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Research Article

# Outstanding Photo-bioelectrochemical Cell by Integrating $TiO_2$ and Chlorophyll as Photo-bioanode for Sustainable Energy Generation

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**Abstract**. Photosynthesis is a technique for converting light energy into chemical energy that is both efficient and sustainable. Chlorophyll in energy-transducing photosynthetic organisms is unique because of their distinctive structure and composition. In photo-bioelectrochemical research, the chlorophyll's quantum trapping efficiency is attractive. Chlorophyll from *Spirulina platensis* is demonstrated to communicate directly with $TiO_2$-modified Indium Thin Oxide (ITO) to generate electricity without the use of any mediator. $TiO_2$-modified ITO with a chlorophyll concentration of 100 % generated the greatest power density and photocurrent of approximately 178.15 mW/m$^2$ and 596.92 mA/m$^2$ from water oxidation under light among all the other materials. While the sensitivity with light was 0.885 mA/m$^2$.lux, and Jmax value was 1085 mA/m$^2$. Furthermore, the power and photocurrent density as a function of chlorophyll content are studied. The polarizability and Van der Waals interaction of $TiO_2$ and chlorophyll are crucial in enhancing electron transport in photo-bioelectrochemical systems. As a result, this anode structure has the potential to be improved and used to generate even more energy.

***Keywords:*** photo-current; Indium Thin Oxide; Van Der Waals interaction; polar interaction; light sensitivity

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## 1. Introduction

Chlorophyll is widely utilized in the manufacture of fuels, hydrogen, and other high-value compounds. Chlorophyll discovered in higher plant and in microalgae are one of the greatest ways to collect light since all the subunits were optimized in a way maximum for photoconversion (Kirchhofer *et al.*, 2012). For these uses, chlorophyll's comparatively basic cellular architecture and ease of use have given it a competitive advantage over their photosynthetic equivalent. Direct energy production using chlorophyll has better benefits than algae or other dissimilar metals microorganisms, as chlorophyll can work for electricity production utilizing the photosynthesis electron transport chain without any outside fuels. Although technology for photosynthetic electrochemical cells is not developed enough for practical applications, ongoing progress in the area can make that technology a viable alternative to photovoltaics or comparable technologies today. In terms of biodegradability, low costs and no dependence on inorganic material, photosynthetic electrochemical cells provide distinct benefits than any similar technology (Sekar *et al.*, 2014).

Photosynthesis-based energy conversion in the anode of photo-electrochemical cells has been studied utilizing isolated photosynthetic reaction centers such as thylakoids or chlorophyll Chlorophyll's photochemical characteristics can be adjusted to structural alterations (Wang *et al.*, 2006; Wang *et al.*, 2007). Chlorophyll-driven photosynthesis just requires light and water without an extra organic carbon source and so has a great potential to produce a clean, sustainable and environmentally acceptable alternative energy source (Sekar and Ramasamy, 2015). The further benefit of chlorophyll molecules is that J-type aggregates can form, directed by π-π stacking with neighboring molecules, which increases the mobility of their charging carrier (Duan *et al.*, 2017; Amao & Komori, 2004). There are serious limitations to employing whole cell of algae since they need costly, labor demanding isolation processes, use sophisticated immobilization methods, low redox activity and have a lower long-term stabilization for practical use. Using chlorophyll in electrochemical cells as a photo-biocatalyst might circumvent such precautions. The extra light energy used by chlorophyll gives the electrical surface a higher stability.

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Due to its low cost, high stability, non-toxicity, biological inertness and redox capability, and environmentally friendly, $TiO_2$ was extensively investigated as the potential photocatalyst for carbon conversion, water splitting and degradation of hazardous contaminants in the aqueous and gaseous system (Rossettu *et al*., 2015; Venkatkarthick *et al*., 2015; Chen *et al*., 2016; Chen *et al*., 2015; Ferrari-Lima *et al*., 2015). $TiO_2$ is employed in several areas, including as solar cells, water and air purification, carcinoma treatment, and antibacterial self-cleaning materials due to the great stability redox characteristics (Liu *et al*., 2014; Luan *et al*., 2012). In case of $TiO_2$, the electron-holes are generated by irradiation by solar-light. The electrons in the conduction band (CB) convert the $H^+$ ions to $H_2$ and oxidize $H_2O$ to create $O_2$ in the valence band (Gao *et al*., 2015)

In photosynthesis, chlorophyll pigment plays an essential role in transforming sunlight into chemical energy. The presence of $TiO_2$ in the chlorophyll structure plays an important part in light absorption. Using a $TiO_2$, we eliminate the need for costly metal-based catalytic to immobilize photosynthetic machinery on electrode surfaces and increase the efficiency of photocatalytic activity (Li *et al*., 2018; Qi *et al*., 2018; Omar and Abd Rahim, 2020). Chlorophyll absorbs light in different wavelengths and achieves a green wavelength color. In photo-bioelectrochemical cells, the study into chlorophyll dyes has attracted significant interest.

We intend in this work to modify $TiO_2$ with chlorophyll which has been isolated from microalgae *Spirulina platensis* and afterwards coated in ITO surface as a photo-bioelectrochemical cell photoanode for sustainable energy generation. Polarization and voltage would be studied and chlorophyll-$TiO_2$ bonding would be chemically investigated. Similar structures including chlorophyll and TiO2 are commonly employed in the fabrication of solar cells, not photo-bioelectrochemical cells, therefore this is an academic novelty of this research. It will therefore be able to contribute even more to the development of photo-bioanodes for photo-bioelectrochemical cells, allowing for the generation of more sustainable and environmentally friendly electrical energy.

