

**SYNTHESIS AND CHARACTERIZATION OF *LAURUS NOBILIS*
(BAY LEAVE) AND MEDITERRANEAN OLIVE LEAVE AS
NATURAL SENSITIZERS FOR DYE-SENSITIZED SOLAR CELLS**

BY
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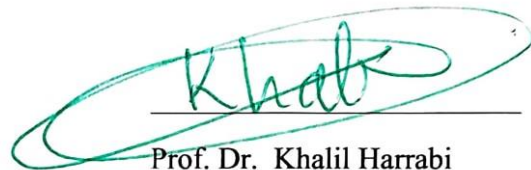
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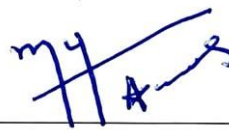


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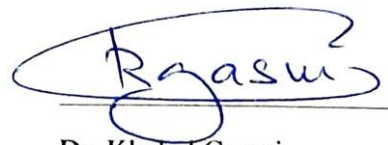
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In a symphony of gratitude, this dedication harmoniously resonates with the unwavering support and spirited encouragement generously provided by my beloved parents, family, brothers, teachers, and colleagues, turning the mundane notes of life into a melodious composition of shared triumphs.

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LIST OF ABBREVIATIONS

BL: Bay leaf

OL: Olive leaf

OLDI2: olive leaves dried under indoor condition for two weeks

OLDS1: olive leaves dried under direct sunlight for one month

DSSC: Dye-sensitized solar cell

NDSSC: Natural dye-sensitized solar cell

E_F: Fermi energy

N_{CB}: effective density of states in the semiconductor CB

V_{oc}: Open-circuit voltage

I_{oc}: Short-circuit current

TCO: Transparent Conducting Oxide

FTO: Fluorine-doped Tin Oxide

ITO: Indium-doped Tin Oxide

Pt: Platinum

CE: Counter electrode

LUMO: Lowest Unoccupied Molecular Orbital

HOMO: Highest Occupied Molecular Orbital

I-V: Current-voltage

J-V: Current density-voltage

P-V: Power density-voltage

UV-Vis: Ultraviolet-visible

FTIR: Fourier Transform Infrared

SEM-EDX: Scanning Electron Microscopy-Energy Dispersive X-ray

XPS: X-ray Photoelectron Spectroscopy

XRD: X-ray diffractometry

CV: Cyclic Voltammetry

EIS: Electrochemical Impedance Spectroscopy

ABSTRACT

Full Name : Ryan Nur Iman

Thesis Title : Synthesis and characterizations of *Laurus nobilis* (Bay leave) and Mediterranean Olive leave as natural sensitizers for Dye-Sensitized Solar Cell

Major Field : Physics

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The rise in global energy demand in 2022 was primarily driven by emerging economies, experiencing a 6.63 Exajoules (EJ) increase compared to the previous year, reaching a record-high total consumption of 604.04 EJ. Worldwide energy demand is projected to increase by 28% between 2015 and 2040. Notably, the Middle East region is expected to exhibit a significant rise in energy demand, reaching a rate of 45%. Solar energy is considered a highly promising option among various alternatives, mainly credited to its claimed capability to generate approximately 4.3×10^{20} joules of energy with one hour of sunlight exposure. Dye-sensitized solar cells (DSSCs), representing a third photovoltaic (PV) technology, appear to be a viable and cost-effective alternative to traditional PV technology. Due to synthetic dyes being toxic, involving complex synthetic routes, high costs, and posing environmental challenges, discovering a new, non-toxic, stable, and optoelectronically enhanced material necessitates a significant investment of time, with natural dyes emerging as a highly promising alternative.

In this thesis, the natural sensitizer from bay leaves and olive leaves were synthesized with two different drying times. The optical properties of the extracted natural dye and the dye-coated TiO_2 film were studied by Ultraviolet–visible (UV–Vis) and Fourier-transform infrared (FTIR) spectroscopy. Cyclic voltammetry (CV) was utilized to study the

electrochemical characteristics of the extracted natural dye. The crystalline structure and crystallinity degree before and after dye adsorption were studied by X-ray diffraction (XRD). The morphology and elemental composition of TiO₂ film pre and post dye adsorption were examined by scanning electron microscopy-energy dispersive X-ray (SEM-EDX). The electronic and chemical bonding characteristics of the TiO₂ film before and after dye adsorption were analyzed by X-ray photoelectron spectroscopy (XPS). The photo-electrochemical properties of NDSSC devices were studied using electrochemical impedance spectroscopy (EIS). The photovoltaic performance of NDSSC devices was examined by I-V solar simulator. Furthermore, the effect of two different TCO (FTO and ITO) substrates on bay leaf and olive leaf-based NDSSC performance was investigated.

The findings indicate that the fabricated NDSSC using BL and OL extracts depends on the conductive substrate, with the FTO/TiO₂/dye configuration proving to be the most optimal. This is attributed to the increased stability exhibited by the FTO configuration after thermal treatment (annealing at 500°C), resulting in a reduction of charge transfer resistance and consequently enhancing charge collection efficiency. Overall, parametric and performance indicators show that BL and OL dyes are promising candidates for NDSSC applications.

Keywords: Global energy demand, Photovoltaic, Bay leaf, Olive leaf, Chlorophyll, NDSSC.

ملخص الرسالة

الاسم الكامل: ريان نور ايمان

عنوان الرسالة: تخليق وتوصيف أوراق شجرة الغار (*Laurus nobilis*) وأوراق شجرة الزيتون البحرية كمحسسات طبيعية للخلية الشمسية المحسنة بالأصباغ.

التخصص: الفيزياء

تاريخ الدرجة العلمية: ١٣ ديسمبر ٢٠٢٣

ارتفاع الطلب العالمي على الطاقة في عام 2022 كان بشكل أساسي بفعل الاقتصادات الناشئة، حيث شهدت زيادة قدرها 6.63 إكساجول (EJ) مقارنة بالعام السابق، وبلغ إجمالي استهلاك الطاقة مستوى قياسياً مرتفعاً يبلغ 604.04 إكساجول. يتوقع زيادة الطلب العالمي على الطاقة بنسبة 28% بين عامي 2015 و2040. يُتوقع خاصة أن تظهر منطقة الشرق الأوسط زيادة كبيرة في الطلب على الطاقة، وتصل إلى معدل 45%. يُعتبر الطاقة الشمسية خياراً واعداً للغاية بين البدائل المختلفة، يُرجى إلى حد كبير لقدرتها المُرَعة على توليد نحو 4.3×10^{20} جول من الطاقة بساعة واحدة من تعرضها لأشعة الشمس. خلايا الطاقة الشمسية المحسنة بالأصباغ (DSSCs)، التي تُمثل تكنولوجيا الخلايا الضوئية الثالثة، تظهر كبديل قابل للتحقيق وفعال من حيث التكلفة لتكنولوجيا الخلايا الضوئية التقليدية. ونظراً لكون الأصباغ الاصطناعية سامة وتتطلب طرقاً اصطناعية مُعقّدة وتكاليف عالية وتُطرح تحديات بيئية، فإن اكتشاف مادة جديدة غير سامة ومستقرة وتحسّن إلكترونياً يتطلب استثماراً كبيراً من الوقت، حيث تظهر الأصباغ الطبيعية كبديل واعد للغاية.

في هذه الرسالة، تم تخليق المحسّس الطبيعي من أوراق الغار وأوراق الزيتون بزمنين جفاف مختلفين. تمت دراسة الخصائص البصرية للأصباغ الطبيعية المستخرجة والفيلم المغلف بالصبغة TiO_2 باستخدام الطيف فوق بنفسجي-مرئي (UV-Vis) والطيف الفوري-تحويل الأشعة تحت الحمراء (FTIR). تم استخدام التردد الدوري لدراسة الخصائص الكهروكيميائية للصبغة الطبيعية المستخرجة. تم توصيف الهيكل البلوري ودرجة التبلور قبل وبعد امتصاص الصبغة باستخدام تفريق الأشعة السينية (XRD). تم فحص التركيب والتركيب العنصري للفيلم TiO_2 قبل وبعد امتصاص الصبغة باستخدام المجهر الإلكتروني بالمسح-الأشعة السينية الانتشارية الطاقة (SEM-EDX). تم تحليل الخصائص الإلكترونية والرابطة الكيميائية لفيلم TiO_2 قبل وبعد امتصاص الصبغة باستخدام طيف الفوتونات الإلكترونية السينية (XPS). تم دراسة الخصائص الفوتوكهروكيميائية لأجهزة NDSSC باستخدام طيف تحليل الانتشار الكهروكيميائي (EIS). تم فحص الأداء الفوتوفولطي لأجهزة NDSSC باستخدام محاكي الطاقة الشمسية I-V. علاوة على ذلك، تم استكشاف تأثير طبقتي TCO (ITO و FTO) المختلفتين على أداء أجهزة NDSSC القائمة على أوراق الغار وأوراق الزيتون.

تشير النتائج إلى أن الخلية الشمسية الحساسة الطبيعية المصنوعة باستخدام استخلاصات OL و BL تعتمد على الطبقة الناقلة الموصلة، حيث ثبت أن التكوين $\text{FTO}/\text{TiO}_2/\text{dye}$ هو الأمثل. يُرجع ذلك إلى الاستقرار المتزايد الذي.

الكلمات المفتاحية: ورق الغار، ورق الزيتون، NDSSC، الكلوروفيل، الطلب العالمي على الطاقة، الطاقة الشمسية (الضوئية).

CHAPTER 1

INTRODUCTION

1.1 Background

The global energy framework is currently surrounded by significant uncertainty in the short, intermediate, and long terms. Ongoing conflicts in Europe, a pressing require to mitigate greenhouse gas emissions, and various other influencing factors make it essential to examine long-term energy. Such projections offer valuable perspectives for evaluating the diverse array of potential scenarios concerning global energy consumption and gas emissions [1].

In 2022, primary energy consumption saw a substantial increase of 6.63 Exajoules (EJ) compared to the previous year, reaching a record-high total consumption of 604.04 EJ (**Fig. 1a**). Global energy usage is anticipated to surge by 28% from 2015 to 2040, with a particularly striking increase forecasted for the Middle East, where energy demand is projected to skyrocket by an impressive 45% [2]. Since 2013, the Saudi government has announced various renewable energy objectives. The most recent goal, set for 2030, aims for 50% of electricity to come from renewable sources [3]. During 2022, Saudi Arabia consumed around 11.50 EJ, still heavily reliant on oil resources, as depicted in **Fig. 1b**.

However, this surge in global energy consumption comes at a cost to the environment, as carbon dioxide emissions from various sources continued to rise. Specifically, emissions

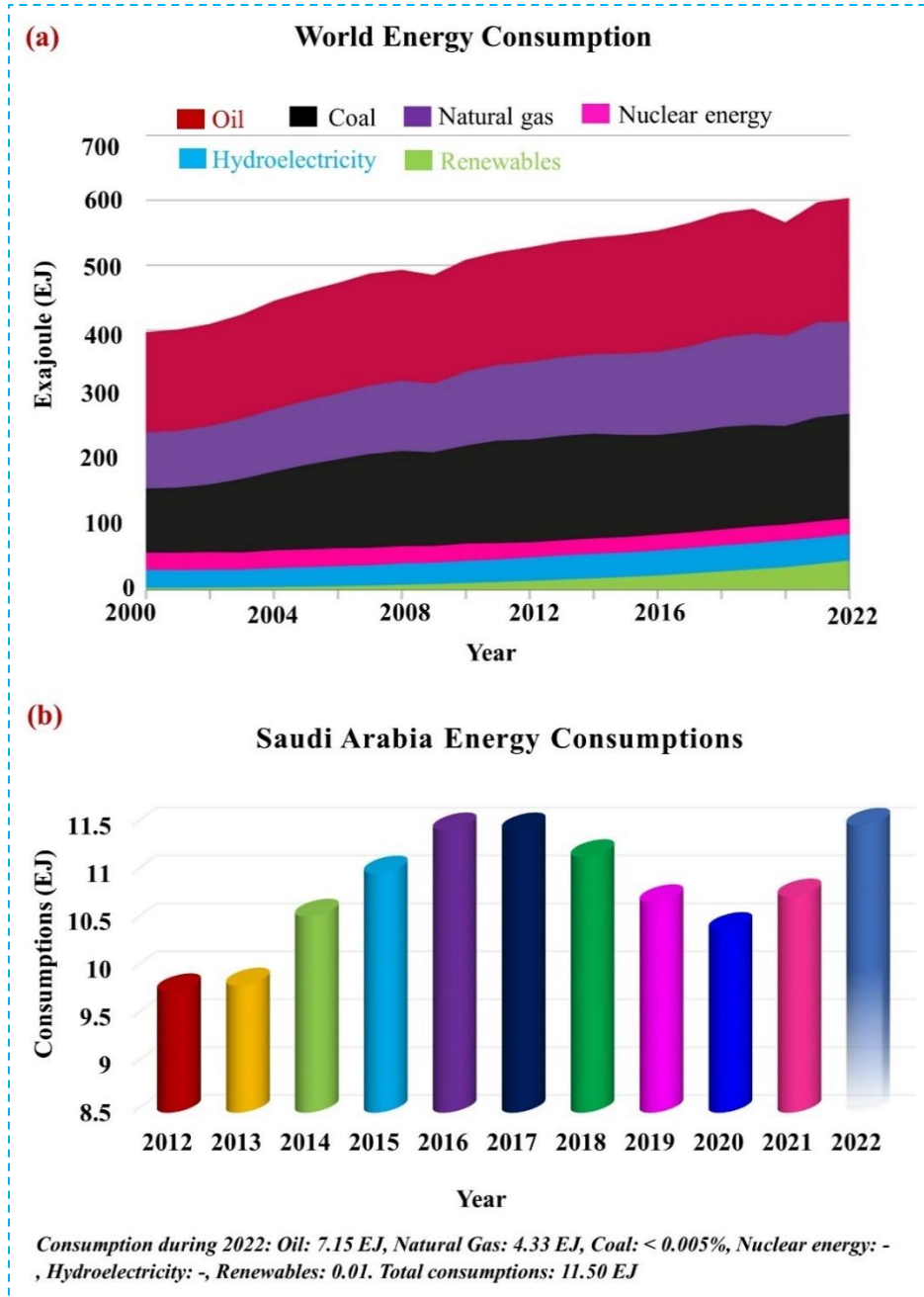


Figure 1 (a) The worldwide utilization of primary energy and (b) the energy consumption specific to Saudi Arabia in the year 2022. The illustration has been modified based on the cited reference [4].

from energy use, industrial processes, flaring, and methane, measured in carbon dioxide equivalent terms, experienced a 0.8% increase in 2022, reaching a staggering 39.3 Gigatons (GT) of CO₂ equivalent emissions (see **Fig. 2**). Emissions from energy use grew by 0.9%,

reaching 34.4 GT of CO₂ equivalent emissions [2]. The increasing concerns over environmental sustainability have catalysed a widespread exploration of alternative and eco-friendly energy production methods.

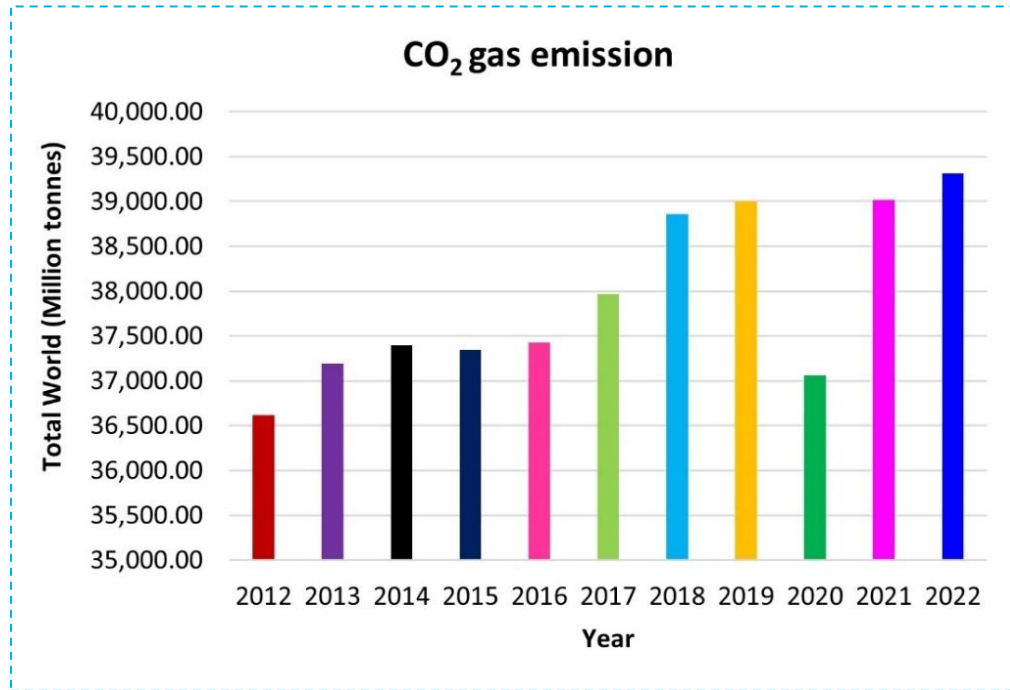


Figure 2 Global CO₂ emissions. (The CO₂ emissions mentioned encompass the total of carbon dioxide emissions resulting from various sources, including energy production, flaring, methane emissions, as well as emissions tied to the fossil fuel industry's production, transportation, and distribution, along with carbon dioxide emissions stemming from industrial processes [4]).

A diverse range of renewable energy sources exhibit various advantages and disadvantages. Renewable energy sources that have gained recognition include tidal, geothermal, wind, small-hydel, solar, and biomass energy [5–8]. Solar energy is considered a highly promising option among the various alternatives. Approximately 4.3×10^{20} joules of solar energy reach the Earth within a one-hour timeframe through the transmission of electromagnetic waves, embodied as photons [9]. The quantity above is approximately equal to the total energy consumption (4.1×10^{20} joules) of the planet on a

global scale throughout a full calendar year [9,10]. Solar energy can be efficiently harnessed through the application of photovoltaic (PV) technology by converting the sunlight to electricity. PV technology is categorized into three generations, with the initial generation utilizing solar cells constructed from silicon wafers. The second generation incorporates solar cells that utilize materials like CdTe, CIGS, and GaAs. The third generation introduces innovative technologies such as DSSCs, perovskites solar cell (PSC), and quantum dot solar cells (QdSC). Every generation signifies progress and variety in the quest for enhancing the conversion of solar energy [11–14].

In the coming decade, there is an anticipated surge in the need for silicon [15], inevitably leading to an increase in its price. Addressing this challenge, a promising solution emerges through the adoption of photovoltaic (PV) technology reliant on dye sources. This innovative approach involves harnessing sunlight to generate clean and cost-effective electrical energy [16]. A pivotal milestone in this trajectory occurred in 1991 when O'Regan and Gratzel introduced DSSCs. The architecture of their device was structured with a glass conductive substrate, a sensitizer, a semiconductor layer, a counter electrode (CE) , and a redox couple [17]. This breakthrough offers a sustainable alternative, potentially mitigating the impending rise in silicon demand and costs.

The DSSC has distinctive features over Si-based PV. These include a high molar absorption coefficient, inexpensive fabrication cost, ability to be processed at ambient temperature, capable of achieving superior performance in elevated temperatures compared to other PV technologies [18], straightforward manufacturing process, printability on flexible substrates, availability in various colors, and potential to perform optimally in varied lighting environments (diffuse light conditions), leading to suit

for indoor applications [19]. According to NREL data, as shown in **Fig. 3**, the certified highest efficiency of DSSCs is 13% [20].

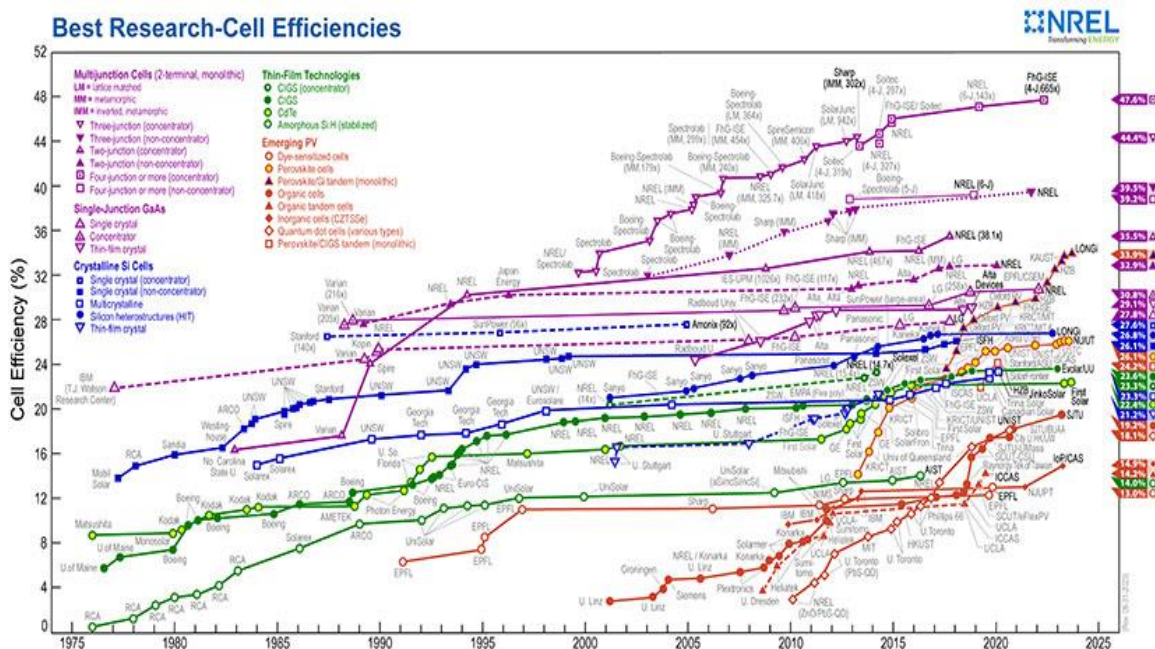


Figure 3 Best efficiency of various types of the solar cells [20].

Enhancing the photo-current conversion efficiency (PCE) of DSSCs has been a focal point for numerous researchers who have delved into the optimization of DSSC devices through the exploration and modification of diverse configurations including adjustments to semiconductor design, dye formulations, electrolytes, and cathode materials [21–29].

Dyes assume a role akin to semiconductors, facilitating the creation of electron-hole pairs. Given the pivotal role played by dyes, there has been a pronounced interest in the development and refinement of innovative categories of metal complexes and organic dyes [6,29–32]. The highest reported efficiency achieved by DSSCs employing synthetic dyes is 11.2% within the metal complex dye category [33] and 14.7% for metal-free organic dyes [34]. Nevertheless, synthetic dyes necessitate intricate and expensive synthetic

procedures, often involving toxic heavy metals, leading to environmental concerns and the generation of byproducts and waste materials through chemical processes [35–37]. Hence, discovering a non-toxic, stable, and opto-electronically enhanced material emerges as a highly promising alternative, particularly when utilizing natural dyes.

Despite their lower efficiency, investigations on natural dye-sensitized solar cells (NDSSCs) remain under the scope of diversity studies due to their potential applicability in compact devices. Researchers have employed naturally derived dyes, such as anthocyanin [38], betacyanin [39], betalain [40], chlorophyll [41,42], carotenoid [43], and flavonoid [44], as sensitizer in NDSSCs. Natural dyes exhibit key characteristics, including simple of extraction, environmental friendliness and cost-effectiveness.

1.2 Objectives

This thesis aims to fabricate the NDSSC by synthesizing a single natural dye and applying different technique in synthesizing dyes and conductive substrates. The NDSSC fabricated was characterized by an I-V solar simulator, electron impedance spectroscopy, XRD, SEM, cyclic voltammetry (CV), XPS, FTIR, and UV-Vis spectroscopy.

1) Synthesis of natural dye

The dye should possess an absorption range in UV-Vis, be non-degradable, and have excited states with energy levels higher than the semiconductor's conduction band minimum.

The dyes were extracted from natural source to obtain the properties mentioned above.

- Synthesis of bay leave extract solution.

- Synthesis of olive leave extract solution with two different drying conditions.

2) Observation of methods

A maceration technique was employed to extract pigments from both bay leaves and olive leaves. For olive leaves extraction, it was treated with two different drying conditions before applying the maceration technique.

A doctor blade technique was employed to deposit the semiconducting paste onto the active layer of the FTO substrate. This method involved a blade moving uniformly over the substrate at a certain contact angle and height, ensuring even distribution of the TiO_2 paste and resulting in the creation of a thick film. Then, the semiconducting material-coated FTO was submerged into the dye solution. Afterward, the effect of dye molecules that were anchored to the semiconducting layer was investigated.

3) Observation of different conductive substrates

Two different transparent conductive oxide (TCO) substrates were utilized to investigate the effect of the TCO substrates on NDSSC device performance and to find the optimum parameters.

In accordance with the three main objectives outlined above, achieving them could result in the optimal configuration for an NDSSC device. These configurations would, in turn, facilitate the more efficient collection of electrons and holes, ultimately enhancing the overall performance of the NDSSC.

1.3 Thesis Overview

Within this section, a comprehensive overview of the contents of each chapter is presented.

1.3.1 Chapter Two

In Chapter 2, an extensive literature review is presented, offering a comprehensive analysis of DSSCs. This chapter delves into the significance of solar cell technology, highlighting its potential for future applications and its pivotal role in addressing pressing environmental challenges, including the issue of global warming. On the other hand, the working principle, model, and components of DSSC are also discussed.

1.3.2 Chapter Three

This chapter offers a detailed account of the experimental procedures conducted for this thesis, covering the materials used, fabrication methods employed, characterization parameters, and equipment specifications.

1.3.3 Chapter Four

Chapter 4 provides the outcomes, discussion, and conclusion of each work:

- Fabrication and Characterization of natural dye-sensitized solar cells using an efficient natural sensitizer derived from *Laurel nobilis L.*
- Fabrication of Efficient Natural Dye-sensitized Solar Cells using Mediterranean Olive Leaves as Natural Dye sensitizer.

CHAPTER 2

LITERATURE REVIEW

This section provides an in-depth and detailed exploration of the working principle, the mathematical model, and the existing literature on DSSCs and NDSSCs, offering a comprehensive review of the subject matter.

2.1 Working principles

2.1.1 P-N junction

The framework of a P-N junction involves the integration of two semiconductors, specifically the P-type and N-type semiconductors, each contributing distinct properties to the overall configuration. Upon the junction of these semiconductors, a diffusion-reaction transpires, causing the ionization of designated P-type regions, generating negative ions, and the ionization of specified N-type regions, leading to the formation of positive ions. This region of ionization is termed the depletion region, sustaining an electric field (E) even in the absence of an externally applied voltage [45].

When illuminated by the light, the P-N junction produces electron-hole pairs within the depletion region. These pairs give rise to a photocurrent (I_L) that travels towards the reverse bias direction, generating a forward bias voltage across a resistive load and producing a forward-bias current (I_F) in the opposite direction of I_L . Consequently, the overall current can be expressed as **Eq. 1**, which the ideal diode equation is applied:

$$I = I_L - I_F = I_L - I_s \left[e^{\frac{eV}{kT}} - 1 \right] \quad (1)$$

Where the I_s is the saturation current (10^{-12} amps). Now, a diode becomes forward-biased, causing the electric field produced in the depletion region to decrease consistently in the same direction without reaching zero.

There are two intriguing conditions. Firstly, when the resistance R is reduced to zero, the voltage V equals 0, resulting in what is called a short-circuit condition. Under these circumstances, the generated current may be expressed as having a relationship with the short-circuit current I_{sc} (**Eq. 2**).

$$I = I_L - 0 = I_{sc} \quad (2)$$

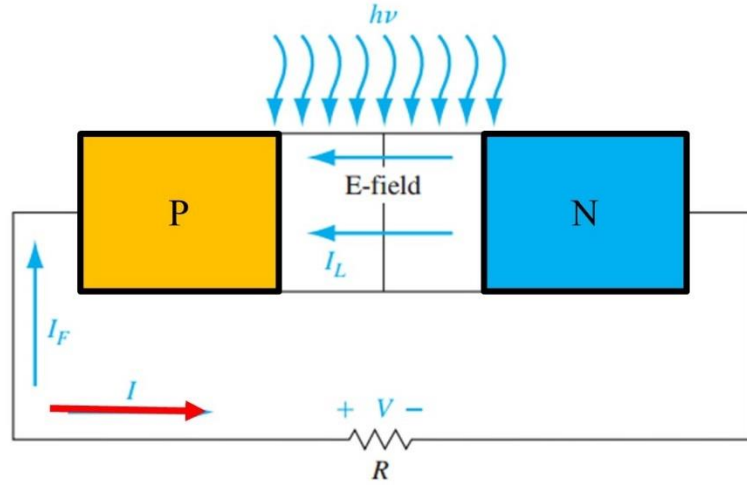


Figure 4 A schematic of P-N junction in solar cell with resistive load.

The second condition arises when R approaches infinity, termed the open-circuit condition, resulting in a net current of zero [45]. In this state, the forward-biased junction current counterbalances the photocurrent in the contrary direction as depicted in **Fig. 4**. Consequently, **Eq. 1** transforms as follows,

$$I = 0 = I_L - I_s \left[e^{\frac{eV_{oc}}{kT}} - 1 \right] \quad (3)$$

By integrating **Eq. (3)**, it is possible to derive the voltage in an open-circuit condition (V_{oc}):

$$V_{oc} = V_t \ln \left(\frac{I_L}{I_s} + 1 \right) \quad (4)$$

V_t correspond to the voltage generated within the PN-junction due to temperature ($V_t \approx kT/e$, ~ 0.026 Volt). The plot of current and voltage produced is known as the I-V characteristics (**Fig. 5**). Moreover, it can be represented in terms of and voltage (V) current density (J) by dividing it by the area of the active cell.

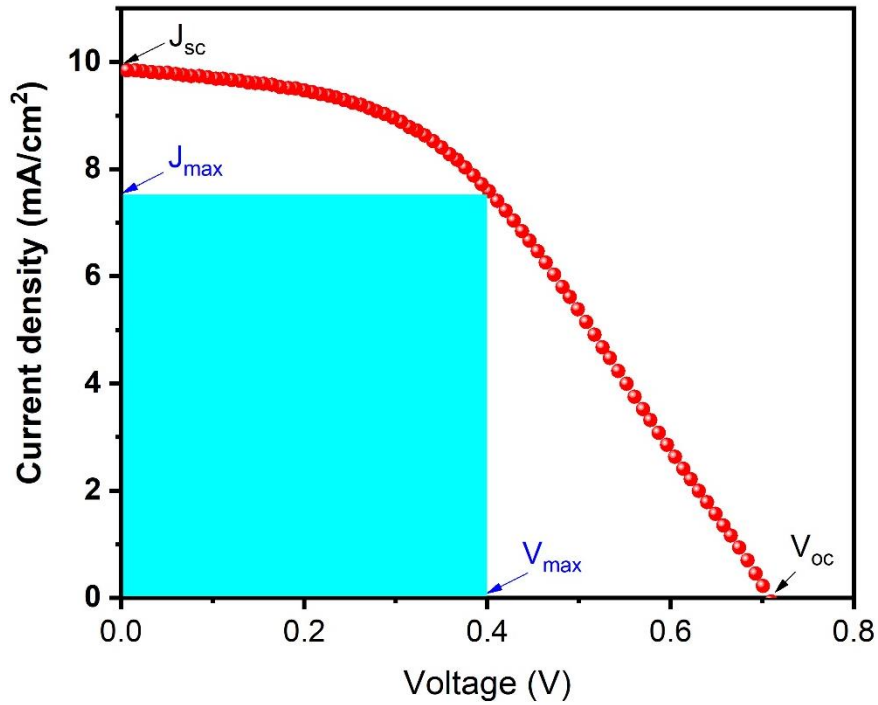


Figure 5 Typical J-V curves of DSSCs device.

The photovoltaic efficiency (PCE) is formally described as the quotient of the maximum power (P_{max}) divided by the primary optical power (P_{in}), expressed in **Eqs. 5 and 6** [46]:

$$\eta = \frac{P_m}{P_{in}} \times 100\% = \frac{J_{max} \times V_{max}}{P_{in}} \times 100\% \quad (5)$$

OR,

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \times 100\% \quad (6)$$

$$FF = \frac{I_{max} \times V_{max}}{I_{SC} \times V_{OC}} \quad (7)$$

Where FF represents the fill factor, defines a ratio of $I_{max}V_{max}$ and $I_{sc}V_{oc}$ (**Eq. 7**) that measures the power achievable from the cell. Typically, the fill factor (FF) falls between 0.7 and 0.8.

2.1.2 P-N junction in DSSC

P-N junction is commonly used to describe the fundamental principle of DSSC. In DSSCs, the photoanode layer is designated as the N-type semiconductor, contrasting with the electrolyte, which is identified as the P-type semiconductor. In addition, the dye is considered as the material can generate the electron hole pairs. The fundamental principle of DSSCs involves transforming light into electrical energy. When the DSSC is illuminated by sunlight, the dye absorbs the light, creating electron-hole pairs. Inside the cell, electrons undergo excitation from the HOMO to the LUMO level of the dye. Following this, electrons are transferred into the conduction band (CB) of the semiconducting layer, usually made of TiO_2 . These electrons are then transferred to the CE via an external circuit, engaging in a reduction reaction within the electrolyte to establish an electrical circuit [47]. The electrolyte functions as a medium to enable the electron's transition from the CE back to the HOMO level of the dye, with an electron transfer constant estimated at

approximately 10^{-12} . **Fig. 6** provides a representative schematic that elucidates the operational concept of a DSSC.

