

Review

# Chlorophyll Sensitization of TiO<sub>2</sub>: A Mini-Review

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**Abstract:** Recent studies have shown that chlorophyll sensitization can improve the performance of semiconductors like TiO<sub>2</sub> 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-TiO<sub>2</sub> combination, presenting the most relevant aspects affecting chlorophyll extraction and TiO<sub>2</sub> sensitization.

**Keywords:** Chlorophyll; TiO<sub>2</sub>; dye sensitization; photocatalysis; DSSC

## 1. Introduction

Titanium dioxide (TiO<sub>2</sub>) is a semiconductor widely used in photocatalytic and photo-electrochemical processes, since the first works describing reactions involving TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub>-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 CO<sub>2</sub> 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., H<sub>2</sub>, CO, CH<sub>3</sub>OH, CH<sub>4</sub>) using sunlight, which are also known as solar fuels [13,14].

The cited processes are based on TiO<sub>2</sub>'s ability to form electron (e<sup>-</sup>)/hole (h<sup>+</sup>) pairs under UV irradiation. When the energy of the photons absorbed by TiO<sub>2</sub> 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<sup>-</sup>/h<sup>+</sup> pairs can recombine inside the photocatalyst particle or migrate to the surface and undergo recombination. If this does not occur, e<sup>-</sup>/h<sup>+</sup> 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 TiO<sub>2</sub> applications combined with solar radiation, which includes predominantly visible light and less than 5% of



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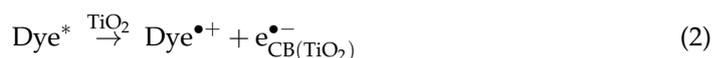
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UV radiation [19]. As one of the possible alternatives, dye sensitization of wide band-gap semiconductors ( $>3.0$  eV), such as  $\text{TiO}_2$ , has been the subject of different studies for improved solar light harvesting technologies [20]. In dye 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].

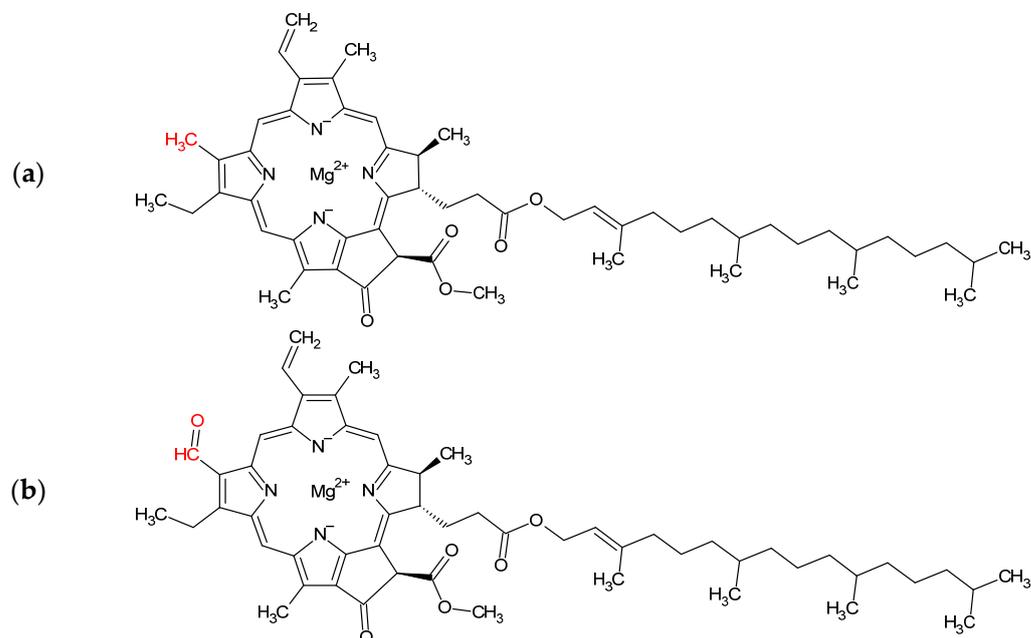
Among natural dyes, chlorophyll has undoubtedly shown exciting results. As reported by [29], spinach extract produced the best efficiency results among the different natural extracts used in sensitizing  $\text{TiO}_2$  solar cells. Compared to the other natural dyes (black rice, dragon fruit, red cabbage, 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  $\text{TiO}_2$  nanoparticles sensitized with chlorophyll promoted higher percentages of degradation (85%) than those sensitized with curcumin (75%) [30]. Thus,  $\text{TiO}_2$  sensitized with chlorophyll has gained space in DSSC [31] and photocatalysis applications, including pollutant degradation [32],  $\text{CO}_2$  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  $\text{TiO}_2$  sensitization for different applications described in the literature.