## 2. Materials and Methods

### *2.1 Chlorophyll Extraction*

Extraction of *Spirulina* using the technique introduced by Tong *et al*., (2012) with slight modifications. *Spirulina* powder was purchased from Neoalgae Indonesia Makmur (Sukoharjo, Indonesia). A glass bottle containing 10 grams of *Spirulina* was filled with 100 mL of ethanol (Sigma Aldrich, St. Louis, USA). The mixture was then sonicated for 1 hour to aid in the extraction process (Christwardana *et al*., 2021). The mixture was then filtered, and the filtrate was collected. To avoid auto-oxidation, the filtrate is placed in a dark bottle. The UV-Vis spectra of chlorophyll extract can be shown in Figure 1 and its concentration was 120.72 ppm, obtained by using equation (1) to (3) from Arnon (1949).

$$C_a\left(\frac{mg}{L}\right) = 12.74A_{663} - 2.69A_{645} \quad (1)$$

$$C_b\left(\frac{mg}{L}\right) = 22.9A_{645} - 4.68A_{663} \quad (2)$$

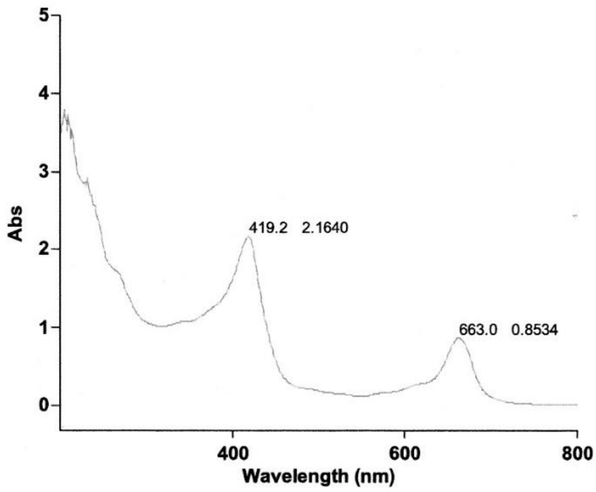


**Fig. 1** UV-Vis spectra of chlorophyll extract of *Spirulina platensis*

$$C_{total}\left(\frac{mg}{L}\right) = C_a + C_b \quad (3)$$

where the $A_{663}$ and $A_{645}$ are the absorbance of chlorophyll at wavelength of 663 and 645 nm, respectively. While $C_a$, $C_b$, and $C_{total}$ are the concentration of chlorophyll-a, chlorophyll-b, and total chlorophyll, respectively.

### *2.2 Photo-anode Modification*

In the first stage, commercial ITO glass was sterilized for 15 minutes by sonication with ethanol as the medium. The ITO glass was then put on tissue paper. Each edge of the ITO glass was sealed, ensuring that the $TiO_2$ paste forms properly in the middle during the coating process. During the $TiO_2$ coating preparation procedure, 0.25 g $TiO_2$ (Merck, Darmstadt, Germany) was blended with 2 mL ethanol. The liquid was mixed until it becomes a paste, then poured over ITO glass that has been isolated on all four edges. Using a ruler, $TiO_2$ paste was uniformly spread on the surface of the ITO glass. The ITO glass was then annealed in the oven for 15 minutes at 240 °C. The ITO glass was then cooled to room temperature before being dripped with various concentration of chlorophyll as shown in Table 1, and let to stand for one day. $TiO_2$-chlorophyll on the surface of the ITO glass was washed with ethanol before to use as a photo-bioanode to eliminate unbound chlorophyll. The reaction mechanism between $TiO_2$ and chlorophyll was illustrated in Figure 2a and the photograph of photo-bioanode can be shown in Figure 2b.

**Table 1**
The concentration of Chlorophyll-a, Chlorophyll-b, and Total Chlorophyll from chlorophyll extract of *Spirulina platensis*

| Chlorophyll Concentration (% v/v) | Chlorophyll – a (ppm) | Chlorophyll – b (ppm) | Total Chlorophyll (ppm) |
|---|---|---|---|
| 100 | 78.24 | 42.48 | 120.72 |
| 50 | 34.12 | 21.24 | 60.36 |
| 25 | 19.56 | 10.62 | 30.18 |
| 0 | 0 | 0 | 0 |

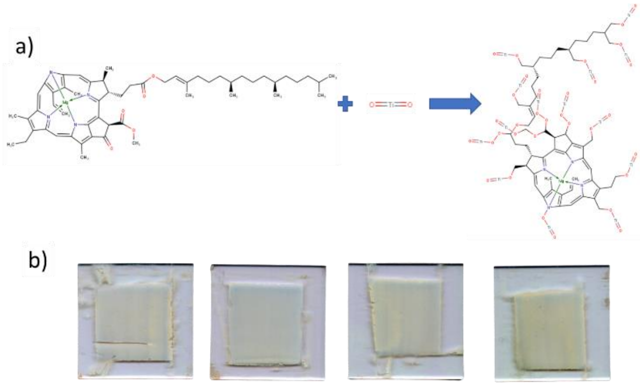


**Fig. 2** a) Bonding mechanism between chlorophyll and $TiO_2$, while b) is photographs of $TiO_2$-Chlorophyll photo-bioanode in the surface of ITO glass