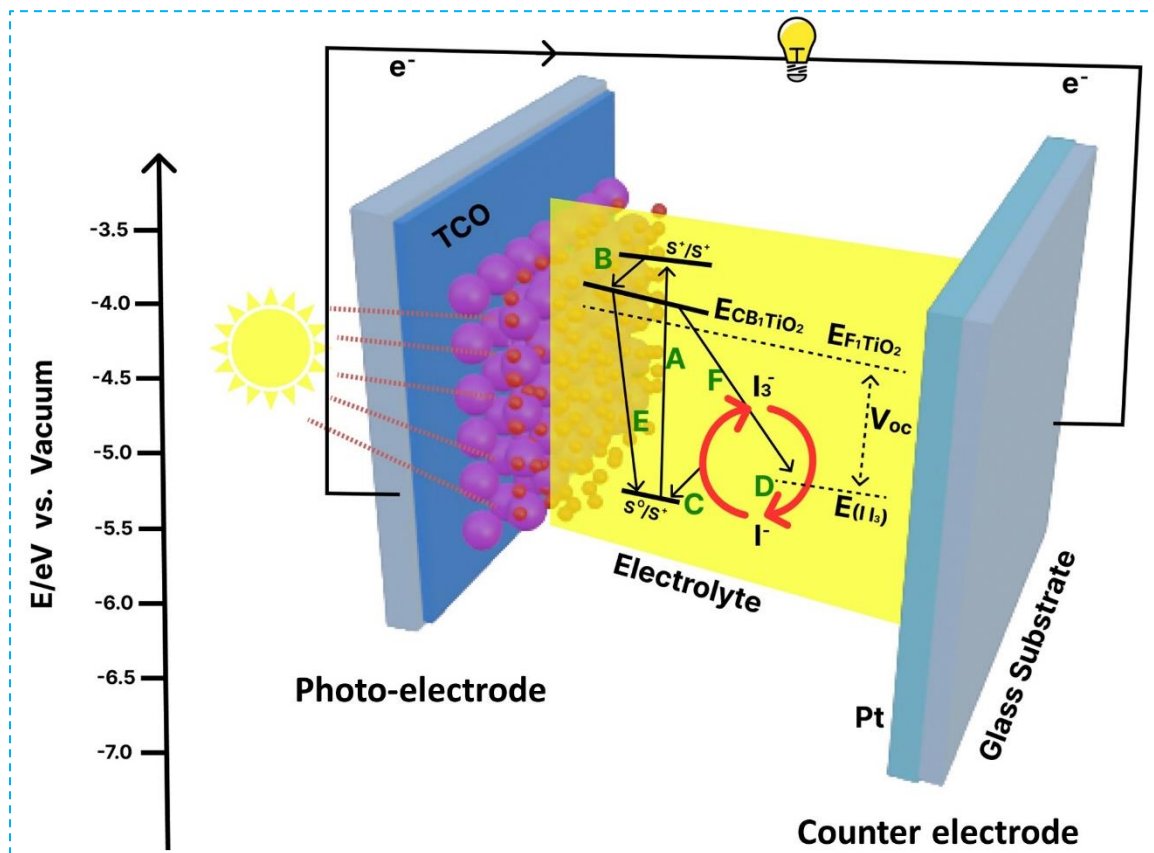


Figure 6 A schematic diagram of DSSC.

2.2 DSSC Models

The operation of DSSC relies on essential processes, such as charge separation within the semiconductor and charge transport at the semiconductor (SC)/electrolyte (EE) interface. Within these theoretical frameworks, the central focus revolves around the primary mobile entities—namely, electrons within the CB of the semiconductor layer and redox couple ions present in the liquid electrolyte. These models incorporate a specific recombination reaction order parameter denoted as β . Concurrently, ongoing efforts are directed towards

the development of comprehensive DSSC models to gain a holistic understanding of the entire phenomenon in this device. It's worth noting that the models presented in this section are limited, particularly in excluding the dimensionless equation model. Despite these limitations, the existing models significantly contribute to advancing our understanding of the phenomena within DSSC devices, especially in the context of current-voltage (I-V) characteristics.

Early experiments analyzed results through the lens of a model established by Gerischer in the 1960s [48,49]. It is important to highlight that in the semiconductor, the separation of photogenerated electron-hole pairs occurs owing to an electric field, often referred to as a depletion layer [50].

Through the application of the diffusion equation and the exclusion of recombination within the depletion layer, Gartner derived (**Eq. 8**) a formula for the photocurrent density (J) by establishing the concentration of minority charge carriers in the bulk semiconductor [51]. The variables in the equation encompass Φ , which signifies incident light intensity; α , representing the length of reciprocal absorption; w , indicating the broad of the depletion layer; and L , denoting the length of minority carrier diffusion.

$$J = q\Phi \left(1 - \frac{e^{-\alpha w}}{1 + \alpha L} \right) \quad (8)$$

Originally formulated for a Schottky barrier established between a semiconductor and a metal [51]. Butler subsequently broadened the utilization of this equation to liquid junctions [52].

Södergren et al. wrote the formula of J-V characteristics for semiconductor/electrolyte (SE) and electrolyte/electrode (EE) interfaces by applying two assumptions [50]: firstly, Initially, the movement of electrons within the semiconductor occurs via diffusion. Secondly, the electron diffusion length within the semiconductor remains consistent throughout the microporous film, under the assumption that recombination processes adhere to first-order kinetics, and the photon flux Φ is a constant. The derivation initiated from the continuity equation governing electrons within the microporous semiconductor film, as stated in **Eq. 9**.

$$Dn''(x) - \frac{n(x) - n_0}{\tau} + \Phi\alpha e^{-\alpha x} = 0 \quad (9)$$

D stands for the electron diffusion constant, $n(x)$ represents surplus electron density, n_0 is the dark electron density, and r , Φ , and α maintain their meanings as defined in Eq. 8. The derivation holds equivalently for holes as charge carriers within the porous film.

The determination of the J-V characteristic involves adjusting the external voltage in opposition to the photovoltage while simultaneously monitoring the current. Furthermore, the J-V characteristics can be ascertained through the variation of an external resistance. The alteration in potential at the semiconductor (V_{SC}) and back contact interface are expressed as follows [50]:

$$V_{SC} = \frac{kT}{q} \ln \frac{n}{n_0} \quad (10)$$

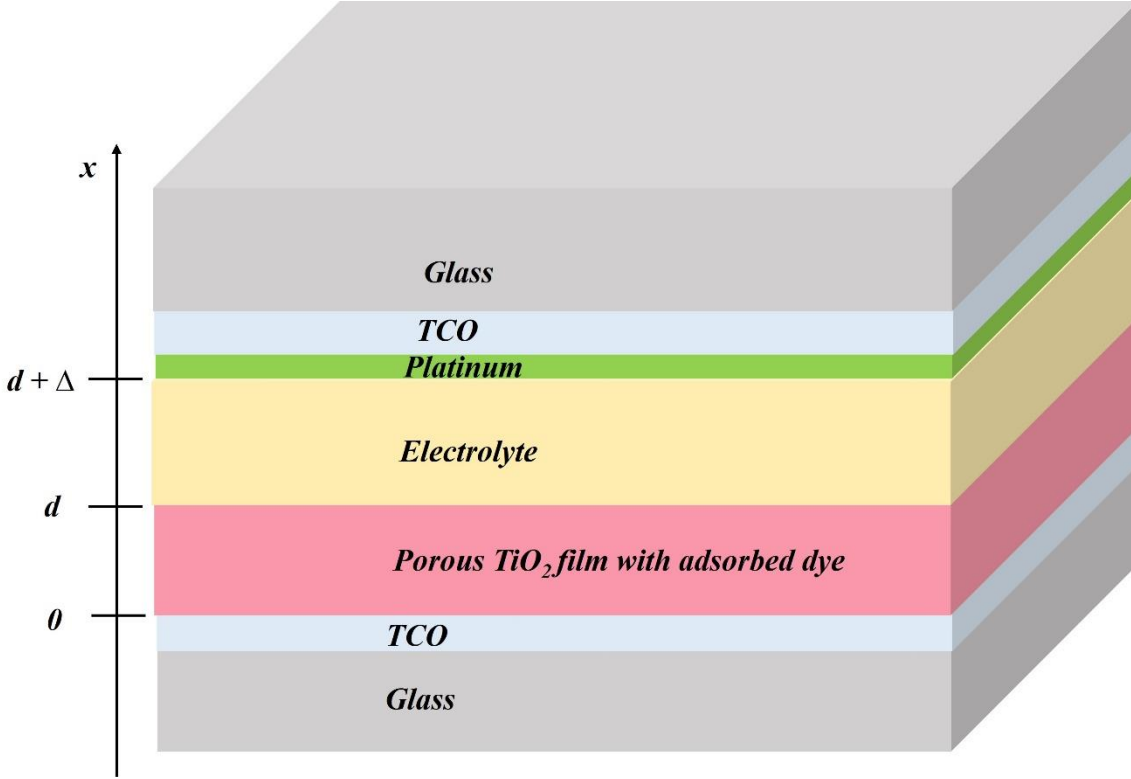


Figure 7 Structure of the modeled DSSC. The figure is adapted from ref. [53].

The generated current density can be obtained by solving **Eq. 9** using the following boundary conditions are depicted in **Fig. 7**. First boundary conditions (Eq. 11) stated that at $x = 0$ (back contact), the application of an external voltage will lead to an elevation in electron concentration $n(x)$ [50].

$$n(0) = n \quad (11)$$

When x reaches d (the outermost layer of TiO_2), it is indicated that the electrons will experience reflection and subsequently disperse back into the inner layers of the film. This leads to the establishment of the second boundary condition, as expressed in Eq. 12.

$$\left. \frac{dn(x)}{dx} \right|_{x=d} = 0 \quad (12)$$

$$J_{SE} = J_{SE}^0 - \frac{qDn_0 \sinh\left[\frac{d}{L}\right]}{L \cosh\left[\frac{d}{L}\right]} \left(e^{\frac{qV}{kTm}} - 1\right) \quad (13)$$

The value of J_{SE}^0 is directly related to the derivative of $n(x)$ at the back contact ($x = 0$) [50], as expressed by **Eq. 14**.

$$J_{SE}^0 = q\Phi \frac{[-L\alpha \cosh\left\{\frac{d}{L}\right\} + \sinh\left\{\frac{d}{L}\right\} + L\alpha e^{-d\alpha}] L\alpha}{[1 - L^2\alpha^2] \cosh\left[\frac{d}{L}\right]} \quad (14)$$

For an ideal solar cell, it is essential that the film thickness is smaller than the diffusion length ($d < L$), resulting in

$$J_{SE} = J_{SE}^0 - \frac{qDn_0 d}{L^2} \left(e^{\frac{qV}{kTm}} - 1\right) \quad (15)$$

They also obtained the photocurrent (**Eq.18**) by using *EE* illumination with the boundary conditions as follows (see **Eqs. 16** and **17**):

$$n(d) = n \quad (16)$$

And,

$$\left. \frac{dn(x)}{dx} \right|_{x=0} = 0 \quad (17)$$

$$J_{EE} = J_{EE}^0 - \frac{qDn_0 \sinh\left[\frac{d}{L}\right]}{L \cosh\left[\frac{d}{L}\right]} \left(e^{\frac{qV}{kTm}} - 1\right) \quad (18)$$

With J_{EE}^0 is expressed by **Eq. 19** [50],

$$J_{EE}^0 = q\Phi \frac{[L\alpha \cosh\left\{\frac{d}{L}\right\} + \sinh\left\{\frac{d}{L}\right\} - L\alpha e^{d\alpha}] L\alpha e^{-d\alpha}}{[1 - L^2\alpha^2] \cosh\left[\frac{d}{L}\right]} \quad (19)$$

According to two illumination conditions aforementioned above, it concludes that the difference between SE and EE illumination relies on the sign of generated current as can be seen in Eqs. 14 and 19.

There are many efforts developed the model of DSSC devices such as Cao et al. [54] expanded the prevailing model to encompass temporal considerations, thereby formulating the primary partial differential equation (PDE) governing electron diffusion over time. Moreover, this investigation introduced the initial nonlinear iteration of the equation, featuring a diffusion coefficient $D(n)$, where $D(n) = n$. Mathews et al. defined the photo current density (J_p) as the saturation current density (J_{sat}) times by injection efficiency Φ_{inj} . Additionally, the injection efficiency (**Eq. 20**) depends on the rate constants of decay (k_{decay}) and injection (k_{inj}) [55].

$$\Phi_{inj} = \frac{k_{inj}}{k_{inj} + k_{dec}} \quad (20)$$

Huang et al. stated that the photocurrent density as the subtraction of current density injection (J_{inj}) to the current density recombination (J_r) in the surface, assuming the recombination from sensitizer neglected [56]. The J_{inj} corresponds to the light intensity of the source (qAI_0). Then they explored details the recombination reaction equation from the oxidize species of electrolyte in solution and obtained the complete equation for photogenerated current density under short-circuit (SC) condition, as written in **Eq. 21**.

$$qAI_0 = J_{sc} - qk_{et}n_0^{u\alpha} \left[\left(\frac{c_{ox}^0}{c_{ox}^0 - \frac{J_{sc}d}{2ZF D}} \right)^{u\alpha} - 1 \right] \left[(c_{ox}^0)^2 + \frac{1}{3} \left(\frac{J_{sc}d}{2ZF D} \right)^2 \right] \quad (21)$$

The concentration function $c_{ox}(x)$ denotes the extent of oxidized species in the solution at a particular position x , situated between the platinum counter electrode (CE) ($x = d$) and the TCO/TiO₂ interface ($x = 0$). Essential factors encompass q is the electronic charge, and F corresponds to the Faraday constant, A corresponds to the proportion of absorbed photon flux to I_0), z corresponds to the quantity of electrons moved from TiO₂ to an oxidized species, and D is attributed to the diffusion coefficient. According to **Eq. 21**, the photocurrent is affected by the concentration gradient of oxidized species in the solution.

In the following year, Stangl et al. tackled the constraints present in the model derived by Södergren et al., which overlooked the mass transport of the electrolyte [50]. They employed the continuity equation to encompass all electroactive species within the system., including electrons, reduced electrolyte (El_{Red}), oxidized electrolyte (El_{Ox}), and cation (Kat^+). Additionally, they implemented a Boltzmann relaxation approximation for the reverse reaction to clarify particle currents densities within the cell [57].

$$-i_{ext} = e_0[j_{e^-}(x) + j_{red^-}(x) + j_{ox^-}(x)] = e_0j_{e^-}(0) = e_0[j_{red^-}(d) + j_{ox^-}(d)](22)$$

At steady-state, the lack of cation current is represented by $j_{Kat^+}(x) = 0$. Moreover, the j athroughout the entire cell remains uniform and is equivalent to the external electric current density, as specified in **Eq. 22**. At the boundaries of the cell, this current is solely influenced by electrons (at $x = 0$) or by the electrolyte alone (at $x = d$, where d represents the depth of the semiconductor/dye/electrolyte interface).

Pichot and Gregg conducted a comparative analysis of two existing models, namely the kinetic model [50,58] and junction model [59], while focusing on the experimental section to examine the photovoltage. Their research indicates that the photovoltage is not regulated

by the electrical potential difference at the dark interfacial zone, as suggested by the junction model. Instead, the photovoltage shows a significant level of independence from the substrate's work function, aligning with the predictions of the kinetic model [60].

Feber et al. [61] proposed that particle diffusion is driven by concentration gradients, and simultaneously, the induction of the diffusion process occurs due to an electric field E in the x -direction, resulting from disparities in local particle concentrations within the bulk. Consequently, the current densities of the respective charged particles under consideration are influenced by these two factors, as written in **Eqs. 23-26**.

$$\frac{1}{e_0} j_e = D_e \frac{dn_e}{dx} + \mu_e n_e E \quad (23)$$

$$\frac{1}{e_0} j_{I^-} = D_{I^-} \frac{dn_{I^-}}{dx} + \mu_{I^-} n_{I^-} E \quad (24)$$

$$\frac{1}{e_0} j_{I_3^-} = D_{I_3^-} \frac{dn_{I_3^-}}{dx} + \mu_{I_3^-} n_{I_3^-} E \quad (25)$$

$$\frac{1}{e_0} j_c = -D_c \frac{dn_c}{dx} + \mu_c n_c E = 0 \quad (26)$$

With the boundary conditions Eqs. 27-29. Representing initial concentrations using an upper index "0."

$$\int_0^d \left[\frac{1}{2} n_{e^-}(x) + \frac{1}{3} n_{I^-}(x) \right] dx = \left[\frac{1}{2} n_{e^-}^0 + \frac{1}{3} n_{I^-}^0 \right] \cdot d \quad (27)$$

$$\int_0^d \left[n_{I_3^-}(x) + \frac{1}{3} n_{I^-}(x) \right] dx = \left[n_{I_3^-}^0 + \frac{1}{3} n_{I^-}^0 \right] \cdot d \quad (28)$$

$$\int_0^d \left[n_{I_3^-}(x) + \frac{1}{3} n_{I^-}(x) \right] dx = \left[n_{I_3^-}^0 + \frac{1}{3} n_{I^-}^0 \right] \cdot d \quad (29)$$

The current traversing the interface is solely attributed to electrons, as articulated in Eq. 30. Additionally, at $x=0$, the current densities of iodide and triiodide, outlined in Eqs. 31 and 32, are null:

$$j_e(0) = j_g \quad (30)$$

$$j_{I^-}(0) = 0 \quad (31)$$

$$j_{I_3^-}(0) = 0 \quad (32)$$

Given the absence of an electrical link between platinized/TCO and TiO_2 , the electron current density (j_e) within the TiO_2 conduction band at the position $x = d$ is diminished to zero. (**Eq. 33**).

$$j_e(d) = 0 \quad (33)$$

Therefore, the net current density (j) for the charge transfer at $x = d$ (**Eq. 34**) is equal to the net current density (j_g) [61].

$$j(d) = j_g = j_0 \left[\sqrt{\frac{n_{I_3^-}(d) n_{I^-}^{OC}(d)}{n_{I_3^-}^{OC}(d) n_{I^-}(d)}} e^{(1-\beta)\frac{e_0}{kT} U_{Pt}} - \frac{n_{I^-}(d)}{n_{I^-}^{OC}(d)} e^{-\beta \frac{e_0}{kT} U_{Pt}} \right] \quad (34)$$

Another study utilized the impedance results to understand the phenomenology in DSSC devices. A recent electrical impedance studies [62] suggest that the photovoltage is influenced by two factors: shifts in the Fermi level (E_F) of semiconductor nanoparticles and changes in the potential drop across the back contact. The photovoltage model,

described in **Eq. 35** [63], was introduced as illumination-dependent under open-circuit conditions. In this equation, the maximum slope, denoted as $(dV_{oc}/d \log \Phi_0)$, is approximately 60 mV and is attained when β' is equal to 1. Where the β' signifies the reaction order and CB (conduction band).

$$\frac{dV_{oc}}{d \log \Phi_0} = \frac{2.3 kT}{\beta' q} \quad (35)$$

In the next year, Ni et al. developed the TiO_2/TCO interfacial model, incorporating a Schottky barrier (ϕ_b) into continuity equation to explore the J-V characteristics [64]. Assuming the cell operating at a high temperature ($\sim 300\text{K}$) and TiO_2 is minimally doped in a DSSC, the significance of electron tunneling is negligible, and electron transfer is primarily governed by thermionic emission. Consequently, only thermionic emission is taken into account in their J-V characteristics model, expressed as Eq. 36.

$$V = \frac{kTm}{q} \ln \left[\frac{(J_{sc} - J)L \cosh\left(\frac{d}{L}\right)}{qDn_0 \sinh\left(\frac{d}{L}\right)} + 1 \right] - \frac{kT}{q} \ln \left[1 + \frac{J}{A^*T^2 \exp\left(-\frac{q\phi_b}{kT}\right)} \right] \quad (36)$$

A^* represents the Richardson constant equivalent to $6.71 \times 10^6 \text{ A/m}^2\text{K}^2$ for TiO_2 , with the remaining variables holding the same meaning as mentioned above. In instances where Schottky barrier heights are low, the influence of the TiO_2/TCO interface on J–V features is negligible. Nevertheless, surpassing a critical value, the impact at the interface becomes notable.

One of the important parameter influence the DSSC performance is a recombination process. Early study showed that the recombination constant is an inversely related to the electron lifetime [50]. Equation 25 distinctly illustrates the separation of a lifetime into two

fundamental components [65]. This decision is grounded in the composition of resistance recombination R_{rec} , which includes a density term, a chemical capacitance C , and a kinetic constant (k_r). Consequently, the product in **Eq. 37** isolates only the kinetic constant. This particular time aligns with the angular frequency.

$$\tau_0 = R_{rec} C_{\mu}^{cb} = \frac{1}{k_r} \quad (37)$$

The recombination resistance and capacitance terms of Bisquert's models are shown in **Eqs. 38** and **39**, respectively.

$$R_{rec} = \frac{1}{A} \left(\frac{\partial j_{rec}}{\partial V_F} \right)^{-1} = \frac{k_B T}{ALq^2 k_r} n_c^{-1} = R_0^{cb} \exp \left[-\frac{qV_F}{k_B T} \right] \quad (38)$$

$$C_{\mu}^{cb} = ALq \frac{\partial n_c}{\partial V_F} = \frac{q^2 AL n_c}{k_B T} = C_{\mu 0}^{cb} \exp \left[\frac{qV_F}{k_B T} \right] \quad (39)$$

Villanueva et al. introduced an additional charge transfer term from the TCO/electrolyte interface into the diffusion equation (see **Eq. 39**), and they compared it with experimental results [66]. Utilizing the same boundary conditions as previous studies, the model was applied in the numerical solution. However, it is important to note that this model has its limitations. If the charge transfer at the electrolyte/ FTO interface is neglected, the model anticipates perfect behavior in the photovoltage-light intensity graph and accurately reproduces the theoretical representation of voltage decay. Furthermore, the model's applicability can be expanded to simulate cells lacking blocking layers by incorporating suitable parameters.

$$\frac{\partial n(x, t)}{\partial t} = \frac{\partial}{\partial x} \left(\frac{D(n) \partial n(x, t)}{\partial x} \right) + G(x) - k_r(n)(n(x) - n_0) + \frac{J_{Tco}}{ed} \quad (39)$$

$G(x)$ signifies the generation, J_{TCO} denotes the current density at the TCO/electrolyte interface, and d represents the depth of the film.

Halme et al. [67] employed the first-order recombination kinetics inherent in the diffusion equation, as derived by Södergren et al. [50]. Building upon the diffusion equation with consistent boundary conditions from a prior study, they introduced the recombination current i_{rec} and the recombination resistance within the TiO_2 layer R_{TiO_2} to characterize the I-V curves. The relationship between electron diffusion length and both the photocurrent and recombination current is evident in **Eq. 40**, underscoring their connection to electron transport and recombination within the film. Significantly, although the recombination current is influenced by the electron diffusion length, it differs from the photocurrent as it is solely an electrical characteristics governed by the potential at the contact.

$$i_{cell}(V_{TiO_2}) = i_{SC,TiO_2} - i_{rec,0} \left(e^{-\frac{qV_{TiO_2}}{mk_B T}} \right) \times \frac{\tanh\left(\frac{d}{L}\right)}{\frac{d}{L}} \quad (40)$$

Here, i_{SC,TiO_2} represents the short-circuit current density of the electrode, aligning with findings in reference [68]. The $i_{rec,0} = \frac{qdn_0}{\tau}$ is explicitly defined as the exchange current density of the recombination reaction. Moreover, **Eq. 40** allows for the derivation of the photovoltage. The differentiation of **Eq. 41** provides the overall resistance of the photoelectrode layer (R_{TiO_2}), encompassing both electron recombination and diffusion within the layer, as expressed in **Eq. 42**.

$$V_{TiO_2}(i_{cell}) = -\frac{mk_B T}{q} \times \ln\left(\frac{d}{L} \coth\left(\frac{d}{L}\right) \cdot \frac{i_{SC,TiO_2} - i_{cell}}{i_{rec,0}} + 1\right) \quad (41)$$

$$R_{TiO_2}(i_{cell}) = R_{rec,0} \left(\frac{i_{SC,TiO_2} - i_{cell}}{i_{rec,0}} + \frac{\tanh\left(\frac{d}{L}\right)}{\frac{d}{L}} \right)^{-1} \quad (42)$$

Andrade et al. formulated a transient phenomenological model to juxtapose the experimental Electrochemical Impedance Spectroscopy (EIS) findings with theoretical data [53]. They started from the continuity equation and used the Fick's law to define the diffusion D equation (**Eq. 43**), where the j is the carrier flux.

$$j = -D \frac{\partial n}{\partial x} \quad (43)$$

With the generation rate (G) is expressed by **Eq. 44**, where η_{inj} corresponds to injection coefficient, and I_0 is attributed to the incident photon flux.

$$G = \eta_{inj} \alpha(\lambda) I_0 e^{-\alpha(\lambda)x} \quad (44)$$

The diffusion equation end up a bit similar to **Eq. 9** (Södergren's model). The charge equilibrium at $x = 0^+$ (surface close to semiconductor layer) is equal to $x = 0^-$ (external surface of TCO). Hence, the current density at that interface is expressed by $J_e^- = J_e^+$, where J_e^+ represents the electron diffusion passed through the TiO_2 . In a steady state, this current, denoted as J_{cell} , constitutes the overall current generated by the cell. The condition at the boundary where $x = 0$ is outlined in **Eq. 45**:

$$J_e^+ = J_{cell} = -qD_e \left. \frac{\partial n_{e^-}}{\partial x} \right|_{x=0^+} \quad (45)$$

At $x = d$, the notable feature is the lack of electron transport from the CE to the electrolyte (refer **Fig. 7**). This state is achieved by having an electrolyte layer in immediate proximity to the cathode, and the thickness is accurately dictated by the spacer ring employed for cell

sealing. This design guarantees the avoidance of direct contact between the CE and the TiO₂, ensuring that electrons are returned and reflected into the layers of the TiO₂ film [50]. Then, the final solution ends up to Södergren's model for J-V characteristics.

Andrade et al. investigated an alternate model encompassing electrons outside the nanoporous semiconductor. The initial model within this realm, introduced by Papageorgiou et al. [69], acts as a basis, even though it does not account for the impact of electrons in the conduction band on the electrolytes. Nevertheless, it establishes the framework for such an extension. Subsequently, Andrade et al. formulated a model for the I⁻/I₃⁻ electrolyte couple utilizing the following diffusion equations:

$$D_{I^-} \frac{\partial^2 n_{I^-}(x, t)}{\partial x^2} - \frac{3}{2\varepsilon_p} \left[\eta_{inj} \alpha(\lambda) I_0 e^{-\alpha(\lambda)x} - \frac{n_{e^-}(x, t) - n_{eq}}{\tau_{e^-}} - \frac{\partial n_{e^-}(x, t)}{\partial t} \right] = \frac{\partial n_{e^-}(x, t)}{\partial t} \quad (46)$$

$$D_{I_3^-} \frac{\partial^2 n_{I_3^-}(x, t)}{\partial x^2} + \frac{1}{2\varepsilon_p} \left[\eta_{inj} \alpha(\lambda) I_0 e^{-\alpha(\lambda)x} - \frac{n_{e^-}(x, t) - n_{eq}}{\tau_{e^-}} - \frac{\partial n_{e^-}(x, t)}{\partial t} \right] = \frac{\partial n_{I_3^-}(x, t)}{\partial t} \quad (45)$$

The terms n_{I^-} and $n_{I_3^-}$ are attributed to the respective densities of I⁻/I₃⁻ electrolyte, and D_{I^-} and $D_{I_3^-}$ stand for the diffusion coefficients associated with I⁻/I₃⁻. Additionally, the variable ε_p denotes the porosity of TiO₂.

Accompanying the initial conditions:

$$t = 0, \quad n_{I^-}(x, 0) = n_{I^-}^{initial}; \quad n_{I_3^-}(x, 0) = n_{I_3^-}^{initial}; \quad (46)$$

And the boundary conditions:

$$x = 0, \quad \frac{\partial n_{I^-}(0, t)}{\partial x} = 0; \quad \frac{\partial n_{I_3^-}(0, t)}{\partial x} = 0; \quad (47)$$

$$x = d, \quad \int_0^d n_{I^-}(x) dx = dn_{I^-}^{initial}; \quad \int_0^d n_{I_3^-}(x) dx = dn_{I_3^-}^{initial}; \quad (48)$$

Through the integration of the continuity equation in conjunction with **Eqs. 47** and **48**, it becomes possible to compute the current density (J) at the TCO/CE interface. This derivation presupposes the lack of resistances within the external circuit load. In this scenario, electrons actively participate in the I^-/I_3^- reaction, facilitated by the CE layer applied to the TCO. Hence, the current density at this interface can be ascertained utilizing the Butler–Volmer equation.

$$J_{cell} = J_0 \left[\frac{n_{I_3^-}(d)}{n_{I_3^-}^{oc}(L)} e^{\frac{\beta q \eta_{ce}}{k_B T}} - \frac{n_{I^-}(d)}{n_{I^-}^{oc}(L)} e^{\frac{-(1-\beta) q \eta_{ce}}{k_B T}} \right] \quad (49)$$

Eq. 49 describes the exponential growth of the current produced from the electrochemical reaction at $x = d$ in relation to the activation overvoltage η_{ce} . It is crucial to highlight that this overvoltage represents the voltage applied to surpass the energy stimulation barrier [53,70].

Belarbi et al. [71] refined the model [61] through the inclusion of a term delineating the concentration of charge carriers. Adhering to the principle of conserving particle numbers, the integral representing the charge carriers concentration consistently equals the equilibrium concentration of the species (**Eqs. 50** and **51**).

$$\int_0^{t_{TiO_2}} \left[\frac{1}{2} n_{e^-}(x) + \frac{1}{3} n_{I^-}(x) \right] dx = \left[\frac{1}{2} \bar{n}_{e^-} + \frac{1}{3} \bar{n}_{I^-} \right] \cdot p \cdot t_{TiO_2} \quad (50)$$

$$\int_0^{t_{TiO_2}} \left[n_{I_3^-}(x) + \frac{1}{3} n_{I^-}(x) \right] dx = \left[\bar{n}_{I_3^-} + \frac{1}{3} \bar{n}_{I^-} \right] \cdot p \cdot t_{TiO_2} \quad (51)$$

Equations (50) and (51) are denoted by $\bar{n}_{I^-} = C_{I^-}^0$, and $\bar{n}_{I_3^-} = C_{I_3^-}^0$, where $C_{I^-}^0$ and $C_{I_3^-}^0$ represent the initial concentrations of I^-/I_3^- , respectively. The variables of p and t_{TiO_2} correspond to porosity and the semiconductor layer thickness.

The J_{SC} and V_{OC} obtained are similar with the previous works [50,53,64,68], a maximum voltage (V_{mp}) and transient (τ_{tr}) terms as written in Eqs. 52 and 53.

$$V_{mp} = -\frac{mk_B T}{q} \times \ln \left(\frac{L(J_{SC} - J_{mp})}{qDn_{eq} \tanh\left(\frac{t_{TiO_2}}{L}\right)} + 1 \right) \quad (52)$$

$$\tau_{tr} = \frac{t_{TiO_2}^2}{\varrho D} \quad (53)$$

Here, ϱ is the numerical factor. The improved model has facilitated the exploration of the influence of distinct parameters on the efficiency of DSSCs.

In conclusion, the reviewed models suggest a widespread preference among researchers, especially those proposed by Södergren et al. [50] at the TCO/semiconductor interface. Ferber's and Andrade's models for TCO/electrolyte interfaces [53], are widely favored among researchers [71,72,81–90,73,91–96,74–80].

2.3 Component of DSSC

2.3.1 Conductive glass

In solar cell technology, the choice of substrate plays a crucial role. Ideally, the substrate should be transparent and deposited with a transparent conductive oxide (TCO) layer on one side. This dual-purpose design allows the substrate to transmit incident light while also providing an electrically conductive path for electrons [97].

One important consideration when selecting a substrate material is its ability to block undesired wavelengths. For instance, a glass substrate with rigid properties can effectively block infrared wavelengths, making it suitable for absorbing a UV light range. In addition, the conductive layer within the TCO substrate must meet specific criteria. It should have low resistance, typically around 10–20 Ω/sq , and possess a bandgap of approximately 3.3 eV [98].

Among frequently utilized transparent conductive oxide (TCO) materials, three noteworthy options include indium–doped tin oxide (ITO), aluminum–doped zinc oxide, and fluorine–doped tin oxide (FTO), typically composed of a glass sheet. Each of these materials has different characteristics that make them suitable for particular applications. ITO, for instance, exhibits a resistivity of approximately 18 Ω/sq [99], while silica boasts a slightly lower resistivity of 12.2 Ω/sq [100]. In contrast, FTO stands out as a superior option due to its exceptional attributes. It not only offers an even lower resistivity of around 8 Ω/sq [99], making it an excellent conductor, but it also surpasses in terms of temperature stability. These features make FTO a preferred choice for applications in solar cell technology.

2.3.2 Semiconducting Layer

The semiconducting layer acts a crucial role by supporting sensitizer incorporation and promoting the transport of excited electrons to the external circuit. To create a highly efficient photoanode, several critical qualities must be met. Firstly, it should feature a substantial surface area to facilitate the loading of dye molecules, enhancing its ability to absorb light and generate electrons. Additionally, a highly porous structure is essential, promoting efficient dye adsorption and facilitating electron transport within the material. Furthermore, the photoanode must be transparent in the visible light region, allowing incident light to penetrate and interact with the dye molecules. It's crucial for the CB of the photoanode to be positioned beneath the LUMO to minimize electron losses during photoexcitation. Moreover, the photoanode should exhibit chemical inertness when subjected to the redox electrolyte solution, diminishing the chances of electron recombination and preserving overall photovoltaic efficiency. High electron mobility is another vital characteristic, ensuring rapid transport of photocurrent to the external circuit. Lastly, the presence of defects and hydroxyl groups can enhance dye loading, promoting increased light absorption and electron generation [98,101]. Various semiconductor mesoporous layers, including TiO_2 , ZnO , SnO_2 , MgO , and WO_3 , have been used in DSSCs [101–103].

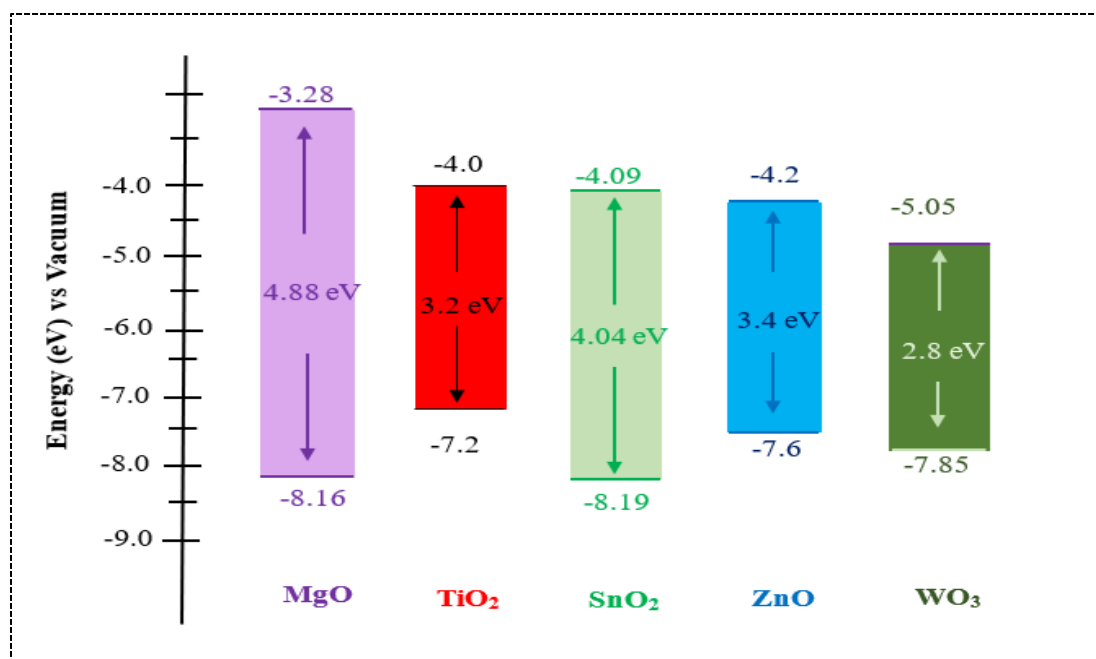


Figure 8. The energy level of different semiconductor materials.

