

Review

Chlorophyll Sensitization of TiO₂: A Mini-Review

Maria E. K. Fuziki ^{1,*} , Angelo M. Tusset ² , Onélia A. A. dos Santos ¹ and Giane G. Lenzi ² 

¹ Department of Chemical Engineering, State University of Maringá, Colombo Av. 5790, Maringá 87020-900, Paraná, Brazil; oneliaandreo@hotmail.com

² Department of Production Engineering, Federal University of Technology-Paraná, Doutor Washington Subtil Chueire St. 330, Ponta Grossa 84017-220, Paraná, Brazil; tusset@utfpr.edu.br (A.M.T.); gianeg@utfpr.edu.br (G.G.L.)

* Correspondence: mariafuziki@gmail.com

Abstract: Recent studies have shown that chlorophyll sensitization can improve the performance of semiconductors like TiO₂ in photocatalytic reactions and light-harvesting technologies, such as solar cells. Faced with the search for renewable energy sources and sustainable technologies, the application of this natural pigment has been gaining prominence. The present work addresses some of the main possibilities of chlorophyll-TiO₂ combination, presenting the most relevant aspects affecting chlorophyll extraction and TiO₂ sensitization.

Keywords: Chlorophyll; TiO₂; dye sensitization; photocatalysis; DSSC

1. Introduction

Titanium dioxide (TiO₂) is a semiconductor widely used in photocatalytic and photo-electrochemical processes, since the first works describing reactions involving TiO₂ and UV radiation [1] and the Fujishima–Honda effect were reported in the 1960s [2]. In the early 1970s, Fujishima and Honda investigated the behavior of the rutile form of TiO₂ under light irradiation, discussing the similarities between the observed phenomenon and the initial stages of photosynthesis, focusing on studying the mechanism of the latter [3]. Over the years, the number of studies about TiO₂-based materials combined with light irradiation have multiplied, spreading to different areas of application, such as the oxidation of organic compounds [4], the degradation of pollutants such as pharmaceuticals and pesticides [5,6], the removal of heavy metals from water [7], bactericidal activity [8], hydrogen production [9–11], and CO₂ reduction for solar fuel synthesis [12]. Notably, this last example has contributed to a strengthening of the aspiration for an artificial photosynthesis process, which, similarly to natural photosynthesis, consumes simple products, such as water and carbon dioxide, to produce energetic substances (e.g., H₂, CO, CH₃OH, CH₄) using sunlight, which are also known as solar fuels [13,14].

The cited processes are based on TiO₂'s ability to form electron (e⁻)/hole (h⁺) pairs under UV irradiation. When the energy of the photons absorbed by TiO₂ is more significant than its band gap, the electrons in the valence band (VB) are promoted to the conduction band (CB) of the semiconductor, generating holes in the VB, and electrons in the CB [15,16]. The photogenerated e⁻/h⁺ pairs can recombine inside the photocatalyst particle or migrate to the surface and undergo recombination. If this does not occur, e⁻/h⁺ pairs at the surface can promote reduction or oxidation reactions of adsorbed species [15,17]. This phenomenon is the basis of the various photocatalytic processes. As it can generate highly active radical species, e.g., hydroxyl radicals, photocatalysis can be classified as an advanced oxidation process (AOP) [16].

Despite its low toxicity, outstanding activity, and considerable chemical stability [18], titanium dioxide is only active under UV light, restricting TiO₂ applications combined with solar radiation, which includes predominantly visible light and less than 5% of



Citation: Fuziki, M.E.K.; Tusset, A.M.; dos Santos, O.A.A.; Lenzi, G.G. Chlorophyll Sensitization of TiO₂: A Mini-Review. *Reactions* **2023**, *4*, 766–778. <https://doi.org/10.3390/reactions4040044>

Academic Editor: Michela Signoretto

Received: 12 September 2023

Revised: 4 November 2023

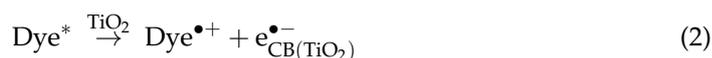
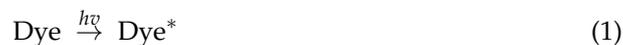
Accepted: 28 November 2023

Published: 1 December 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

UV radiation [19]. As one of the possible alternatives, dye sensitization of wide band-gap semiconductors (>3.0 eV), such as TiO_2 , has been the subject of different studies for improved solar light harvesting technologies [20]. In dye sensitization, the dye molecule bonded to the semiconductor surface injects electrons into the conduction band of the semiconductor upon photoexcitation, as described in Equations (1) and (2) [21,22].



Based on this principle, one of the third-generation solar cell technologies has gained ground, driven by growing energy demand and the search for renewable energy sources: dye-sensitized solar cells (DSSCs) [23,24]. This type of device aims to convert sunlight into electricity, consisting of a substrate made up of a glass conductor, a dye-sensitized semiconductor (metal oxide), and a catalyst counter electrode, separated from the other electrode using an electrolyte solution [24]. Although this technology still suffers from limitations in terms of efficiency and long-term stability, there is an excellent expectation regarding its development, especially concerning the use of new dyes that improve its performance [25]. In this context, natural dye extracts have gained attention due to the abundance, low cost, and environmentally friendly nature of the raw material [25–28].

Among natural dyes, chlorophyll has undoubtedly shown exciting results. As reported by [29], spinach extract produced the best efficiency results among the different natural extracts used in sensitizing TiO_2 solar cells. Compared to the other natural dyes (black rice, dragon fruit, red cabbage, and blends), the spinach UV-Vis absorption spectrum presented the highest absorption peak at approximately 662 nm [29], which can be associated with chlorophyll-a. Haghightazadeh, in a study about phenol photocatalytic degradation under visible light irradiation, observed that TiO_2 nanoparticles sensitized with chlorophyll promoted higher percentages of degradation (85%) than those sensitized with curcumin (75%) [30]. Thus, TiO_2 sensitized with chlorophyll has gained space in DSSC [31] and photocatalysis applications, including pollutant degradation [32], CO_2 reduction [33], and even artificial photosynthesis processes involving light harvesting and oxygen production [34]. In this context, the present work aims to present some of the main practical aspects involved in the extraction of chlorophyll and its use in TiO_2 sensitization for different applications described in the literature.

2. Chlorophyll

Chlorophyll is a natural pigment of the porphyrin class, which has a Mg^{2+} ion coordinated to the four rings [35], as shown in Figure 1. The Mg^{2+} ion in the molecule plays a vital role in the light absorption phenomenon, being essential for the excited state of the molecule and affecting the efficiency of the excitation transfer between chlorophyll molecules in the chloroplast [35–37], giving chlorophyll a prominent position in photosynthesis and promoting solar energy conversion into chemical energy [38]. The green color of chlorophyll pigments is due to their high absorption in the red and blue regions of the light spectrum [39]. In the absorption spectrum, the ranges of 350 nm to 480 nm can be attributed to the charge transfer transitions of the porphyrin and the Mg ion [38].

While chlorophyll-a is a pigment common to all photosynthetic plants, chlorophyll-b is characteristic of algae and vascular plants [38]. As for the molecular structure, the two pigments are distinguished by the presence of a methyl group (chlorophyll-a, Figure 1a) or an aldehyde group (chlorophyll-b, Figure 1b) at position 3 [35]. Green plants usually contain both chlorophyll-a and chlorophyll-b, the former being the major pigment [35]. There are reports of an increase in the proportion of chlorophyll-b in shade plants, given that this pigment would be more effective in absorbing low-intensity light [35]. Despite the slight differences between the pigments, it is quite common to use extracts containing both to sensitize TiO_2 , whether in extracts obtained from plants [19] or other sources, such

as *Spirulina* [40]. Even so, there are reports of the isolated use of chlorophyll-a [41] and chlorophyll-b [42] as TiO₂ modifiers.