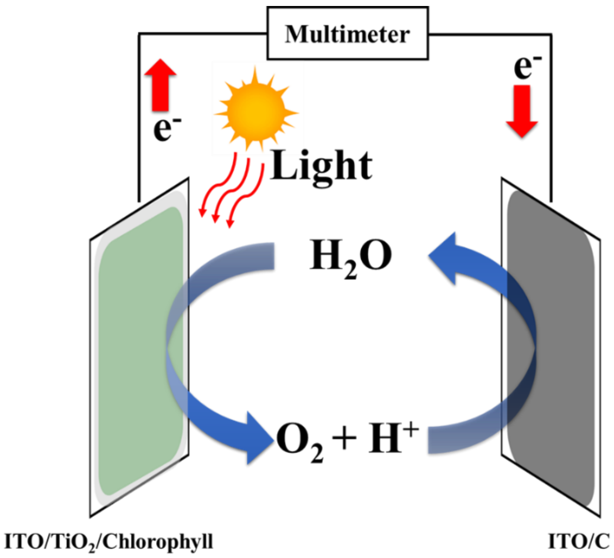


**Fig. 3** The schematic diagram of anode and cathode of photo-bioelectrochemical cell

*2.3 Photo-bioelectrochemical Cell Configuration*

The anode was ITO/$TiO_2$ containing chlorophyll, whereas the cathode was ITO/C placed a specific distance away from the anode. The reaction chamber's distance between the anode and cathode was measured to be 5cm, as illustrated in Figure 3. The cathode in the reaction chamber reduces the oxygen emitted from the anode surface and converts it to water. The anode and cathode electrodes were serially linked and put in a reaction cell made of a beaker glass. In this experiment, water act as the electrolyte solution for photo-bioelectrochemical cell. The photocurrent experiments were carried out with the help of a solar simulator and a special photo-biochemical system consisting of a modified light chamber equipped with a desk LED lamp of varying light intensity as a light source and a digital light meter LX1010B to measure the real-time light intensity inside the light chamber. The photo-bioelectrochemical was then placed within a modified light chamber and closed so that no light from the surroundings could enter. This analysis is performed in duplicate, and the findings presented are the averages.

*2.4 Electrochemical Characterization*

A multimeter device UNI-T UT-61E was systematically linked to the electrode of a photo-bioelectrochemical cell without the inclusion of any external resistance, which may be related to Open Circuit Voltage (OCV). After that, chronoamperometry (CA) measurement was determined and all CA measurements were taken using a multimeter under cyclic on-off illumination at a light intensity of 1600 lux within the light chamber. Various light intensity between 900 to 1600 lux was used to measure photocurrent of cell for sensitivity determination purpose. Various resistor values (10 MΩ – 100 Ω) were utilized to calculate the polarization and power curves under Closed-Circuit Voltage (CCV). The voltage values were read, and the electrical current was calculated by dividing the voltage by the resistance load, while the power density was calculated using Ohm's law and polarization curves were drawn following equation (4), (5) and (6) (Christwardana *et al.*, 2020; Hadiyanto *et al.*, 2021).

$$I = V/R \tag{4}$$

$$J = I/A \tag{5}$$

$$P = V \times J \tag{6}$$

where I and J are current (mA) and current density (mA/m$^2$), respectively, V is voltage (V), R is resistance (Ω), A is electrode area (m$^2$), and P is power density (mW/m$^2$).

*2.5 FTIR and Molecular Dynamics Characterization*

FTIR measurements have been performed using a spectrometer Shimadzu IRAffinity-1S (Kyoto, Japan). The molecular dynamic of photo-bioanode was modeled using Marvinsketch 21.3 software while it undergoing molecular interaction such as polarizability and Van der Waals surface area. Menu calculations → charge → polarizability and calculations → geometry → molecular surface area (3D) was used to analyze the polarizability and Van der Waals surface area, respectively, on the structures of chlorophyll, $TiO_2$, and chlorophyll/$TiO_2$ composites.

## 3. Results and Discussion

*3.1 Molecular Dynamic Simulation Analysis*

The interaction of chlorophyll with $TiO_2$ is very interesting to investigate at the molecular level. Non-polar bonds dominate the bonding that happens in chlorophyll (left picture) in Figure 4a. Meanwhile, the $TiO_2$ bond (middle image) clearly demonstrates the polar connection between Ti and O. When chlorophyll interacts with $TiO_2$, some portions of the chlorophyll functional group bind to O in $TiO_2$. According to the results of molecular dynamic simulation, the interaction formed between $TiO_2$ and chlorophyll is dominated by polar bonds (right figure) with a more compact shape than chlorophyll's structure. This polarizability is critical because it is associated to $TiO_2$-chlorophyll conductivity in transferring electrons to the external circuit. As a result, more $TiO_2$-chlorophyll in the photo-bioanode will improve the electron transfer rate in the oxidation process at the anode side, improving the photo-bioelectrochemical cell's performance.