Additionally, it is mandatory for the semiconducting layer to have a suitable band gap width owing to electron transfer easily. The energy band gap of various semiconducting materials is depicted in **Fig. 8**. Among these options, TiO₂-anatase emerges as the preferred choice for several reasons. Notably, it boasts an extensive surface area, which facilitates the chemical adsorption of sensitizers onto the TiO₂ surface. Furthermore, a TiO₂ film exhibits high porosity, effectively capturing incoming photons and achieving remarkable cell efficiencies of up to 14.7% [104]. In addition, TiO₂ is recognized for its non-toxic nature, abundance, and compatibility with biological systems [105].

2.3.3 Dye

The dye acts to absorb light and subsequently inject its excited molecule into the CB of the semiconducting layer [101]. To optimize its functionality, the dye must possess luminescence and cover a broad spectrum, including UV-Vis (400-800 nm) and near-IR

regions [106]. Additionally, anchoring groups such as $-\text{COOH}$, $-\text{H}_2\text{PO}_3$, or $-\text{SO}_3\text{H}$ are essential for effective binding to the semiconducting surface [107]. For effective electron transfer, the energy level of the excited dye must surpass the semiconductor's CB. Additionally, the successful regeneration of oxidized dye relies on the oxidized state level of the dye being more negative (Energy vs Vacuum) than the redox potential of the electrolyte [103]. Furthermore, it must exhibit stability to facilitate approximately 10^8 turnovers, corresponding typically to 20 years of cell performance [101].

2.3.4 Electrolyte

An electrolyte serves as a medium for a redox reaction to occur. The process involves oxidizing iodide into triiodide, releasing electrons, and reducing triiodide back into iodide with a CE. Currently, three types of electrolytes—liquid, gel, and solid—are under study, each with its pros and cons [40,103,108,109]. The investigation into these electrolytes is ongoing due to their potential impact on both open-circuit voltage and short-circuit current density. Efficient electrolyte incorporation is crucial for inhibiting recombination reactions that could otherwise diminish J_{sc} and V_{oc} .

2.3.5 Counter electrode (CE)

Within these devices, the electrocatalyst layer emerges as a crucial element, playing a pivotal role in facilitating electron accumulation from the external circuit and promoting the intricate process of electrolyte reduction [110]. The CE comprises TCO coated with either carbon or platinum, constituting a fundamental layer in the mechanism. This specific layer is strategically applied atop the active TCO layer, serving as a catalyst for the redox couple [106]. This catalyst facilitates the efficient transfer of electrons into the electrolyte,

initiating the regeneration of a redox couple [103]. Unlike a spontaneous reduction reaction at CE, the process is intricately governed by the intrinsic electrocatalytic prowess of the material chosen. An adept CE for DSSCs must demonstrate a noteworthy exchange current density in comparison to the photoanode. This is exemplified by its capability to effectively reduce the I^-/I_3^- redox couple and facilitate the seamless and rapid diffusion of triiodide ions, emphasizing the indispensable attributes necessary for optimal DSSC performance.

2.4 Synthetic dyes-based DSSC

Since O'Regan and Graetzel discovered an advanced type of solar cell recognized as DSSCs in 1991 [17], the DSSC has garnered considerable interest in recent times owing to its characteristics as elucidated previously. The researchers are continuously working on their development to improve their harvesting efficiency. Currently, the synthetic dyes can perform very well. At an intensity of 1 sun, the N3 sensitizer achieved an efficiency of 11.18%, while the N621 sensitizer achieved an efficiency of 9.57% [33]. Chiba et al. used black dye with a different haze of TiO_2 to obtain the PCE up to 11.1% [111]. Yella et al. successfully synthesized zinc porphyrin dye and facilitated its conjugation with a $Co^{(II/III)}$ -based electrolyte, resulting to a cell efficiency of 12.3% [112]. By modifying the porphyrin dye through molecular engineering, the same porphyrin dye with the $Co^{(II/III)}$ -based electrolyte exhibited 13% of PCE [113]. Currently, the top efficiency achieved in DSSCs using collaboratively ADEKA-1 and LEG-4 dyes with liquid electrolytes (LEs) based stands at approximately ~14.7% [104]. Despite high efficiency, synthetic dye entails high manufacturing costs and complex synthesis routes and readily pollutes the environment [114,115]. In contrast, natural dyes are economical, inexpensive, easy to collect and extract, and eco-friendly in comparison to their synthetic counterparts. Therefore, the

adoption of natural dyes as sensitizers emerging as a compelling and eco-friendly alternative.

2.5 Natural Dye-sensitized solar cell

The natural dye-sensitized solar cell (NDSSC) is the kind of DSSC that employs the natural source as a sensitizer. These dyes encompass pigments such as anthocyanins, betalains, carotene, chlorophyll, and flavonoid, obtained from various plant sources [32,35,37,39,116]. Additionally, carotene and chlorophyll can also be sourced from other organisms like bacteria and algae [114,117,118]. The structure of those pigments is depicted in **Fig. 9**. Natural dyes exhibit key characteristics, including accessibility, environmental friendliness, and cost-effectiveness [39,119,120].

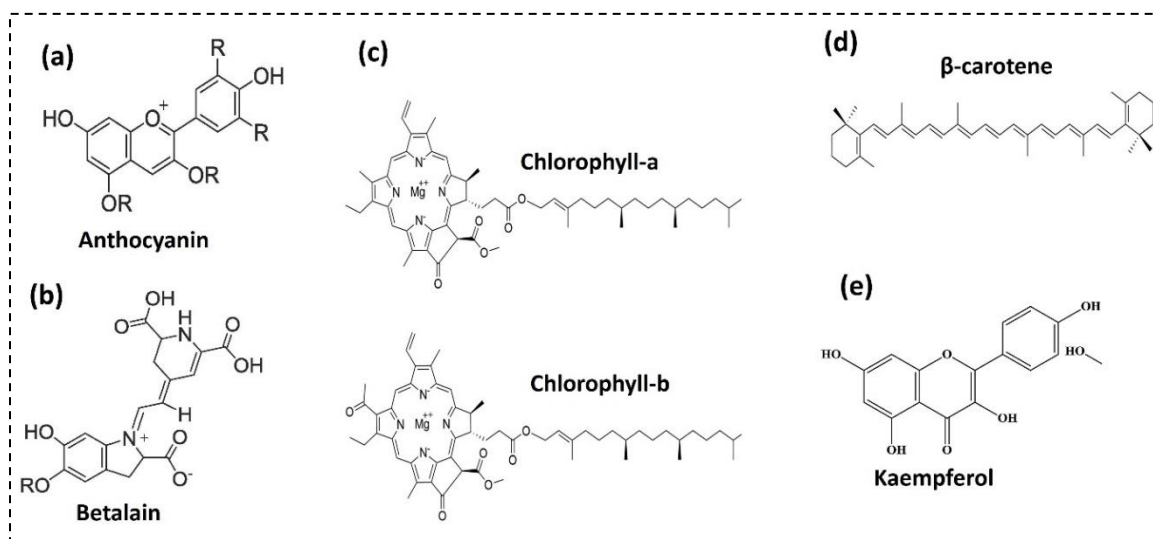


Figure 9. The molecular structure of (a) anthocyanin, (b) betalain [121], (c) chlorophyll, (d) carotenoid [122], and (e) Kaempferol (type of flavonoids) [44].

2.5.1 Anthocyanin

In NDSSC, anthocyanin, a primary component of various natural colors found in fruits, flowers, roots, and plant leaves, plays a central role [123–129]. **Fig. 9a** illustrates the molecular structure of anthocyanin, featuring six sub-molecular structures [119]. Significantly, the existence of hydroxyl and carbonyl groups in anthocyanin molecules allows them to bind to the semiconductor layer's surface, thereby aiding the efficient transfer of electrons from the sensitizer to the conduction band. Anthocyanin displays light absorption characteristics within the peak wavelength range of 420 nm to 580 nm, efficiently directing this energy through resonance energy transfers to pairs of anthocyanins located in the photosystem's reaction center, contributing to improved performance [128]. Researchers have explored the potential of anthocyanin-based natural dyes in DSSCs, harnessing a variety of sources. Maiaugree et al. explored the utilization of carbonized peel from mangosteen as a dual-purpose natural photosensitizer and counter electrode, resulting in an impressive efficiency of 2.63% in their DSSC based on mangosteen [129]. Prima et al. utilized black rice as a source of anthocyanin pigment, extracting and purifying it through maceration, resulting in an efficient electron transport system and an efficiency of 2.17% [130]. Li et al. harnessed red cabbage extract, which covers a broad UV region extending nearly to NIR (300–900 nm), achieving an optimum efficiency of 2.9% after 24 hours of immersion, showcasing successful hydroxyl group binding to semiconductor oxide through chemical bonding [131]. A different extraction method of the same dye yielded an anthocyanin based NDSSC with an impressive efficiency of approximately $1.337 \pm 0.04\%$ at a dye concentration of 3.0 mM [132]. The anthocyanin extract from pomegranate fruit showed strong absorption in the visible spectrum, peaking at 510 nm,

leading to effective photon absorption and an notable efficiency of 2% [124]. Rahul et al. obtained a slightly lower efficiency of 0.028% from pomegranate fruit extract, attributed to the use of a PEO-based solid polymer electrolyte affecting electron collection [133]. Ammar et al. extracted anthocyanin from red onion, with observed wavelengths ranging from 350-800 nm and peaks at 544 nm and 486 nm, achieving an efficiency of 0.06% [22]. Furthermore, various other anthocyanins sourced from dragon fruit, purple cabbage, barberry root, blueberry, cranberry, blue pea, Melinjo skin, red rose, Chinese rose, begonia, Bauhinia, black carrot, and flower knotweed have exhibited efficiencies in the range of 0.04-1.56%, as outlined in **Table 1**.

2.5.2 Betalain

Betalain are yellow and red pigments found in the part of plants, as well as in the petals of flowers. Natural color extraction is a straightforward and perhaps green technique. Betalain can be subdivided into betacyanins and betaxanthins [119]. The condensation of different amines and amino acids resulted in the formation of betaxanthins, a more straightforward subclass of betalain. Betanin pigments offer a lot of promise for converting solar energy. Betanin pigments, recognized for their water solubility and nitrogen content, showcase unique chemical attributes. Within this pigment family, betaxanthin takes center stage with its notable trait of fluorescence absorption, emitting discernibly within the visible range of the electromagnetic spectrum. In contrast, the other subgroup of betacyanins does not demonstrate any responsiveness to fluorescence. Typically, the absorption spectrum of red dye is discerned within the wavelength range of 350–640 nm, with absorption bands showing a peak absorbance at 559 nm [40]. The utilization of natural dyes in DSSCs not only capitalizes on their absorption properties but also aligns with the growing interest in

sustainable and eco-friendly approaches to energy conversion. The **Fig. 9b** illustrates the molecular structure of betalain.

Kabir et al. published a paper on NDSSCs utilizing beet root as a betalain source, achieving an efficiency of 0.47% with $J_{sc} = 1.857 \text{ mA/cm}^2$ [134]. Guzel et al. investigated NDSSCs using Pokewood fruit (PF) and stalk (PS) sensitizers, where betanidin extract, a betalain derivative, achieved a conversion efficiency of 3.04% (PF) [121]. The high efficiency is because of a good binding between the dye and nanocrystalline semiconductor, leading to broader absorption. Rani et al. conducted a study on the utilization of blood berries (BB) for light harvesting, resulting in a notable enhancement of efficiency from $\eta = 0.86\%$ to 2.06%. The improvement was ascribed to the interaction between the $-\text{COOH}$ functional group present in BB dye and TiO_2 molecules [40]. Purushothamreddy et al. employed prickly pear fruit as a source of natural dye, successfully extracting betacyanin pigment with an absorbance peak at 543 nm. The attachment of dye molecules to the TiO_2 surface was attributed to the presence of hydroxyl and carbonyl groups in the prickly pear extract, leading to a PCE of 0.56% [39]. Additionally, various other natural dyes such as violet flower [135], cockscomb [136], beetroot [137], ivy gourd [138], gardenia yellow [139], grapes [140], golden trumpet [141], and capsicum fruit [142] have been studied.

2.5.3 Carotenoid

Carotenoids, comprising eight isoprenoid units, are penetrative compounds in nature, significantly illustrated in **Fig. 9d**. These compounds are classified into two distinct classes determined the presence of oxygen derivatives: xanthophylls, containing oxygen, and carotenes, which consist solely of hydrocarbons, devoid of oxygen. Particularly, various carotenoids (α -carotene, β -carotene, γ -carotene, and β -cryptoxanthin) possess the shared

characteristic of the β -ionone ring [143]. Within this group, beta-carotene demonstrates noteworthy features, absorbing light within the 400 to 600 nm wavelength range. It also shows impressive photoconductivity in dark ($8.2 \times 10^{-4} \Omega \cdot \text{m}^{-1}$) and illuminated conditions ($28.3 \times 10^{-4} \Omega \cdot \text{m}^{-1}$), respectively [144].

A study was conducted by exploring natural dyes like orange, carrot, and tomato, yielding the PCE of 0.02%, 0.009%, and 0.03%, respectively. The best efficiency observed with tomato was attributed to its strong binding with TiO_2 , enhancing electron transfer [145]. Sinha et al. conducted a study on curcumin-based NDSSC, revealing that the stability and elevated electron affinity of the curcumin dye were confirmed by the optical band gap energy. These attributes render the dye highly suitable for light-harvesting applications, as they promote the seamless transfer of electrons from the dye to either the semiconductor or the interface between them [116]. Ruhane et al. explored curcumin as a natural sensitizer source for NDSSCs. They applied two different conditions to curcumin: raw curcumin (without drying) and dry curcumin subsequently soaked in various solvents such as ethanol, methanol, and acetone. In each solvent, the NDSSCs using dry curcumin displayed superior performance. The solvent extract from dry turmeric contained a higher concentration of curcuminoids per unit volume compared to raw turmeric, owing to the absence of water and other compounds [26]. Until now, the cell efficiency of this group reached up to 1.6% [116,146–148].

2.5.4 Flavonoid

As another intriguing pigment, flavonoids compose a diverse group of natural dyes with a distinctive carbon structure known as the phenylbenzopyran functionality ($\text{C}_6\text{--C}_3\text{--C}_6$), as shown in **Fig. 9e** [149], featuring two phenyl rings linked by three carbon bridges and

creating a third ring. The vibrant colors exhibited by flavonoids stem from variations in the oxidation degree of the phenyl rings (C-ring) [150]. When adsorbed onto the mesoporous TiO₂ surface, flavonoids display rapid adsorption kinetics, displacing OH counter ions from Ti sites through proton donation [44].

A study showed that the flavonoids extract from *Punica granatum* peel exhibit noteworthy photovoltaic performance, boasting a $J_{sc} = 9.4 \text{ mA/cm}^2$, a $V_{oc} = 0.35 \text{ V}$, an FF = 38%, and an impressive cell efficiency of 1.26% [151]. Narayan et al. extracted into the study of flavonoid pigments, specifically focusing on Sulfur cosmos. These flower dyes, soluble in methanol, yield a luminous deep yellow hue. Their absorption spectrum spans a wide range from 300 to 630 nm, with a peak at 442 nm. The primary coloring agent in *Cosmos sulphureus* is pentahydroxy chalcone hexoxide, a flavonoid generically referred to as coreopsin, which belongs to the anti-chlorine class. This flavonoid achieves an efficiency of 0.54% [152]. Zhou et al. explored flavonoids sourced from Tangerine peel, characterized by an absorption range of 400-500 nm. Photovoltaic assessments reveal an PCE of 0.28% [135]. In a separate endeavor, Singh et al. harnessed *Tacoma stans* dye as a photosensitizer. Through UV-Vis analysis, the dye displayed an absorption spectrum spanning 300-500 nm. Intriguingly, the solvent choice during the dye extraction process impacted its absorption characteristics. Prior to anchoring with TiO₂, the dye dissolved in an ethanol-water mixture solvent exhibited higher absorbance. However, after anchoring with TiO₂, the ethanol solvent-based dye showcased superior absorbance. Remarkably, despite the solvent variations, the energy levels of the two dyes remained consistent. Photovoltaic assessments showed an efficiency of the ethanol solvent-based dye at 0.13%, surpassing that of the mixture solvent-based dye at 0.09% [153].

2.5.5 Chlorophyll

Chlorophyll gives a green color to the plants and algae. Plants use chlorophyll to capture the light required for photosynthesis [154]. Chlorophyll has six different types of pigments that exist in nature. Among these, chlorophyll-a is the most prevalent, succeeded by chlorophyll-b. The molecular structure differs based on these categories, including a chlorin ring centered with magnesium, various side chains, and a hydrocarbon tail (see **Fig. 9c**). Chlorophyll is fat-soluble and insoluble in water due to the lengthy hydrocarbon tail linked to the porphyrin ring [155]. The hydroxyl and carbonyl groups in the chlorophyll can strongly anchor with TiO₂. Additionally, chlorophyll possesses dual absorbance bands, characterized by red and blue bands [41,156,157].

Reference [158] reported the investigation of dyes derived from pandan, spinach, and sawi leaves, revealing that using the maceration method for dye extraction yielded efficiencies of 0.57%, 0.44%, and 0.40%, respectively. Khan et al. combined chlorophyll-a and b pigments extracted from *Mitragyna speciosa* leaves, achieving a PCE of 0.12%. They further incorporated a chemical additive into the extracted pigment to stabilize positive ions, using additives like MgSO₄ in the chlorophyll-based dye solution. This intervention played a crucial role in managing and preventing the quick deterioration of chlorophyll due to the loss of Mg²⁺, resulting in an improved cell efficiency of 0.24% [41]. Taya et al. conducted a study using fresh and dried Spinach oleraceae to design NDSSCs with a natural sensitizer. Extracts from dried Spinach oleraceae exhibited superior performance, yielding a PCE of 0.29%, compared to the fresh counterpart (0.08%) [159]. Zhou and coworkers investigated 20 natural dyes from traditional China medicine, which five of them has chlorophyll pigment. *Perilla*, *Herba artemisiae scopariae*, *Broadleave holyleave*, China

Leropetel, and Petunia were extracted to yield the chlorophyll. Their absorption showed in the range 400-700 nm. The photovoltaic parameters of J_{sc} and V_{oc} are 0.85-1.36 mA/cm² and 0.484-0.616 V [135]. The kelp also can be used as a sensitizer which has chlorophyll pigment. The absorption shows in the range 400-680 nm. Photo-current density and open circuit voltage were reached 0.433 mA/cm² and 0.441 V, respectively, the cell efficiency was obtained 0.12% [142]. Otherwise, the efficiency of the rest in the chlorophyll group is lower than 0.5% [156,157,159,160]. Summarize of the natural dye-based solar cell showed in **Table 1**.

Table 1 The resume of performance from single natural dye.

Year	Plant	Pigment	E	CE	Jsc (mA/cm ²)	Voc (V)	FF (%)	η (%)	Ref.
2023	<i>Chrysanthemum</i> green	ATC	I ⁻ /I ₃ ⁻	Pt	0.99	0.48	0.41	1.229	[161]
2023	<i>Chrysanthemum</i> blue	ATC	I ⁻ /I ₃ ⁻	Pt	0.34	0.47	0.48	0.485	[161]
2023	<i>Chrysanthemum</i> violet	ATC	I ⁻ /I ₃ ⁻	Pt	0.85	0.58	0.44	1.348	[161]
2022	Malabar spinach fruit	ATC	I ⁻ /I ₃ ⁻	C	0.0227	0.487	32.0	0.10	[123]
2022	<i>Rubus idaeus</i>	ATC	LiLH ₂ O	Graphite	0.56	0.338	33.09	0.644	[162]
2021	Barbados flower	ATC	I ⁻ /I ₃ ⁻	Pt	0.74	0.71	48.0	0.25	[157]
2020	Roselle	ATC	I ⁻ /I ₃ ⁻	C	10	0.803	69.0	1.47	[163]
2020	Rice	ATC	I ⁻ /I ₃ ⁻	C	9.8	0.552	66.0	0.95	[163]
2020	Black rice	ATC	I ⁻ /I ₃ ⁻	Pt	6.46	0.614	66.7	2.65	[130]
2019	Allium cepa (Red Onion)	ATC	I ⁻ /I ₃ ⁻	Pt	0.24	0.48	46.63	0.06	[22]
2019	Rose petal	ATC	I ⁻ /I ₃ ⁻	Pt	7.3	0.63	69.0	2.32	[164]
2018	Purple cabbage	ATC	I ⁻ /I ₃ ⁻	C	0.29	0.35	50.0	0.10	[165]
2018	Barberry fruit	ATC	I ⁻ /I ₃ ⁻	Pt	5.47	0.57	64.0	2.01	[121]
2018	Barberry root	ATC	I ⁻ /I ₃ ⁻	Pt	7.46	0.58	54.0	2.35	[121]
2018	Coralberry	ATC	I ⁻ /I ₃ ⁻	C	0.45	0.30	33	0.04	[166]
2018	Red spinach	ATC	I ⁻ /I ₃ ⁻	C	-	-	-	0.051	[167]
2017	Blueberry	ATC	I ⁻ /I ₃ ⁻	C	2.72	0.42	38.0	0.40	[124]
2017	Blackberry	ATC	I ⁻ /I ₃ ⁻	C	11.16	0.47	26.0	1.40	[124]
2017	Cranberry	ATC	I ⁻ /I ₃ ⁻	C	6.78	0.41	42.0	1.20	[124]
2017	Pomegranate fruit	ATC	I ⁻ /I ₃ ⁻	C	12.20	0.39	41.0	2.00	[124]

2017	Dragon fruit	ATC	I ⁻ /I ₃ ⁻	C	0.75	0.437	-	0.81	[125]
2014	Blue pea	ATC	I ⁻ /I ₃ ⁻	Pt	0.00016	0.318	-	0.02	[156]
2014	Melinjo skin	ATC	I ⁻ /I ₃ ⁻	Pt	0.00036	0.424	-	0.04	[156]
2013	Red frangipani	ATC	I ⁻ /I ₃ ⁻	Pt	0.94	0.495	65.0	0.30	[138]
2013	Ixora sp. (Rubiaceae)	ATC	I ⁻ /I ₃ ⁻	Pt	6.26	0.384	44.0	0.96	[168]
2013	Canarium odontophyllum	ATC	I ⁻ /I ₃ ⁻	Pt	2.45	0.385	62.0	0.59	[168]
2013	Red cabbage	ATC	I ⁻ /I ₃ ⁻	Pt	11.2	0.59	43.37	2.90	[131]
2012	Hibiscus	ATC	I ⁻ /I ₃ ⁻	Pt	0.161	0.388	60.0	0.75	[140]
2012	Raspberries	ATC	I ⁻ /I ₃ ⁻	Pt	0.269	0.429	64.8	1.50	[140]
2011	Rhododendron	ATC	I ⁻ /I ₃ ⁻	Pt	1.61	0.585	60.9	0.57	[135]
2011	Lily	ATC	I ⁻ /I ₃ ⁻	Pt	0.51	0.498	66.7	0.17	[135]
2011	Red rose	ATC	I ⁻ /I ₃ ⁻	Pt	0.97	0.595	65.9	0.38	[135]
2011	Chinese rose	ATC	I ⁻ /I ₃ ⁻	Pt	0.90	0.483	61.9	0.27	[135]
2011	Bauhinia	ATC	I ⁻ /I ₃ ⁻	Pt	0.96	0.572	66.0	0.36	[135]
2011	Lithospermum	ATC	I ⁻ /I ₃ ⁻	Pt.	0.14	0.337	58.5	0.03	[135]
2011	Black raspberry	ATC	I ⁻ /I ₃ ⁻	Pt	0.672	0.400	59.0	0.16	[127]
2011	Begonia	ATC	I ⁻ /I ₃ ⁻	Pt	0.63	0.537	72.2	0.24	[135]
2011	Rosella	ATC	I ⁻ /I ₃ ⁻	Pt	0.79	0.428	47.0	0.16	[127]
2011	Black carrot	ATC	I ⁻ /I ₃ ⁻	Pt	1.302	0.400	47.0	0.25	[127]
2006	Black rice	ATC	I ⁻ /I ₃ ⁻	Pt	1.142	0.551	52.0	0.33	[142]
2011	Flowery knotweed	ATC	I ⁻ /I ₃ ⁻	Pt	0.60	0.554	62.7	0.21	[135]
$\text{Co}^{2+/\beta}$ +									
2021	Blood berry	BTL	blend ed, I ⁻ /I ₃ ⁻	Pt	8.10	0.635	40.11	2.06	[40]
2019	Turmeric	BTL	I ⁻ /I ₃ ⁻	C	1.857	0.507	50.4	0.47	[134]
2018	Pokeweed fruit	BTL	I ⁻ /I ₃ ⁻	Pt	8.57	0.608	57.0	2.97	[121]
2018	Pokeweed stalk	BTL	I ⁻ /I ₃ ⁻	Pt	9.08	0.632	53.0	3.04	[121]
2016	Cockscomb	BTL	I ⁻ /I ₃ ⁻	Pt	2.53 X 10 ⁻⁴	0.10	46.7	0.11 X 10 ⁻	[136]
2014	Beetroot	BTL	I ⁻ /I ₃ ⁻	C	0.75	0.60	63.0	0.27	[137]
2013	Ivy gourd	BTL	I ⁻ /I ₃ ⁻	Pt	0.24	0.644	49.0	0.07	[138]
2013	Gardenia yellow	BTL	I ⁻ /I ₃ ⁻	Pt	0.96	0.54	62.0	0.32	[139]
2013	Gardenia blue	BTL	I ⁻ /I ₃ ⁻	Pt	0.53	0.44	69.0	0.16	[139]
2012	Grapes	BTL	I ⁻ /I ₃ ⁻	Pt	0.091	0.340	61.1	0.38	[140]
2011	Red	BTL	I ⁻ /I ₃ ⁻	C	2.344	0.26	74.0	0.45	[169]
	Bougainvillea glabra								
2011	Red Bougainvillea glabra	BTL	I ⁻ /I ₃ ⁻	C	2.291	0.28	76.0	0.48	[169]
2011	Violet Bougainvillea	BTL	I ⁻ /I ₃ ⁻	C	1.860	0.23	71.0	0.31	[169]

2011	Violet	BTL	I ⁻ /I ₃ ⁻	C	1.881	0.25	73.0	0.35	[169]
	Bougainvillea spectabilis								
2011	Violet flower	BTL	I ⁻ /I ₃ ⁻	Pt.	1.02	0.498	64.5	0.33	[135]
2011	Marigold	BTL	I ⁻ /I ₃ ⁻	Pt.	0.51	0.542	83.1	0.23	[135]
2011	Fructus lycii	BTL	I ⁻ /I ₃ ⁻	Pt.	0.53	0.689	46.6	0.17	[135]
2011	Yellow rose	BTL	I ⁻ /I ₃ ⁻	Pt	0.74	0.609	57.1	0.26	[135]
2011	Golden trumpet	BTL	I ⁻ /I ₃ ⁻	Pt	0.878	0.405	54.0	0.40	[141]
2010	Red turnip	BTL	I ⁻ /I ₃ ⁻	Pt	9.5	0.425	37.0	1.70	[139]
2006	Capsicum fruit	BTL	I ⁻ /I ₃ ⁻	Pt	0.225	0.412	63.0	0.06	[142]
2023	<i>Caulerpa lentillifera</i>	CLP	Iodide /PVD F-HFP	Pt	0.52	0.58	0.65	0.20	[42]
2022	Kratom leaves	CLP	I ⁻ /I ₃ ⁻	C	1.80	0.52	28.0	0.26	[41]
2021	Waterleave	CLP	I ⁻ /I ₃ ⁻	Pt	0.65	0.56	49.0	0.18	[157]
2021	Pumpkin leave	CLP	I ⁻ /I ₃ ⁻	Pt	0.63	0.69	46.0	0.20	[157]
2018	Pandan leaves	CLP	I ⁻ /I ₃ ⁻	C	2.96	0.305	0.39	0.35	[160]
2014	Grass leaves	CLP	I ⁻ /I ₃ ⁻	Pt	0.00015	0.287	-	0.01	[156]
2014	Broccoli	CLP	I ⁻ /I ₃ ⁻	Pt	0.00022	0.560	-	0.07	[156]
2013	Arugula	CLP	I ⁻ /I ₃ ⁻	Pt	0.788	0.599	42.0	0.20	[159]
2013	Arugula [Dried]	CLP	I ⁻ /I ₃ ⁻	Pt	0.713	0.594	43.0	0.18	[159]
2013	Parsley	CLP	I ⁻ /I ₃ ⁻	Pt	0.535	0.455	34.0	0.07	[159]
2013	Parsley [Dried]	CLP	I ⁻ /I ₃ ⁻	Pt	0.448	0.553	40.0	0.09	[159]
2013	Dill (Anethum graveolens)	CLP	I ⁻ /I ₃ ⁻	Pt	0.965	0.579	40.0	0.22	[159]
2013	Dill (Anethum graveolens)[Dried]	CLP	I ⁻ /I ₃ ⁻	Pt	0.454	0.562	32.0	0.08	[159]
2013	Green alge	CLP	I ⁻ /I ₃ ⁻	Pt	0.134	0.416	21.0	0.01	[159]
2013	Green alge [Dried]	CLP	I ⁻ /I ₃ ⁻	Pt	0.397	0.559	44.0	0.10	[159]
2011	China Leropetel	CLP	I ⁻ /I ₃ ⁻	Pt	0.84	0.518	62.6	0.27	[135]
2010	Spinach	CLP	I ⁻ /I ₃ ⁻	Pt	0.467	0.550	51.0	0.13	[170]
2006	Kelp	CLP	I ⁻ /I ₃ ⁻	Pt	0.433	0.441	62.0	0.12	[142]
2019	Cassia fistula	FLV	I ⁻ /I ₃ ⁻	Pt	0.51	0.549	-	0.21	[44]
2014	Linn coffee	FLV	I ⁻ /I ₃ ⁻	C	-	-		0.26	[171]
2013	Jathopha curcas	FLV	I ⁻ /I ₃ ⁻	C	0.69	0.054	87.0	0.12	[172]
2011	Tangerine peel	FLV	I ⁻ /I ₃ ⁻	Pt	0.74	0.592	63.1	0.28	[135]
2011	Sulfur cosmos	FLV	I ⁻ /I ₃ ⁻	Pt	1.041	0.447	61.0	0.54	[141]
2010	Punica granatum peel	FLV	I ⁻ /I ₃ ⁻	Pt	9.4	0.350	38.0	1.26	[151]
2022	<i>Curcuma longa</i>	CRT		Graphite	30.67x10 ⁻³	0.238	29.62	2.16	[162]
2020	Tecoma stans flower	CRT	I ⁻ /I ₃ ⁻	Pt	0.790	0.293	46.0	0.13	[153]

2011	Mangosteen pericarp	CRT	I ⁻ /I ₃ ⁻	Pt	2.69	0.686	63.3	1.17	[135]
2018	Orange	CRT	I ⁻ /I ₃ ⁻	Pt	0.37	0.06	58.0	0.02	[145]
2018	Carrots	CRT	I ⁻ /I ₃ ⁻	Pt	0.36	0.04	64.0	0.01	[145]
2018	Tomato	CRT	I ⁻ /I ₃ ⁻	Pt	0.51	0.14	37.0	0.03	[145]
2006	Erythrina	CRT	I ⁻ /I ₃ ⁻	Pt	0.776	0.484	55.0	0.21	[142]
2006	Sulfur cosmos	CRT	I ⁻ /I ₃ ⁻	Pt	0.225	0.412	58	0.05	[142]

Note: ATC: anthocyanin, BTL: betalain, CLP: chlorophyll, FLV: flavonoid, CRT: curcumin.

The previous literature overview leads to the conclusion that there is substantial potential for enhancing the efficiency of NDSSCs, especially in the chlorophyll groups pigment, while concurrently addressing their cost reduction and numerous availability due to the other pigment having a conflict with the “food availability”. *Laurus nobilis L* (bay leaf: BL) and Mediterranean olive leave (OL) were used as the source of chlorophyll and utilized as a natural sensitizer in fabricating NDSSC devices. These leaves are abundant in the Middle East region, posing no conflict with food availability. The focus of this thesis is on identified areas for enhancement with the aim of improving performance, stability, and environmental friendliness of photovoltaic technologies based on natural sensitizer. Our efforts also extend to improving the cost-effectiveness of these photovoltaics.

CHAPTER 3

MATERIALS AND CHARACTERIZATIONS

This chapter describes the detailed experiments such as materials, synthesis, fabrication of NDSSC device, and characterization parameters conducted for this thesis.

3.1 Synthesis of Bay leave-base sensitizer

3.1.1 Materials

The bay leaves (BLs) were collected from a home garden. A fluorine-doped tin oxide (FTO) glass substrate, N3 dye, TiO₂ paste with an anatase phase (T/SP 14451), platinum paste, and an electrolyte (Iodolyte Z-50) were acquired from Solaronix, Switzerland. The indium-doped tin oxide (ITO) substrate was purchased from OPVTech, China. Methanol solvent (A412-1) was purchased from Fisher Chemical, USA, and super glue gel (B09KCGPSPG) was purchased locally from Pattex.

3.1.2 Preparation of Bay leave sensitizer

The BLs were purchased from the market as dry. The chlorophyll content in the BLs are 79.57 mg/100 g DM (dry mass) [173]. The dry BLs were sorted to select only those with a green color. A small amount of alcohol was used to clean the surfaces of the BLs from the dust, which were then allowed to dry in air for 20 min. The dried leaves were ground in a coffee grinder for 15 min to obtain a fine powder. One gram of the powder was dissolved in 22 mL of methanol solution to procure a dye concentration of 4×10^{-5} mol/L using Eq. 23, which is commonly used in natural dye experiments (3 to 10×10^{-5} mol/L), particularly with chlorophyll pigments [157,170,174,175]. The prepared solutions were sonicated for

30 min and then stored for 24 h in dark. They were subsequently filtered through Whatman paper to separate the mixture remnants from the final pigment solution. The filtered (green) solution was stored in dark until use.

$$C = \frac{m}{V} \times \frac{1}{MW} \quad (23)$$

Where C is the BLs concentration, m is the dry mass of BLs powder, V is the volume of solvent, and MW is the molecular weight of chlorophyll (893.51 g/mol). The photographic of dry BLs, powder, and solution as depicted in Figures 11a-c.

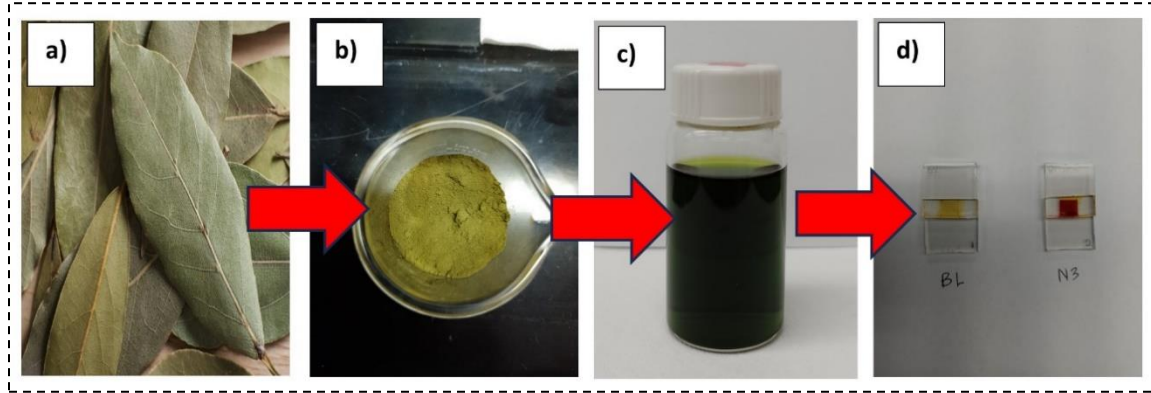


Figure 10 a) dry bay leaves, b) powder, c) solution, d) NDSSC devices of bay leave and N3.