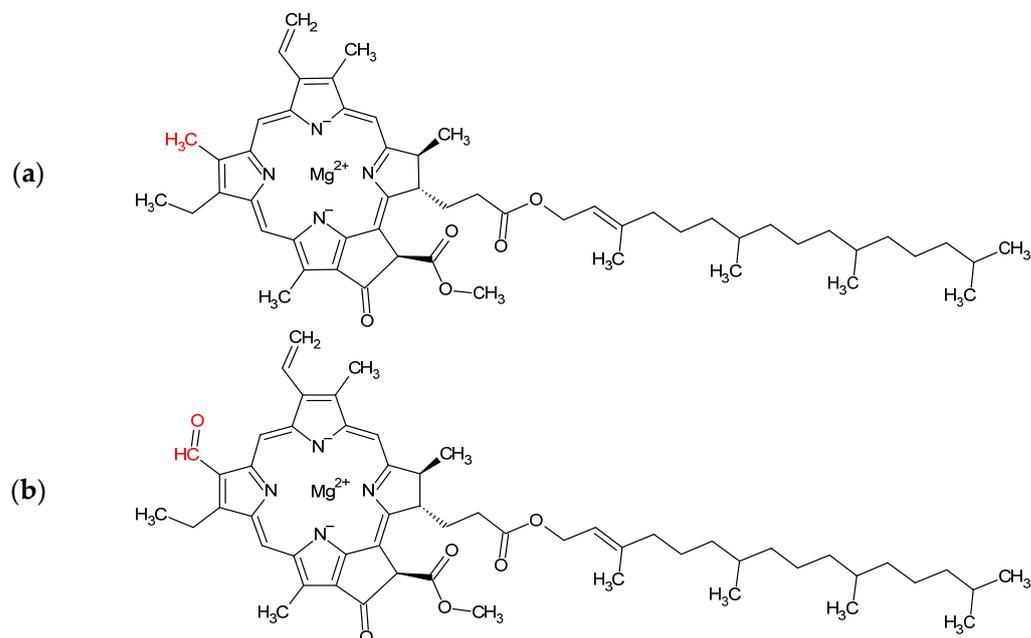


Figure 1. Chlorophyll-a (a) and Chlorophyll-b (b).

Chlorophyll-a's two maximum absorption peaks are at approximately 432 and 670 nm [35]. However, the chlorophyll absorption spectrum may vary slightly depending on the solvent [35]. Shen et al., for example, reported a variation in the chlorophyll-a absorption maxima in different solvents, changing from 420 nm and 661 nm in chloroform to 421 nm and 667 nm in ethanol and 440 nm and 673 nm in phosphate-buffered saline (0.01 M, pH 7) [34]. This type of phenomenon is closely related to the polarity of the solvent, and it is common to observe a red shift as the polarity of the solvent increases [43,44].

Through a theoretical study using density functional theory (DFT) and time-dependent DFT (TD-DFT), Faiz et al. concluded that the solvent can also reduce the LUMO–HOMO band gap and affect the light-harvesting energy (LHE) [45]. Among the results obtained, the authors observed that water could improve chlorophyll's performance in injecting electrons, even though chlorophyll is not soluble in water [45]. Similarly, Sabagh et al. reported that the solvent improves the LHE in a comparative study between water and the gas phase [46].

2.1. Chlorophyll-a and Chlorophyll-b Concentration Estimations

The concentration of chlorophyll-a and chlorophyll-b can be determined directly and simultaneously using spectrophotometry through calculations considering a system of two equations [35]. The equations may vary slightly since the solvent can affect the absorption spectrum [35]. Krishnan et al., for example, considered the chlorophyll optical densities (OD) in the extract—which were calculated by subtracting the absorbance at 750 nm from absorbances at 647 nm (OD_{647}) and 664 nm (OD_{664})—to estimate the concentrations of chlorophyll-a and chlorophyll-b in mg L⁻¹ [19]. Pai et al., in turn, used the absorbance value to estimate the concentration of the two pigments [39]. Some examples are provided in Table 1.

Table 1. Different equations described in the literature used to determine the concentration of chlorophyll-a and chlorophyll-b for different solvents.

Equations	Solvent	Ref.
$\text{Chl}_a \left(\text{mg L}^{-1} \right) = 11.93 \cdot (OD_{664}) - 1.93 \cdot (OD_{647})$ $\text{Chl}_b \left(\text{mg L}^{-1} \right) = 20.36 \cdot (OD_{647}) - 5.50 \cdot (OD_{664})$	90% Aqueous acetone	[19]
$\text{Chl}_a \left(\mu\text{g mL}^{-1} \right) = 12.21 \cdot (A_{663}) - 2.81 \cdot (A_{646})$ $\text{Chl}_b \left(\mu\text{g mL}^{-1} \right) = 20.13 \cdot (A_{646}) - 5.03 \cdot (A_{663})$	Acetone/ petroleum ether	[39]
$\text{Chl}_a \left(\mu\text{g mL}^{-1} \right) = 13.95 \cdot (A_{665}) - 6.88 \cdot (A_{649})$ $\text{Chl}_b \left(\mu\text{g mL}^{-1} \right) = 24.96 \cdot (A_{649}) - 7.32 \cdot (A_{665})$	95% Ethanol	[47]

2.2. Extraction of Chlorophyll

Natural chlorophyll extracts can be produced from different raw materials including plants [32,39] and microorganisms [22]. Among the plant species, we can mention leaves of fresh spinach [19], pandan [48], weeds such as *Chromolaena odorata* [39], and parsley [30]. Among microorganisms, the cyanobacteria stand out, among which we can mention *Spirulina* sp. [22].

The chlorophyll molecule is composed of a hydrophilic part and a hydrophobic part [39], and its extraction is commonly performed by using organic solvents such as methanol [22], ethanol [40], acetone [19], and petroleum ether [39], among others. Najihah et al. observed that polar organic solvents tend to promote better chlorophyll extraction (acetone > ethanol > methanol > acetic acid > acetonitrile) than non-polar solvents (hexane) [49]. This result justifies the widespread use of acetone in chlorophyll extraction [29]. Krishnan and Shrivastav, for example, extracted chlorophyll from ground fresh spinach leaves (after removing their midrib) using a 90% acetone aqueous solution, which was kept in contact with the leaves for 2 h in the dark at 4 °C. The extract was centrifuged for 20 min at 3000 rpm. The authors were able to produce an extract containing 0.39 ± 0.05 mg of chlorophyll per gram of spinach [19].

Other commonly used solvents are ethanol and methanol. Al-Alwani et al., for example, reported that ethanol showed the best performance in extracting chlorophyll from pandan leaves (*P. amaryllifolius*) compared to methanol, chloroform, ethyl ether, and acetonitrile [48]. Kathiravna et al. [22] extracted chlorophyll from a cyanobacteria *Spirulina* sp. using a 90% methanol solution and centrifugation as the separation method.