## 2. Chlorophyll

Chlorophyll is a natural pigment of the porphyrin class, which has a  $\text{Mg}^{2+}$  ion coordinated to the four rings [35], as shown in Figure 1. The  $\text{Mg}^{2+}$  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  $\text{TiO}_2$ , 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 TiO<sub>2</sub> 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*<sub>647</sub>) and 664 nm (*OD*<sub>664</sub>)—to estimate the concentrations of chlorophyll-a and chlorophyll-b in mg L<sup>-1</sup> [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  $0.39 \pm 0.05$  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 TiO<sub>2</sub> surface [49].

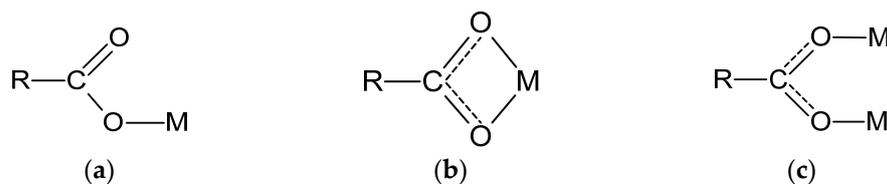
Phongamwong et al. did not perform the chlorophyll extraction. Still, they incorporated *Spirulina* directly into the TiO<sub>2</sub> using the incipient wetness impregnation method, using deionized water to disperse the ground *Spirulina* and then adding it to the N-TiO<sub>2</sub>, which was kept under 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 TiO<sub>2</sub>

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 TiO<sub>2</sub> and the chlorophyll extract for a certain period. In the case of Chl-TiO<sub>2</sub> 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 TiO<sub>2</sub> 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  $\text{TiO}_2$  through interactions between some of its functional groups and the O of titanium dioxide, with a predominance of polar bonds.  $\text{TiO}_2$  FTIR spectra typically show peaks at approximately  $3400\text{ cm}^{-1}$  (O–H stretching),  $1630\text{ cm}^{-1}$  (O–H bending mode), and  $800\text{--}400\text{ cm}^{-1}$  (O–Ti–O stretching) [19,51]. Chlorophyll's presence in  $\text{TiO}_2$ -sensitized samples is normally indicated by the peaks associated with the symmetric C–H stretching vibration of methine (CH), methyl ( $\text{CH}_3$ ), or methylene ( $\text{CH}_2$ ) groups, which has already been reported by different authors to occur at  $2975\text{ cm}^{-1}$  [52],  $2932\text{ cm}^{-1}$  [53], or  $2920\text{ cm}^{-1}$  [51]. Several authors also highlighted the peak referring to C=O stretching in the region between  $1632$  and  $1641\text{ cm}^{-1}$ , which is associated with ketone or aldehyde groups, highlighting the importance of C=O for chlorophyll anchoring on  $\text{TiO}_2$ . [51–53]. The FTIR spectra of chlorophyll extracted from different sources also tend to show a broad peak in the region at approximately  $3500\text{ cm}^{-1}$  associated with the OH group, as already described by [49] ( $3700\text{--}3000\text{ cm}^{-1}$ ), [38] ( $3600\text{--}3400\text{ cm}^{-1}$ ), [52] ( $3296\text{ cm}^{-1}$ ), and [48] ( $3350\text{ cm}^{-1}$ ).

The presence of alkyl groups instead of hydroxyl or carboxyl groups in the chlorophyll molecule can impair the Chl- $\text{TiO}_2$  interaction due to steric effects, hindering the electron transfer from the dye to the electrode [48]. The dye sensitization of  $\text{TiO}_2$  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.