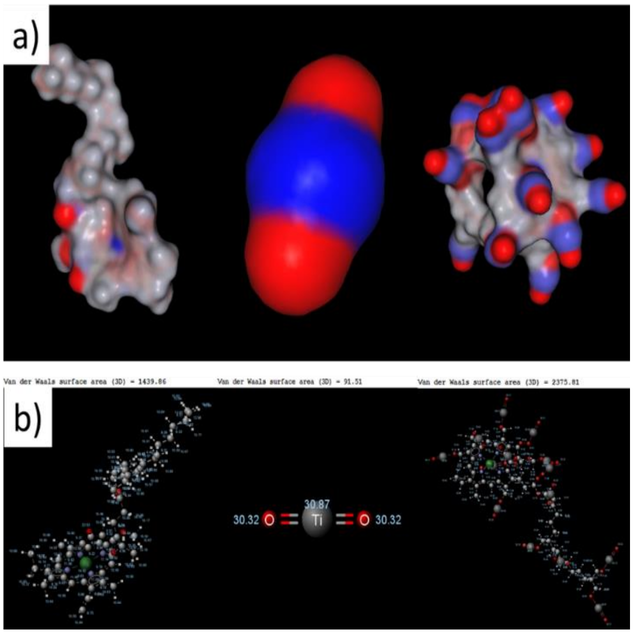


**Fig. 4** a) Polar interaction in the molecule of chlorophyll (left), $TiO_2$ (middle), and $TiO_2$-Chlorophyll (right), while b) its Van der Waals surface area. Red and blue color show polar area, while grey color show non-polar area

In addition to the polarizability of the interaction between $TiO_2$ and chlorophyll, the Van der Waals surface area was estimated to further understanding of the two materials' interactions. The Van der Waals surface area was discovered to be linearly related to polarizabilities. In Figure 4b, the Van der Waals surface area of chlorophyll (left picture) is 1439.86 A$^2$, whereas $TiO_2$ (middle image) has a surface area of 91.51 A$^2$, which includes 60.64 A$^2$ on O (30.32 A$^2$ each) and 30.87 A$^2$ on Ti. Meanwhile, the Van der Waals surface area of chlorophyll modified $TiO_2$ (right image) is 2375.81 A$^2$, which is approximately 65% higher than chlorophyll. This demonstrates that the interaction of $TiO_2$ with chlorophyll increases the surface area of the photo-anode indirectly, which affects the performance of the photo-bioelectrochemical cell.

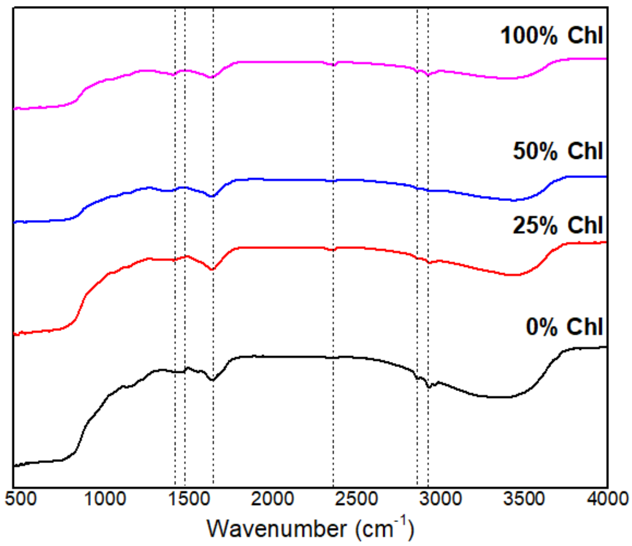


**Fig. 5** FTIR spectra of $TiO_2$ loaded with 0, 25, 50, and 100% concentration of chlorophyll

### *3.2 FTIR Analysis*

Identifying the chemical bonding development between $TiO_2$ and chlorophyll during anode synthesis is critical as shown in Figure 5. In the undoped $TiO_2$ photo-anode, the peak at 2863 - 2931 cm$^{-1}$ and 3228 - 3331 cm$^{-1}$ were attributed to the stretching vibration of the O–H bond or Ti-OH, as well as different interactions between hydroxyl groups and the $TiO_2$ surface (Lv *et al.*, 2017). While the peak at 1640 cm$^{-1}$ corresponds to the bending H–O–H bond vibration of water molecules absorbed on the $TiO_2$ surface (Lv *et al.*, 2017), the peak at 1631 - 1635 cm$^{-1}$ results in the C=O stretching vibration. At 425 - 721 cm$^{-1}$, a broad peak O-Ti-O or Ti-O-Ti stretching adsorption band in the TiO2 lattice appeared (Jiang *et al.*, 2008). When chlorophyll was added to $TiO_2$, the peak intensity of hydroxyl groups at 2869 - 2934 cm$^{-1}$ decreased as increased in chlorophyll concentration. In the FTIR spectra of chlorophyll-sensitized $TiO_2$, a new absorption peak at 2338 - 2359 cm$^{-1}$ showed that hydroxyl groups were depleted owing to chemical interactions between chlorophyll molecules and the surface of $TiO_2$ (Saikia & Parthasarathy, 2010). A small peak at 1317 cm$^{-1}$ appeared, corresponding to species with C-N bonds or nitrogen oxide species (Lv *et al.*, 2017). While C=O stretching was seen in conjugated ketone and carbonyl groups at 1631 - 1635 cm$^{-1}$, CN stretching in chlorophyll was observed at 1405 cm$^{-1}$ (Dhafina *et al.*, 2020; Nan *et al.*, 2017). Those observations therefore clearly show that *Spirulina* chlorophyll is strongly bound to the surface of $TiO_2$.