Regardless of the raw material or solvent used, the extraction process usually follows similar steps under mild conditions and relatively simple procedures to ensure the extraction of chlorophyll by the solvent. The initial steps involved preparing the raw material, generally with the reduction of the sample through crushing and grinding [19,22,30,49]. In some cases, it is also necessary to preliminarily remove the midrib of plant leaves [19] or carry out a drying step [48]. Once the sample is prepared, it proceeds to the next step, in which the contact between the raw material and the solvent is promoted for a defined time, which can vary from a few hours (1 h [22] or 2 h [19]) or days (from 24 h [29] up to 1 week [30,48,50]). The sample can be sonicated during this period to promote extraction [40]. Then, the extract is separated from solid waste using centrifugation [19,22] or filtration [29,30,40,48,49]. In some cases, it is also possible to increase the extract concentration in a rotary evaporator [29,48]. Some extraction conditions are summarized in Table 2.

Even though these are the most common procedures, there are alternative processes that can differ significantly from the extraction methods described, such as the procedure followed by Phongamwong et al., who obtained the chlorophyll extract after a short incubation period (2 min) of *Spirulina* at 70 °C, at the end of which the mixture was centrifuged and the supernatant collected [51].

Table 2. Some extraction conditions described in the literature.

Source	Solvent	Contact Time	Separation	Ref.
Spinach leaves	90% aqueous acetone	2 h	Centrifugation	[19]
Spinach leaves	Ethanol	20 min	Filtration	[41]
<i>Spirulina</i> sp. (cyanobacteria)	90% methanol	1 h	Centrifugation	[22]
<i>Spirulina</i>	Methanol and water (incubated for 2 min in a water bath at 70 °C)	2 min (70 °C, incubated)	Centrifugation	[51]
<i>Spirulina</i>	Ethanol	1 h (sonicated)	Filtration	[40]
Pandan leaves (<i>P. amaryllifolius</i>)	96% Ethanol	1 week	Filtration	[48]
Parsley leaves	96 Ethanol	7 days	Filtration	[30]
Pumpkin (<i>Cucurbita maxima</i>) leaves	Ethanol	36 h	Filtration	[28]

Chlorophyll tends to be unstable, suffering from the action of temperature, light, oxygen, or other chemical reactions [35]. After the extraction, it is essential to take care of the extract's storage conditions to avoid its degradation, whether that be by keeping it at low temperatures (4 °C [19,22,30]) or by protecting it from exposure to atmospheric air [48] or light [22,29,39,40,48] to prevent autoxidation [40]. Furthermore, it is necessary to consider that the extract obtained from plants and microorganisms may contain other organic compounds, such as sugars and amino acids, which may lead to chlorophyll degradation during storage or even the detachment of the dye from the TiO₂ surface [49].

Phongamwong et al. did not perform the chlorophyll extraction. Still, they incorporated *Spirulina* directly into the TiO₂ using the incipient wetness impregnation method, using deionized water to disperse the ground *Spirulina* and then adding it to the N-TiO₂, which was kept under constant stirring at 40 °C until the complete evaporation of water [33]. In a later work, the authors compared the incorporation of *Spirulina* (Sp) and chlorophyll (Chl) to P25 using the incipient wetness impregnation method. They observed that, although both contributed to a significant improvement in P25 performance, the incorporation of extracted chlorophyll led to superior results. While P25 presented a rate constant of $k = 8.05 \pm 0.23 (10^{-3} \text{ min}^{-1})$ in the degradation of Rhodamine B, the modified catalysts 0.5Sp/P25 and 0.5Chl/P25 presented rate constants equal to $k = 23.53 \pm 0.91 (10^{-3} \text{ min}^{-1})$ and $k = 60.80 \pm 2.21 (10^{-3} \text{ min}^{-1})$, respectively [51].

3. Chlorophyll Fixation on TiO₂

Dye sensitization can occur through electrostatic, hydrophobic, or chemical interactions between the dye and the semiconductor surface [21]. An adequate interaction between the pigment and the semiconductor film is fundamental for improving the energy conversion and charge transfer in DSSCs [29]. The simplest and most common form of sensitization described in the literature involves promoting direct contact between the TiO₂ and the chlorophyll extract for a certain period. In the case of Chl-TiO₂ electrodes, it is common to dip the electrode in the dye extract [39]. An essential factor to consider is the contact time, which can take a few hours, 24 h [48,49], or longer [41]. Mahadik et al. prepared Chl-a-sensitized TiO₂ nanorods by dipping the synthesized thin films horizontally in a Chl-a ethanol solution for 10–40 h [41]. As for photocatalytic processes, several works reported applying the incipient wetness impregnation method to sensitize catalysts [19]. Phongamwong et al. applied the incipient wetness impregnation method, promoting contact between the chlorophyll extract and the catalyst overnight under agitation at 40 °C until the solvent evaporated [51].

According to the molecular dynamic simulations performed by Christwardana et al. [40], chlorophyll binds to TiO_2 through interactions between some of its functional groups and the O of titanium dioxide, with a predominance of polar bonds. TiO_2 FTIR spectra typically show peaks at approximately 3400 cm^{-1} (O–H stretching), 1630 cm^{-1} (O–H bending mode), and $800\text{--}400\text{ cm}^{-1}$ (O–Ti–O stretching) [19,51]. Chlorophyll's presence in TiO_2 -sensitized samples is normally indicated by the peaks associated with the symmetric C–H stretching vibration of methine (CH), methyl (CH_3), or methylene (CH_2) groups, which has already been reported by different authors to occur at 2975 cm^{-1} [52], 2932 cm^{-1} [53], or 2920 cm^{-1} [51]. Several authors also highlighted the peak referring to C=O stretching in the region between 1632 and 1641 cm^{-1} , which is associated with ketone or aldehyde groups, highlighting the importance of C=O for chlorophyll anchoring on TiO_2 . [51–53]. The FTIR spectra of chlorophyll extracted from different sources also tend to show a broad peak in the region at approximately 3500 cm^{-1} associated with the OH group, as already described by [49] ($3700\text{--}3000\text{ cm}^{-1}$), [38] ($3600\text{--}3400\text{ cm}^{-1}$), [52] (3296 cm^{-1}), and [48] (3350 cm^{-1}).

The presence of alkyl groups instead of hydroxyl or carboxyl groups in the chlorophyll molecule can impair the Chl- TiO_2 interaction due to steric effects, hindering the electron transfer from the dye to the electrode [48]. The dye sensitization of TiO_2 can be directly influenced by the number and distribution of carboxyl groups in the dye molecule [54]. The three possible coordination modes of carboxylate groups to metal are represented in Figure 2 [20]:

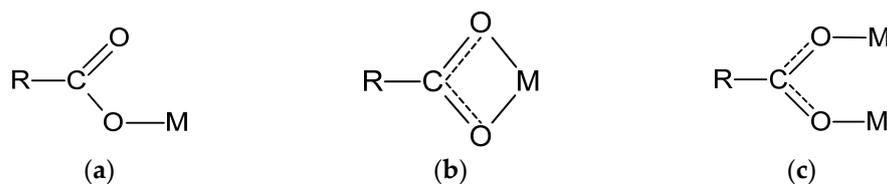


Figure 2. Representation of (a) unidentate, (b) bidentate chelating, and (c) bridging coordination modes.

Since there are no carboxyl, carbonyl, or hydroxyl groups in the chlorophyll molecule that favor its anchorage to the surface [39,55], its fixation on TiO_2 can be improved with the help of some fatty acids with a long carbon chain such as myristic acid, stearic acid, and cholic acid [55]. The fatty acids bind to the TiO_2 surface via carboxylate groups, while their hydrophobic domains allow the anchoring of chlorophyll molecules [55]. The long hydrophobic part of the chlorophyll molecule facilitates its interaction with lipids and its consequent insertion into lipid bilayers [34].

