  $1479\text{ cm}^{-1}$  (porphyrin 2:2:01), and  $1483\text{ cm}^{-1}$  (porphyrin 2:2:02) represented symmetrical strain vibrations of the carboxylate group. A peak at  $1726\text{ cm}^{-1}$  (chlorophyll),  $1734\text{ cm}^{-1}$  (porphyrin 2:2:01), and  $1728\text{ cm}^{-1}$  (porphyrin 2:2:02) corresponded to the carbonyl, indicating a sol-gel reaction [45]. A peak in the  $850\text{--}997\text{ cm}^{-1}$  range is associated with stretching the Zn-O band. Similar behaviour was observed for the three conditions, as their respective bands appeared in the  $652\text{ cm}^{-1}$  region, easily comparable with Zn-O. At  $1386\text{--}1535\text{ cm}^{-1}$  (chlorophyll),  $1394\text{--}1568\text{ cm}^{-1}$  (porphyrin 2:2:01), and  $1398\text{--}1560\text{ cm}^{-1}$  (porphyrin 2:2:02) for mixed oxides, only ZnO can create an asymmetric stretching mode in the presence of oxygen in the sample [46-49].

#### EDX Characteristics

EDX detects X-ray signals to produce elemental analysis. Because each element emits different characteristic X-rays, EDX detectors can differentiate and measure the essential presence

and distribution in the scanned area [50]. Characterizing the DSSC layer using EDX aims to determine the elemental composition of the sample surface. Figures 3-5 and Tables 2-4 illustrate the actual content in DSSC.

From the EDX spectra, the analysis results provide data on the composition of elements present on the surface of the  $\text{TiO}_2\text{-ZnO}$ : Al photo-electrode with chlorophyll dye, along with the addition of porphyrin (2:2:0.1) and (2:2:0.2), as shown in Tables 2-4. Figures 3-5 display the EDX spectrum in the DSSC layer with elemental composition.

Table 2 illustrates percentages such as 20.61% for Ti K, 63.44% for O K, 1.47% for Zn K, and 0.87% for Al K.

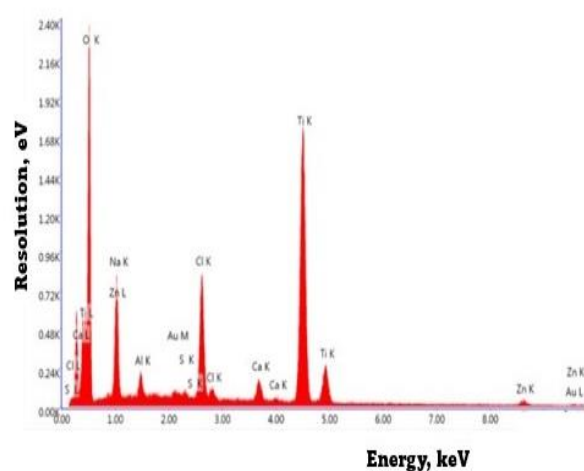


Figure 3.-EDX  $\text{TiO}_2\text{-ZnO}$ : Al with dye chlorophyll.

Table 1

Functional groups of  $\text{TiO}_2\text{-ZnO}$ : Al + chlorophyll and  $\text{TiO}_2\text{-ZnO}$ : Al + porphyrin composite [42,43].

Wavenumbers	Functional groups
1234.5–1238.34	vibration Ti-O-O
1614.47–1633.8	bending vibration of $\text{H}_2\text{O}$ and Ti-OH
2351.3–2374.45	vibration $\text{CO}_2$
3358.23–362.04	H-OH absorbs water

Table 2

Composition of  $\text{TiO}_2\text{-ZnO}$ : Al with dye chlorophyll.

Element	Weight (%)	Atomic (%)	Net Int.
O K	39.91	63.44	506.73
Na K	5.8	6.42	139.21
Al K	0.92	0.87	41.47
Au M	0.63	0.08	13.68
S K	0.31	0.25	14.06
Cl K	7.52	5.39	301.81
Ca K	2.32	1.47	63.63
Ti K	38.82	20.61	837.65
Zn K	3.77	1.47	15.98

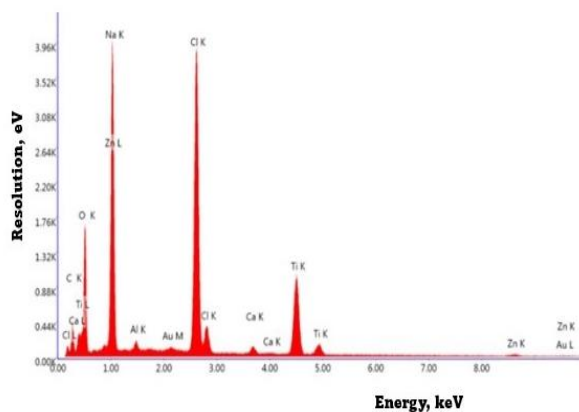
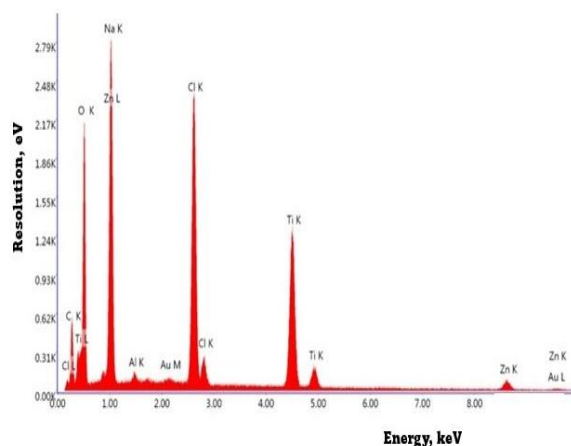
Figure 4. EDX TiO<sub>2</sub>-ZnO: Al with dye porphyrin.Figure 5. EDX TiO<sub>2</sub>-ZnO: Al with dye porphyrin (2: 2: 0.2).