### *3.3 Voltage and Current Density of Photo-bioelectrochemical Cell*

As shown in Figure 6a, the performance of a photo-bioelectrochemical cell incorporating chlorophyll was studied in pulse mode. The stability of the OCV at 0.85 V in light-on mode corresponds to the completely charged state. The inclusion of visible light might significantly improve the system's power output. Contrary, in light-off mode, the OCV drops to 0.65 V and grows up to 0.75 V in the fully charged state. Because the OCV values in the four samples are almost identical, determining the optimal performance of a photo-bioelectrochemical cell based on voltage analysis is extremely challenging. Taking into consideration that operating the anode at the OCV value, which generates low anodic current densities, may result in the photo-bioanode degrading quickly owing to photo-oxidative damage to photosystem II (Pankratova *et al.*, 2017). A change in the voltage decline to lower OCVs during the pulsing of the discharge is due to the rise in the chlorophyll redox potential in electrolyte (Heller, 2006).

CA measurements are used to evaluate the influence of chlorophyll concentration on the electron transfer pathway, as illustrated in Figure 6b. The use of chlorophyll as an electron generator increases the amount of photocurrent produced, which ranges between 3200 and 4000 mA/m$^2$. The greatest resulting current is from ITO/$TiO_2$ with 100% chlorophyll with a value of 4000 mA/m2, followed by 50% with a value of 3800 mA/m$^2$, which is slightly lower. The average photocurrent produced by ITO/$TiO_2$ with 25% and 0% chlorophyll was 3500 and 3100 mA/m$^2$, respectively. This means that

ITO/$TiO_2$ at 50% was optimum since the photocurrent result was comparable to chlorophyll at 100%. Under dark condition, the CA can achieve only 2500 mA/m$^2$. This finding demonstrates that increasing chlorophyll up to a certain extent can increase the photocurrent produced by the cell.