Chlorophyll derivatives containing carboxy groups [56] can be a solution for binding and efficiently injecting electrons into TiO_2 [57]. Another strategy to overcome this limitation is the incorporation of dopants into TiO_2 [39]. Phongamwong et al., for example, added *Spirulina* containing chlorophyll to N-doped TiO_2 catalysts, observing a synergistic effect between doping and chlorophyll loading, achieving a 21.3-fold increase in yield compared to pure TiO_2 [33]. Phongamwong et al. observed that the modification of TiO_2 with *Spirulina* led to a decrease in the catalyst's surface area and pore volume, most likely due to the large size and low porosity of the *Spirulina* particles [33].

3.1. Chlorophyll-Modified TiO_2 as Photocatalyst

Chlorophyll-modified TiO_2 has gained space as a photocatalyst for applications in the environmental area, whether in the degradation of organic pollutants [19,32,51], bactericidal activity [58], or for energy purposes, such as in the synthesis of solar fuels from CO_2 reduction [12,33]. Figure 3 presents a schematic representation of a typical photocatalytic process based on chlorophyll-sensitized TiO_2 . Among the pollutants usually degraded, we can cite dyes such as methylene blue [19] and rhodamine B [51,59]. However, given that the molecules of these dyes are also able to absorb visible photons and donate electrons to TiO_2 , it is necessary to carefully consider the contribution of the dye molecules being

degraded to accurately assess the improvement produced by the addition of chlorophyll to titanium dioxide [19,51].

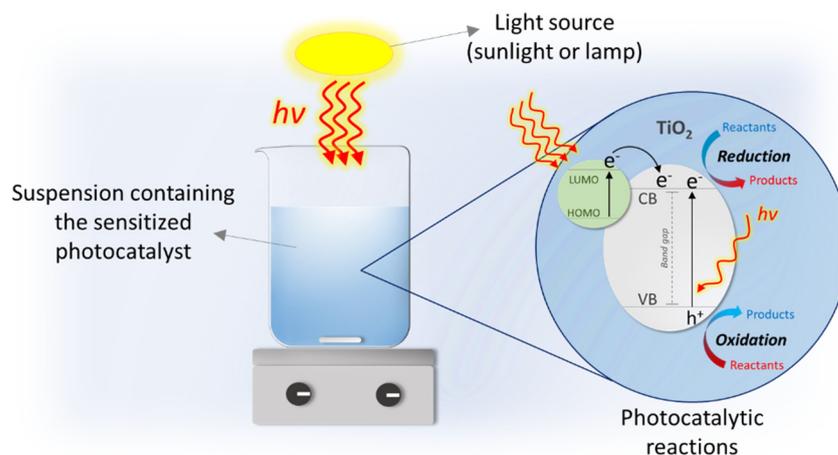


Figure 3. Schematic representation of a typical photocatalytic process based on chlorophyll-sensitized TiO₂.

Furthermore, the association between chlorophyll and TiO₂ has also found space in artificial photosynthesis applications. Shen et al. combined chlorophyll-a and TiO₂ into a fascinating structure mimicking the thylakoid membrane [34]. By applying the synthesized chlorophyll-TiO₂-liposomes, the authors achieved O₂ productions that were approximately three times greater than free chloroplasts.

The improved visible light response is one of the main advantages pointed out in studies on incorporating chlorophyll into TiO₂. TiO₂ thin films sensitized with a cyanobacterial biomass showed approximately 25% methylene blue degradation in 140 min of visible light irradiation compared to less than 10% removal from bare TiO₂ films in the same time interval, as described by Patiño-Camelo et al. [60]. Phongamwong et al. described an increase in the kinetic degradation rate of rhodamine B under visible light after P25 sensitization using chlorophyll, rising from $8.05 \times 10^{-3} \text{ min}^{-1}$ using pure P25 to $60.80 \times 10^{-3} \text{ min}^{-1}$ after dye incorporation [51]. Phongamwong et al. also reported a decrease in the band gap of Chl/P25 samples from 3.02 eV of pure P25 to 2.82–2.87 eV after chlorophyll incorporation [51]. This result was in agreement with that stated by Patiño-Camelo [60], who observed a band-gap reduction from 3.2 eV (TiO₂) to 2.55 eV (sensitized TiO₂).

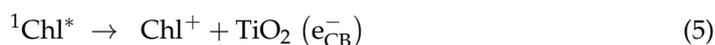
This improvement in performance under visible light is directly related to the sensitizing role of chlorophyll, which acts as an electron donor to the conduction band of the photocatalyst the pigment is incorporated into [51]. When chlorophyll in the ground state (Chl) absorbs photons in the visible light region of the spectrum (around 457 nm), the electrons present in its highest occupied molecular orbital (HOMO) acquire energy to be promoted to last unoccupied molecular orbital (LUMO), resulting in a singlet excited state (¹Chl*, Equation (3)) [19].



Some of the chlorophyll electrons in the singlet state can undergo intersystem crossing (ISC), leading to the triplet state (³Chl*, Equation (4)), or even a return to the ground state by releasing energy [19,51].



Chlorophyll in an excited state can donate electrons to TiO₂, transferring them to the conduction band of the photocatalyst, resulting in the formation of the cationic form of chlorophyll (Chl⁺, Equation (5)) [19]. The electron transfer mechanism is represented in Figure 4.



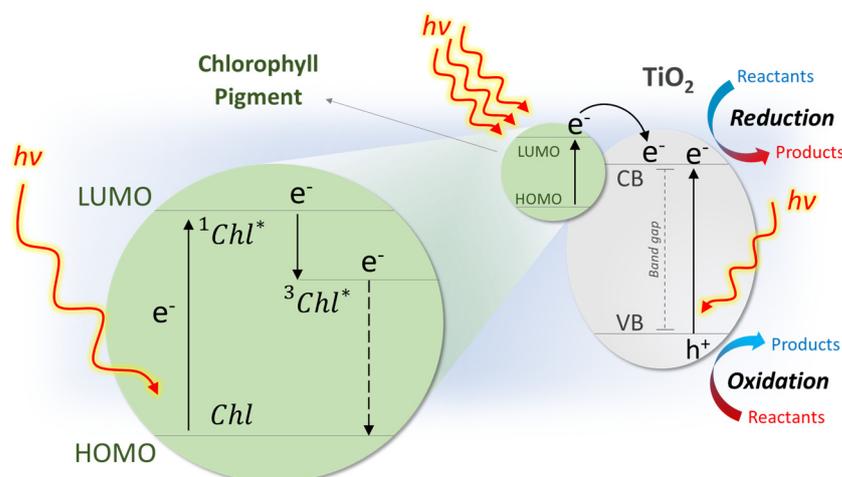
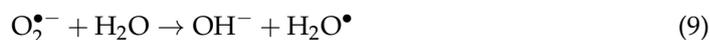
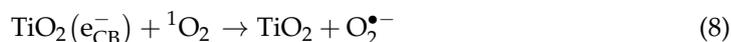
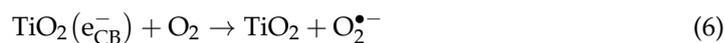


Figure 4. Schematic representation of chlorophyll pigment excitation (left) and excited electrons transfer from chlorophyll to TiO_2 conduction band (right).

The photogenerated electrons can then participate in reactions (Equations (6)–(11)), forming superoxide ($\text{O}_2^{\bullet-}$) and hydroxyl radicals (OH^\bullet), which can promote the degradation of various compounds [19,61].