3.1.3 Preparation of N3 dye solution

As a reference, the same concentration of N3 solution was used. The N3 dye (0.629 mg) was dissolved in methanol (22 mL) and mixed using a sonicator for 30 min. The N3 dye was used for comparison with the natural dye.

3.2 Synthesis of Olive leave-base sensitizer

3.2.1 Materials

Olive trees grow widely in Mediterranean countries. In this study, leaves from Tunisian olive trees were collected for use as a sensitizer source for dyes. FTO, anatase TiO_2 paste

(14451), N3 dye, electrolyte (Z-50), and platinum (Pt) paste (Plastisol T) were purchased from Solaronix (Switzerland). The ITO substrates were purchased from OPV-Tech (China). Methanol, isopropanol, and acetone were purchased from Fisher Chemical Company (United States). The glue gel was purchased from Pattex.

3.2.2 Preparation of Olive leaves sensitizer

Maceration was used to extract pigments from olive leaves that followed the method of ref. [44] with a quite modification. The olive leaves were dried under different conditions: OLDI2, dried indoors for two weeks, and OLDS1, dried for one month under sunlight. The



Figure 11 a) fresh olive, b) dry olive leaf under ambient condition for two weeks (OLDI2), c) powder of OL1, d) concentrated extract of OLDI2, e) dry olive leaf under sunlight condition for four weeks (OLDS1), f) powder of OLDS1, and g) concentrated extract of OLDS1.

dark green leaves were selected for OLDI2, while the green-brownish leaves were selected for the OLDS1. The colour criteria and the extracted solutions of olive leaves are shown in **Fig. 11**. Both leaves were separately ground for 15 min in a coffee grinder to obtain a fine powder. Afterward, one gram of each powder was placed in a glass beaker and dissolved in 22 mL of methanol. Each sample was sonicated for 30 min using a sonicator (BRANSON 2800). The mixture was kept for 24 h, covered with aluminum foil, and placed in the dark. Finally, the remnant was filtered through Whatman paper, and the pigment solution was stored in the dark until use. Both bay leaf and olive leaf based NDSSCs devices were fabricated with the same method.

3.3 Photoanode preparation

The conductive layer on the glass substrate (FTO or ITO) was sequentially cleaned with deionized water, acetone, and isopropanol for 10 min. The glass substrates were then dried in an oven for 20 min at 60 °C. The photoanodes were fabricated by coating a thin layer of anatase-TiO₂ paste onto the glass substrate (FTO or ITO) employing the doctor blade technique, with an active area of 0.2 cm². This method involved a blade moving uniformly over the substrate at a specific contact angle and height, ensuring even distribution of the TiO₂ paste and resulting in the formation of a thin film [27]. They were then calcined for 10 min at 200 °C, followed immediately by annealing at 500 °C for 20 min. The photoanodes were cooled and soaked in different dyes for 48 h.

3.4 Counter electrode preparation

The subsequent step involved the fabrication of the counter electrode, where Pt paste was utilized. Similar to the process used for the photoanode, Pt paste was tape-cast onto FTO

and ITO substrates, each with an active area of 0.2 cm². These Pt-deposited substrates underwent annealing at 200°C for 10 minutes, followed by immediate annealing at 500°C for 20 minutes.

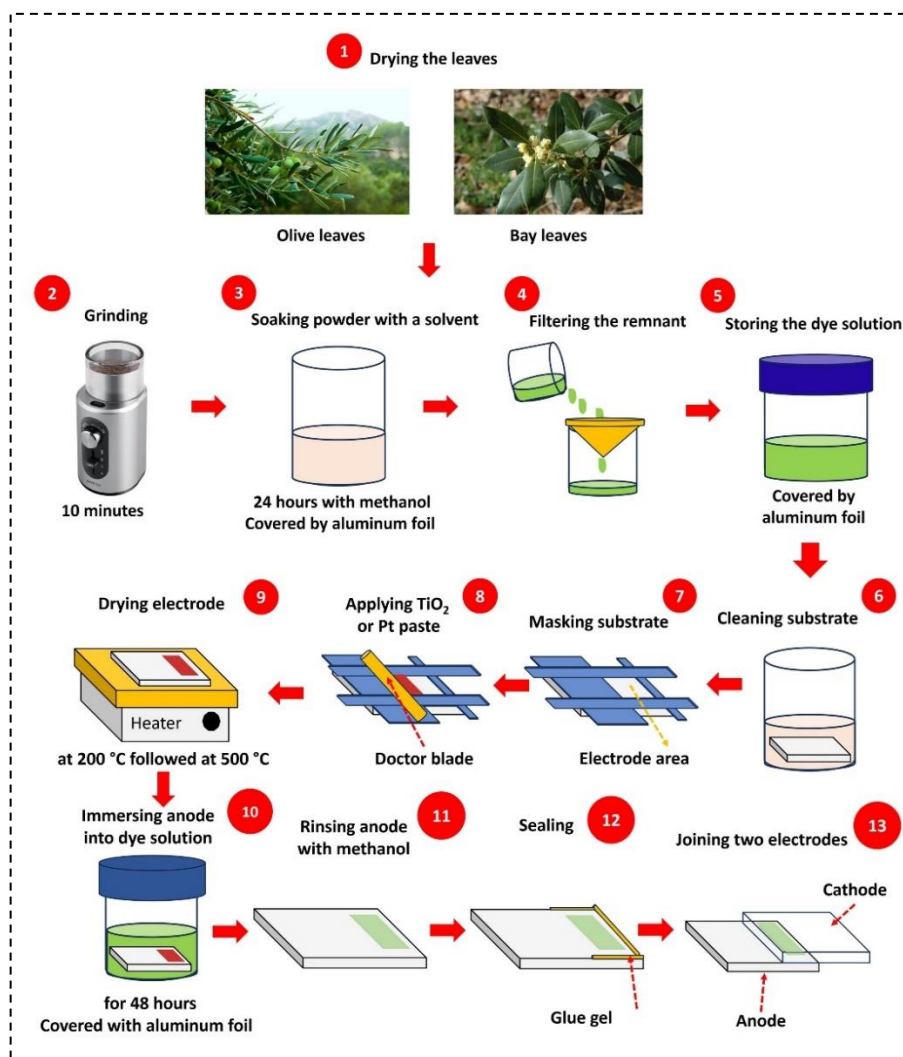


Figure 12 Schematic diagram for NDSSCs fabrication.

3.5 Cells Fabrication

After 48 h, the immersed photoanode was taken out of the beaker glass and rinsed with methanol solvent to remove un-adsorbed dye. Subsequently, a small amount of glue gel

was placed slightly away from the active area on the three edges of the anode. The cathode was then flipped and attached to the anode. Pressure was avoided to prevent the spread of the glue and to overcome the active area of the cell. The iodide/triiodide solution was slowly dropped between the anode and cathode. The cell was left for 3–5 minutes to allow the electrolyte solution to diffuse into the volume between the anode and cathode. The schematic diagram of the NDSSC fabrication is depicted in **Fig. 12** and the photographic of olive-based NDSSC devices were shown in **Fig. 13**.

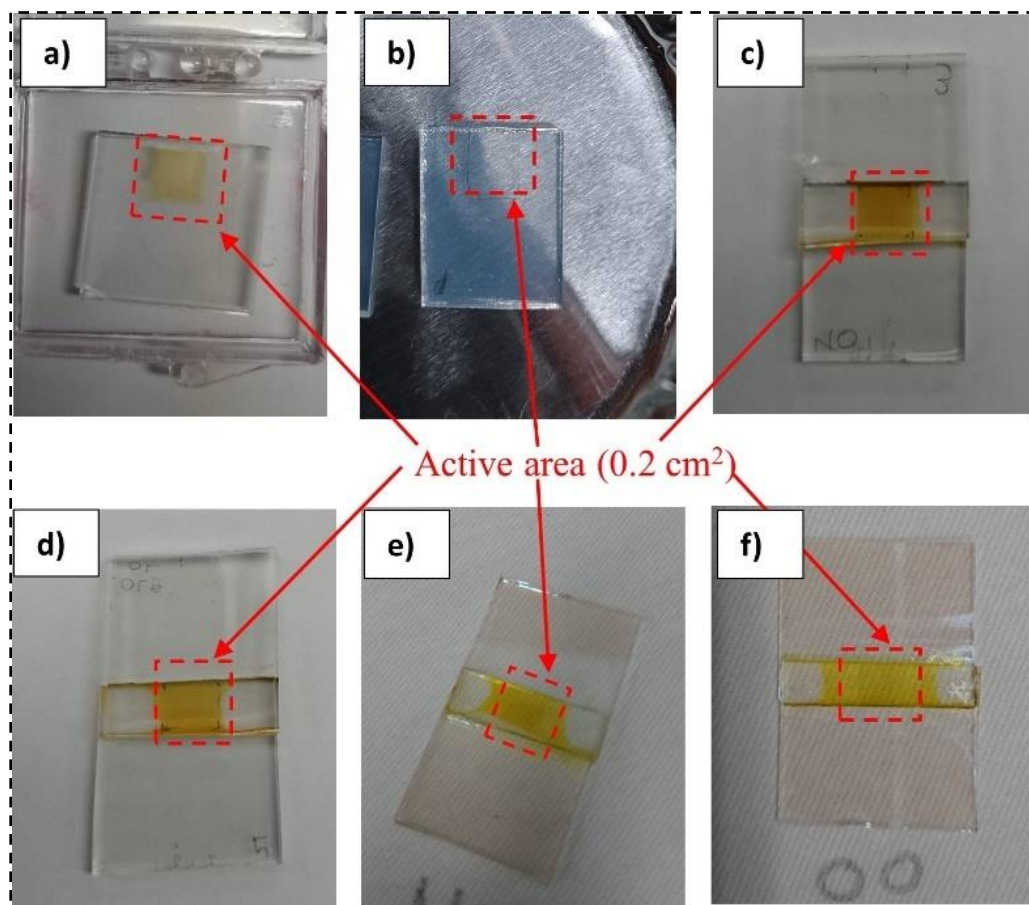


Figure 13 a) photoanode, b) counter electrode, NDSSC device of c) OLDI2 with FTO, d) of OLDS1 with FTO, e) OLDI2 with ITO, d) OLDS1 with ITO substrates. Figure 13b is very transparent so it will be quite difficult to see the active area.

3.6 Characterizations of NDSSC

3.6.1 Optical characterizations

The UV-Vis spectrophotometer double beam Jasco V-670 (Photovoltaic Laboratory I, IRC-REPS, KFUPM) was utilized to characterize the optical properties of the dye solution, TiO₂/TCO and dye/TiO₂/TCO. The absorption of the samples were examined in the range of 200-800 nm wavelength.

The functional group of the dye was characterized in the wavenumber range of 400-4000 cm⁻¹ employing Fourier Transform Infrared (FT-IR) spectroscopy (Model: NICOLET 6700) available at Laser Group, Physics, KFUPM. The spectra were analyzed using a reference book and published article that suited their functional groups.

3.6.2 I-V characterizations

To evaluate the photovoltaic (PV) performance of the fabricated NDSSCs devices with different substrates (FTO and ITO), an I-V solar simulator (IV-5, PV Measurement Ltd. USA) was utilized delivering 100 mW/cm², equipped with a Keithley 2400 SCS source digital meter and a silicon reference cell. **Eqs. 54** and **55** were applied to determine the parameters of the NDSSCs:

$$FF = \frac{P_{max}}{J_{sc} \cdot V_{oc}} \quad (54)$$

$$\eta(\%) = \frac{V_{oc} \cdot J_{sc} \cdot FF}{P_{in}} \times 100\% \quad (55)$$

The key performance parameters of our study are defined as follows: J_{sc} represents the short-circuit current density (mA/cm²), V_{oc} stands for the open-circuit voltage (V), P_{max} denotes the maximum power density (mW/cm²), P_{in} represents the induced/source power

(mW/cm^2), FF is the fill factor (%) calculated as the area under the square from the J-V curve, and η signifies the photocurrent conversion efficiency (PCE) (%) of the fabricated NDSSC. The visual representation of the experimental setup and the I-V measurement of the NDSSC devices are shown in **Fig. 14**.

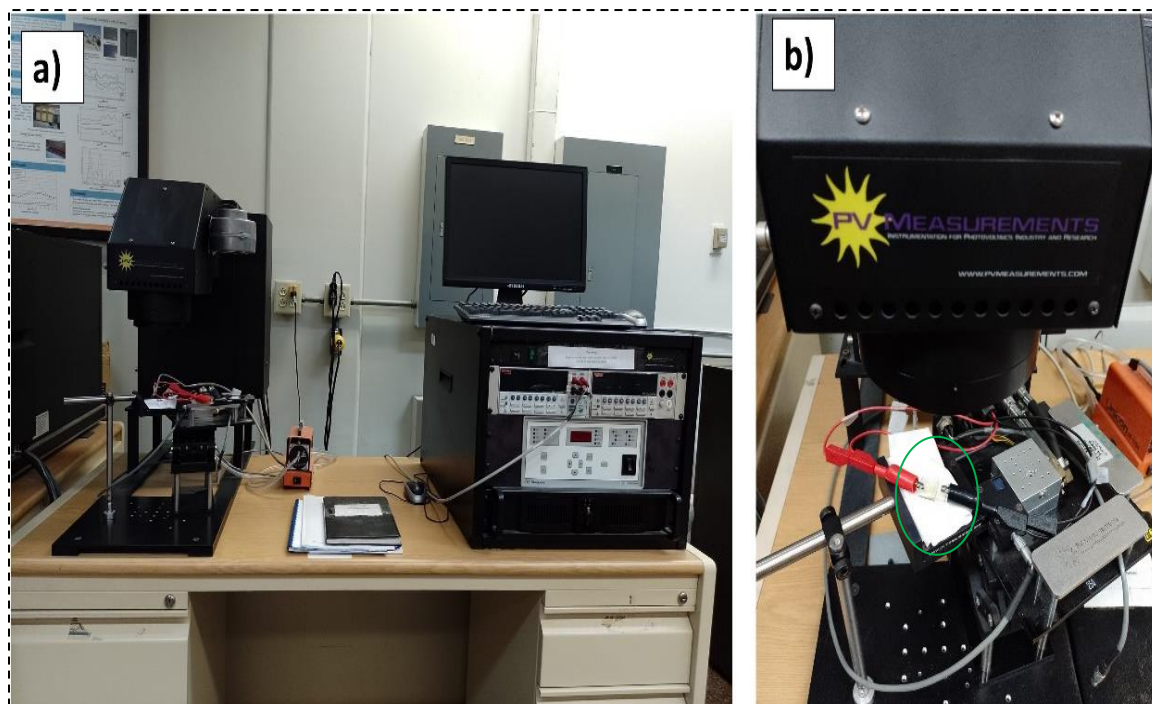


Figure 14 a) Complete set of I-V solar simulator machine (Model# IV-5, PV Measurement Ltd. USA), b) Measurement of the NDSSC device. The device was connected to two connections (red and black cables) inside the green circular sign.

3.6.3 Electrochemical characterizations

The Electrochemical Impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV) techniques were employed to study the electrochemical characteristics. The multichannel Potentiostat from Biologic Instruments, VMP3, was employed to measure the energy levels of the dye solution. The reaction between the electrolyte and dye is examined to study the

kinetic of reduction and oxidation reactions of the dye. Various cycles were employed to assess their stability. The energy levels of the dye's LUMO (E_{LUMO}) and HOMO (E_{HOMO}) were calculated using **Eqs. 56 and 57** [176]. The E_{red} corresponds to the reduction potential, E_{ox} corresponds to the oxidation potential, and the value of -4.4 eV corresponds to a known reference value of the supporting electrolyte (energy level of I^-/I^{3-} is -4.9 eV [177] and its standard potential redox is 0.5 V vs NHE (normal hydrogen electrode) [178].

$$E_{LUMO} = \left[-4.9 - \left(E_{red} - E_{\frac{1}{2}}(iodide) \right) \right] eV \quad (56.a)$$

$$E_{LUMO} = -(E_{red} + 4.4) eV \quad (56.b)$$

$$E_{HOMO} = \left[-4.9 - \left(E_{ox} - E_{\frac{1}{2}}(iodide) \right) \right] eV \quad (57.a)$$

$$E_{HOMO} = -(E_{ox} + 4.4) eV \quad (57.b)$$

EIS curves were examined using the same instrument to investigate electron transfer at the interfaces between various layers, such as the dye/semiconducting layer and electrolyte, the counter electrode and electrolyte, as well as electrolyte diffusion itself. Additionally, the chemical capacitance of TiO_2 was examined.

3.6.4 Morphological and elemental characterizations

The morphological structure acts a vital role in anchoring the dye to semiconducting porous layer. Scanning Electron Microscope and Energy Dispersive X-Ray (SEM-EDX) (model: JEOL JSM6610LV) equipment were employed to study the morphological structure of the dye/ TiO_2 films and the elemental compositions within the bulk.

3.6.5 Surface characterizations

For closer look at the interface between the dye (OL or BL) and TiO₂ was studied using XPS using the Thermo-Scientific (Model: ESCALAB 250Xi) system (Al-K α x-rays) with an energy resolution of 0.5 eV. The Advantage v5.932 software was used to deconvolute the spectra. The XPS spectra were calibrated by employing the adventitious C1s peak at a binding energy of 284.8 eV as a reference. All the peaks were fitted with a combined Gaussian-Lorentzian peak shape.

3.6.6 Crystal structure analysis

The crystal structures and crystalline size of TiO₂ films before and after dye adsorption were studied using an X-ray diffractometer Rigaku ULTIMA IV in the 2θ range of 10-90° with a scan rate of 2°/minute, Cu K α radiation at a continuous scanning mode (40 mA, 40 kV, and $\lambda = 0.15418$ nm).

CHAPTER 4

RESULTS AND DISCUSSION

This chapter provides the results, discussions, and the conclusions of this thesis. The results include the absorption spectra analysis, electrochemical, functional groups, morphology structure, crystallite structure, I-V characteristics, and recombination reactions study.

4.1 Fabrication and Characterization of Natural Dye-Sensitized Solar Cells using an Efficient Natural Sensitizer Derived from *Laurus nobilis L* (Bay Leave)

4.1.1 Summary

Herein, a novel natural dye extracted from *Laurus nobilis L* (bay leaf: BL) for application in natural dye-sensitized solar cells (NDSSCs) was studied. The dye was extracted using a maceration method with methanol as the solvent. The NDSSCs fabricated using FTO and ITO as substrates were compared. The extracted natural dye and fabricated NDSSCs were characterized using UV–Vis, FTIR, SEM–EDX, XPS, I-V simulator, and EIS equipment. The bonding of chlorophyll (a component of interest in the extracted dye) to the surface of TiO₂ was confirmed using UV–Vis and FTIR spectroscopy. The absorbance spectrum of the BL dye was broad, and the adherence of the BL dye to the TiO₂ surface was confirmed using UV–Vis spectroscopy. Surface morphology analysis performed using SEM revealed a uniform distribution of the BL dye on the TiO₂ surface. An EDX analysis was performed to confirm the composition of the dye. XPS analysis confirmed the existence of the

chlorophyll pigment to the TiO₂ surface. Upon optimization, the NDSSC fabricated using the BL and FTO substrate achieved a J_{sc} of 0.528 ± 0.0015 mA/cm², V_{oc} of 0.615 ± 0.0012 V, FF of 0.699 ± 0.0016 , and η of $0.227 \pm 0.0007\%$ under one solar illumination. However, the cell with the ITO substrate exhibited a low performance with V_{oc} , J_{sc} , P_{max} , FF , and η values of 0.591 ± 0.0015 V, 0.394 ± 0.0030 mA/cm², 0.16 mW/cm², 0.699 ± 0.0013 , and $0.163 \pm 0.00001\%$, respectively. Furthermore, an EIS analysis was presented to study the charge transport properties of the fabricated NDSSCs. Here, the best-performing FTO-NDSSC with the BL dye demonstrated a recombination resistance (R_2) of 90.8Ω and photoanode–electrolyte interface resistance of 83.2Ω , which is higher than that of the N3-based DSSC. The overall parametric and performance indicators showed that the BL dye is a promising candidate for diverse applications and further investigations.

4.1.2 Absorption spectra

Absorbance spectra were recorded using UV–Vis spectroscopy (see **Figs. 15-17**). The absorbance range of the BL solution was 200–800 nm with broad peaks at approximately 300–500 nm and 600–685 nm. Peaks appeared at 315, 412, 438, 469, and 664 nm, with strongest peak at 315 and 664 nm for the BL dye solution (**Fig. 15**). Notably, peaks for the BL dye adsorbed on the TiO₂-coated FTO substrate were observed at 344 and 670 nm. The absorbance peak at 664 nm represents $n \rightarrow \pi^*$ conjugated molecule transitions. In these transitions, electrons are shifted from a nonbonding electron pair (n) to an antibonding π^* orbital, resulting in a molar absorptivity of less than 2000 and the emergence of a blue band, signifying interactions with the solvent. The presence of the absorbance peak at 315 nm signifies the occurrence of $\pi \rightarrow \pi^*$ conjugated molecule transitions, wherein the electron is transferred from the bonding electron pair (π) to the antibonding (π^*) orbital,

which generally appears at a short wavelength as $\pi \rightarrow \pi^*$ transitions necessitate higher energy than $n \rightarrow \pi^*$ transitions [179]. These spectral regions correspond to chlorophyll pigments, as reported by [41,160,179].

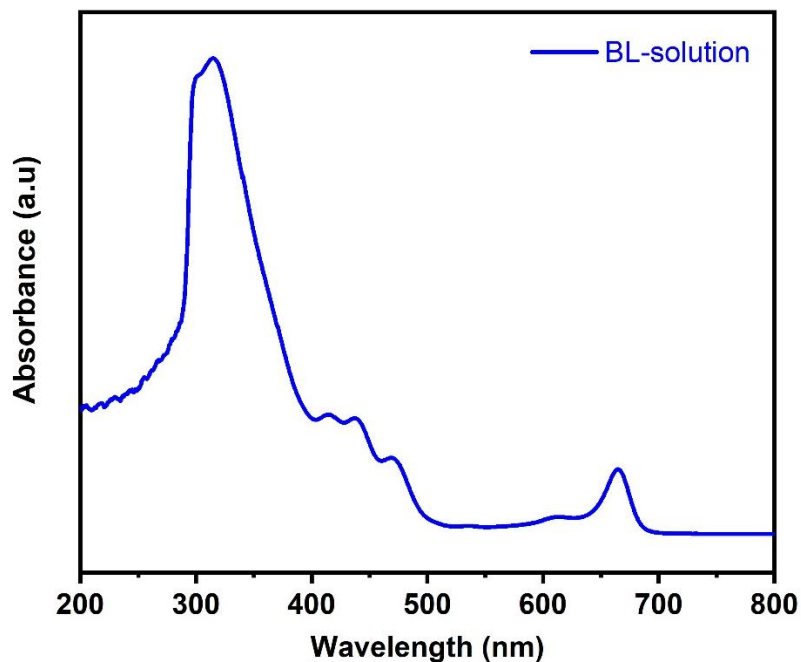


Figure 15 Absorbance spectra of bay leave (BL) dye solution.

A methanol solution was used to dissolve chlorophyll because it has a porphyrin ring that can be dissolved only with an organic solvent, such as methanol [155]. The absorbance of the BL exhibits a red shift after the TiO_2 film adsorbs the chlorophyll pigment, lowering the π^* energy level, indicating the binding between Ti^{4+} and carboxyl groups in the chlorophyll molecules of the BL [8,16,180]. As shown in **Fig. 17**, the absorbance spectrum of the BL-adsorbed TiO_2 film widens (blue line) compared to those of pure TiO_2 (black line) and the BL solution only (blue line). This observation revealed that the dye-adsorbed TiO_2 could harvest a significant amount of light to generate electron-hole pairs and subsequently convert these pairs to a photocurrent. **Fig. 18** reveals the band gap energy

determination is illustrated through the application of the Tauc plot method, which relies on the analysis of absorption data. The energy of the bandgap is measured to be 3.29 eV, which aligns with the point of absorption within the spectrum at 380 nm.

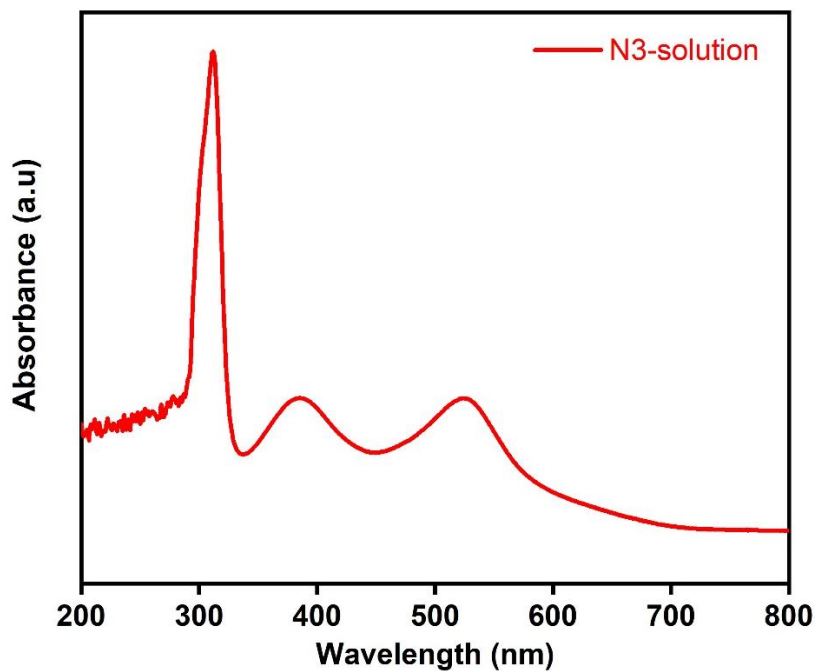


Figure 16 Absorbance spectra of N3 dye solution.

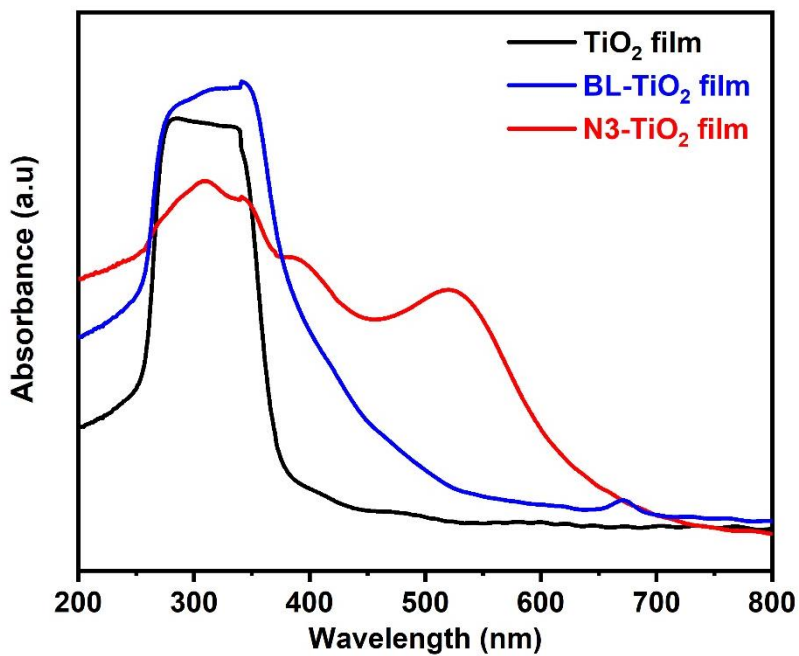


Figure 17 Absorbance spectra of pure TiO_2 , BL- TiO_2 , and N3- TiO_2 films.

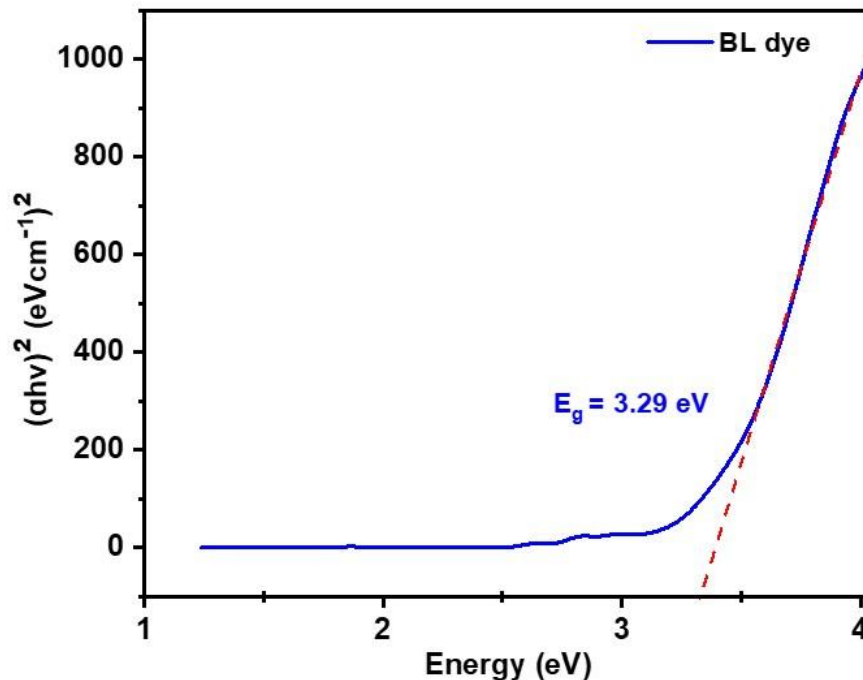


Figure 18 Tauc's plot photon energy determination of BL dye solution.

Additionally, the conventional dye (N3) exhibited a spectrum with three peaks at 312, 380, and 530 nm (**Fig. 16**). The use of methanol resulted in an additional peak at 312 nm, compared with the spectrum reported in [11]. The authors of [11] used ethanol and observed only two peaks at 380 and 525 nm. This was because different organic solvents have different solubilities. The absorbance of the BL dye solution is higher than that of the N3 dye solution at the same concentration (0.04 mM). However, after the dye was adsorbed on the TiO₂ film, the absorbance peak of N3-TiO₂ became broader and stronger than that of BL/TiO₂. This can be attributed to the effective binding between N3 molecules and TiO₂, as reported in reference [16]. This binding significantly influences the absorption of light and the generation of electron–hole pairs.

4.1.3 Cyclic voltammetry (CV) analysis of the BL dye

The dye serves an important role as a light absorber for generating electron–hole pairs. The difference in energy levels between the conduction bands (CBs) of the semiconducting layer and dye and the electrolyte potential affect charge collection. The experiments were conducted at different scan rates between 80 and 140 mV/s in increments of 10 mV/s to study the stability of the dye. For comparison, CV was performed for different cycles at a scan rate of 80 mV/s. An initial potential of +3.0 V was applied to prevent the electrolysis of I^- when the electrode was switched on. Thereafter, the potential was scanned negatively in the forward direction toward -2.5 V to reduce I^- . Pt, glassy carbon and Ag/AgCl were used as the counter, working, and reference electrodes, respectively. The supporting electrolyte for the experiment consisted of an iodide/triiodide redox couple dissolved in acetonitrile.

Figs. 19a-c display the voltammograms of the BL dye at 80 mV/s, different scan rates, and different numbers of cycles, respectively. The curves clearly show forward and reverse ramps with the appearance of two peaks, which indicate the oxidation and reduction reactions between the electrolyte and the dye. Dye stability was observed via CV analysis at different scan rates and cycles. **Fig. 19b** illustrates the stability of the dye extract in the electrolyte (I^-/I_3^-) at different scan rates, in which similar voltammograms are observed. To further confirm the dye stability, CV analysis was conducted for various cycles at 80 mV/s, as shown in **Fig. 19c**. As the number of cycles increased, the oxidation peak shifted to a low potential, and the current density decreased. The oxidation potential (E_{ox}) was +2.7 eV, and the reduction potentials were -0.27 (E^1_{red}) and -1.4 eV (E^2_{red}). The second peak (E^2_{red}) appears at the reduction potential corresponding to chlorophyll-b, as reported by

Bernal et al., who revealed that BLs consist of several chlorophyll-b pigments [181], which have one additional oxygen atom and two fewer hydrogen atoms ($C_{55}H_{70}MgN_4O_6$) compared with chlorophyll-a ($C_{55}H_{72}MgN_4O_5$). Consequently, the reduction of chlorophyll-b occurred in a highly negative potential region. Because chlorophyll-a is dominant, we effectively used the potential in the reduction region of E^I_{red} (-0.27 eV), which is consistent with the band gap energy calculated using the Tauc plot method in the following discussion.