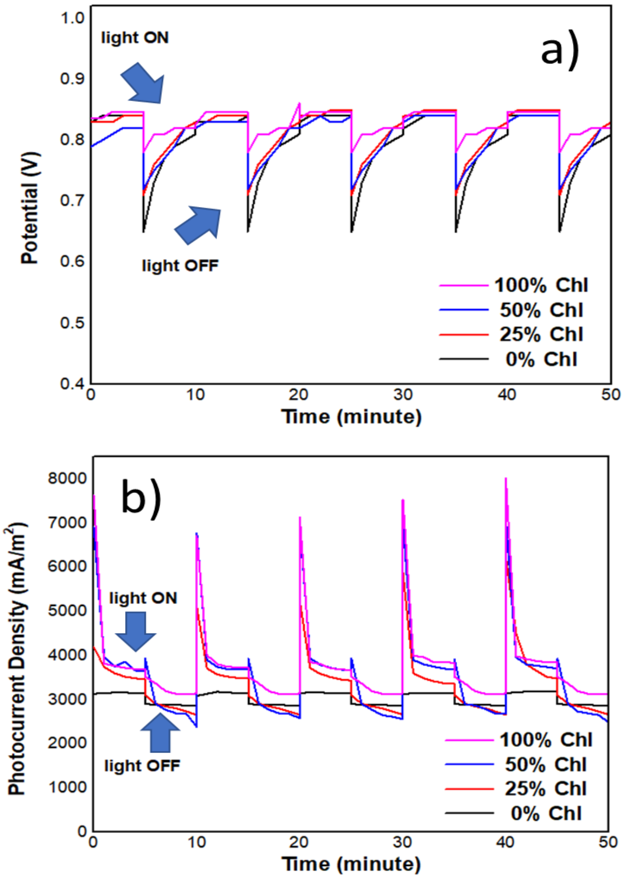


**Fig. 6** a) OCV and b) photo-current density of photo-bioelectrochemical cell with and without illumination

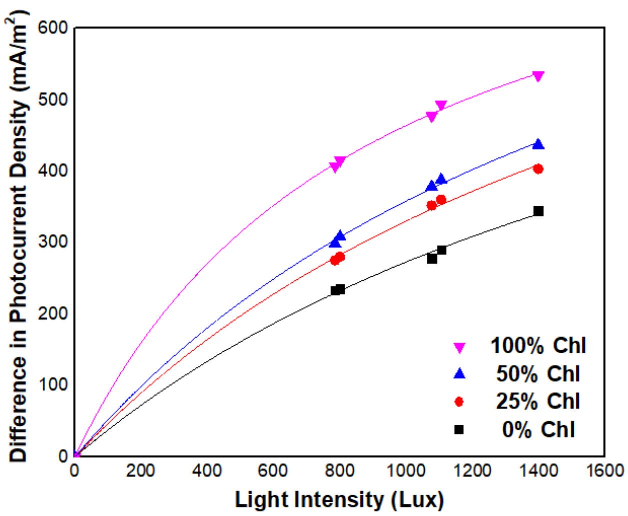


**Fig. 7** Correlation between light intensity and difference in photo-current density of photo-bioelectrochemical cell

### 3.4 Sensitivity of Photo-bioelectrochemical Cell

The impact of the light intensity on the electrical current produced by photo-bioelectrochemical cells should be studied very importantly, given that the cell's performance is one indicator for the sensitivity between biocatalyst and substrate. The Michaelis-Menten plot was therefore calculated for every photo-bioanode catalyst to get the apparent-Michaelis-Menten constant value (Figure 7). The difference in maximum photocurrent density ($J_{max}$) of ITO/$TiO_2$ with 0, 25, 50, and 100% chlorophyll were 889, 1009, 1041, and 1085 mA/m2. While, the lowest Km values were ITO/$TiO_2$ with 100% chlorophyll with values of 908 lux, followed by 50, 25, and 0% chlorophyll with 1907, 2054, and 2257 lux values, respectively. The lower the Km value, the more sensitive the catalyst photo-bioanode is to light. The amount of chlorophyll connected to $TiO_2$ undoubtedly underlies this sensitivity, so that, the more chlorophyll is attached, the more protons and electrons in the presence of light are produced. The slope of each curve is determined to support the sensitivity. Among the four samples with values of 0.885 mA/m$^2$.lux, the sensitivity of ITO/$TiO_2$ with 100% chlorophyll continues to dominate, followed by 50% chlorophyll with value of 0.488 mA/m$^2$.lux, then 25 and 0% chlorophyll with value of 0.437 and 0.345 mA/m$^2$.lux, correspondingly.

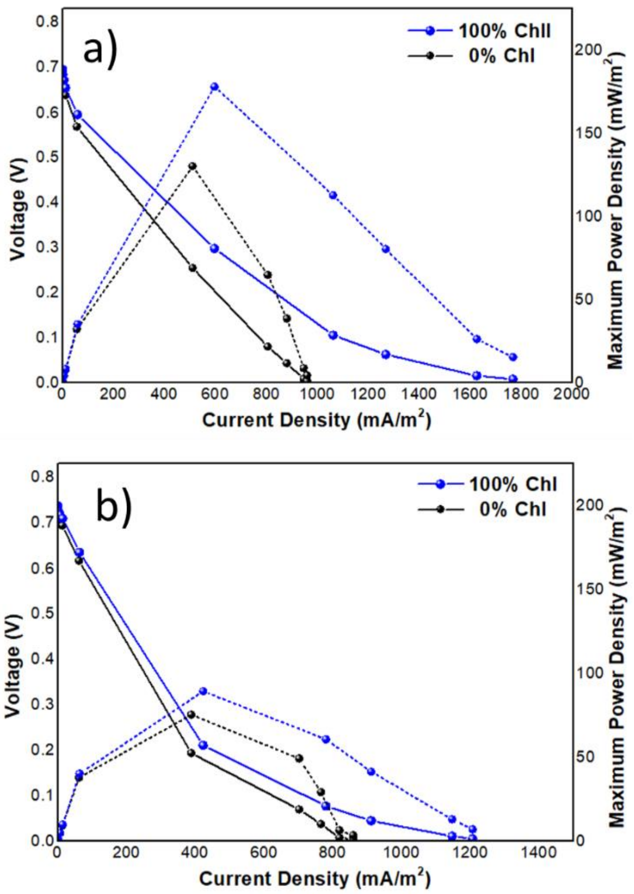


**Fig. 8** Polarization and Power Curves of Photo-bioelectrochemical a) with and b) without illumination addition

**Table 2**
Comparison the performance of photo-bioelectrochemical cell with other researches

| Photo-anode | Cathode | MPD ($mW/m^2$) | Reference |
|---|---|---|---|
| GE/P(DTP-Ph-$NH_2$)/CytC/thylakoid membrane | GE/P(DTP-NNaphthyl-$NH_2$)/BOD | 4.9 | Cevik *et al.*, 2018 |
| GE/Os/ thylakoid membrane | GE/AuNPs/BOx | 26 (2.6 $\mu W/cm^2$) | Pankratova *et al.*, 2017 |
| NOS/CNT | laccase/CNT | 35 | Sekar *et al.*, 2014 |
| pMBQ/PSII | pMBQ/ PSII//BOD/CNTs | 180 (18 $\mu W/cm^2$) | Yehezkeli *et al.*, 2014 |
| ITO/$TiO_2$/Chlorophyll | ITO/C | 178.15 | *This work* |

### *3.5 Performance Photo-bioelectrochemical Cell*

The performance of the photo-bioelectrochemical cell was further examined by performing discharge tests with varied external resistances, as shown in Figure 8a. Under the light, a maximum power output of around 178.15 $mW/m^2$ was obtained when 100% chlorophyll concentration was loaded in $TiO_2$, followed by 0% chlorophyll concentrations with values of 130.39 $mW/m^2$, or 27% lower than with 100% chlorophyll. Power generation in the dark condition was also tested (Figure 8b), with power density values of 75.53 and 89.46 $mW/m^2$ obtained from $TiO_2$ coupled without and with 100% chlorophyll concentrations, respectively. This result is comparable or higher than others which can be shown in Table 2.