Table 3

Composition of TiO<sub>2</sub>-ZnO: Al with dye porphyrin (2: 2: 0.1).

Element	Weight (%)	Atomic (%)	Net Int.
C K	9.93	19.75	55.75
O K	19.67	29.36	350.35
Na K	20.52	21.32	867.06
Al K	0.51	0.45	31.12
Au M	0.53	0.06	16.97
Cl K	28.2	19	1494.9
Ca K	1.08	0.65	36.79
Ti K	17.09	8.52	474.97
Zn K	2.46	0.9	13.98

Table 4

Composition of TiO<sub>2</sub>-ZnO: Al with dye porphyrin (2: 2: 0.2).

Element	Weight (%)	Atomic (%)	Net Int.
C K	13.52	25.67	102.66
O K	25.06	35.72	453.07
Na K	14.27	14.16	539.21
Al K	0.19	0.16	11.04
Au M	0.28	0.03	8.21
Cl K	17.65	11.36	927.58
Ti K	21.79	10.38	613.13
Zn K	7.24	2.53	40.35

Table 3 continues with percentages like 8.52% for Ti K, 29.36% for O K, 0.9% for Zn K. Table 4 illustrates the composition of TiO<sub>2</sub>-ZnO: Al with dye porphyrin (2:2:0.2), showcasing percentages such as 10.38% for Ti K, 35.72% for O K, 2.53% for Zn K, 25.67% for C K, and 0.16% for Al K. The elements Ti, Zn, Al, and O indicate the formation of TiO<sub>2</sub> and ZnO compounds, which aligns with previous studies [51,52]. Additionally, elements C, K, and Ca in chlorophyll and Na and Cl are identified as elements found in FTO glass.

The C and O elements in TiO<sub>2</sub> act as electron transfer connectors within its porous structure. Compounds of carbon in the hexagonal three-electron layer form covalent bonds with neighboring carbon atoms. The fourth electron acts as a free electron that moves across the coating's surface, enabling the conduction of electric currents. Element O, as an electron acceptor, captures the electrons generated from the dye. In the presence of elemental C, O, and P in TiO<sub>2</sub>, the charge of the dye can be captured by the molecules of C, O, and P. This charge can then be rapidly transferred to the next TiO<sub>2</sub> particle.

Tables 2-4 highlight the presence of elements Au, Ca, Cl, K, Mg, Na, O, and S. Ca, K, S, and Mg that are essential elements in chlorophyll, with the used chlorophyll originating from *Syzygium Paniculatum*, a plant belonging to the Myrtaceae family. The Na element is derived from the NaOH ligand, while Cl comes from aluminium nitrate (AlCl<sub>3</sub>) as a dopant compound. The presence of gold may be attributed to contamination during sample preparation or handling.

#### Current-Voltage (I-V) Testing

This point on the I-V curve represents the optimal combination of current and voltage where the solar cell produces maximum power. The coordinates of the Maximum Power Point are often denoted as (*Imp*, *Vmp*).

#### Measurement of the I-V Curve

The current-voltage (I-V) curve measurement is a crucial method for estimating the power conversion efficiency of solar cells. The speed of voltage scanning (vs) may induce a capacitive current depending on the cell's capacitance, potentially affecting the shape of the I-V curve. S-shaped I-V characteristics are common challenges in the development of new solar cell materials and device architectures [53]. These characteristics typically indicate a charge transport bottleneck, often at one of the selective contact layers. Overcoming this bottleneck through interface engineering and doping is essential for achieving high fill factors and enhancing power

conversion efficiencies [54]. For I-V curves, the maximum power point significantly shifts toward lower voltages, as illustrated in Figure 6.

The smallest fill factor (*FF*) values were observed when using the method proposed in this paper, in comparison to those presented in [55]. Additionally, the proposed method achieves an excellent match between the measured and estimated curves, as demonstrated in Table 5.