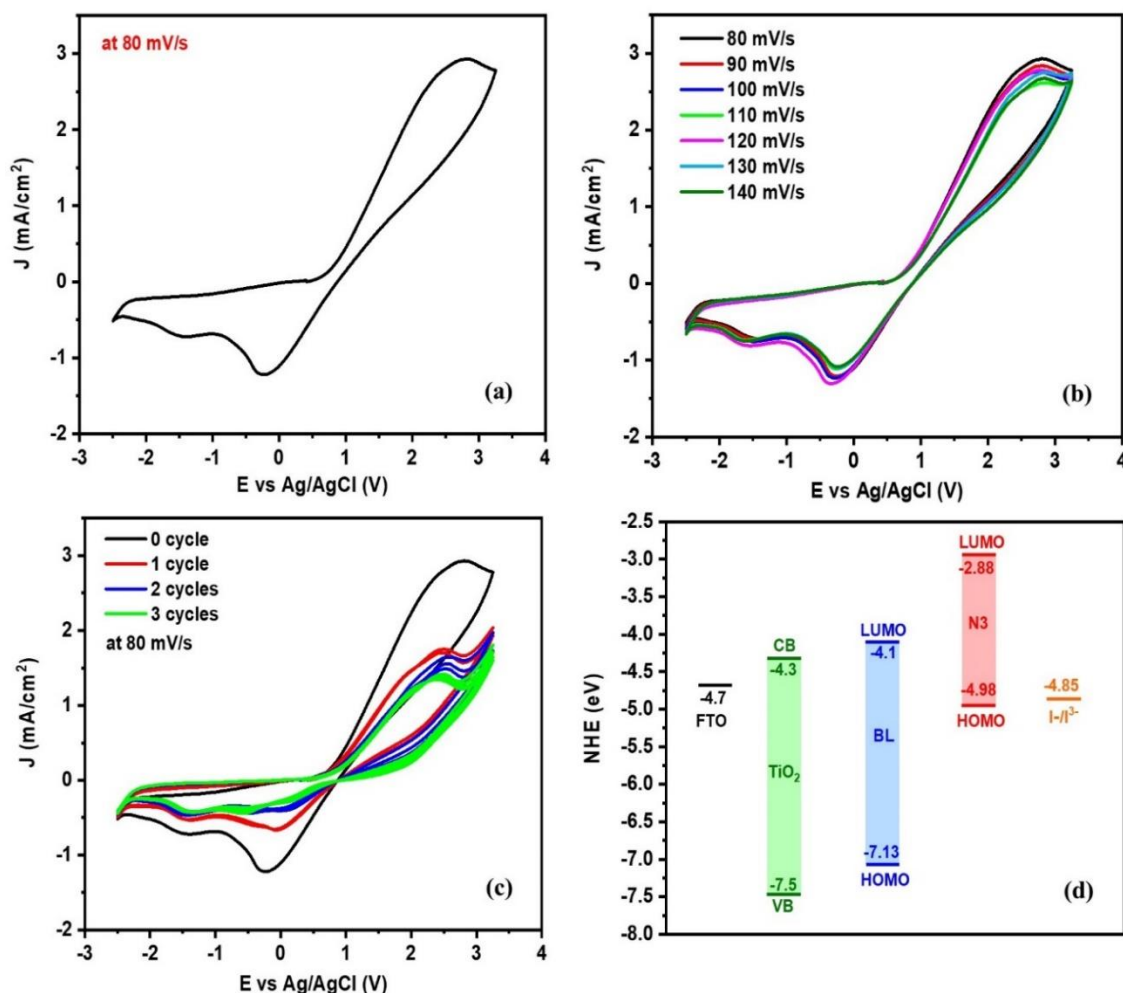


Figure 19 (a) Cyclic voltammograms of the BL dye at 80 mV/s, (b) different scan rates, and (c) different numbers of cycles at 80 mV/s scan rate. (d) Energy level diagram of TiO₂, BL dye, N3, and I⁻/I₃⁻ electrolyte. Values of the CB and valence band (VB) of TiO₂ are adapted from [182].

The calculated HOMO and LUMO values were -7.13 and -4.1 eV, respectively. This resulted in a bandgap energy of 3.03 eV. This value is approximately equivalent to the bandgap energy obtained using the Tauc plot method. The synthetic N3 dye exhibited LUMO and HOMO levels of -2.879 and -4.98 eV, respectively, with a bandgap of 2.011 eV [183]. Because the bandgap for N3 is significantly smaller than that of the BL, more electron-hole pairs will be generated, and more electrons from N3 will be available for collection at the CB of TiO₂. Moreover, N3 binds better with TiO₂ than the BL; therefore, the chances of charge recombination are lower for BL. Furthermore, the HOMO level of the BL is considerably a bit far than the I⁻/I₃⁻ redox level, resulting in fewer opportunities for BL dye regeneration. Conversely, as the HOMO energy level approaches the I⁻/I₃⁻ potential, the amount of oxidized dye regenerated by the electrons increases. This helps increase the efficiency of charge accumulation and photovoltaic conversion in solar cells [38,130]. **Fig. 19d** illustrates the energy levels of each component.

4.1.4 FTIR spectra analysis

The FTIR spectrum presented in **Fig. 20** provides a detailed analysis of the molecular structure of the natural dye solution obtained from BLs. The existence of chlorophyll functional groups, mainly hydroxyl and carbonyl functional groups in BLs was substantiated; these groups regulate the adsorption and attachment to the TiO₂ surface [179]. The C–O vibration peak was observed at 1029 cm⁻¹, and a weak C=C vibration peak was observed at 1114 cm⁻¹. The peak related to the C=N vibration of the porphyrin ring was observed at 1449 cm⁻¹, and C=C and C=O vibrational peaks were observed at 1608 and 1700 cm⁻¹, respectively. C–H₂ and C–H₃ vibrational peaks were observed at 2848 and 2920 cm⁻¹, respectively. The vibrational peak relating to O–H was found at 3309 cm⁻¹, and

the broadest peak was related to the O–H group of the solvent. All peaks were verified based on literature [115,157]. The adherence of these functional groups, particularly the carbonyl (C=O) and hydroxyl (O-H) groups, in the BL extract confirmed that the BL dye could strongly anchor to the TiO₂ surface [41]. Hence, the chlorophyll dye extracted from BLs is suitable as a sensitizer.

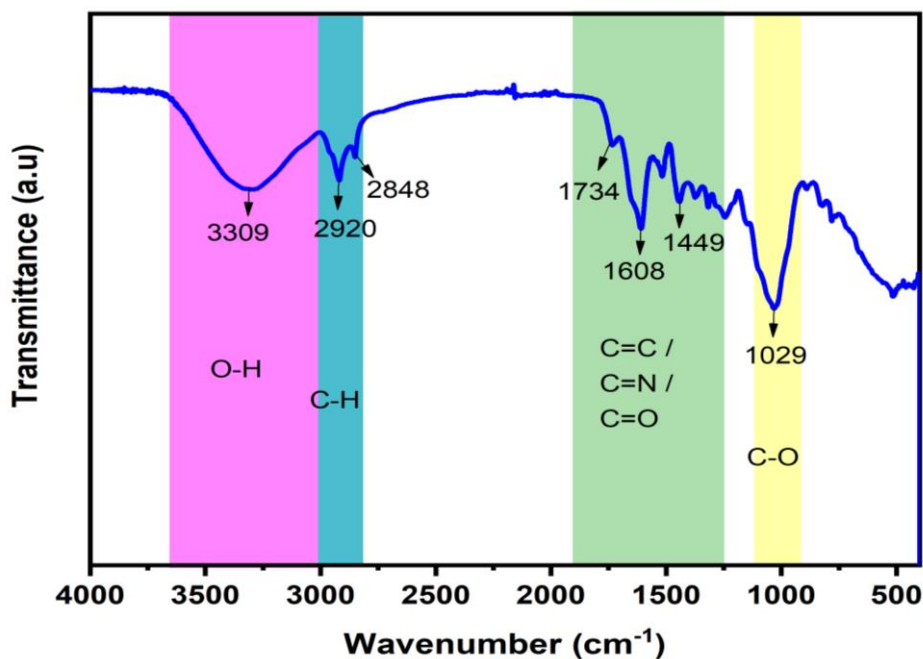


Figure 20 Functional group of natural dye from bay leaves.

4.1.5 Crystal Structure Analysis

Pure TiO₂ and dye-adsorbed TiO₂ crystal structures were examined using XRD in the 2θ range of 10°–80° with a scan rate of 2°/min. The diffraction patterns are shown in **Fig. 21**. The sharp peaks at (25.32°), (37.8°), (48.24°), (51.52°), (54.04°), (65.56°), (70.52°), and (75.24°) correspond to TiO₂ anatase as per the JCPDS No. 96-900-9087 standard card [184]. The peaks at (26.56°), (33.76°), (55.28°), (61.6°), (62.92°), (68.88°), and (78.52°)

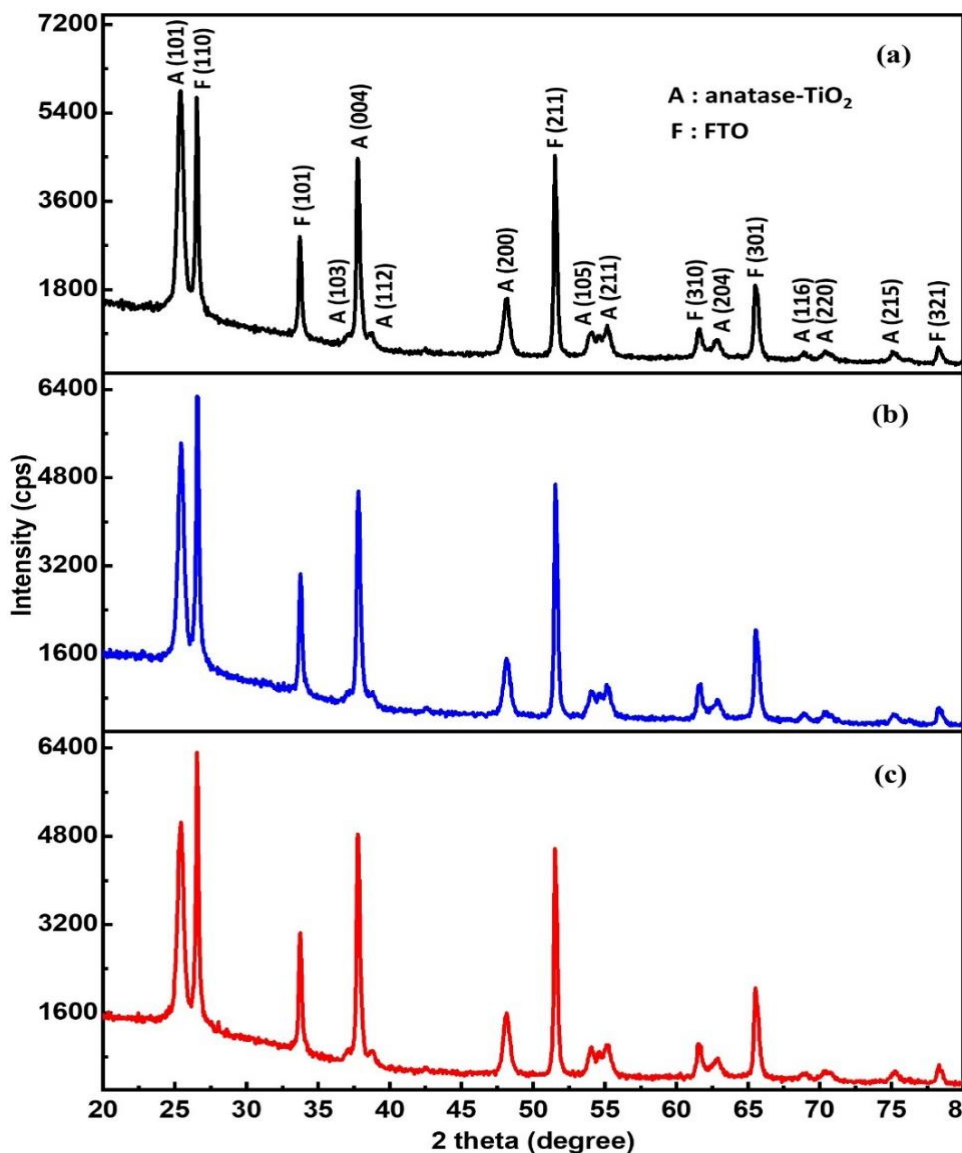


Figure 21 XRD patterns of thin films on FTO substrates: (a) pure TiO_2 , (b) BL/ TiO_2 , and (c) N3- TiO_2 films.

correspond to FTO as per JCPDS No. 041–1445 [185]. All the samples showed the same diffraction pattern, with no change in the 2θ position, which implied that dye adsorbed into TiO_2 did not affect the crystal structure. Additionally, the intensity of the peak at $2\theta = 25.32^\circ$ decreased as the dye was adsorbed onto the TiO_2 surface. This demonstrates the

effects of dye adsorption process on the crystallinity of TiO_2 . The adherence of chlorophyll on the TiO_2 surface decreased the crystallinity, which aligned with the results obtained by Najihah et al. [179].

4.1.6 Surface morphology and elemental compositions analysis

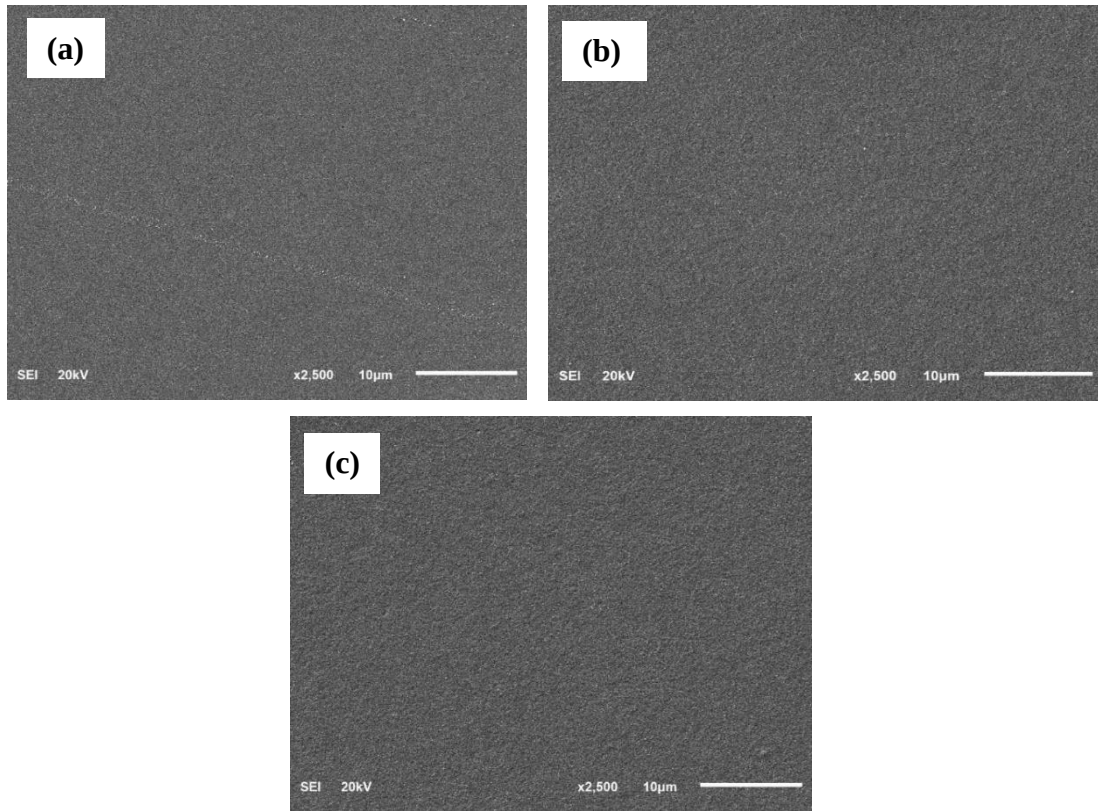


Figure 22 SEM image of the morphological surface of (a) TiO_2 , (b) BL- TiO_2 , and (c) N3- TiO_2 films.

The surface morphologies of the pure TiO_2 and dye-adsorbed TiO_2 films were investigated using SEM **Fig. 22**. It shows the pure TiO_2 film with a uniform and porous surface morphology deposited onto the FTO substrates (see **Fig. 22a**). The surface morphology exhibited interconnected particles and a large contact area. This will improve the electrical conduction inside the particles and the anchoring capacity of the TiO_2 particle connections,

facilitating the conversion of photons into electrons, thereby enhancing the electrical and optical properties of TiO₂ films [186].

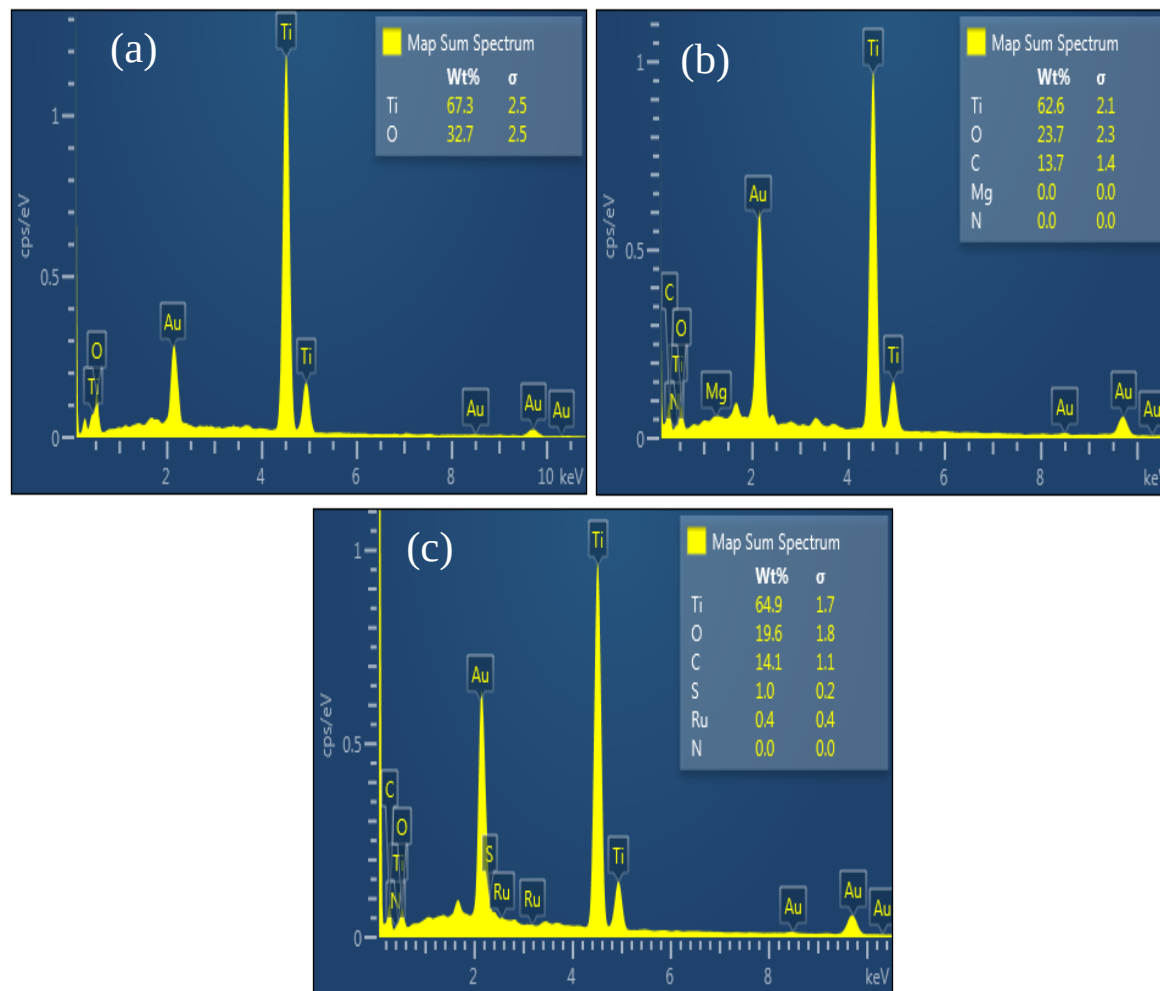


Figure 23 Elemental compositions analysis using EDX of (a) pure TiO₂, (b) BL/TiO₂, and (c) N3-TiO₂ films.

Fig. 22b shows the surface morphology and pores of BL-adsorbed TiO₂, exhibiting a difference compared with those of pure TiO₂; the surface of BL-adsorbed TiO₂ was slightly sharper, and the color of the SEM image was darker than those of pure TiO₂. This was because of the adsorption of BL molecules onto the TiO₂ surface. Hence, the surface was

more compact than that of pure TiO₂. **Fig. 22c** shows the N3 dye adsorbed on TiO₂, revealing the aggregation of the dye molecule on the top of the TiO₂ surface. The N3 molecule adsorbed on TiO₂ renders the film more compact and sharper, as indicated by the darker surface color. This further revealed that numerous N3 molecules were attached to the TiO₂ surface. The higher the degree of attachment of the dye molecule to the TiO₂ surface, the higher the capacity for light harvesting.

EDX spectroscopy was used to determine the elemental compositions. **Fig. 23a** shows the fundamental interpretation of **Fig. 22a** that verifies that only the TiO₂ components are attached to the FTO substrate. The two different peaks belong to Ti (67.3%) and oxygen (32.7%). The presence of Au is due to the coating, which is a requirement for SEM measurements. **Fig. 23b** corresponds to **Fig. 22b**, revealing the BL-TiO₂ composition. The highest-intensity peak corresponds to Ti, followed by those of O, C, Mg, and N, with weight percentages of 62.6, 23.7, and 13.7 for Ti, O, and C, respectively. We could not conduct quantitative analyses of Mg and N because they existed in small quantities at the depth of the micrometer region. However, this can be verified by a mapping analysis, as shown in **Fig. 25**. The results indicated that the dye was successfully adsorbed onto the TiO₂ surface. Similarly, **Fig. 23c** shows the elements corresponding to **Fig. 22c**; Ti, O, C, S, and Ru are detected. All the elements detected are consistent with the composition of the N3 dye [51], which is successfully adsorbed by TiO₂.

Elemental analysis of Ti, O, Mg, N, C, Ru, and S elements was confirmed by EDX-mapping. **Fig. 24** shows the mapping of TiO₂ film, which confirms the adherence of Ti and O without any impurities. Titanium is more dominant than oxygen. **Fig. 25** reveals the Mg, N, C, and O elements of the BL dye, which are distributed uniformly on the TiO₂ film.

These results confirmed the presence of Mg and N, which were not quantified using EDX.

Fig. 26 shows the elemental mapping of N3-TiO₂, which indicates that N3 dye is adsorbed by TiO₂. N3 dye (C₂₆H₁₆N₆O₈RuS₂) is distributed uniformly on the TiO₂ surface.

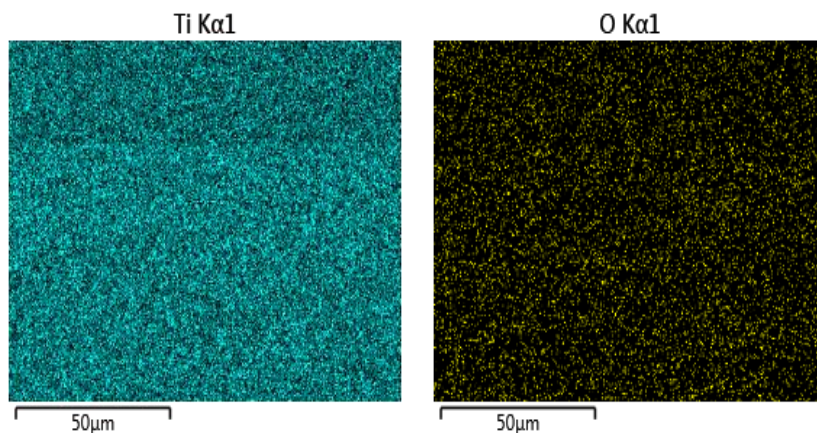


Figure 24 X-ray mapping of pure TiO₂ film.

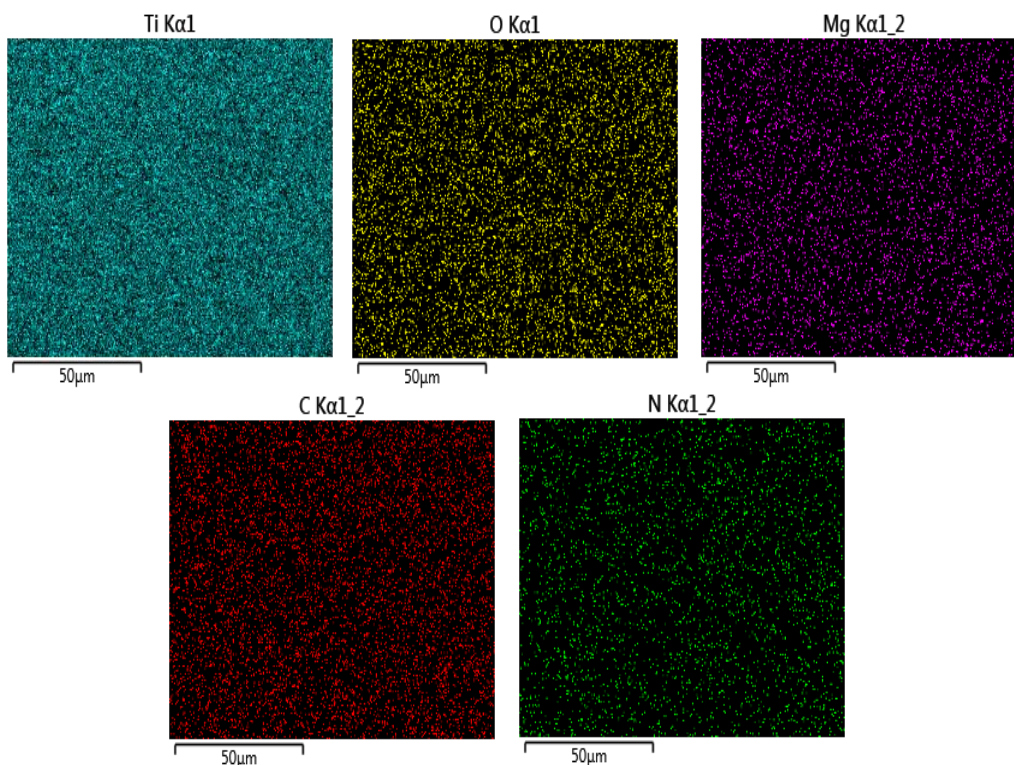


Figure 25 X-ray mapping of BL dye adsorbed TiO₂ film.

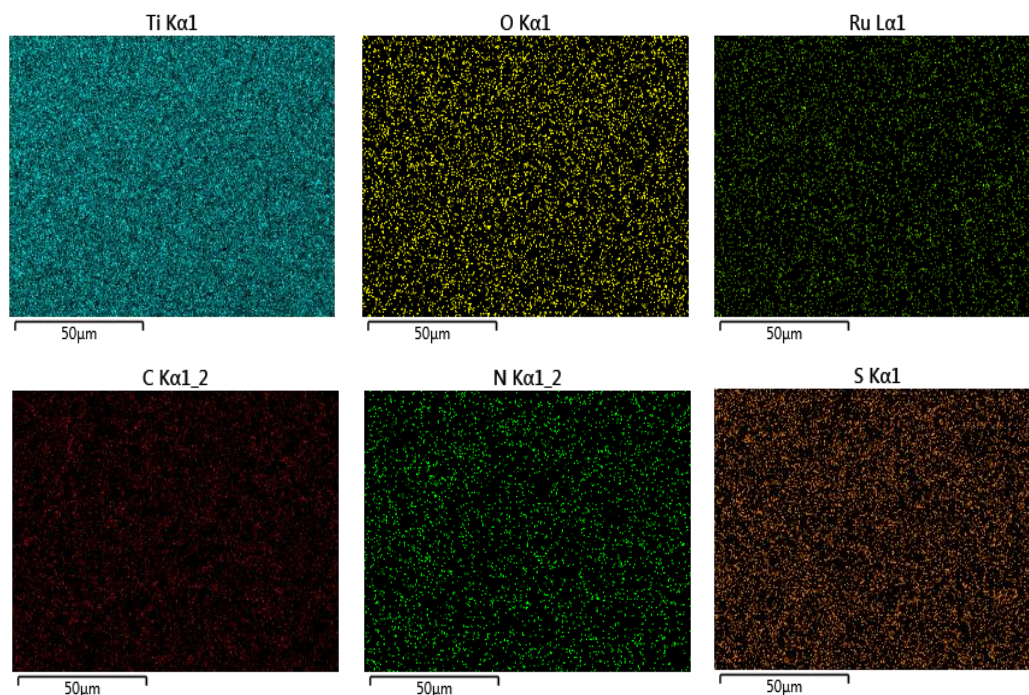


Figure 26 X-ray mapping of N3-TiO₂ film.

4.1.7 X-ray photoelectron spectra analysis

The XPS spectra were analyzed to study the electronic properties of the chemical states of the films. **Fig. 27** shows wide-scan XPS spectra in the binding energy range of 0–700 eV for the three samples. Ti 2p and O 1s core levels were observed in the spectrum of the pure TiO₂ sample. The core levels of Ti 2p, O 1s, C 1s, Mg 2p, N 1s, Ru 3d, and S 2p were detected in the N3-TiO₂ sample spectrum, whereas the Ti 2p, O 1s, C 1s, Mg 2p, and N 1s core levels were observed in the BL-TiO₂ sample spectrum. The adherence of Mg 2p and N 1s peaks in the BL-TiO₂ sample spectrum indicated that the BL dye was adsorbed by TiO₂ [188]. All peaks corresponding to the aforementioned core levels were confirmed using the XPS handbook [189].

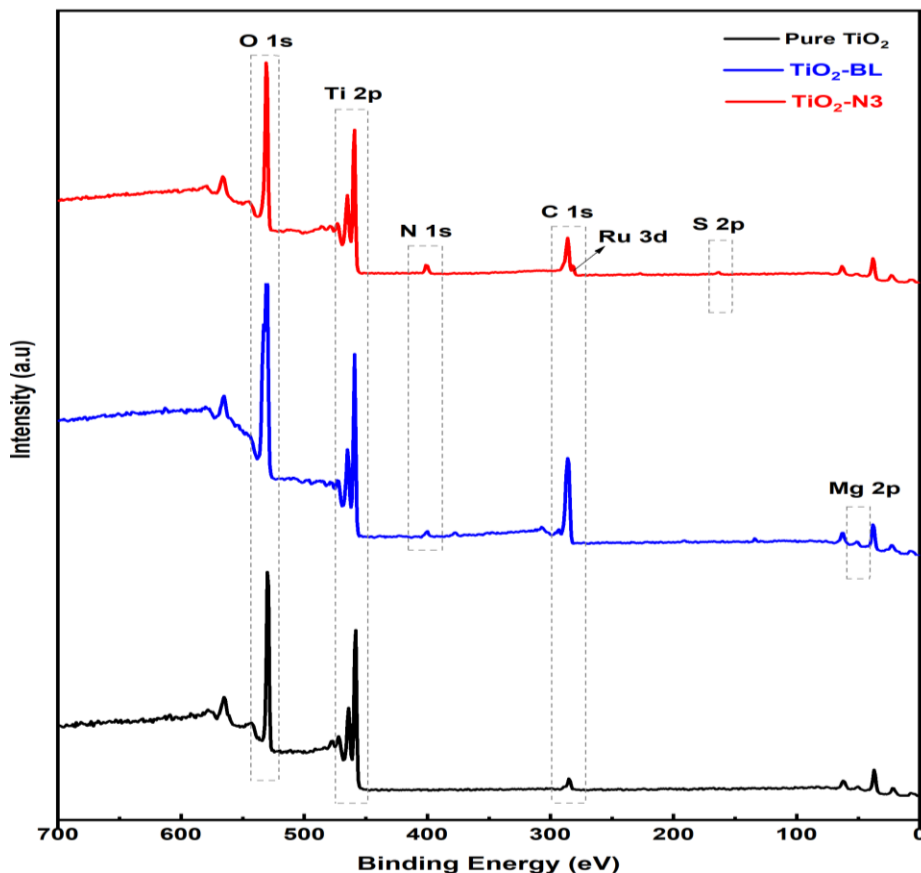


Figure 27 Wide scan of XPS spectra for pure TiO₂, BL/TiO₂, and N3/ TiO₂ in the binding energy range 0 to 700 eV.

Furthermore, all the peaks in each spectrum were compared, as shown in **Fig. 28**. The high-resolution C 1s core levels result in one main peak and two shoulder peaks. However, one peak corresponding to C–C bonding overlapped with that of Ru 3d_{3/2} in the N3-TiO₂ sample spectrum [190]. The characteristics of the Ru 3d core level (**Fig. 28a**) show that the splitting results in two peaks owing to the spin-orbit doubling of the Ru 3d level [190,191]. It shows that the highest carbon-peak intensity is observed for the BL-TiO₂ film because it has a higher carbon content (C₅₅H₇₂MgN₄O₅) than the N3 dye (C₂₆H₁₆N₆O₈RuS₂). **Fig. 28b** reveals the characteristic Ti 2p core-level spectrum, which split into two peaks owing to the spin-orbit doubling of the Ti 2p level [39]. **Fig. 28c** reveals the characteristics of the

O 1s core level spectrum, which shows one main peak and a shoulder peak at a high binding energy on the main-peak side. The decrease in the intensity of the Ti 2p and O 1s core level peaks observed for the N3-TiO₂ and BL-TiO₂ samples is due to other types of chemical bonding that occurs on the TiO₂ surface [192], such as C–C, C–O–C, O–C=O, and RuO₂.

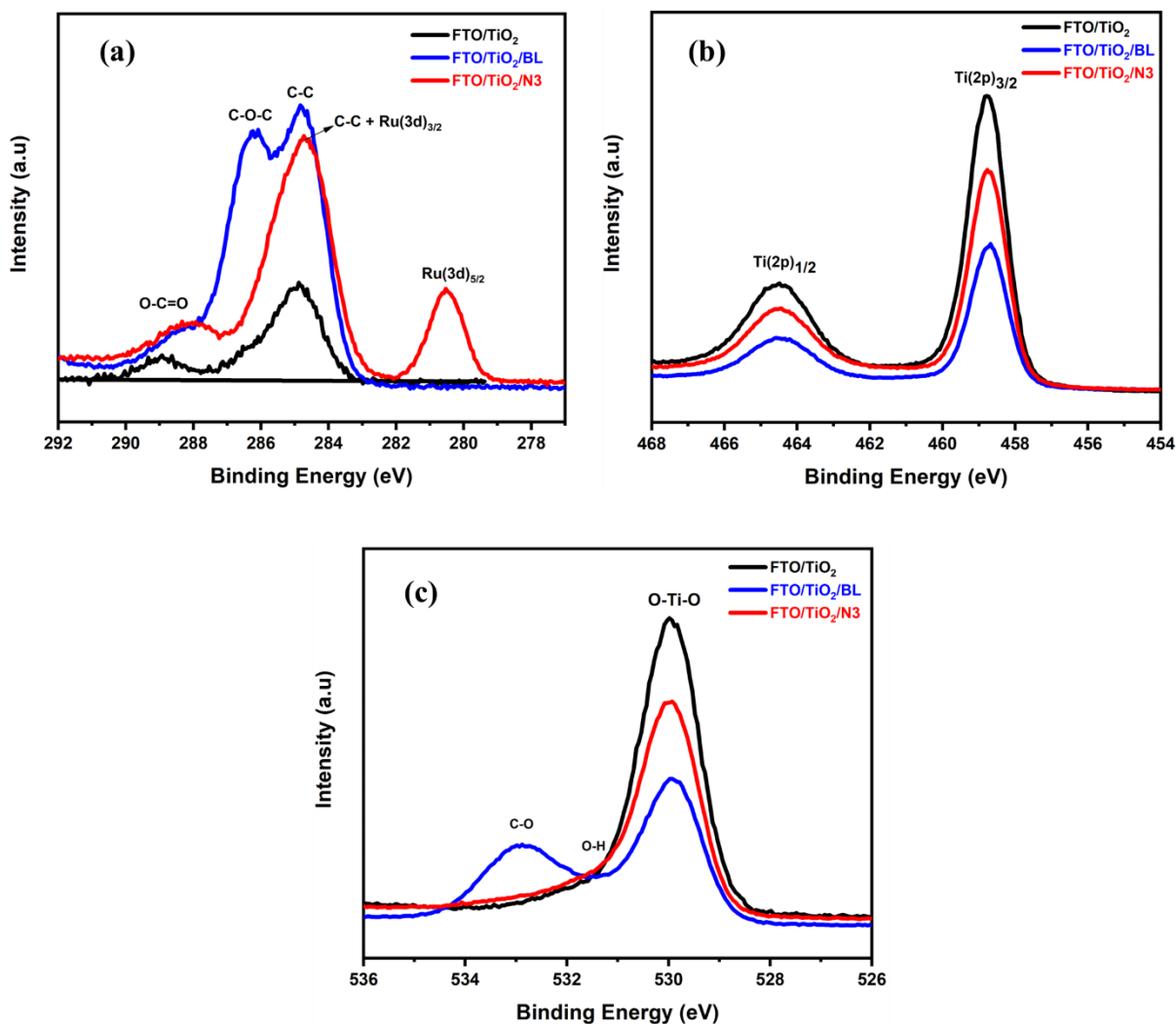


Figure 28 Stacking of XPS spectra of pure-TiO₂, BL/TiO₂, and N3/ TiO₂ in (a) C 1s, (b) Ti 2p, and (c) O 1s core levels.