### *3.6 Limitation and Future Outlook*

This article explores the use of chlorophyll derived from the cyanobacterium Spirulina platensis as an anode photo-biocatalyst in photo-bioelectrochemical cells by altering it with $TiO_2$ on ITO substrates. The binding process between $TiO_2$ and chlorophyll, which affects electron transport, is the important process in this study. Because the quantity of chlorophyll linked to $TiO_2$ influences the performance of photo-bioelectrochemical cells, optimization is required. Binding chlorophyll to $TiO_2$ may be accomplished in numerous methods, including I dipping followed by immersion and (ii) dripping chlorophyll on $TiO_2$ that has been cast on the substrate.
Advances in the usage of chlorophyll and $TiO_2$ as photo-anodes of photo-bioelectrochemical cells suggest that man-made photonic materials that mirror the notion of chlorophyll photosynthesis may be created in a viable manner. To improve electron transport, the electrode must be modified by boosting its conductivity. Lastly, the integration of modified anodes may result in not only photo-bioelectrochemical cells that convert light energy into electric power, but also chemical fuels (e.g., hydrogen) simultaneously. Furthermore, for increasingly complicated photo-bioelectrochemical cell applications, photocatalyst printing on flexible substrates is desirable.

## 4. Conclusion

$TiO_2$ loaded with chlorophyll extracted from *Spirulina platensis* and coated in ITO glass was created as visible-light-driven photocatalysts for energy production in aqueous electrolyte solutions in this study. By using bio-electrons, this coupling photocatalytic system greatly increases the energy generation of a photo-bioelectrochemical cell. OCV can achieve 0.85 V under light conditions, whereas OCV can only achieve 0.65 V under dark conditions. Under light conditions, the current density may reach 4000 $mA/m^2$, which is 1.3 times higher than the 3100 $mA/m^2$ without chlorophyll, and 2500 $mA/m^2$ in the absence of light. The Michaelis-Menten constant was 908 lux and the sensitivity with light was 0.885 $mA/m^2$.lux, while $J_{max}$ value was 1085 $mA/m^2$. The power density generated from polarization curve was 178.15 $mW/m^2$ at current density of 596.92 $mA/m^2$. The polarizability of the interaction between $TiO_2$ and chlorophyll causes an enhancement in the performance of the photo-bioelectrochemical cell in the presence of chlorophyll. This polarizability allows electrons to be caught by the electrodes and pass through the external circuit more efficiently. As a relatively new sustainable energy system, the synthesis of chlorophyll and $TiO_2$ and loading on ITO glass as its photocatalyst shows tremendous potential for improved performance of photo-bioelectrochemical cells.

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**Author Contributions**: M.C.: Conceptualization, methodology, writing—original draft, writing—review and editing A.A.S.; formal analysis, resources, validation, L.A.Y.; supervision, writing—review and editing, project administration, validation. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

## References

Arnon, D. I. (1949). Copper enzymes in isolated chloroplasts. Polyphenoloxidase in Beta vulgaris. *Plant physiology*, 24(1), 1.

Cevik, E., Carbas, B. B., Senel, M., & Yildiz, H. B. (2018). Construction of conducting polymer/cytochrome C/thylakoid membrane based photo-bioelectrochemical fuel cells generating high photocurrent via photosynthesis. *Biosensors and Bioelectronics*, 113, 25-31.

Chen, H., Tang, M., Rui, Z., Wang, X., & Ji, H. (2016). ZnO modified TiO2 nanotube array supported Pt catalyst for HCHO removal under mild conditions. *Catalysis Today*, 264, 23-30.

Chen, J., Cen, J., Xu, X., & Li, X. (2016). The application of heterogeneous visible light photocatalysts in organic synthesis. *Catalysis Science & Technology*, 6(2), 349-362.

Christwardana, M., Septevani, A. A., & Yoshi, L. A. (2021). Sustainable electricity generation from photo-bioelectrochemical cell based on carbon nanotubes and chlorophyll anode. *Solar Energy*, 227, 217-223.

Dhafina, W. A., Daud, M. Z., & Salleh, H. (2020). The sensitization effect of anthocyanin and chlorophyll dyes on optical and photovoltaic properties of zinc oxide based dye-sensitized solar cells. *Optik*, 207, 163808.

Duan, S., Chen, G., Li, M., Chen, G., Wang, X. F., Tamiaki, H., & Sasaki, S. I. (2017). Near-infrared absorption bacteriochlorophyll derivatives as biomaterial electron donor for organic solar cells. *Journal of Photochemistry and Photobiology A: Chemistr*y, 347, 49-54.

Ferrari-Lima, A. M., De Souza, R. P., Mendes, S. S., Marques, R. G., Gimenes, M. L., & Fernandes-Machado, N. R. C. (2015). Photodegradation of benzene, toluene and xylenes under visible light applying N-doped mixed TiO2 and ZnO catalysts. *Catalysis Today*, 241, 40-46.

Gao, M., Zhu, L., Ong, W. L., Wang, J., & Ho, G. W. (2015). Structural design of TiO 2-based photocatalyst for H 2 production and degradation applications. *Catalysis science & technology*, 5(10), 4703-4726.

Heller, A. (2006). Electron-conducting redox hydrogels: design, characteristics and synthesis. *Current opinion in chemical biology*, 10(6), 664-672.

Jiang, D., Xu, Y., Wu, D., & Sun, Y. (2008). Visible-light responsive dye-modified TiO2 photocatalyst. *Journal of Solid State Chemistry*, 181(3), 593-602.