#### DSSC Performance Metrics

Current, voltage, and efficiency measurements are crucial for evaluating the performance of each DSSC, as depicted in Table 5. The performance of DSSCs relies on parameters, such as short-circuit current ( $I_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), fill factor (*FF*), and energy conversion efficiency ( $\eta$ ). The efficiency of DSSCs was assessed by incorporating dyes (chlorophyll, porphyrin 2:2:0.1, and porphyrin 2:2:0.2) and

analysing the current-voltage (I-V) curves under halogen lamp irradiation. Table 5 shows that the DSSC with added chlorophyll achieved the highest values for  $I_{sc}$  (269.3  $\mu$ A),  $V_{oc}$  (78 mV), and efficiency (13.32%). The addition of porphyrin 2:2:0.2 resulted in an  $I_{sc}$  of 212.6  $\mu$ A,  $V_{oc}$  of 105 mV, and an efficiency of 13.95%. The improved performance in DSSCs are attributed to the addition of dyes, which facilitate electron transfer by acting as bridges between the porous TiO<sub>2</sub> and ZnO: Al molecules, thus reducing barriers in the electron transfer process [56]. This study achieved efficiencies surpassing those of non-ruthenium research using  $I_2/I_3^-$  electrolytes, which reported an efficiency of 11.5% [57].

This phenomenon shortens the charge delivery distance, leading to increased electric current and improved DSSC performance.

Table 5

Performance of DSSC.								
Photo-electrode and dye	$V_{sc}$ (mV)	$I_{sc}$ ( $\mu$ A)/cm <sup>2</sup>	$V_{max}$ (mV)	$I_{max}$ ( $\mu$ A)/cm <sup>2</sup>	<i>FF</i>	$P_{max} \times 10^9$ (W/cm <sup>2</sup> )	$P_{in} \times 10^7$ (W/cm <sup>2</sup> )	$\eta$ (%)
TiO <sub>2</sub> -ZnO: Al and chlorophyll	53	269.3	45.0	163.7	0.516	7364.8	777.4	9.47
	72	266.9	58.5	172.1	0.524	10069.6	821.3	12.3
	58.4	262.1	46.1	177.9	0.536	8204.4	825.7	9.9
	42.2	257.4	29.5	192.0	0.521	5664.0	834.5	6.8
	78	193.7	69.3	160.0	0.733	11074.6	831.6	13.3
TiO <sub>2</sub> -ZnO: Al and porphyrin (2:2:0.1)	28.3	276.3	20.0	197.1	0.504	3946.3	833.0	4.7
	32.5	276.2	21.1	189.0	0.444	3985.6	775.9	5.1
	40.2	278.4	22.1	198.1	0.391	4375.9	846.2	5.2
	37	278.1	22.3	238.0	0.516	5309.5	620.7	8.6
	38.6	278.7	23.4	238.5	0.518	5572.6	625.1	8.9
TiO <sub>2</sub> -ZnO: Al and porphyrin (2:2:0.2)	47	111.7	29.5	83	0.472	2477.9	412.9	6
	42	152.9	32.0	85	0.424	2722.8	420.2	6.5
	54	212.6	46.6	87	0.353	4054.2	761.4	5.3
	97	132.5	92.9	86	0.662	7994.3	790.6	10.1
	105	87.2	96.0	69.6	0.730	6683.9	479.0	13.9

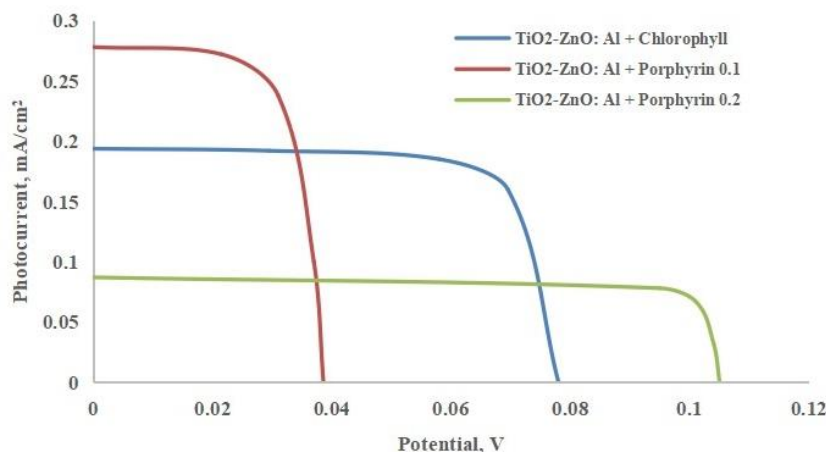


Figure 6. Series of I-V curves.

## Conclusion

The integration of natural dyes (chlorophyll and porphyrin) into DSSC was successfully achieved. Adding dye to the composite fills voids between TiO<sub>2</sub>-ZnO: Al molecules, decreasing gaps and accelerating electron transfer, ultimately reducing electron recombination rates. The study reveals that incorporating dye into TiO<sub>2</sub>-ZnO: Al enhances DSSC performance, showcasing optimal characteristics in absorptivity, optical band gap, and electrical parameters. The highest DSSC efficiency achieved is 13.95%, emphasizing the interdependence of absorbent layer quality with photovoltaic performance.

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## Supplementary information

Supplementary data are available free of charge at <http://cjm.ichem.md> as PDF file.

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