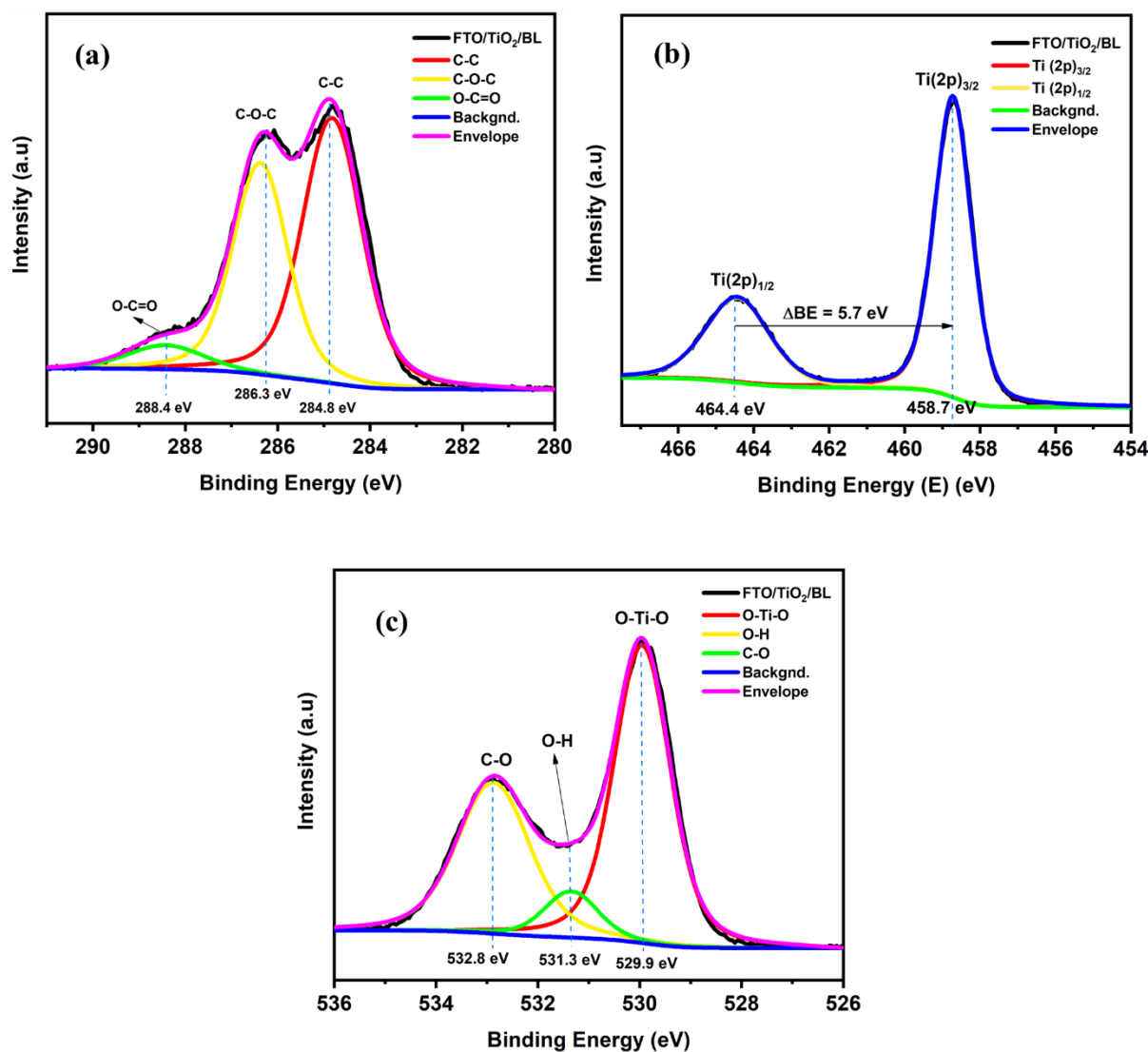


Figure 29 XPS spectra and fitting analysis of FTO-TiO₂-BL in (a) C 1s, (b) Ti 2p, and (c) O 1s core levels.

High-resolution Ti 2p, O 1s, and C 1s spectra were fitted to that of the BL-TiO₂ sample, as shown in **Fig. 29**. **Fig. 29a** shows three types of carbon: C-C at 284.8 eV, C-O-C at 286.3 eV, and O-C=O at 288.4 eV [37]. The peak at 284.8 eV is due to carbon contamination from the atmosphere, whereas the two small peaks are caused by the carbon present in the BL dye as the chlorophyll pigment. These results align with the FTIR spectral analysis results. Based on **Fig. 29b**, the Ti 2p narrow scan spectra are disintegrated into

doublets of Ti 2p_{3/2} and Ti 2p_{1/2}, conforming to binding energies of 458.7 and 464.4 eV, respectively, with the doublet energy separation of 5.7 eV, which suggests the existence of Ti⁴⁺ in the film [188]. Similar values were obtained for the doublet energy separation in the pure TiO₂ and N3-TiO₂ films. The fitted high-resolution O 1s spectra are shown in **Fig. 29c**. The O 1s core level spectra revealed three peaks at binding energies of 532.8, 531.3, and 529.9 eV. These peaks are characteristic of the C–O (532.8 eV) and O–H (531.3 eV) functional groups of chlorophyll on the TiO₂ surface [188,193] and the presence of oxygen (529.9 eV) within the TiO₂-anatase lattice [16].

Moreover, the atomic composition of TiO₂ was determined to be 32.8% Ti and 67.2% O. In contrast, the atomic composition for TiO₂-N3 comprised 19.1% Ti and 41.6% O. The additional peaks corresponding to atomic percentages of 0.1% (Ru), 1.5% (S), 32.9% (C), and 4.8% (N) were observed, further confirming the presence of the N3 dye adsorbed onto TiO₂ [190]. The atomic composition of TiO₂-BL was determined to be 11.6% Ti, 43.3% O, 39.9% C, 1.8% N, and 3.4% Mg. Mg and N are the central atoms of the porphyrin ring in chlorophyll [188].

4.1.8 I-V characteristics

The performance of cells with the BL and different substrates (FTO/ITO) and N3 dye was investigated under standard conditions using one-sun illumination at ambient temperature and a power of 100 W/cm² at an air mass of 1.5G. The *I*–*V* curves were converted to current density–voltage (*J*–*V*) curves by dividing with the active area (0.2 cm²) **Fig. 30**. The PCE of the BL and N3 DSSCs were calculated using **Eq. 5**.

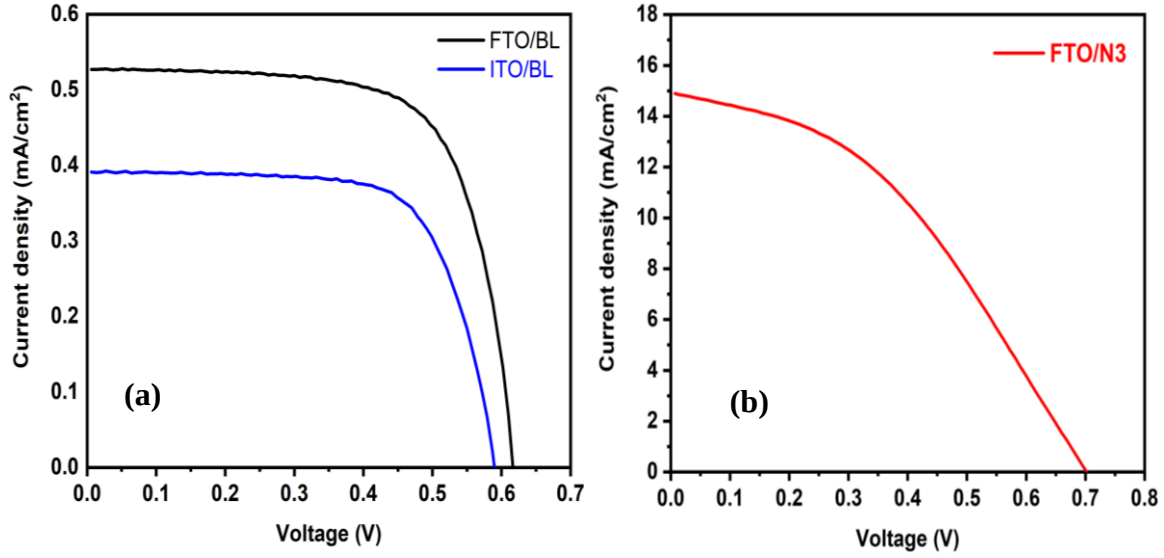


Figure 30 I-V characteristics: (a) FTO/BL and ITO/BL devices, (b) FTO/N₃ device.

Table 2 Photovoltaic parameter of chlorophyll-based dye NDSSC.

Sample	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)	Ref.
BLs (FTO)	0.528 ± 0.0015	0.615 ± 0.0012	0.699 ± 0.0016	0.227 ± 0.0007	This study
BLs (ITO)	0.394 ± 0.0030	0.591 ± 0.0015	0.699 ± 0.0013	0.163 ± 0.00001	This study
N3	14.695 ± 0.2455	0.703 ± 0.0008	0.406 ± 0.0019	4.191 ± 0.0005	This study
Spinach	0.467	0.550	51.0	0.13	[170]
Arugula	0.713	0.594	43.0	0.18	[159]
Parsley	0.448	0.553	40.0	0.09	[159]
Kelp	0.433	0.441	62.0	0.12	[142]
Water leaves	0.65	0.56	49.0	0.18	[157]
Pumpkin leaves	0.63	0.69	46.0	0.20	[157]

The NDSSC fabricated using the FTO/BL dye in methanol exhibited maximum absorption at 315 and 664 nm. Following parameters were observed for the as-fabricated NDSSC: $V_{oc} \approx 0.615 \pm 0.0012$ V, $J_{sc} \approx 0.528 \pm 0.0015$ mA/cm², $P_{max} = 0.227 \pm 0.0007$ mW/cm², and $FF = 0.699 \pm 0.0016$. The overall efficiency was approximately $0.227 \pm 0.0007\%$. In the case with the ITO substrate, $V_{oc} = 0.591 \pm 0.0015$ V, $J_{sc} = 0.394 \pm 0.0030$ mA/cm², $P_{max} = 0.163 \pm 0.0014$ mW/cm², and $FF = 0.699 \pm 0.0013\%$. The overall efficiency was approximately $0.163 \pm 0.00001\%$. **Table 2** summarizes the features of the aforementioned two cell types. Considering the performances of the FTO and ITO substrates, which varied solely in terms of the transparent conducting oxide, FTO exhibited clearly superior characteristics compared to ITO. This can be attributed to the comparatively lower losses observed for the FTO substrate than those for the ITO substrate. After thermal treatment, the resistivity of FTO was more stable than that of ITO [99].

Taya et al. [159] compared the natural dyes of dry arugula and parsley with efficiencies of 0.18% and 0.09% and FF values of 43% and 40%, respectively. Hao et al. [142] obtained an efficiency of 0.12% and an FF of 62% using kelp as the source of chlorophyll. In comparison, Ezike et al. [157] used water leaves and pumpkin leaves and obtained efficiencies of 0.18% and 0.20% and FF values of 49% and 46%, respectively. Based on [142,159,170], BL-based NDSSCs exhibit high V_{oc} , FF , and efficiency values. This is caused by the anchoring of the hydroxyl and carbonyl groups in the BL dye on the TiO₂ surface and the effective regeneration of I^-/I^{3-} electrolytes [135]. Consequently, numerous electrons are collected in the cell. Additionally, compared with the cells considered in [41], BL-based NDSSCs exhibit slightly lower efficiencies and J_{sc} values. However, the V_{oc} and

FF values for the BL-NDSSC are higher than those reported in literature [41], which indicates the superiority of the TiO_2 /BL device compared to the other previously devices. The V_{oc} and FF of the BL-based cell were comparable to those of the DSSC with a commercial dye (N3), although J_{sc} and efficiency values were lower than those of the N3 dye. The high efficiency of the N3 dye was because of its high extinction coefficient [151]. However, in this case, the BL-chlorophyll-based NDSSC anchored with TiO_2 showed a higher efficiency than other previously reported chlorophyll-based NDSSCs. The photovoltaic parameters of several previously reported chlorophyll-based NDSSCs are listed in **Table 2**.

4.1.9 Electrochemical Impedency Spectra (EIS) Analysis

EIS spectra were obtained to investigate the charge transport and recombination properties of the fabricated NDSSCs. **Fig. 31a** shows the Nyquist plot and its equivalent diagram circuit (**Fig. 31c**) as well as the Bode plot (**Fig. 31b**). Two semicircles are observed in the Nyquist plot (**Fig. 31a**). The first and second semicircles correspond to the high-frequency (smaller semicircle) and mid-frequency (larger semicircle) regions, respectively. The small semicircle corresponds to the counter electrode/electrolyte interface. The width corresponds to the charge-transfer resistance R_1 . The large semicircle represents the photoanode/dye/electrolyte interface. The width of this semicircle corresponds to the electron and hole recombination resistance R_2 [29,39]. The R_1 , R_2 , and R_s values were 42.2, 90.8, and 22.9 Ω , respectively, for the FTO/BL cell. For the ITO/BL cell, R_1 , R_2 , and R_s values were 102, 189, and 68.3 Ω , respectively. Consequently, the FTO/BL cell performed better than the ITO/BL cell because the former demonstrated lower charge-transfer and

sheet resistances than the latter and facilitated current flow, thereby enhancing the photoelectrochemical characteristics.

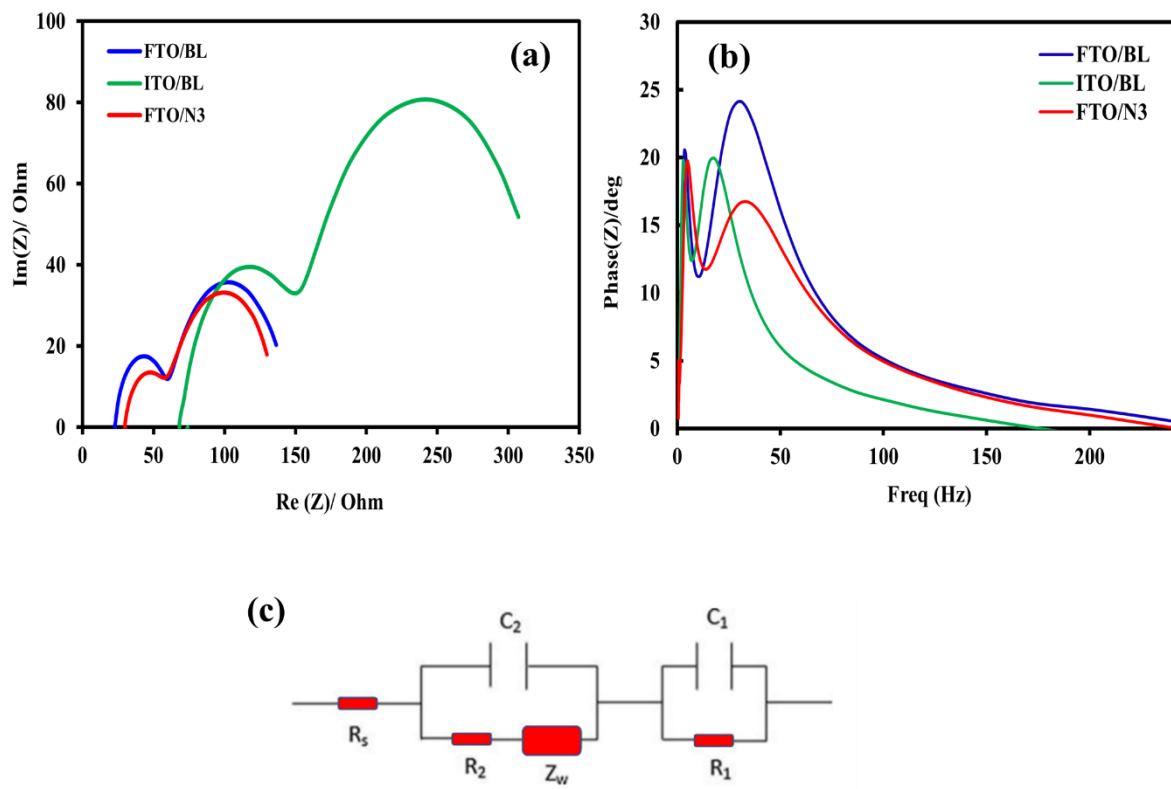


Figure 31. a) Electrochemical impedance spectra for Nyquist plot; b) the Bode phase plot of the DSSC; c) equivalent diagram circuit with Nyquist plot.

The values of R_1 (37.1 Ω) and R_2 (83.2 Ω) for the N3-based reference cell are lower than those for the FTO/BL cell (R_1 and R_2 of 42.2 and 90.8 Ω , respectively), as listed in **Table 2**. The value of R_2 for the BL-DSSC indicates a slightly higher degree of electron transfer at the $\text{TiO}_2/\text{BL}/\text{electrolyte}$ interfaces than that observed for the N3 cell. Electron motion and recombination reactions are shown in **Fig. 32**.

Additionally, a third semicircle is expected to be present at a low-frequency region, representing the disappearance of the diffusion characteristic of the I^- redox couple

electrolytes, as R_2 is higher than the Warburg impedance (Z_w). Z_w is the charge-carrier resistance or impedance of the electrolyte. Additionally, the fabricated FTO-based DSSCs had approximately equal sheet resistances R_s [41], which did not start from zero and belonged to the FTO substrate.

Table 3 Circle fitting of the equivalent circuit of the Nyquist electrochemical impedance spectra and the calculated electron recombination lifetimes.

Cell structure	$R_s (\Omega)$	$R_1 (\Omega)$	$R_2 (\Omega)$	$\tau_e (ms)$
FTO/TiO ₂ /BL/Pt	22.9	42.2	90.8	47.1
ITO/TiO ₂ /BL/Pt	68.3	102	189	55.8
FTO/TiO ₂ /N3/Pt	30.1	37.1	83.2	33.4

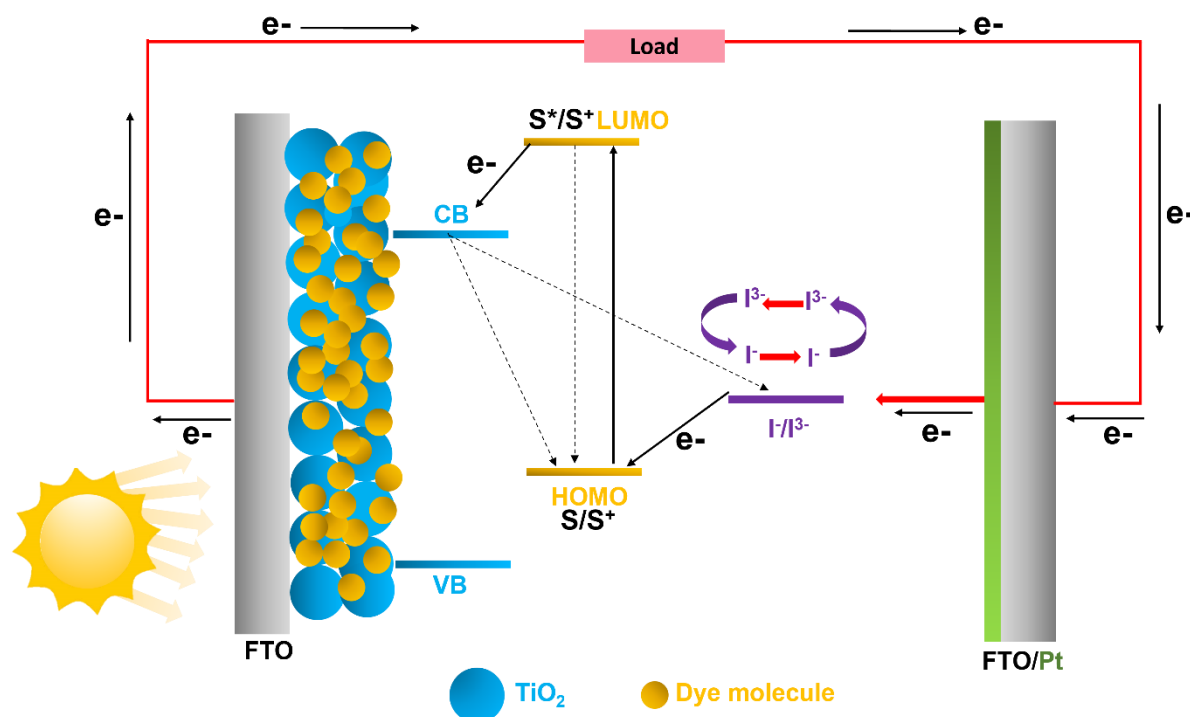


Figure 32 Schematic diagram of electron movement and recombination reactions in NDSSC.

Electron recombination lifetime (τ_e) or electron back transfer can be used to explain the recombination reactions between excited electrons with oxidized dye or between injected electrons (electrons in the CB of TiO₂) with the electrolyte and/or oxidized dye [194], as shown in **Fig. 31a**. This indicates the time required for an electron to travel before recombining with a cation. This time scale is larger than the electron transfer time, which is a few milliseconds [29]. The electron recombination lifetime can be determined from the Bode phase plots (**Fig. 31b**) using **Eq. 25**.

$$\tau_e = \frac{1}{2\pi f_{max}} \quad (25)$$

where f_{max} corresponds to the highest phase peak in the mid-frequency region of the Bode plot. A longer electron recombination time indicates slower recombination. The calculated τ_e indicates that the BL has a longer electron recombination lifetime than the N3 dye, as shown in **Table 3**. Furthermore, chlorophyll extracted from BLs exhibits a longer electron recombination lifetime than other reported natural dyes, such as chlorophyll extracted from *Costus woodsonii* leaves (2 ms) in methanol solvent [179], chlorophyll extracted from pandan leaves (2.52 ms) [160], and betacyanin extracted from prickly fruit (0.12 ms) [39]. Therefore, the chlorophyll extracted from BLs is competitive with other natural dyes.

4.2 Fabrication of Efficient Natural Dye-sensitized Solar Cells using Mediterranean Olive Leaves as Natural Dye sensitizer

4.2.1 Summary

The synthesis of synthetic dyes employed in dye-sensitized solar cells (DSSCs) is often associated with substantial costs and environmental concerns. As a result, there is gaining attention in utilizing natural dyes as sensitizers for DSSCs (NDSSCs). This paper presents a comprehensive investigation of natural dyes extracted from Mediterranean olive leaves using a methanol-based solution, with a particular focus on the impact of different drying times during the dye extraction process on the efficiency of fabricated solar cells. The extracted olive leaf dyes were systematically characterized, encompassing their optical properties analyzed through UV-Vis and FTIR spectroscopy, electrochemical behavior, photovoltaic performance, crystallographic and morphological structures, as well as elemental composition. The research findings unveiled distinctive attributes of the olive leaf dyes, attributable to variations in their charge transfer processes to the band edge of the TiO_2 semiconductor. These outcomes were substantiated through comprehensive analyses involving UV-Vis, FTIR, XRD, and SEM–EDX spectroscopy. Notably, the olive leaf dye subjected to a longer drying time (referred to as OLDS1) exhibited an energy level of the LUMO closer to that of the CB of TiO_2 , facilitating efficient electron transfer. Furthermore, X-ray photoelectron spectroscopy revealed alterations in elemental composition upon dye adsorption onto the TiO_2 surface, with a notable reduction in the intensities of the Ti 2p and O 1s peaks. The OLDS1 dye demonstrated lower charge transfer resistance and recombination rates compared to the shorter drying time for both FTO and ITO substrates-based natural DSSCs (NDSSCs). Importantly, the choice of substrate

material, specifically FTO and ITO, significantly influenced the NDSSC performance. The FTO/TiO₂/OLDS1 configuration exhibited remarkable characteristics, including a high fill factor (FF) of approximately 0.724 ± 0.0019 and an efficiency of $0.306 \pm 0.00003\%$, accompanied by a short-circuit current density of $0.655 \pm 0.0045 \text{ mA/cm}^2$ and an open-circuit voltage of $0.643 \pm 0.0002 \text{ V}$. These results highlight the crucial role of drying time and substrate selection in the fabrication of NDSSCs utilizing Mediterranean olive leaf extracts, with the FTO/TiO₂/OLDS1 configuration emerging as the most promising and efficient combination.

4.2.2 Crystal structure analysis

X-ray diffraction (XRD) analysis was employed to examine the crystalline phases of TiO₂ both before and after the adsorption of OL dyes. All diffraction patterns exhibited identical peak positions across all samples, as depicted in in **Fig. 33**. Specifically, the peaks observed at 2θ values of 25.4° , 37.04° , 37.8° , 38.84° , 48.12° , 54.12° , 55.36° , 62.96° , 68.84° , 70.84° , and 75.2° corresponded to the anatase phase of TiO₂, associated with lattice planes (101), (103), (004), (112), (200), (105), (211), (204), (116), (220), and (215), respectively. These XRD patterns were in excellent agreement with the standard data found in JCPDS card No. 96-900-9087 [184]. The remaining peaks were attributed to FTO and matched the JCPDS card No. 041–1445 [185]. Upon adsorbing chlorophyll pigment from olive leaves, a slight change in peak intensity was observed at $2\theta = 25.44^\circ$. This change indicated an alteration in the crystallinity of the TiO₂ film. The Debye-Scherrer equation was applied to determine the crystallite size (D) of TiO₂ before and after dye adsorption using **Eq.58** [195,196]:

$$D = K \frac{\lambda}{\beta \cos \theta} \quad (58)$$

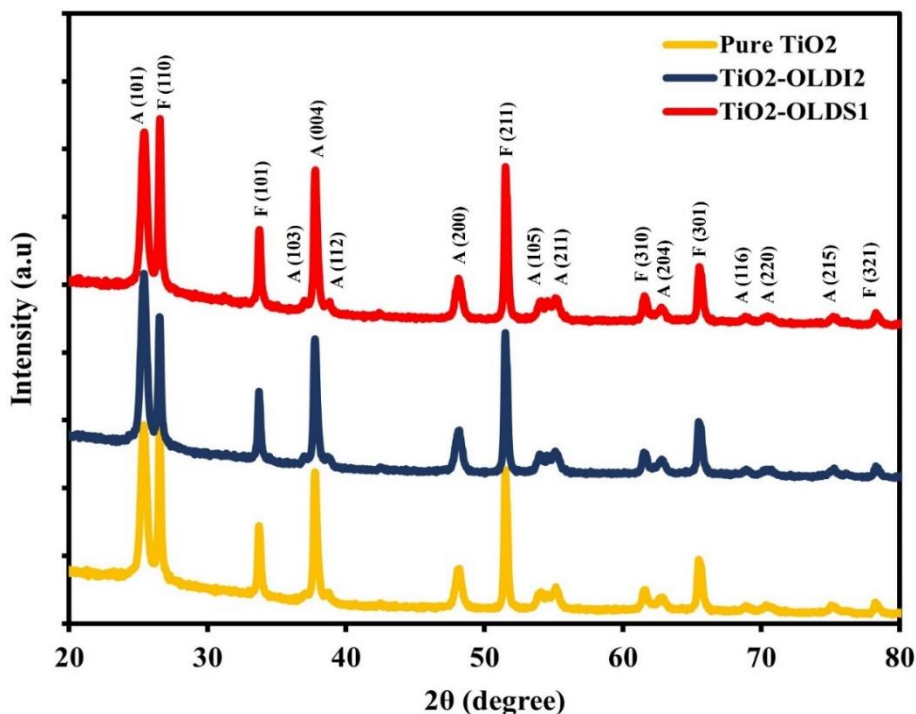


Figure 33 Crystal phase of pure TiO₂ (yellow line), TiO₂-OLDI2 (navy line), and TiO₂-OLDS1 (red line). Letter A and F are attributed to anatase-TiO₂ and FTO substrates, respectively.

In this context, the parameter λ represents the wavelength utilized by the XRD equipment, which corresponds to CuK α radiation (0.15406 nm). K , known as the Scherrer constant, holds a value of 0.9 [195], and β signifies the full width at half maximum (FWHM) of the diffraction peak observed at $2\theta = 25.4^\circ$.

The calculated crystallite sizes for pure TiO₂, TiO₂-OLDI2, and TiO₂-OLDS1 were approximately 28 nm, 28 nm, and 26 nm, respectively. It is noteworthy that the crystallite sizes of pure TiO₂ and TiO₂-OLDI2 were quite similar. However, the discernible intensity variation between them confirms the binding of chlorophyll to the TiO₂ surface [39,179].

Furthermore, the smallest crystallite size observed indicates the strongest adherence of the dye extract to the TiO₂ film surface [179].

4.2.3 Surface morphology and chemical analysis

SEM images provided conclusive evidence of the adherence of chlorophyll on the TiO₂ substrate. As illustrated in **Fig. 34**, the presence of minute particles affirmed that the film possessed a nanoscale structure. The surface of pure TiO₂ displayed a porous nature (**Fig. 34a**), characterized by pores formed through the nucleation and amalgamation of nanoparticles [41]. Following the adsorption of dye, it exhibited dye aggregation on the TiO₂ surface resulting in a smoother and more compact surface [26,39,179] compared to the porous structure of pure TiO₂ (refer to **Figs. 34b** and **34c**). Notably, **Fig. 34c** showcased an even smoother and denser surface compared to **Fig. 34b**. It signifies a higher chlorophyll content from OLDS1 that was adsorbed by the TiO₂ film, thereby enhancing light absorption to facilitate electron generation from the dye molecules.

The observed alteration in the XRD pattern's intensity aligns with the transformation of the TiO₂ surface into a smoother and denser configuration, as evident in **Fig. 34**. This transformation underscores the successful adsorption of chlorophyll pigment onto the TiO₂ substrate, a phenomenon previously reported by Najihah et al. when employing *Costus woodsonii* as a pigment source [179].

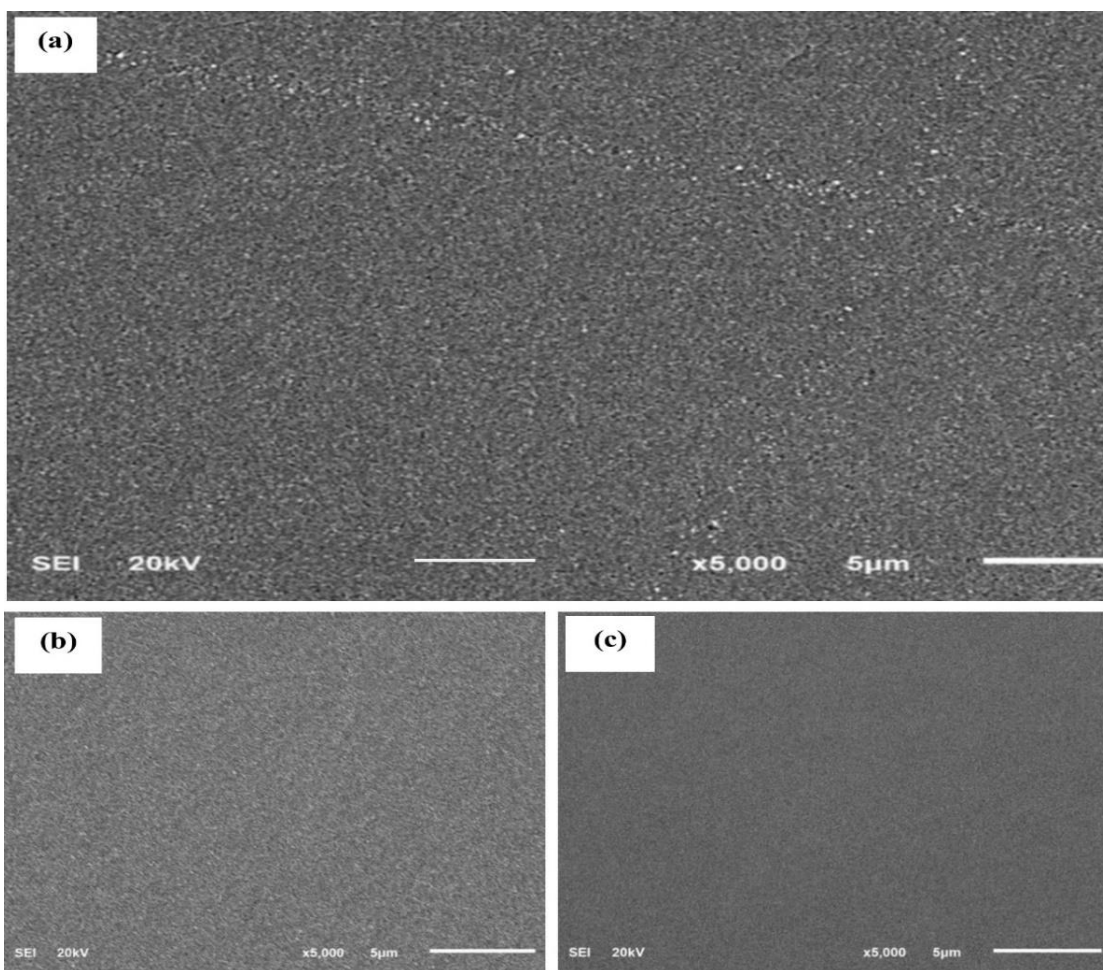


Figure 34 SEM image of (a) pure-TiO₂, (b) OLDI2-TiO₂, (c) OLDS1-TiO₂.