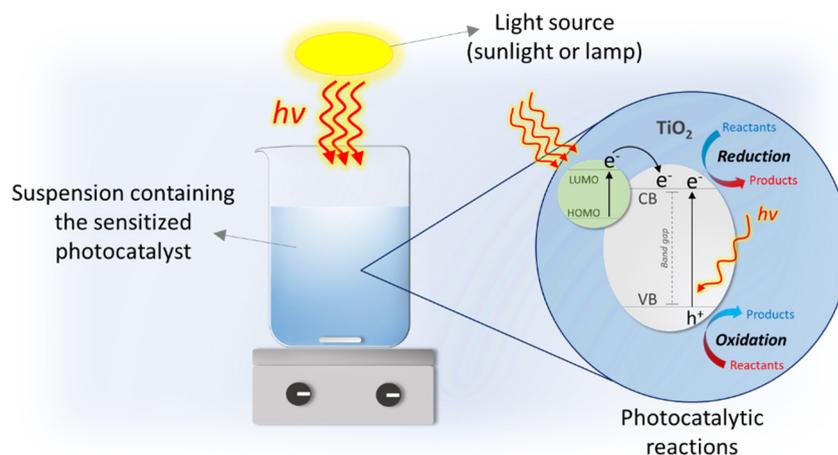
Since there are no carboxyl, carbonyl, or hydroxyl groups in the chlorophyll molecule that favor its anchorage to the surface [39,55], its fixation on  $\text{TiO}_2$  can be improved with the help of some fatty acids with a long carbon chain such as myristic acid, stearic acid, and cholic acid [55]. The fatty acids bind to the  $\text{TiO}_2$  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  $\text{TiO}_2$  [57]. Another strategy to overcome this limitation is the incorporation of dopants into  $\text{TiO}_2$  [39]. Phongamwong et al., for example, added *Spirulina* containing chlorophyll to N-doped  $\text{TiO}_2$  catalysts, observing a synergistic effect between doping and chlorophyll loading, achieving a 21.3-fold increase in yield compared to pure  $\text{TiO}_2$  [33]. Phongamwong et al. observed that the modification of  $\text{TiO}_2$  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 $\text{TiO}_2$ as Photocatalyst

Chlorophyll-modified  $\text{TiO}_2$  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  $\text{CO}_2$  reduction [12,33]. Figure 3 presents a schematic representation of a typical photocatalytic process based on chlorophyll-sensitized  $\text{TiO}_2$ . 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  $\text{TiO}_2$ , 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].

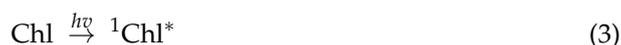


**Figure 3.** Schematic representation of a typical photocatalytic process based on chlorophyll-sensitized TiO<sub>2</sub>.

Furthermore, the association between chlorophyll and TiO<sub>2</sub> has also found space in artificial photosynthesis applications. Shen et al. combined chlorophyll-a and TiO<sub>2</sub> into a fascinating structure mimicking the thylakoid membrane [34]. By applying the synthesized chlorophyll-TiO<sub>2</sub>-liposomes, the authors achieved O<sub>2</sub> 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 TiO<sub>2</sub>. TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 (TiO<sub>2</sub>) to 2.55 eV (sensitized TiO<sub>2</sub>).

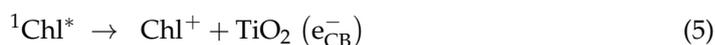
This improvement in performance under visible light is directly related to the sensitizing role of chlorophyll, which acts as an electron donor to the conduction band of the photocatalyst the pigment is incorporated into [51]. When chlorophyll in the ground state (Chl) absorbs photons in the visible 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 (<sup>1</sup>Chl\*, Equation (3)) [19].

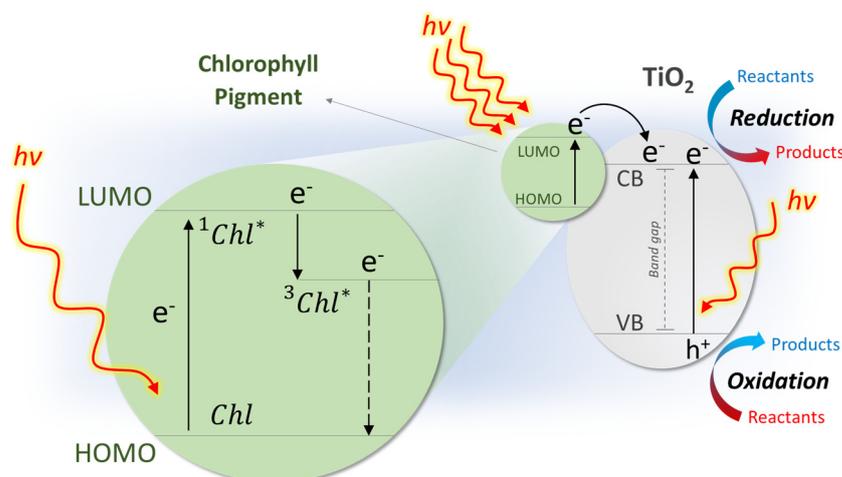


Some of the chlorophyll electrons in the singlet state can undergo intersystem crossing (ISC), leading to the triplet state (<sup>3</sup>Chl\*, Equation (4)), or even a return to the ground state by releasing energy [19,51].