However, the excessive loading of chlorophyll in the catalyst can compromise its photocatalytic activity by forming recombination centers in the catalyst. Phongamwong et al. reported a decrease in Rhodamine B degradation from 64% to 61% in 1 h of testing when the chlorophyll loading was increased from 0.5 to 1.0 wt.% [51]. There was a slight decrease in photocatalyst activity with the excessive addition of *Spirulina*, probably because it started acting as a recombination center for photogenerated electron–hole pairs [33].

Phongamwong et al. reported an enhanced photocatalytic stability of N-doped TiO_2 catalysts after *Spirulina* incorporation, in contrast to non-sensitized materials, which showed a decrease in H_2 production after 4 h of irradiation [33]. In the same sense, 0.5 Chl-0.1 Mg/P25 catalysts prepared by Phongamwong et al. were considerably stable even after seven cycles of photocatalysis, making it possible to maintain a degradation efficiency greater than 75% of rhodamine B. FTIR analyses carried out with used catalysts compared to fresh ones indicated that, at the end of the tests, only 88% of the chlorophyll was still present in the catalyst, and it was possible to observe this because the intensity of the peak was located at 2920 cm^{-1} . The authors attributed the excellent stability of chlorophyll to the incorporation of Mg into the catalyst, which would have contributed to the inhibition of chlorophyll degradation [51].

Phongamwong et al. described the increased selectivity in CO₂ reduction towards C₂₊ products. According to the authors, the greater availability of electrons from chlorophyll could probably favor chain growth during hydrocarbon formation [33].

3.2. Chlorophyll Sensitization in TiO₂ Solar Cells

DSSCs can be manufactured by sensitizing TiO₂ with extracts from different sources, as shown in Table 3. Figure 5 represents a typical DDSC based on chlorophyll-sensitized TiO₂. The spinach extract is a typical example. Ahliha et al. prepared DSSCs with spinach dye extracted, achieving a voltage of 0.639 mV, a current of 0.33 mA, an FF equal to 0.337, and an efficiency of 0.0713% [29]. Yang et al. used spinach leaf extract to sensitize TiO₂ solar cells with light-harvesting complex II (LHCII) pigment [62].

Table 3. Types of Extracts for TiO₂ sensitizing.

Dye/Pigment	DSSC Configuration	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	η (%)	Ref.
Spinach extract	Spinach dye-sensitized TiO ₂ /FTO electrode, Pt/FTO counter electrode	0.33	0.639	0.337	0.0713	[29]
Spinach extract	Chlorophyll-a-sensitized TiO ₂ nanorods and DSSC devices as described in [63]	0.2566	0.5327	0.5621		[41]
<i>C. woodsonii</i> extract	<i>C. woodsonii</i> -sensitized TiO ₂ /FTO electrode and Pt/FTO counter electrode	2.25	0.57	0.51	0.65	[49]
<i>P. amaryllifolius</i> extract	Chl-TiO ₂ /conductive glass electrode, I ⁻ /I ³⁻ electrolyte solution in acetonitrile.	0.4	0.55	0.6051	0.1	[48]
Chl-e ₆ in ethanol	Chl-e ₆ -TiO ₂ electrode, Pt-coated OTE electrode	1.47	0.425	0.57	0.4	[64]
<i>Plectranthus amboinicus</i> extract	Dye-sensitized TiO ₂ /FTO electrode, Pt counter electrode, I ₃ ⁻ /I ⁻ redox couple.	0.99	0.637	0.63	0.46	[38]
<i>Coriandrum sativum</i> extract		0.62	0.626	0.615	0.28	
<i>Murraya koenigii</i> extract		0.63	0.621	0.595	0.27	
H ₂ Chl and ZnChl	Chl-based biosolar cell (ZnChl) _n /TiO ₂ -H ₂ Chl/TiO ₂ /FTO electrode	4.49	0.67	0.44	1.33	[57]

One of the critical aspects in preparing chlorophyll-based DSSCs is the promotion of the interaction between the pigment and TiO₂. Amao and Kato [55] improved the chlorophyll-a anchoring to the nanocrystalline TiO₂ electrodes by using three fatty acids as modifiers: myristic acid (Myr), stearic acid (Ste), and cholic acid (Cho). The photocurrent responses obtained by the authors were equal to 0.27, 0.19, and 0.19 mA cm⁻² for Chl-a/Ste-TiO₂, Chl-a/Myr-TiO₂, and Chl-a/Cho-TiO₂ electrodes, respectively. The incident photon to current efficiency (IPCE) at 660 nm was 5.0, 4.1, and 4.1%, respectively [55]. These results highlight the relevance of the adequate chlorophyll anchorage to TiO₂ for an improved performance of DSSCs. The adsorption of chlorophyll-a on TiO₂ films is complex in many cases, impairing the performance of solar cells despite the relatively high short-circuit current density [39].

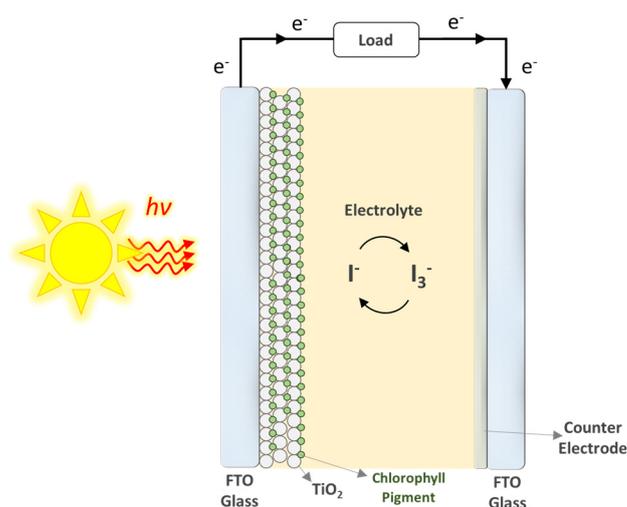


Figure 5. Schematic representation of a typical DDSC based on chlorophyll-sensitized TiO₂.

The proper contact of the dye with the TiO₂ electrode is fundamental for the efficient transport of electrons between them, justifying the need to promote a good incorporation of chlorophyll in the sensitization step, as well as preventing the detachment of the dye from the TiO₂ surface, which may lead to a DSSC performance decrease over time [49]. As for the light-harvesting device's stability, Najihah et al. observed the decrease in the J_{SC} and η at 96 h to 84% and 63% of the as-fabricated values, respectively, and attributed the reduction in the DSSC performance to the detachment of chlorophyll from the TiO₂ surface, probably caused by the presence of impurities in the dye extract [49]. TiO₂ nanotubes sensitized by Tsui et al. with bacteriochlorophyll-C showed photocurrent stability for 14 min under simulated sunlight [50].

In the work of Yang et al. [62], the measured short-circuit current density (J_{SC}) was $1.386 \mu\text{A cm}^{-2}$ for the TiO₂ electrode modified with large LHCII aggregates with 100% of adequate surface coverage (ESC), in comparison to $0.876 \mu\text{A cm}^{-2}$ for the bare APTES-TiO₂ electrodes. This corresponded to a 58.2% increase in the J_{SC} value after incorporating LHCII aggregates in the electrode [62]. Interestingly, the authors observed the excellent stability of the sensitized solar cell and the improvement over time of properties such as J_{SC} , fill factor, and power conversion efficiency during the 30-day interval.