The presence of chlorophyll within the TiO₂-coated substrate was validated using Energy Dispersive X-ray (EDX) Spectroscopy. The corresponding energy spectra can be observed in **Fig. 35** for both pure TiO₂ and the adsorbed dyes. **Fig. 35a**, the spectrum for pure TiO₂ exclusively shows the presence of titanium (Ti) and oxygen (O), with weight percentages of 69.2% and 30.8%, respectively. It's worth noting that the presence of aurum (Au) originates from the conductive film and was utilized to improve the accuracy of SEM-EDX measurements. No impurities contributing to the TiO₂ film were detected, affirming its

high purity. It is also supported by **Fig. 35d**, illustrating the X-ray mapping of the TiO_2 film, highlighting the uniform dispersion of Ti and O across the film

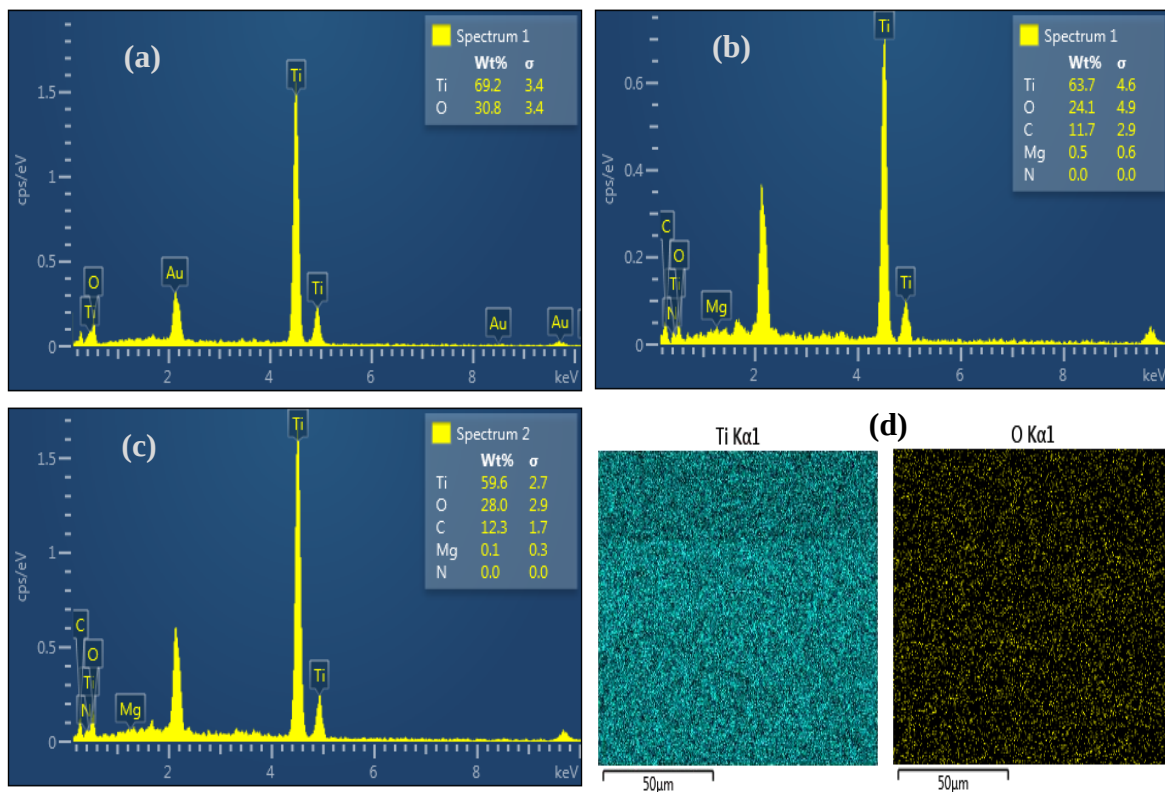


Figure 35 Energy spectrum of (a) pure- TiO_2 , (b) OLDI2- TiO_2 , (c) OLDS1- TiO_2 , and (d) mapping elements of pure- TiO_2 .

Figs. 35b and **35c** reveals the presence of elemental carbon (C), nitrogen (N), and magnesium (Mg), indicating the successful adherence of these elements due to chlorophyll dye molecules. Notably, the reduction in the percentage of oxygen (O) confirms that the TiO_2 surface effectively adsorbed the chlorophyll dye molecule. The weight percentages for the TiO_2 -OLDI2 film were found to be 63.7% Ti, 24.1% O, 11.7% C, 0.5% Mg, along with trace amounts of N. Additionally, the elemental composition of carbon (C) and oxygen

(O) in TiO₂-OLDS1 (**Fig. 35c**) exhibited higher weight percentages compared to TiO₂-OLDI2. This observation indicates that TiO₂-OLDS1 adsorbed a greater number of dye molecules from OLDS1. At a microscopic scale, the nitrogen (N) content in both TiO₂-OLDI2 and TiO₂-OLDS1 samples was minimal. However, the adherence of nitrogen was validated through the X-ray mapping and XPS analysis.

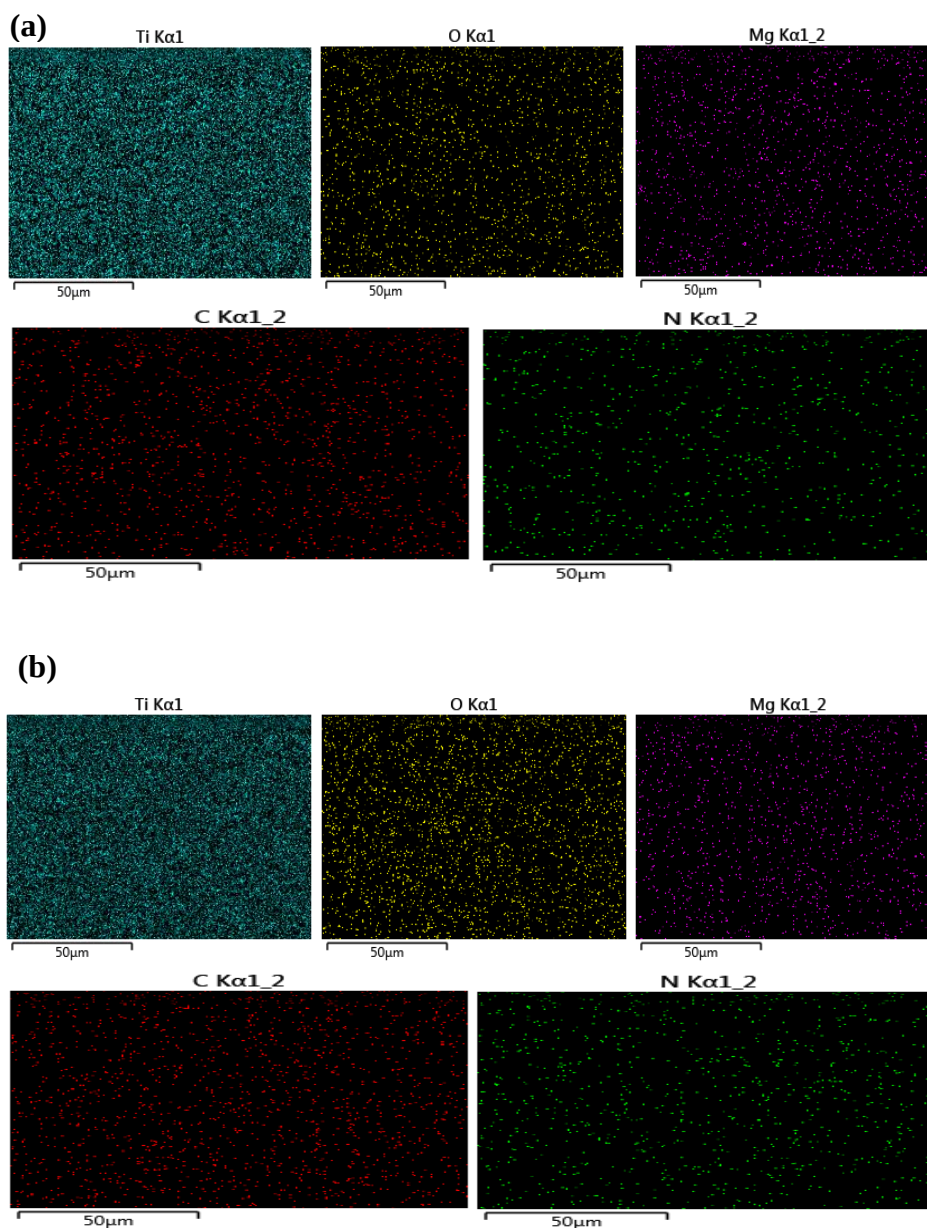


Figure 36 X-ray mapping of dye-absorbed TiO₂ film: a) OLDI2 and b) OLDS1.

X-ray mapping, as depicted in **Fig. 36**, provided definitive evidence of nitrogen (N) adherence. **Fig. 36a** illustrates the successful adsorption of pigment from OLDI2 onto the TiO₂-coated substrate, a crucial step for efficient light harvesting [114]. **Fig. 36b** validated the adhesion of all chlorophyll elements (C, N, Mg, and O) in the TiO₂-OLDS1 film. The EDX spectrum and elemental mapping clearly demonstrated the attachment of OLDI2 and OLDS1 pigments to the TiO₂ surface. The distinct elemental distributions observed in the X-ray mapping results correspond to the light-harvesting capabilities, which are evident in the photovoltaic performance illustrated in **Fig. 44**.

4.2.4 Absorption spectra

In **Fig. 37**, we observe the absorbance spectra of OLDI2 and OLDS1 within the visible light range, spanning approximately 200–800 nm. Four distinct peaks were notable in the case of OLDI2 at 330, 437, 473, and 667 nm, while OLDS1 displayed minor peaks at 410, 437, and 473 nm, alongside a prominent peak at 326 nm and another at 667 nm. The absorbance at 330 nm (OLDI2) and 326 nm (OLDS1) could be attributed to $\pi \rightarrow \pi^*$ transitions, characterized by high-energy transitions. In contrast, the absorption at 667 nm in both cases was ascribed to the $n \rightarrow \pi^*$ transition of conjugated molecules, representing lower-energy transitions [179,197]. These absorption peaks were attributed to the adherence of chlorophyll pigments, corroborating findings in the literature [25,38].

Chlorophyll possesses a porphyrin ring featuring a central Mg atom, a hydrocarbon tail, and various side chains [155,198]. The porphyrin ring exhibits hydrophobic properties, whereas the magnesium ions at its core are hydrophilic [199]. This inherent polarity renders chlorophyll soluble in methanol. Additionally, it's worth noting that OLDI2 exhibited slightly higher absorbance than OLDS1, a difference attributed to the drying time of the

pigment. Enhanced absorption is advantageous as it contributes to the generation of more electrons, thereby potentially increasing cell efficiency.

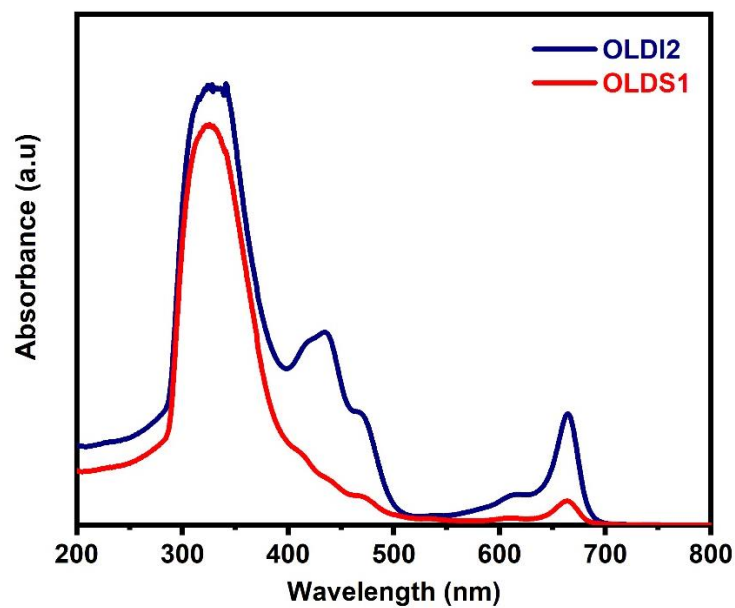


Figure 37 Absorbance spectra for OLDI2 and OLDS1 solution.

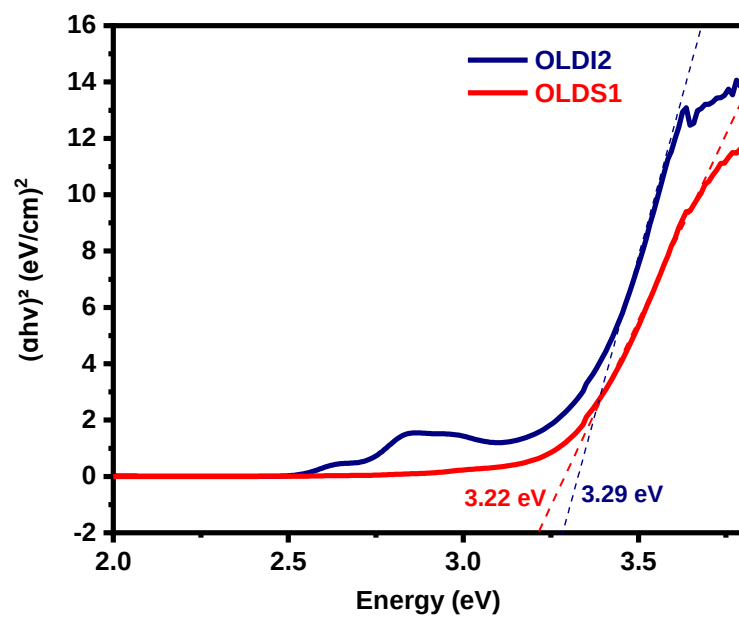


Figure 38 Band gap determination using Tauc plot technique.

The Tauc relationship shown in **Eq.16** can be employed to determine the bandgap energy [200]. This technique assumes that the absorption coefficient α varies with the energy. The γ factor is the specific characteristic of the electron transition and is equivalent to $\frac{1}{2}$ or 2 in the context of direct and indirect transition band gaps [200]. The h , ν , and E_g are defined as Planck constant, frequency of photon, and band gap energy, respectively.

$$(\alpha h\nu) = (h\nu - E_g)^\gamma \quad (16)$$

The Tauc plot depicted in **Fig. 38** reveals that the band gap energy values for the extracted dye were 3.29 eV for OLDI2 and 3.22 eV for OLDS1. Remarkably, these values closely match the previously reported bandgap energy of chlorophyll found in *Ocimum gratissimum* [201]. It's worth underscoring that OLDS1 possessed a lower bandgap energy compared to OLDI2. This distinction suggests that, under identical incident light conditions within the cell, an NDSSC based on OLDS1 is poised to demonstrate superior electron collection capabilities. This advantage stems from the more efficient extraction of electrons from the HOMO to the LUMO state of the dye [26,36].

4.2.5 Cyclic voltammogram analysis

Cyclic Voltammetry (CV) is a widely employed technique for studying the mechanisms governing electron transfer reactions and the kinetics associated with redox processes. In this particular investigation, we utilized CV to explore the electrochemical properties of the extracted natural dyes. The generation of photocurrent hinges on the seamless flow of electrons from the LUMO of the dye to the Conduction Band (CB) of TiO₂. Consequently, it is imperative that the LUMO level of the natural dye is positioned above the CB of TiO₂, while the HOMO level of the dye remains below both the CB of TiO₂ and the

iodine/triiodide electrolyte level [202]. This arrangement serves to diminish the recombination rate within TiO_2 and enhances the stability of the dye employed in NDSSCs [116].

Fig. 39 presents the cyclic voltammograms obtained from the olive leaf extracts, revealing distinctive reduction (cathodic) and oxidation (anodic) peaks. Notably, the redox peaks located on the left side of this range exert a discernible impact on the Photovoltaic Conversion Efficiency (PCE) of NDSSC, while the corresponding redox peaks on the right-hand side do not exhibit a substantial influence [24]. The energy levels of the LUMO and HOMO for the extracted dyes were determined by analyzing the reduction and oxidation reactions, following the equations provided in reference [165], **Eqs. 24** and **25**.

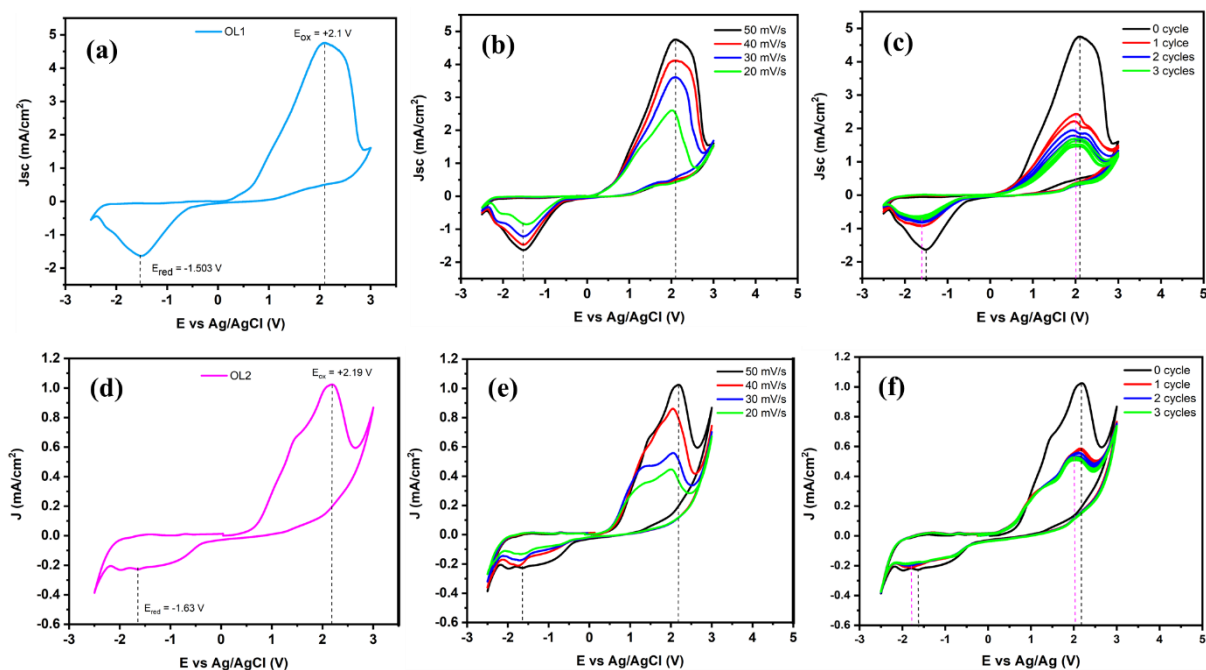


Figure 39 Cyclic voltammogram curve: (a) OL1 dye, (b) OL1 dye at different scan rates, (c) OL1 dye at a different number of cycles, (d) OL2 dye, (e) OL2 dye at different scan rates, and (f) OL2 dye at a different number of cycles.

The anodic (E_{ox}) and cathodic (E_{red}) redox responses were observed at $E = +2.1$ V and -1.503 V for OLDI2 and $E = +2.19$ V and -1.63 V for OLDS1, as depicted in **Figs. 39a** and **d**. These reactions were deemed irreversible due to the disparity between E_{ox} and E_{red} . Notably, both dyes exhibited higher generated current densities in comparison to previously reported studies [38,157,203,204]. This observation underscores the prospect of olive extract as a potential sensitizer candidate for NDSSC with the outlook of achieving enhanced photocurrent conversion efficiency.

The calculated LUMO energy values for OLDI2 and OLDS1 were determined to be -2.897 eV and -2.77 eV, respectively. It's noteworthy that the LUMO energy of the extracted dye surpasses that of the CB of TiO_2 (-4.3 eV) [205], facilitating the efficient injection of electrons from the LUMO of the dye into the CB of TiO_2 .

Another critical attribute of a viable dye is its ability to maintain chemical and electrochemical stability in electrolytic environments [140,206]. A dye must endure at least 10^8 redox processes [140]. Information about the stability of the redox processes of the dyes can be obtained through different scan rates and cycles [206]. The application of Cyclic Voltammetry (CV) was employed to assess the electrochemical stability of olive extracts as sensitizers.

The hysteresis loops generated during the oxidation and reduction processes exhibited similarity. As the scan rate increased, so did the current density for both dyes (**Figs. 39b** and **e**), and the potential peaks displayed a slight shift towards higher potentials with increasing scan rate [207]. This phenomenon can be ascribed to the accelerated migration of ions towards the electrode surface at higher scan rates, indicating the dependency of

both dyes on the scan rate [208]. Furthermore, **Figs. 39c** and **f** illustrate the utilization of cyclic voltammetry to evaluate the long-term compatibility of olive extracts with the solution. These measurements were conducted at a scan rate of 50 mV/s. The current density initially decreased after one cycle but remained stable from one to three cycles. Interestingly, the current density peaks of cycles one to three demonstrated that OLDS1 exhibited superior stability compared to OLDI2 [209]. The curve patterns of OLDI2 exhibited two variations in the maximum current density for each cycle number, whereas OLDS1 consistently displayed the same maximum current density.

In summary, the CV analysis of the extract through cyclic voltammetry showcases its electrochemical stability and electrocatalytic activity in the existence of a redox electrolyte. The influence of drying time emerges as a crucial optimization parameter in this NDSSC configuration, reinforcing its potential as a stable, eco-friendly, and economical sensitizer for NDSSC, serving as a viable alternative to conventional or synthetic dyes.

4.2.6 FTIR spectra analysis

The FTIR spectra displayed in **Fig. 40** depict the variations in olive leaf compositions following different drying durations. In the figure, the navy line spectrum represents OLDI2, while the red line spectrum represents OLDS1. In OLDI2's spectrum, the vibration at 1020 cm^{-1} is attributed to C-O and C-N groups, the faint peak between $1378\text{--}1546\text{ cm}^{-1}$ signifies the aromatic C=C group, the stretch at 1619 cm^{-1} is attributed to the C=O group, the stretch ranging from $2849\text{--}2922\text{ cm}^{-1}$ is attributed to the C-H group, and the stretch at 3281 cm^{-1} is ascribed to the O-H group. On the other hand, OLDS1 exhibits a spectrum that closely resembles OLDI2, with many peaks displaying shifts in either higher or lower frequencies due to variations in drying times for each olive leaf. Despite these noticeable

peak shifts, all peaks still correspond to the same functional groups found in OLDI2's spectrum. The existence of the O-H (hydroxyl) and C=O (carbonyl) groups in both OLDI2 and OLDS1 spectra facilitates the anchoring of chlorophyll to the TiO₂ surface [41,179].

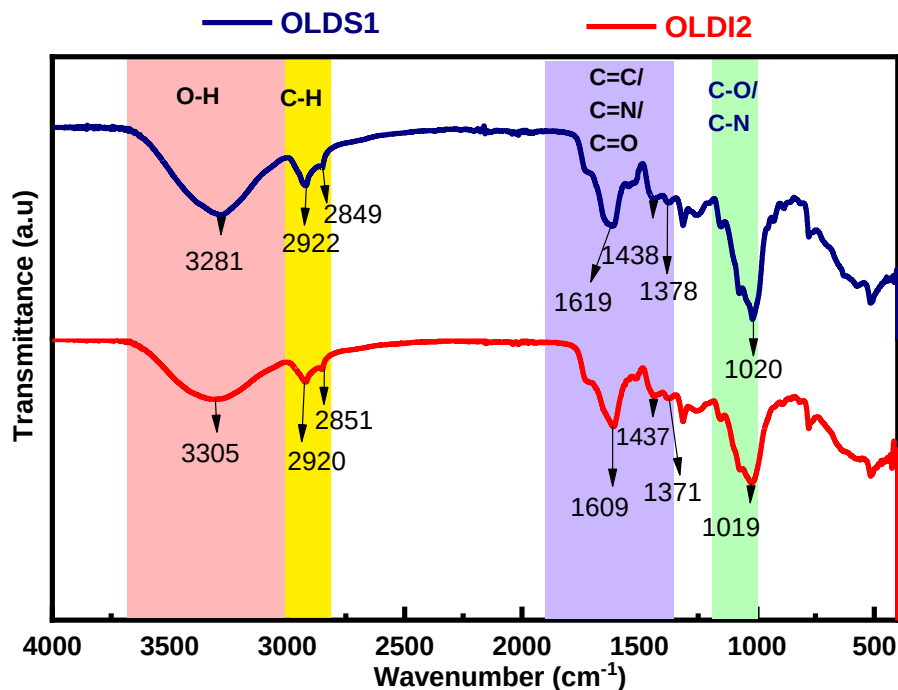


Figure 40 FTIR spectrum of olive leaf extract.

4.2.7 X-ray photoelectron spectra analysis

X-ray Photoelectron Spectroscopy (XPS) had been employed to delve into the electronic characteristics of the elements constituting the surface film of NDSSC. The survey scans of the XPS spectra for TiO₂, both pre and post-dye adsorption, are illustrated in **Fig. 41**. The spectral analysis unveiled that the recorded peaks corresponded to the elements Ti and O, as expected, in the pristine TiO₂ sample. However, in the TiO₂-OLDI2 and TiO₂-OLDS1 samples, additional peaks emerged, corresponding to the elements Ti, C, O, Mg, and N.

This observation confirmed the presence of Mg and N from the chlorophyll structure on the TiO_2 surface in the TiO_2 -OLDI2 and TiO_2 -OLDS1 films [188].

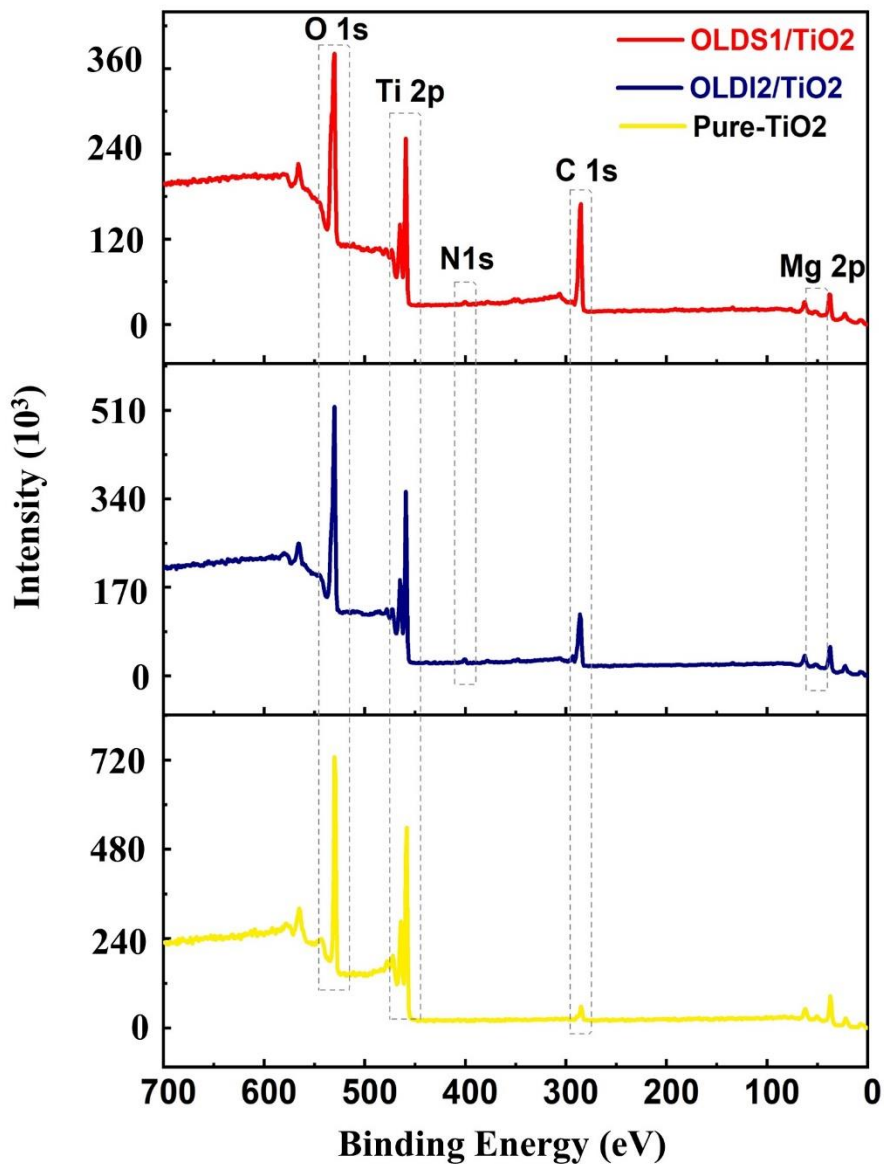


Figure 41 Survey scan of XPS for pure- TiO_2 (black spectrum), OLDI2/ TiO_2 (blue spectrum), and OLDS1/ TiO_2 (red spectrum) in the binding energy range 0 to 700 eV.

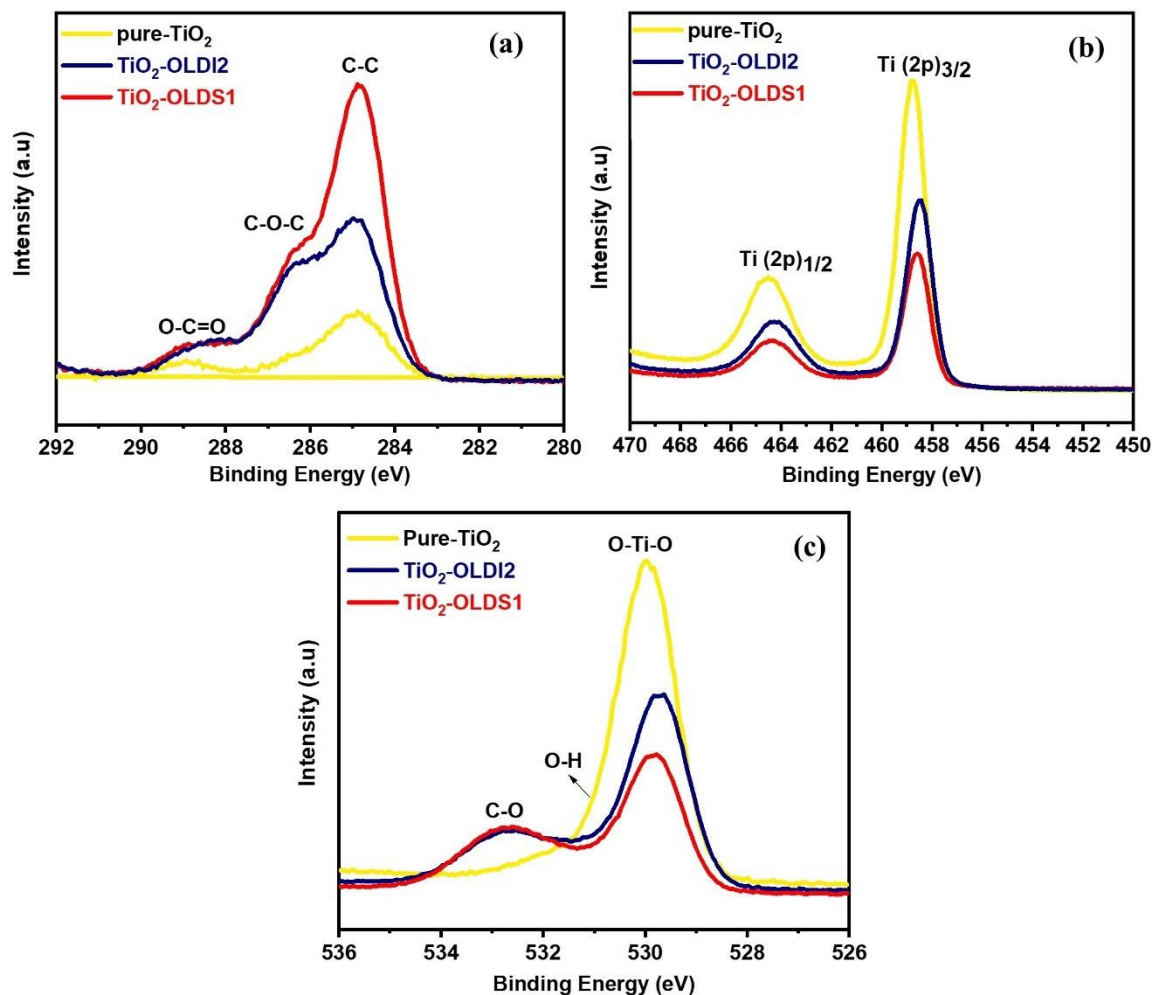


Figure 42 Stacking high-resolution XPS spectra of C 1s, Ti 2p, and O 1s core levels for pure-TiO₂, TiO₂-OLDI2, and TiO₂-OLDS1.

A more in-depth analysis of the high-resolution C1s XPS spectra (**Fig. 42a**) revealed a prominent main peak with two accompanying shoulders on the higher binding-energy side. **Fig. 42b** depicted the Ti 2p core level with two discernible peaks attributed to the spin-orbit splitting of the Ti 2p level. As for the O1s core level peaks (**Fig. 42c**), they displayed a main peak along with a shoulder at a higher binding energy relative to the main peak. Upon the adsorption of dye molecules, the intensities of the Ti 2p and O 1s core-level peaks experienced a reduction (as evident in **Fig. 42b** and **c**). It conveys that the decrease was ascribed to the existence of other chemical bonds on the TiO₂ surface like O-C=O, C-O-C,

and O-H [192], which resembled the composition of chlorophyll. Subsequently, these findings were corroborated by examining the atomic percentages (%), as discussed later in this section.

In contrast to the Ti 2p and O 1s peaks, the carbon peaks displayed an increase in intensity post-dye adsorption (**Fig. 42a**). The C1s peak with the highest intensity was associated with the TiO₂-OLDS1 sample, indicating a more substantial presence of carbonyl groups (C-O-C) adsorbed on the TiO₂ surface. Collectively, these outcomes provide compelling evidence that the olive leaf extract was effectively adsorbed onto the TiO₂ surface, as suggested in previous studies [39].

The combined Gaussian-Lorentzian fitting results are presented in **Figs. 43a-c**, focusing on the TiO₂-OLDS1 film. **Fig. 43b** showcases the chemical analysis of TiO₂, revealing a splitting of the Ti 2p spin-orbitals into a doublet. Specifically, Ti 2p_{1/2} (464.3 eV) and Ti 2p_{3/2} (458.6 eV) exhibit a binding energy separation of approximately 5.7 eV. A similar separation value was observed when fitting Ti 2p for the pure TiO₂ and TiO₂-OLDI2 films, implying the presence of Ti⁴⁺ in all the films.

In **Fig. 43b**, the curve fitting of the O1s spectrum reveals three distinct components. The first peak at 529.8 eV conforms to the O-Ti-O metal oxide bonding [39]. The second peak at 530.9 eV conforms to O-H group bonding [37], while the third peak at 532.7 eV is indicative of the C-O bonding characteristic of the chlorophyll functional group [210]. The presence of hydroxyl (O-H) groups on the metal oxide surface can enhance photoelectron and hole trapping efficiency, thus decreasing the rate at which electron-hole pairs recombine [39,211].