Kirchhofer, N. D., Rasmussen, M. A., Dahlquist, F. W., Minteer, S. D., & Bazan, G. C. (2015). The photobioelectrochemical activity of thylakoid bioanodes is increased via photocurrent generation and improved contacts by membrane-intercalating conjugated oligoelectrolytes. *Energy & Environmental Science*, 8(9), 2698-2706.

Li, X., Shi, J. L., Hao, H., & Lang, X. (2018). Visible light-induced selective oxidation of alcohols with air by dye-sensitized TiO2 photocatalysis. *Applied Catalysis B: Environmental*, 232, 260-267.

Liu, X., Zhang, H., Liu, C., Chen, J., Li, G., An, T., ... & Zhao, H. (2014). UV and visible light photoelectrocatalytic bactericidal performance of 100%{1 1 1} faceted rutile TiO2 photoanode. *Catalysis Today*, 224, 77-82.

Luan, Y., Jing, L., Meng, Q., Nan, H., Luan, P., Xie, M., & Feng, Y. (2012). Synthesis of efficient nanosized rutile TiO2 and its main factors determining its photodegradation activity: roles of residual chloride and adsorbed oxygen. *The Journal of Physical Chemistry C*, 116(32), 17094-17100.

Lv, L., Li, K., Xie, Y., Cao, Y., & Zheng, X. (2017). Enhanced osteogenic activity of anatase TiO2 film: Surface hydroxyl groups induce conformational changes in fibronectin. *Materials Science and Engineering: C*, 78, 96-104.

Nan, H., Shen, H. P., Wang, G., Xie, S. D., Yang, G. J., & Lin, H. (2017). Studies on the optical and photoelectric properties of anthocyanin and chlorophyll as natural co-sensitizers in dye sensitized solar cell. *Optical Materials*, 73, 172-178.

Omar, A., Ali, M. S., & Abd Rahim, N. (2020). Electron transport properties analysis of titanium dioxide dye-sensitized solar cells (TiO2-DSSCs) based natural dyes using electrochemical impedance spectroscopy concept: A review. *Solar Energy*, 207, 1088-1121.

Pankratova, G., Pankratov, D., Hasan, K., Åkerlund, H. E., Albertsson, P. Å., Leech, D., ... & Gorton, L. (2017). Supercapacitive photo-bioanodes and biosolar cells: a novel approach for solar energy harnessing. *Advanced Energy Materials*, 7(12), 1602285.

Qi, K., Liu, S. Y., Chen, Y., Xia, B., & Li, G. D. (2018). A simple post-treatment with urea solution to enhance the photoelectric conversion efficiency for TiO2 dye-sensitized solar cells. *Solar Energy Materials and Solar Cells*, 183, 193-199.

Ramakrishna, T. R., Mathesh, M., Liu, Z., Zhang, C., Du, A., Liu, J., ... & Yang, W. (2020). Solvent effect on supramolecular self-assembly of chlorophylls a on chemically reduced graphene oxide. *Langmuir*, 36(45), 13575-13582.

Rossetti, I., Villa, A., Compagnoni, M., Prati, L., Ramis, G., Pirola, C., ... & Wang, D. (2015). CO 2 photoconversion to fuels under high pressure: effect of TiO 2 phase and of unconventional reaction conditions. *Catalysis Science & Technology*, 5(9), 4481-4487.

Saikia, B. J., & Parthasarathy, G. (2010). Fourier transform infrared spectroscopic characterization of kaolinite from Assam and Meghalaya, *Northeastern India. J. Mod. Phys*, 1(4), 206-210.

Sekar, N., & Ramasamy, R. P. (2015). Photosynthetic energy conversion: recent advances and future perspective. *The Electrochemical Society Interface*, 24(3), 67.

Sekar, N., Umasankar, Y., & Ramasamy, R. P. (2014). Photocurrent generation by immobilized cyanobacteria via direct electron transport in photo-bioelectrochemical cells. *Physical Chemistry Chemical Physics*, 16(17), 7862-7871.

Venkatkarthick, R., Davidson, D. J., Ravichandran, S., Vengatesan, S., Sozhan, G., & Vasudevan, S. (2015). Eco-friendly and facilely prepared silica modified amorphous titania (TiO 2–SiO 2) electrocatalyst for the O 2 and H 2 evolution reactions. *Catalysis Science & Technology*, 5(11), 5016-5022.

Wang, X. F., Matsuda, A., Koyama, Y., Nagae, H., Sasaki, S. I., Tamiaki, H., & Wada, Y. (2006). Effects of plant carotenoid spacers on the performance of a dye-sensitized solar cell using a chlorophyll derivative: enhancement of photocurrent determined by one electron-oxidation potential of each carotenoid. *Chemical physics letters*, 423(4-6), 470-475.

Wang, X. F., Zhan, C. H., Maoka, T., Wada, Y., & Koyama, Y. (2007). Fabrication of dye-sensitized solar cells using chlorophylls c1 and c2 and their oxidized forms c1′ and c2′ from Undaria pinnatifida (Wakame). *Chemical physics letters*, 447(1-3), 79-85.

Yehezkeli, O., Tel-Vered, R., Michaeli, D., Willner, I., & Nechushtai, R. (2014). Photosynthetic reaction center-functionalized electrodes for photo-bioelectrochemical cells. *Photosynthesis research*, 120(1), 71-85.