4. Conclusions

Using natural pigments has grown in TiO₂ sensitization applications in photocatalytic processes and DSSCs. Chlorophyll is a natural pigment in photosynthetic organisms, such as plants and cyanobacteria, that plays a fundamental role in transforming solar energy into chemical energy. It can be extracted from different biomasses through relatively simple processes involving organic solvents. Once extracted, it can be applied to the sensitization of semiconductors, such as TiO₂, bringing as one of the main benefits its increased response under the action of visible light. This response under visible light directly impacts its performance in photocatalytic processes, affecting its band gap and selectivity in some processes. Furthermore, it is an excellent option for DSSCs, and the main point to be considered is the proper anchoring of chlorophyll to the TiO₂ surface, which is fundamental for the adequate performance of the solar cell. Promoting a good interaction between chlorophyll and TiO₂ has been one of the main points affecting the process, which still requires improvements from the conversion efficiency and stability point of view.

Author Contributions: Conceptualization, M.E.K.F.; writing, review, and editing, M.E.K.F., A.M.T., O.A.A.d.S. and G.G.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data is contained within the article.

Acknowledgments: The authors thank the Capes, Fundação Araucaria, and CNPq agencies.

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

References

- Schneider, J.; Matsuoka, M.; Takeuchi, M.; Zhang, J.; Horiuchi, Y.; Anpo, M.; Bahnemann, D.W. Understanding TiO₂ photocatalysis: Mechanisms and Materials. *Chem. Rev.* **2014**, *114*, 9919–9986. [[CrossRef](#)] [[PubMed](#)]
- Hashimoto, K.; Irie, H.; Fujishima, A. TiO₂ Photocatalysis: A Historical Overview and Future Prospects. *Jpn. J. Appl. Phys.* **2005**, *44*, 8269. [[CrossRef](#)]
- Fujishima, A.; Honda, K. Electrochemical Evidence for the Mechanism of the Primary Stage of Photosynthesis. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1148–1150. [[CrossRef](#)]
- Augugliaro, V.; Bellardita, M.; Loddo, V.; Palmisano, G.; Palmisano, L.; Yurdakal, S. Overview on Oxidation Mechanisms of Organic Compounds by TiO₂ in Heterogeneous Photocatalysis. *J. Photochem. Photobiol. C Photochem. Rev.* **2012**, *13*, 224–245. [[CrossRef](#)]
- Varma, K.S.; Tayade, R.J.; Shah, K.J.; Joshi, P.A.; Shukla, A.D.; Gandhi, V.G. Photocatalytic Degradation of Pharmaceutical and Pesticide Compounds (PPCs) Using Doped TiO₂ Nanomaterials: A Review. *Water-Energy Nexus* **2020**, *3*, 46–61. [[CrossRef](#)]
- Murgolo, S.; De Ceglie, C.; Di Iaconi, C.; Mascolo, G. Novel TiO₂-Based Catalysts Employed in Photocatalysis and Photoelectrocatalysis for Effective Degradation of Pharmaceuticals (PhACs) in Water: A Short Review. *Curr. Opin. Green. Sustain. Chem.* **2021**, *30*, 100473. [[CrossRef](#)]
- Shoneye, A.; Sen Chang, J.; Chong, M.N.; Tang, J. Recent Progress in Photocatalytic Degradation of Chlorinated Phenols and Reduction of Heavy Metal Ions in Water by TiO₂-Based Catalysts. *Int. Mater. Rev.* **2022**, *67*, 47–64. [[CrossRef](#)]
- Bono, N.; Ponti, F.; Punta, C.; Candiani, G. Effect of UV Irradiation and TiO₂-Photocatalysis on Airborne Bacteria and Viruses: An Overview. *Materials* **2021**, *14*, 1075. [[CrossRef](#)] [[PubMed](#)]
- Liao, C.H.; Huang, C.W.; Wu, J.C.S. Hydrogen Production from Semiconductor-Based Photocatalysis via Water Splitting. *Catalysts* **2012**, *2*, 490–516. [[CrossRef](#)]
- Chiarello, G.L.; Dozzi, M.V.; Selli, E. TiO₂-Based Materials for Photocatalytic Hydrogen Production. *J. Energy Chem.* **2017**, *26*, 250–258. [[CrossRef](#)]
- Kumaravel, V.; Mathew, S.; Bartlett, J.; Pillai, S.C. Photocatalytic Hydrogen Production Using Metal Doped TiO₂: A Review of Recent Advances. *Appl. Catal. B* **2019**, *244*, 1021–1064. [[CrossRef](#)]
- Wang, Z.; Zhou, W.; Wang, X.; Zhang, X.; Chen, H.; Hu, H.; Liu, L.; Ye, J.; Wang, D. Enhanced Photocatalytic CO₂ Reduction over TiO₂ Using Metalloporphyrin as the Cocatalyst. *Catalysts* **2020**, *10*, 654. [[CrossRef](#)]
- Roy, N.; Suzuki, N.; Terashima, C.; Fujishima, A. Recent Improvements in the Production of Solar Fuels: From CO₂ Reduction to Water Splitting and Artificial Photosynthesis. *Bull. Chem. Soc. Jpn.* **2019**, *92*, 178–192. [[CrossRef](#)]
- Gust, D.; Moore, T.A.; Moore, A.L. Solar Fuels via Artificial Photosynthesis. *Acc. Chem. Res.* **2009**, *42*, 1890–1898. [[CrossRef](#)] [[PubMed](#)]
- Guo, Q.; Zhou, C.; Ma, Z.; Yang, X. Fundamentals of TiO₂ Photocatalysis: Concepts, Mechanisms, and Challenges. *Adv. Mater.* **2019**, *31*, 1901997. [[CrossRef](#)] [[PubMed](#)]
- Bora, L.V.; Mewada, R.K. Visible/Solar Light Active Photocatalysts for Organic Effluent Treatment: Fundamentals, Mechanisms and Parametric Review. *Renew. Sustain. Energy Rev.* **2017**, *76*, 1393–1421. [[CrossRef](#)]
- Linsebigler, A.L.; Lu, G.; Yates, J.T. Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected Results. *Chem. Rev.* **1995**, *95*, 735–758. [[CrossRef](#)]
- Chen, D.; Cheng, Y.; Zhou, N.; Chen, P.; Wang, Y.; Li, K.; Huo, S.; Cheng, P.; Peng, P.; Zhang, R.; et al. Photocatalytic Degradation of Organic Pollutants Using TiO₂-Based Photocatalysts: A Review. *J. Clean. Prod.* **2020**, *268*, 121725. [[CrossRef](#)]
- Krishnan, S.; Shriwastav, A. Application of TiO₂ Nanoparticles Sensitized with Natural Chlorophyll Pigments as Catalyst for Visible Light Photocatalytic Degradation of Methylene Blue. *J. Environ. Chem. Eng.* **2021**, *9*, 104699. [[CrossRef](#)]
- Finnie, K.S.; Bartlett, J.R.; Woolfrey, J.L. Vibrational Spectroscopic Study of the Coordination of (2,2'-Bipyridyl-4,4'-Dicarboxylic Acid)Ruthenium(II) Complexes to the Surface of Nanocrystalline Titania. *Langmuir* **1998**, *14*, 2744–2749. [[CrossRef](#)]
- Zhang, H.; Zhou, Y.; Zhang, M.; Shen, T.; Li, Y.; Zhu, D. Photoinduced Interaction between Fluorescein Ester Derivatives and CdS Colloid. *J. Colloid. Interface Sci.* **2003**, *264*, 290–295. [[CrossRef](#)] [[PubMed](#)]
- Kathiravan, A.; Chandramohan, M.; Renganathan, R.; Sekar, S. Cyanobacterial Chlorophyll as a Sensitizer for Colloidal TiO₂. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2009**, *71*, 1783–1787. [[CrossRef](#)] [[PubMed](#)]
- Mujtahid, F.; Gareso, P.L.; Arminyah, B.; Tahir, D. Review Effect of Various Types of Dyes and Structures in Supporting Performance of Dye-Sensitized Solar Cell TiO₂-Based Nanocomposites. *Int. J. Energy Res.* **2022**, *46*, 726–742. [[CrossRef](#)]
- Karim, N.A.; Mehmood, U.; Zahid, H.F.; Asif, T. Nanostructured Photoanode and Counter Electrode Materials for Efficient Dye-Sensitized Solar Cells (DSSCs). *Solar Energy* **2019**, *185*, 165–188. [[CrossRef](#)]
- Hosseinneshad, M.; Gharanjig, K.; Yazdi, M.K.; Zarrintaj, P.; Moradian, S.; Saeb, M.R.; Stadler, F.J. Dye-Sensitized Solar Cells Based on Natural Photosensitizers: A Green View from Iran. *J. Alloys Compd.* **2020**, *828*, 154329. [[CrossRef](#)]
- Richhariya, G.; Kumar, A.; Tekasakul, P.; Gupta, B. Natural Dyes for Dye Sensitized Solar Cell: A Review. *Renew. Sustain. Energy Rev.* **2017**, *69*, 705–718. [[CrossRef](#)]