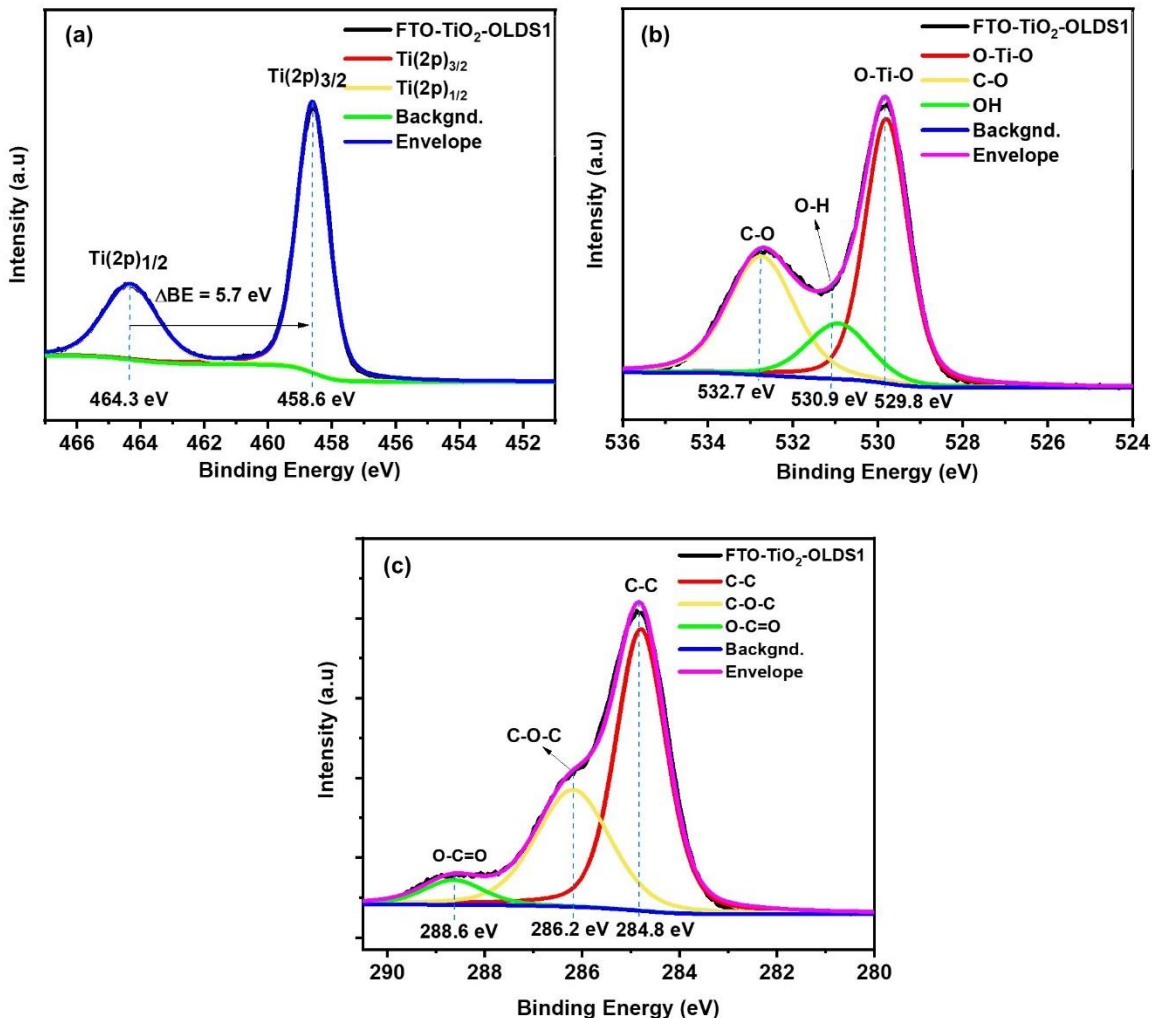


Figure 43 Fitting results of XPS spectra for (a) Ti 2p, (b) O 1s, and (c) C1s core levels of OLDS1-TiO₂.

Fig. 43c exhibits the distinct fitted peaks in the C 1s spectra for TiO₂-OLDS1 at binding energies of 284.8, 286.2, and 288.6 eV, indicating the presence of carbon contamination from the atmosphere (C-C) and O-bound species (O-C=O and C-O-C). These findings align with the FTIR results, confirming the presence of chlorophyll pigment.

Moreover, an analysis of the atomic percentage composition showed that pure TiO₂ consisted of 32.8% Ti and 67.2% O. In contrast, TiO₂-OLDI2 had percentages of Ti, O, C,

N, and Mg at 15.2%, 45.9%, 33.6%, 1.7%, and 3.6%, respectively. TiO₂-OLDS1 exhibited Ti, O, C, N, and Mg contents of 11.2%, 40.1%, 45.4%, 0.7%, and 2.6%, respectively. The decrease in elemental percentages of Ti and O following dye molecule adsorption indicates the existence of these molecules on the TiO₂ surface. TiO₂-OLDS1, in particular, adsorbed more dye molecules than TiO₂-OLDI2, as evidenced by the reduced intensities of the O 1s and Ti 2p peaks. This contributed to the higher photo-to-current conversion efficiency achieved by the NDSSC based on OLDS1, as discussed in Section 4.2.7.

4.2.8 J-V characteristics

Photocurrent Conversion Efficiency (PCE) serves as a pivotal metric for assessing the effectiveness of NDSSCs devices. The precise measurement of PCE holds paramount importance in the quest to enhance the caliber and functionality of NDSSC devices [22,118,157]. In **Fig. 44**, we present the performance characteristics of NDSSC devices operating under two distinct conditions.

The FTO/OLDI2 NDSSC exhibited a V_{oc} of 0.578 ± 0.0005 V, a J_{sc} of 0.548 ± 0.0145 mA/cm², and a PCE of $0.211 \pm 0.0045\%$. In comparison, the FTO/OLDS1-based NDSSC demonstrated superior performance, boasting a PCE of $0.306 \pm 0.00003\%$, accompanied by $V_{oc} = 0.643 \pm 0.0002$ V, $J_{sc} = 0.655 \pm 0.0045$ mA/cm², and $FF = 0.724 \pm 0.0019$. Transitioning to ITO-based NDSSCs, ITO/OLDI2 yielded results with $V_{oc} = 0.583 \pm 0.0005$ V, $J_{sc} = 0.620 \pm 0.0055$ mA/cm², an FF of 0.513 ± 0.0009 , and a PCE of $0.185 \pm 0.00001\%$. Conversely, the ITO/OLDS1 NDSSC outperformed its ITO/OLDI2 counterpart, achieving a $V_{oc} = 0.605 \pm 0.0006$ V and $J_{sc} = 0.597 \pm 0.0140$ mA/cm², coupled with an $FF = 0.605 \pm 0.0006$, ultimately resulting in an elevated PCE of $0.225 \pm 0.00005\%$.

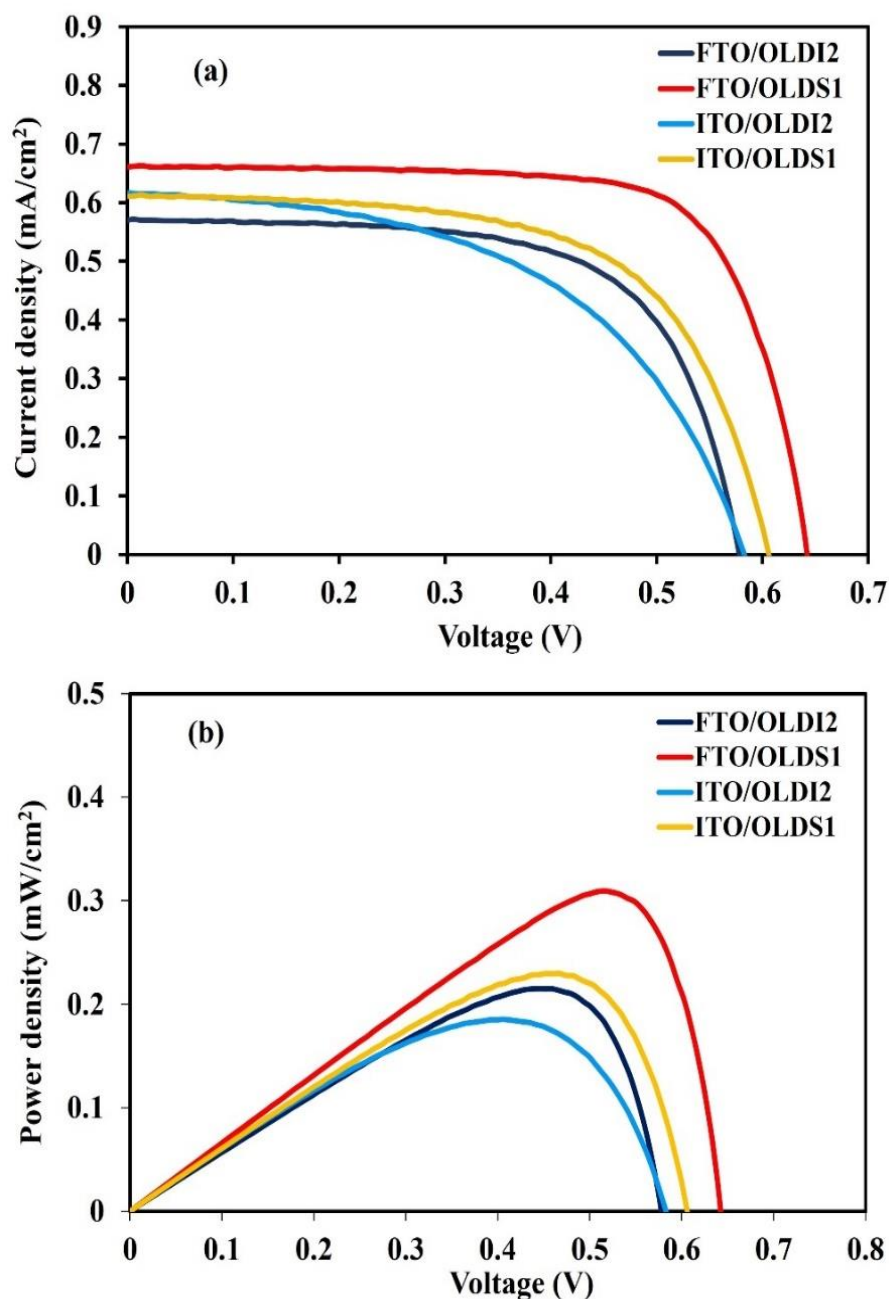


Figure 44 J-V curves of Olive leaf base DSSC.

The performance of the NDSSC was notably influenced by the choice of transparent conducting oxide (TCO) substrate, with FTO outperforming ITO under both drying conditions. This superiority was attributed to the thermal treatment during the annealing of

TiO₂ at 500 °C. It has been reported that higher temperatures, such as 450 °C, during the thermal treatment of TiO₂/TCO/glass led to an increase in the resistivity of ITO, whereas FTO remained unaffected [99]. This phenomenon aligns with the findings of Longo and Paoli, who reviewed the performance of ITO and FTO substrates in DSSC applications and arrived at a similar conclusion [212]. As a result, NDSSCs based on ITO substrates exhibited inferior performance.

Table 4 Photovoltaic parameter of nature and synthetic dye-based DSSC.

Dye	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	η (%)	Ref.
N3	16.8	0.73	0.52	6.33	[11]
Dyename Yellow	14.5	0.75	0.78	8.48	[213]
OLDI2 (FTO)	0.548 ± 0.0145	0.578 ± 0.0005	0.659 ± 0.0039	0.211 ± 0.00448	This work
OLDS1 (FTO)	0.655 ± 0.0045	0.643 ± 0.0002	0.724 ± 0.0019	0.306 ± 0.00002	This work
OLDI2 (ITO)	0.620 ± 0.0055	0.583 ± 0.0005	0.513 ± 0.0009	0.185 ± 0.00001	This work
OLDS1 (ITO)	0.597 ± 0.0140	0.605 ± 0.0006	0.6215 ± 0.0011	0.225 ± 0.00005	This work
Water leave	0.65	0.56	0.49	0.18	[157]
Tecoma stans flower	0.79	0.29	0.46	0.13	[153]
<i>Caulerpa lentillifera</i>	0.52	0.58	0.65	0.20	[42]
<i>Garcinia cola</i>	0.98	0.13	0.90	0.13	[35]
<i>Syzygium cumini</i>	1.29	0.20	0.26	0.27	[214]

<i>Mitragyna speciosa</i> leaves	1.80	0.52	0.28	0.26	[41]
<i>Spinach oleraceae</i> (dry)	1.11	0.58	0.46	0.29	[159]
<i>Spinach oleraceae</i> (fresh)	0.33	0.59	0.42	0.08	[159]
<i>Prickly fruit</i>	1.17	0.56	0.85	0.56	[39]
<i>Scenedesmus obliquus</i>	0.19	0.50	0.69	0.06	[118]
<i>Costus woodsonii</i>	1.03	0.46	0.56	0.56	[179]
Red spinach	-	-	-	0.05	[215]
Spinach	0.41	0.59	0.59	0.17	[22]
<i>Cassia fistula</i>	0.51	0.55	-	0.21	[44]
Curcumin (raw)	0.41	0.45	0.35	0.07	[26]
Curcumin (dry)	0.65	0.57	0.44	0.16	[26]

Examining the V_{oc} of the fabricated NDSSCs, it was observed that the values varied but consistently exceeded those of other natural dyes, as indicated in **Table 4**, where the average listed V_{oc} is 0.47 volts [22,26,159,179,214,215,35,39,41,42,44,118,153,157]. V_{oc} plays a pivotal role in NDSSCs, representing the distinction between the redox and the Fermi level of TiO_2 potential. Achieving a high V_{oc} is crucial for enabling NDSSCs to attain superior efficiency [42,44]. In addition, the PCE of the OLDS1-based NDSSCs exceeds that of the chlorophyll group as presented in **Table 4** [22,41,42,44,157,159]. This improvement can be ascribed to the strong binding between the TiO_2 surface and OLDS1

extract, resulting in a smooth and compact surface. Consequently, the OLDS1-based NDSSC absorbed more light and generated a greater number of electron-hole pairs.

The enhancement in V_{oc} and J_{sc} for OLDS1 in comparison to OLDI2 in both FTO- and ITO-based NDSSCs corroborated earlier findings [26,159]. The primary contributing factors to the successful performance of OLDS1-based NDSSCs were the high J_{sc} and V_{oc} values. According to the SEM and XPS results (**Figs. 34c and 42**), the FTO/OLDS1 NDSSC adsorbed more dye molecules, which correlated with the increased generation of electron-hole pairs, leading to the improved photoelectric performance of the device.

The Power-Voltage (P-V) data were employed to determine the NDSSC output power using the formula $P = J.V$. **Fig. 44b** presents the recorded power density-voltage characteristics for the NDSSCs sensitized with olive leaves. The maximum power (P_{max}) of each NDSSC device was determined, with the maximum current density (J_{max}) and voltage (V_{max}) associated with the maximum power point. The maximum power densities followed the order FTO/OLDS1 > ITO/OLDS1 > FTO/OLDI2 > ITO OLDI2. This order suggests that FTO, with its more stable resistivity, outperforms ITO-based NDSSCs, thus recommending FTO as the preferred substrate for NDSSC configurations over ITO.

Comparing the photovoltaic characteristics of DSSCs sensitized with synthetic dyes such as N3 and L1 (Dyenamo Yellow) to those using natural dyes are listed in **Table 4**. It is evident that NDSSCs sensitized with olive leaf extract exhibited outstanding photovoltaic parameters [22,26,214,215,35,41,42,44,118,153,157,159]. Notably, the OLDS1-based NDSSC demonstrated superior photovoltaic performance when compared to several other natural dyes in terms of V_{oc} , J_{sc} , Fill Factor (FF), and PCE

[22,26,214,215,35,41,42,44,118,153,157,159]. The influence of different drying conditions was also evident, with OLDS1 consistently delivering better photovoltaic performance. This was attributed to the higher pigment content in the extract of dried olive leaves, resulting from the absence of water and other compounds [26,159].

Furthermore, it is worth noting that the V_{oc} of NDSSCs sensitized using olive leaf extract generally compared favorably to that of DSSCs sensitized with synthetic dyes [213]. This achievement holds significant implications, as it signifies that natural dyes, such as OL, can be synthesized through a simpler process compared to synthetic dyes, yet yield comparable V_{oc} levels.

4.2.9 Electrochemical impedance spectra analysis

In solar-cell technology, addressing charge recombination stands as a significant challenge. This phenomenon is visually depicted in **Fig. 45a**. When incident photons excite the dye, generating electrons, these electrons typically move towards the CB of a porous semiconductor layer. Ideally, the external circuit should efficiently capture these excited electrons. However, there are three potential scenarios in which the electrons can follow different pathways: firstly, they may recombine with the holes generated by the excited dye; secondly, they might transfer to a semiconductor and subsequently combine with holes; or thirdly, they could undergo recombination with ionized electrolyte atoms [216].

In this study, we delved into charge recombination within the solar cell by employing EIS Spectroscopy. **Fig. 45b** presents the Nyquist plot of the NDSSC alongside the corresponding equivalent circuit for the Nyquist plot [217]. This plotted data encompasses the frequency response for both real and imaginary impedance (Z). On the graph, the X-

axis represents the real component, while the Y-axis depicts the imaginary component of the equivalent parallel RC circuit of the NDSSC. Impedance is quantified in ohms (Ω).

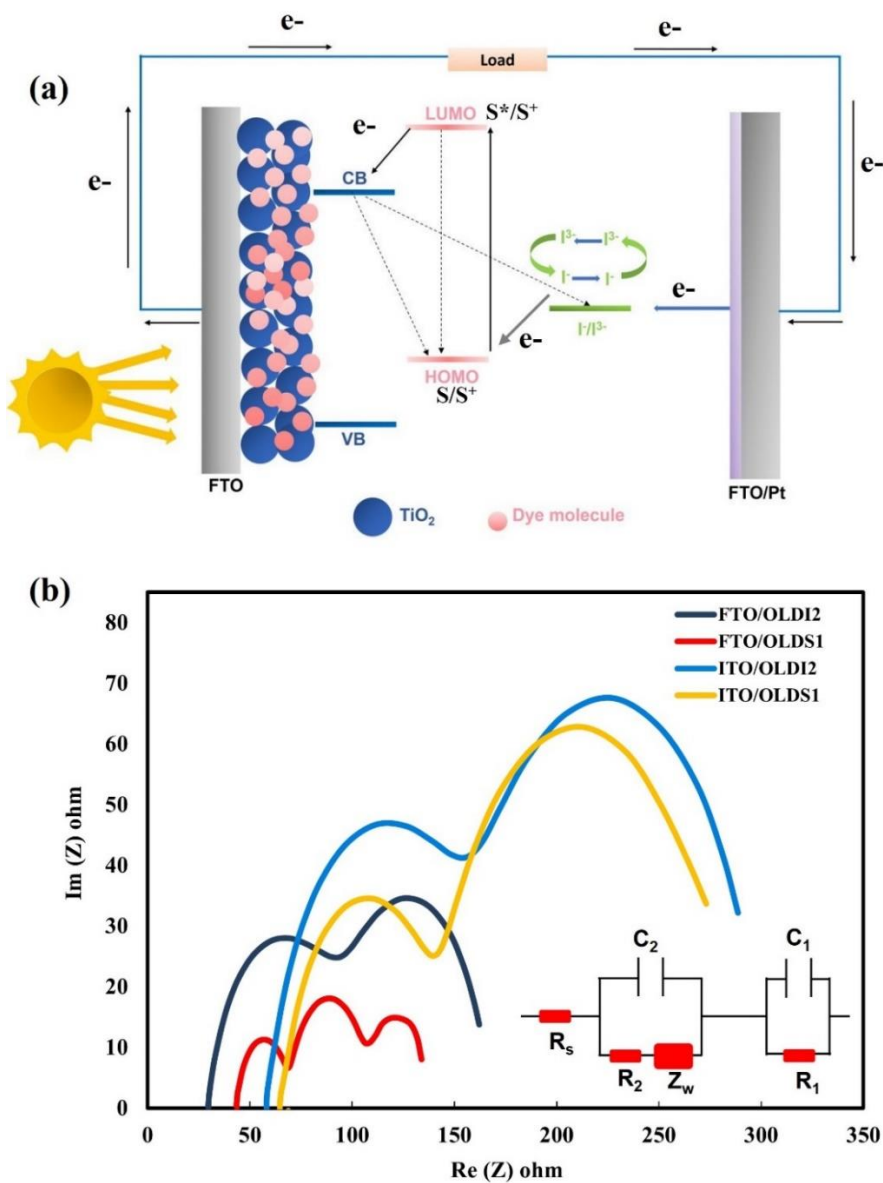


Figure 45 (a) Energy level diagram and recombination illustration in chlorophyll dye-based DSSC, (b) Nyquist plots for OLDI2 and OLDS1, diagram circuit equivalent Nyquist plot.

The EIS spectra revealed three distinct semicircles, each corresponding to specific impedance components within the cell: the interfacial resistance of the Counter Electrolyte (CE) electrolyte (R_1), the photoanode electrolyte (R_2), and the charge diffusion occurring within the electrolyte (Z_w). These components manifest at high, medium, and low frequencies, respectively [35] [218]. C_1 and C_2 denote the capacitances at the interfaces of the counter electrode with the electrolyte and the anode with the electrolyte, respectively. Within **Fig. 45b**, Z_w designates the Warburg impedance, representing the resistance faced by charge carriers as they diffuse inside the electrolyte. R_s refers to the sheet resistance in a series of resistance-capacitance (RC) circuits [22], displaying a subtle variation between OLDI2 and OLDS1.

Table 5 Resistance and capacitance of Olive leave-based DSSCs.

Sample	R_1 (ohm)	R_2 (ohm)	Z_w (ohm)	$C_1(\mu F)$	$C_2(mF)$
FTO/TiO ₂ /OLDI2/electrolyte/Pt	76.9	83.9	-	2.44	520×10^{-4}
FTO/TiO ₂ /OLDS1/electrolyte/Pt	27.4	43.8	32.9	2.11	219×10^{-3}
ITO/TiO ₂ /OLDI2/electrolyte/Pt	119	159	-	2.34	600×10^{-4}
ITO/TiO ₂ /OLDS1/electrolyte/Pt	85.4	158	-	3.26	133×10^{-3}

The resistance and capacitance values for each sample are detailed in **Table 5**. Notably, for FTO/OLDI2, ITO/OLDI2, and ITO/OLDS1 NDSSCs, the Z_w component, associated with the diffusion of redox species in the electrolyte, was omitted from the circuit during the fitting process due to the absence of a discernible semicircular pattern under the specified measurement conditions [218]. Among these NDSSCs, R_2 values were determined as 83.9 Ω (FTO/OLDI2), 43.8 Ω (FTO/OLDS1), 159 Ω (ITO/OLDI2), and 158 Ω (ITO/OLDS1),

respectively. Notably, FTO/OLDS1 exhibited the lowest charge transfer resistance, facilitating enhanced current flow and subsequently boosting photoelectrochemical parameters [157]. In contrast, the other three cells displayed higher charge-transfer resistance (R_1), intensifying recombination reactions and resulting in lower efficiencies of $0.211 \pm 0.0045\%$ (FTO/OLDI2), $0.185 \pm 0.00001\%$ (ITO/OLDI2), and $0.225 \pm 0.00005\%$ (ITO/OLDS1). As previously mentioned, the thermal treatment had the effect of increasing the series resistance in ITO-based NDSSCs, consequently diminishing their performance [99,212]. Thus, the mitigated recombination in FTO/OLDS1 translated into superior performance, yielding a PCE of $0.306 \pm 0.00003\%$.

Comparatively, when evaluating charge transfer resistance within the chlorophyll group NDSSCs [22,42,157], the OLDS1-based NDSSC exhibited lower charge transfer resistance, resulting in a higher photocurrent conversion efficiency. These findings position OLDS1 as a promising choice for NDSSCs incorporating chlorophyll pigment.

CHAPTER 5

CONCLUSION

Dyes extracted from BLs were studied as natural sensitizers of DSSCs. UV–Vis and FTIR studies confirmed the presence of chlorophyll in the extracted dye, which is important for harvesting sunlight. Furthermore, the XRD, XPS, and SEM–EDX analysis results revealed the attachment of chlorophyll onto the TiO₂ surface through the adherence of carbonyl and hydroxyl functional groups. The analysis of *I*–*V* characteristics demonstrated that the *V*_{oc} and *FF* values of the fabricated NDSSCs were comparable to those of the commercial dye (N3)-based cell. The electrochemical impedance study revealed a higher charge-recombination resistance in the photoanode/electrolyte interfaces of the NDSSC (FTO/TiO₂/BL), indicating a lower degree of charge recombination, which leads to the collection of more photogenerated electrons. The performance of the BL-DSSC was better than that of other chlorophyll-based DSSCs. These results indicate that the dye extracted from BLs can be employed in NDSSCs as a natural, low-cost, and environmentally friendly sensitizer for energy-harvesting applications.

A novel natural dyes, specifically chlorophyll pigments extracted from Mediterranean (Tunisia) olive leaves, to sensitize Natural Dye-Sensitized Solar Cells (NDSSCs). The investigation encompassed two distinct drying conditions, shedding light on the potential of olive leaves as a renewable source for efficient sensitizers. UV-Vis and FTIR analyses established that both extracted dyes exhibited significant absorption within the visible light spectrum, making them promising candidates for solar cell sensitization. XRD

measurements provided concrete evidence of the successful anchoring of the dyes onto TiO₂ thin films. Although the 2θ positions remained consistent, variations in peak intensities compared to pure TiO₂ were indicative of the presence of the sensitizing dyes. The influence of drying conditions on the crystallinity of the dye-adsorbed TiO₂ thin films was evident. Notably, extended drying time (OLDS1) resulted in a more pronounced dye adsorption onto TiO₂, enhancing light-harvesting capabilities. This enhancement was clearly reflected in the photovoltaic performance, with OLDS1-based NDSSCs achieving a significantly higher photocurrent conversion efficiency ($0.306 \pm 0.00003\%$) compared to OLDI2 ($0.211 \pm 0.0045\%$). This effect stemmed from the higher pigment concentration in the extract of drier olive leaves (OLDS1) due to the absence of water and other interfering compounds. The findings revealed that FTO-based NDSSCs outperformed their ITO-based counterparts in terms of photovoltaic parameters. This discrepancy was attributed to thermal treatment, which increased the charge transfer resistance of ITO. Consequently, ITO-based cells experienced greater recombination, leading to lower overall efficiency. In conclusion, our study highlights the significance of both drying time and Transparent Conducting Oxide (TCO) substrate choice in influencing the interfacial properties of TiO₂/dye and photoanode/TCO. FTO, with its more stable resistance post-thermal treatment and superior performance when coupled with OLDS1, emerged as the preferred TCO substrate. This study demonstrates the potential of chlorophyll extracted from Mediterranean olive leaves as a viable, low-cost, and eco-friendly alternative for sensitizing NDSSCs. By leveraging natural sources, we pave the way for sustainable and economically viable solar energy solutions.

5.1 Future outlook

The following studies could be conducted in the future:

1. Optimization of Olive and Bay Leaves-Based NDSSC Using Different Solution Concentrations.
2. Fabrication of Olive and Bay Leaves-Based NDSSC Using Different Immersing Times of TiO_2 Photoanode on Dye Solution.
3. Study of the Dye Solution pH of Olive and Bay Leaves on the Efficiency of NDSSC Devices.
4. Characterization of Olive and Bay Leaves-Based NDSSC Stability.
5. Fabrication of Olive and Bay Leaf-Based Carbon as a Blocking Layer for Retarding Charge Recombination.

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Curriculum Vitae

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Publications :

A. Journal Paper

1. **Ryan Nur Iman**, Khalil Harrabi, Muhammad Younas, and Abdelkarim Mekki. 2023. *Fabrication of efficient natural dye-synthesized solar cells using*

Mediterranean Olive leave as natural dye sensitizer. Accepted at **Journal of Photochemistry and Photobiology a: Chemistry**, Elsevier.

2. **Ryan Nur Iman**, Muhammad Younas, Khalil Harrabi, and Abdelkarim Mekki. 2023. *Fabrication and Characterization of natural dye-sensitized solar cells using an efficient natural sensitizer derived from Laurus nobilis L*. Under review at **Dyes and Pigments**, Elsevier.
3. **Ryan Nur Iman**, Muhammad Younas, Khalil Harrabi, and Abdelkarim Mekki. 2023. *Maximizing the Potential of Natural Dye-Sensitized Solar Cells: A Comprehensive Review on Efficiency and Stability Optimization Strategies*. Under review at **Journal of Photochemistry and Photobiology C: Photochemistry**, Elsevier.
4. Yuda Prima Hardianto, **Ryan Nur Iman**, Arif Hidayat, Nandang Mufti, Nurul Hidayat, Sunaryono, and Ahmad Taufiq. *A Facile Route Preparation Of Fe₃O₄/MWCNT/ZnO/PANI Nanocomposite For Enhanced Microwave Absorption Performance*. Under review at **ChemistrySelect**, John Wiley & Sons.
5. Hasniah Aliah, **Ryan Nur Iman**, Andhy Setiawan, Dani Gustaman Syarif , Asti Sawitri, Assa Prima Dasti Putri, Indri Winarti. 2023. *Utilization of Jarosite and Manganite mineral as raw material to fabricate metal-oxide composite film for gas sensor application*. Under review at **Chemical Physical Letters**, Elsevier.
6. Hasniah Aliah, **Ryan N Iman**, Sriwidati Sriwidati, Asti Sawitri, Andhy Setiawan, Assa P.D. Putri, and Fera Kurniawati. 2023. *Study of Optical and Electrochemical Properties of Solvent-dependent natural dye extracted from Rivina humilis L for DSSC Applications*. "Journal of Ecological Engineering." Vol. 24 (9), pp. 312-321. <https://doi.org/10.12911/22998993/169418>
7. Hasniah Aliah, Indri Winarti, **Ryan Nur Iman**, Asti Sawitri, Andhy Setiawan. 2023. *Influence of Sieve Size on Calorific Value and Proximate Properties of Bio-Briquette Composites*. "Journal of Ecological Engineering." Vol. 24 (7), pp. 25-34. <https://doi.org/10.12911/22998993/163309>
8. Hasniah Aliah, Elis Sabilil Hidayah, **Ryan Nur Iman**, Asti Sawitri, Andhy Setiawan. 2023. *Photocatalytic activity of MgFe₂O₄:TiO₂ composite for degrading methylene blue*. "Jurnal Pendidikan Fisika dan Keilmuan (JPFK)". <http://e-journal.unipma.ac.id/index.php/JPFK/article/view/13510>.
9. Hasniah Aliah, **Ryan Nur Iman**, Asti Sawitri, Dani Gustaman Syarif, Andhy Setiawan, Wahyudin Darmalaksana and Adam Malik. (2019). *The optimization of ZnFe₂O₄/Mn₂O₃-based nanocomposite ceramic fabrication utilizing local minerals as an ethanol gas detector*. *Materials Research Express*, 6(9), 095908. <https://doi.org/10.1088/2053-1591/ab2ffe>

B. Conference paper

1. Hasniah Aliah, Indri Winarti, Rizky Safarina Kh, Asti Sawitri, **Ryan Nur Iman**, Ridwan Ramdhani, and Andhi Setiawan. 2023. ***Analysis of Thermal and Mechanical Quality of Briquettes From Arabica Coffee And Rice Husk***. "American Institute of Physics Conference series." *In press*.
2. Aliah, H., Rahmah, B. L., Sawitri, A., **Iman, R. N.**, Syarif, D. G., Setiawan, A., & Nuryadin, B. W. (2023, April). ***Physical properties of briquettes composite from coffee husks (Coffea Arabica L) and Corncob (Zea Mays) for alternative fuel***. In *AIP Conference Proceedings* (Vol. 2646, No. 1). AIP Publishing. <https://doi.org/10.1063/5.0114133>
3. Aliah, H., D. G. Syarif, **R. N. Iman**, A. Sawitri, and A. Setiawan. ***A sensitive thick film as a candidate for ethanol gas sensor from Jarosite-based minerals***. In *Journal of Physics: Conference Series*, vol. 1869, no. 1, p. 012194. IOP Publishing, 2021. <https://doi.org/10.1088/1742-6596/1869/1/012194>
4. Aliah, H., P. Gumarang, **R. Iman**, A. Sawitri, and D. Syarif. ***Electrical Properties of Fe₂O₃-ZnO Thick Film***. In *Proceedings of the 1st International Conference on Islam, Science and Technology, ICONISTECH 2019, 11-12 July 2019, Bandung, Indonesia*. 2021. <http://dx.doi.org/10.4108/eai.11-7-2019.2297560>
5. Aliah, H., Syarif, D.G., **Iman, R.N.**, Sawitri, A., Darmalaksana, W., Setiawan, A., Malik, A. and Gumarang, P., 2019. ***Structure analysis of nanocomposite ZnO: Fe₂O₃ based mineral yarosite as Fe₂O₃ source and its application probability***. *Materials Today: Proceedings*, 13, pp.36-40. <https://doi.org/10.1016/j.matpr.2019.03.183>
6. Aliah, H., D. G. Syarif, **R. N. Iman**, W. Darmalaksana, A. Setiawan, and A. Sawitri. ***Preliminary studies of Mn_(x)Zn_(2-x)FeO₄ (x= 0 and 0.1) thick film semiconductors as an ethanol gas sensor***. In *IOP Conference Series: Materials Science and Engineering*, vol. 434, no. 1, p. 012027. IOP Publishing, 2018. <https://doi.org/10.1088/1757-899X/434/1/012027>
7. Aliah, H., D. G. Syarif, **R. N. Iman**, A. Sawitri, M. Sanjaya WS, M. Nurul Subkhi, and P. Pitriana. ***Semiconductor ceramic Mn_{0.5}Fe_{1.5}O₃-Fe₂O₃ from natural minerals as ethanol gas sensors***. In *IOP Conference Series: Materials Science and Engineering*, vol. 367, no. 1, p. 012041. IOP Publishing, 2018. <https://doi.org/10.1088/1757-899X/367/1/012041>

C. Synthesis, Fabrication, and Characterization expertise

1. Extraction of natural dye with maceration method.
2. Doctor blade and spin coating techniques.
3. Fabrication of DSSC (sandwich).

4. UV-Vis spectroscopy JASCO V-670 [measurement and analysis].
5. Fourier Transform Infrared (FTIR) spectroscopy smart iTR NICOLET iS10 [measurement and analysis].
6. X-ray Photoelectron Spectroscopy (XPS) ESCALAB 250Xi [analysis].
7. X-Ray Diffractometry, Rigaku Ultima IV [analysis]
8. Scanning Electron Microscopy-EDX JEOL JSM6610LV [analysis].
9. IV-5 solar simulator, QEX10, PV Measurement, Inc. Ltd, USA., [measurement and analysis].
10. Electrochemical Impedance Spectroscopy (EIS) with Multichannel Research Grade Potentiostat, BioLogic Science Instruments (Model: VMP3 SAS) [measurement and analysis]
11. Cyclic Voltammetry (CV) with Multichannel Research Grade Potentiostat, BioLogic Science Instruments (Model: VMP3 SAS) [measurement and analysis].
12. Linear Sweep Voltammetry (LSCV) with Multichannel Research Grade Potentiostat, BioLogic Science Instruments (Model: VMP3 SAS) [measurement and analysis].

D. Academic experience

1. **Instructor**, General Physics II (Lab section) August 26th – December 30th , 2023 in Fall Semester at King Fahd University of Petroleum and Minerals (KFUPM).
Assignment: Lab teaching -> Data Analysis, Resonance On String, Specific Heat, Perfect Gas Law, Electric Field Mapping, Capacitors, Ohm's Law, Kirchhoff's Law, E/M Electron, and Current Balance.
2. **Research Assistant**, September 2017 – 2021, Universitas Islam Negeri Sunan Gunung Djati Bandung, Indonesia.
Assignment: doing experiment in the field of Metal Oxide Semiconductor-based Gas Sensor, Bio-briquette, and Photocatalyst.

E. Social work

Voluntary work (Environmental activist)

F. Membership

- Materials Research Society of Indonesia (MRS id) 2018-present.
- Community of Indonesian KFUPM student (Persatuan Pelajar dan Mahasiswa Indonesia) Dhahran, 2021-present.

G. Contact References

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