27. Omar, A.; Ali, M.S.; Abd Rahim, N. Electron Transport Properties Analysis of Titanium Dioxide Dye-Sensitized Solar Cells (TiO₂-DSSCs) Based Natural Dyes Using Electrochemical Impedance Spectroscopy Concept: A Review. *Sol. Energy* **2020**, *207*, 1088–1121. [[CrossRef](#)]
28. Mukhokosi, E.P.; Maaza, M.; Tibenkana, M.; Botha, N.L.; Namanya, L.; Madiba, I.G.; Okullo, M. Optical Absorption and Photoluminescence Properties of Cucurbita Maxima Dye Adsorption on TiO₂nanoparticles. *Mater. Res. Express* **2023**, *10*, 046203. [[CrossRef](#)]
29. Ahliha, A.H.; Nurosyid, F.; Supriyanto, A.; Kusumaningsih, T. The Chemical Bonds Effect of Anthocyanin and Chlorophyll Dyes on TiO₂ for Dye-Sensitized Solar Cell (DSSC). In *Journal of Physics: Conference Series, Proceedings of the International Conference on Science and Applied Science 2017, Solo, Indonesia, 29 July 2017*; Institute of Physics Publishing: Bristol, UK, 2017; Volume 909.
30. Haghghatzadeh, A. Comparative Analysis on Optical and Photocatalytic Properties of Chlorophyll/Curcumin-Sensitized TiO₂ Nanoparticles for Phenol Degradation. *Bull. Mater. Sci.* **2020**, *43*, 52. [[CrossRef](#)]
31. Arof, A.K.; Ping, T.L. Chlorophyll as Photosensitizer in Dye-Sensitized Solar Cells. In *Chlorophyll*; InTech: London, UK, 2017.
32. Krishnan, S.; Shriwastav, A. Chlorophyll Sensitized and Salicylic Acid Functionalized TiO₂ Nanoparticles as a Stable and Efficient Catalyst for the Photocatalytic Degradation of Ciprofloxacin with Visible Light. *Environ. Res.* **2023**, *216*, 114568. [[CrossRef](#)]
33. Phongamwong, T.; Chareonpanich, M.; Limtrakul, J. Role of Chlorophyll in Spirulina on Photocatalytic Activity of CO₂ Reduction under Visible Light over Modified N-Doped TiO₂ Photocatalysts. *Appl. Catal. B* **2015**, *168–169*, 114–124. [[CrossRef](#)]
34. Shen, S.; Wang, Y.; Dong, J.; Zhang, R.; Parikh, A.; Chen, J.G.; Hu, D. Mimicking Thylakoid Membrane with Chlorophyll/TiO₂/Lipid Co-Assembly for Light-Harvesting and Oxygen Releasing. *ACS Appl. Mater. Interfaces* **2021**, *13*, 11461–11469. [[CrossRef](#)] [[PubMed](#)]
35. Gross, J. *Pigments in Vegetables*; Springer: Boston, MA, USA, 1991; ISBN 978-1-4613-5842-8.
36. Murata, N. Control of Excitation Transfer in Photosynthesis II. Magnesium Ion-Dependent Distribution of Excitation Energy between Two Pigment Systems in Spinach Chloroplasts. *Biochim. Biophys. Acta BBA* **1969**, *189*, 171–181. [[CrossRef](#)]
37. Jamali Jaghdani, S.; Jahns, P.; Tränkner, M. The Impact of Magnesium Deficiency on Photosynthesis and Photoprotection in Spinacia Oleracea. *Plant Stress* **2021**, *2*, 100040. [[CrossRef](#)]
38. Mary Rosana, N.T.; Joshua Amarnath, D.; Senthil Kumar, P.; Vincent Joseph, K.L. Potential of Plant-Based Photosensitizers in Dye-Sensitized Solar Cell Applications. *Environ. Prog. Sustain. Energy* **2020**, *39*, e13351. [[CrossRef](#)]
39. Pai, A.R.; Nair, B. Synthesis and Characterization of a Binary Oxide ZrO₂-TiO₂ and Its Application in Chlorophyll Dye-Sensitized Solar Cell with Reduced Graphene Oxide as Counter Electrodes. *Bull. Mater. Sci.* **2015**, *38*, 1129–1133. [[CrossRef](#)]
40. Christwardana, M.; Septevani, A.A.; Yoshi, L.A. Outstanding Photo-Bioelectrochemical Cell by Integrating TiO₂ and Chlorophyll as Photo-Bioanode for Sustainable Energy Generation. *Int. J. Renew. Energy Dev.* **2022**, *11*, 385–391. [[CrossRef](#)]
41. Mahadik, S.A.; Yadav, H.M.; Mahadik, S.S. Surface Properties of Chlorophyll-a Sensitized TiO₂ Nanorods for Dye-Sensitized Solar Cells Applications. *Colloids Interface Sci. Commun.* **2022**, *46*, 100558. [[CrossRef](#)]
42. Heidari, A.; Safa, K.D.; Teimuri-Mofrad, R. Chlorophyll B-Modified TiO₂ Nanoparticles for Visible-Light-Induced Photocatalytic Synthesis of New Tetrahydroquinoline Derivatives. *Mol. Catal.* **2023**, *547*, 113338. [[CrossRef](#)]
43. Chen, C.; Gong, N.; Qu, F.; Gao, Y.; Fang, W.; Sun, C.; Men, Z. Effects of Carotenoids on the Absorption and Fluorescence Spectral Properties and Fluorescence Quenching of Chlorophyll a. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2018**, *204*, 440–445. [[CrossRef](#)]
44. Ungureanu, E.M.; Tatu, M.L.; Georgescu, E.; Boscornea, C.; Popa, M.M.; Stanciu, G. Influence of the Chemical Structure and Solvent Polarity on the Fluorescence of 3-Aryl-7-Benzoyl-Pyrrolo [1,2-c]Pyrimidines. *Dyes Pigments* **2020**, *174*, 108023. [[CrossRef](#)]
45. Faiz, M.R.; Widhiyanuriyawan, D.; Siswanto, E.; Wardana, I.N.G. Theoretical Study on the Effect of Solvents in Chlorophyll Solution for Dye-Sensitized Solar Cell. In *IOP Conference Series: Materials Science and Engineering, Proceedings of the International Conference on Chemistry and Material Science (IC2MS) 2017, Malang, Indonesia, 4–5 November 2017*; Institute of Physics Publishing: Bristol, UK, 2018; Volume 299, p. 299.
46. Sabagh, S.; Izadyar, M.; Arkan, F. Insight into Incident Photon to Current Conversion Efficiency in Chlorophylls. *Int. J. Quantum Chem.* **2021**, *121*, e26483. [[CrossRef](#)]
47. Qiao, L.; Tang, W.; Gao, D.; Zhao, R.; An, L.; Li, M.; Sun, H.; Song, D. UAV-Based Chlorophyll Content Estimation by Evaluating Vegetation Index Responses under Different Crop Coverages. *Comput. Electron. Agric.* **2022**, *196*, 106775. [[CrossRef](#)]
48. Al-Alwani, M.A.M.; Mohamad, A.B.; Kadhum, A.A.H.; Ludin, N.A.; Safie, N.E.; Razali, M.Z.; Ismail, M.; Sopian, K. Natural Dye Extracted from Pandanus Amaryllifolius Leaves as Sensitizer in Fabrication of Dye-Sensitized Solar Cells. *Int. J. Electrochem. Sci.* **2017**, *12*, 747–761. [[CrossRef](#)]
49. Najihah, M.Z.; Noor, I.M.; Winie, T. Long-Run Performance of Dye-Sensitized Solar Cell Using Natural Dye Extracted from Costus Woodsonii Leaves. *Opt. Mater.* **2022**, *123*, 111915. [[CrossRef](#)]
50. Tsui, L.K.; Huang, J.; Sabat, M.; Zangari, G. Visible Light Sensitization of TiO₂ Nanotubes by Bacteriochlorophyll-C Dyes for Photoelectrochemical Solar Cells. *ACS Sustain. Chem. Eng.* **2014**, *2*, 2097–2101. [[CrossRef](#)]
51. Phongamwong, T.; Donphai, W.; Prasitchoke, P.; Rameshan, C.; Barrabés, N.; Klysubun, W.; Rupperechtter, G.; Chareonpanich, M. Novel Visible-Light-Sensitized Chl-Mg/P25 Catalysts for Photocatalytic Degradation of Rhodamine B. *Appl. Catal. B* **2017**, *207*, 326–334. [[CrossRef](#)]
52. Zakaria, P.N.M.; Noor, I.S.M.; Winie, T. *Caulerpa lentillifera* Seaweed Extract as Natural Sensitizer for Dye-Sensitized Solar Cell. *Macromol. Symp.* **2023**, *407*, 2100359. [[CrossRef](#)]

53. Giang, N.T.H.; Thinh, N.T.; Hai, N.D.; Loc, P.T.; Thu, T.N.A.; Loan, N.H.P.; Quang, D.M.; Anh, L.D.; Truong An, V.N.T.; Phong, M.T.; et al. Application of TiO₂ Nanoparticles with Natural Chlorophyll as the Catalyst for Visible Light Photocatalytic Degradation of Methyl Orange and Antibacterial. *Inorg. Chem. Commun.* **2023**, *150*, 110513. [[CrossRef](#)]
54. Ma, T.; Inoue, K.; Yao, K.; Noma, H.; Shuji, T.; Abe, E.; Yu, J.; Wang, X.; Zhang, B. Photoelectrochemical Properties of TiO₂ Electrodes Sensitized by Porphyrin Derivatives with Different Numbers of Carboxyl Groups. *J. Electroanal. Chem.* **2002**, *537*, 31–38. [[CrossRef](#)]
55. Amao, Y.; Kato, K. Chlorophyll Assembled Electrode for Photovoltaic Conversion Device. *Electrochim. Acta* **2007**, *53*, 42–45. [[CrossRef](#)]
56. Hashimoto, Y.; Suzuki, H.; Kondo, T.; Abe, R.; Tamiaki, H. Visible-Light-Induced Hydrogen Evolution from Water on Hybrid Photocatalysts Consisting of Synthetic Chlorophyll-a Derivatives with a Carboxy Group in the 20-Substituent Adsorbed on Semiconductors. *J. Photochem. Photobiol. A Chem.* **2022**, *426*, 113750. [[CrossRef](#)]
57. Zhao, W.; Wang, L.; Pan, L.; Duan, S.; Tamai, N.; Sasaki, S.I.; Tamiaki, H.; Sanehira, Y.; Wei, Y.; Chen, G.; et al. Charge Transfer Dynamics in Chlorophyll-Based Biosolar Cells. *Phys. Chem. Chem. Phys.* **2019**, *21*, 22563–22568. [[CrossRef](#)] [[PubMed](#)]
58. Pan, X.; Dong, W.; Zhang, J.; Xie, Z.; Li, W.; Zhang, H.; Zhang, X.; Chen, P.; Zhou, W.; Lei, B. TiO₂/Chlorophyll S-Scheme Composite Photocatalyst with Improved Photocatalytic Bactericidal Performance. *ACS Appl. Mater. Interfaces* **2021**, *13*, 39446–39457. [[CrossRef](#)] [[PubMed](#)]
59. Valadez-Renteria, E.; Oliva, J.; Rodriguez-Gonzalez, V. A Sustainable and Green Chlorophyll/TiO₂:W Composite Supported on Recycled Plastic Bottle Caps for the Complete Removal of Rhodamine B Contaminant from Drinking Water. *J. Environ. Manage* **2022**, *315*, 115204. [[CrossRef](#)] [[PubMed](#)]
60. Patiño-Camelo, K.; Diaz-Urbe, C.; Gallego-Cartagena, E.; Vallejo, W.; Martinez, V.; Quiñones, C.; Hurtado, M.; Schott, E. Cyanobacterial Biomass Pigments as Natural Sensitizer for TiO₂ Thin Films. *Int. J. Photoenergy* **2019**, *2019*, 7184327. [[CrossRef](#)]
61. Cabir, B.; Yurderi, M.; Caner, N.; Agirtas, M.S.; Zahmakiran, M.; Kaya, M. Methylene Blue Photocatalytic Degradation under Visible Light Irradiation on Copper Phthalocyanine-Sensitized TiO₂ Nanopowders. *Mater. Sci. Eng. B Solid. State Mater. Adv. Technol.* **2017**, *224*, 9–17. [[CrossRef](#)]
62. Yang, Y.; Jankowiak, R.; Lin, C.; Pawlak, K.; Reus, M.; Holzwarth, A.R.; Li, J. Effect of the LHCII Pigment-Protein Complex Aggregation on Photovoltaic Properties of Sensitized TiO₂ Solar Cells. *Phys. Chem. Chem. Phys.* **2014**, *16*, 20856–20865. [[CrossRef](#)]
63. Li, Y.; Yoo, K.; Lee, D.K.; Kim, J.Y.; Son, H.J.; Kim, J.H.; Lee, C.H.; Míguez, H.; Ko, M.J. Synergistic Strategies for the Preparation of Highly Efficient Dye-Sensitized Solar Cells on Plastic Substrates: Combination of Chemical and Physical Sintering. *RSC Adv.* **2015**, *5*, 76795–76803. [[CrossRef](#)]
64. Amao, Y.; Yamada, Y.; Aoki, K. Preparation and Properties of Dye-Sensitized Solar Cell Using Chlorophyll Derivative Immobilized TiO₂ Film Electrode. *J. Photochem. Photobiol. A Chem.* **2004**, *164*, 47–51. [[CrossRef](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.