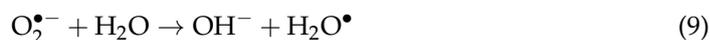
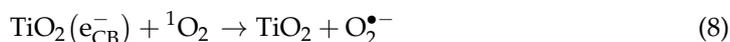
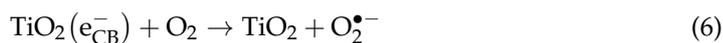
Chlorophyll in an excited state can donate electrons to TiO<sub>2</sub>, transferring them to the conduction band of the photocatalyst, resulting in the formation of the cationic form of chlorophyll (Chl<sup>+</sup>, Equation (5)) [19]. The electron transfer mechanism is represented in Figure 4.





**Figure 4.** Schematic representation of chlorophyll pigment excitation (left) and excited electrons transfer from chlorophyll to  $\text{TiO}_2$  conduction band (right).

The photogenerated electrons can then participate in reactions (Equations (6)–(11)), forming superoxide ( $\text{O}_2^{\bullet-}$ ) and hydroxyl radicals ( $\text{OH}^\bullet$ ), 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  $\text{TiO}_2$  catalysts after *Spirulina* incorporation, in contrast to non-sensitized materials, which showed a decrease in  $\text{H}_2$  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  $2920\text{ cm}^{-1}$ . 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 CO<sub>2</sub> reduction towards C<sub>2+</sub> products. According to the authors, the greater availability of electrons from chlorophyll could probably favor chain growth during hydrocarbon formation [33].

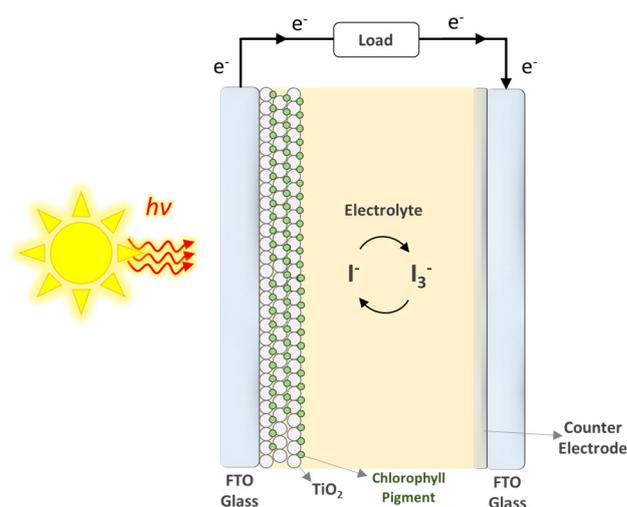
### 3.2. Chlorophyll Sensitization in TiO<sub>2</sub> Solar Cells

DSSCs can be manufactured by sensitizing TiO<sub>2</sub> with extracts from different sources, as shown in Table 3. Figure 5 represents a typical DDSC based on chlorophyll-sensitized TiO<sub>2</sub>. 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 TiO<sub>2</sub> solar cells with light-harvesting complex II (LHCII) pigment [62].

**Table 3.** Types of Extracts for TiO<sub>2</sub> sensitizing.

Dye/Pigment	DSSC Configuration	$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (V)	FF	$\eta$ (%)	Ref.
Spinach extract	Spinach dye-sensitized TiO <sub>2</sub> /FTO electrode, Pt/FTO counter electrode	0.33	0.639	0.337	0.0713	[29]
Spinach extract	Chlorophyll-a-sensitized TiO <sub>2</sub> 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 <sub>2</sub> /FTO electrode and Pt/FTO counter electrode	2.25	0.57	0.51	0.65	[49]
<i>P. amaryllifolius</i> extract	Chl-TiO <sub>2</sub> /conductive glass electrode, I <sup>-</sup> /I <sup>3-</sup> electrolyte solution in acetonitrile.	0.4	0.55	0.6051	0.1	[48]
Chl-e <sub>6</sub> in ethanol	Chl-e <sub>6</sub> -TiO <sub>2</sub> electrode, Pt-coated OTE electrode	1.47	0.425	0.57	0.4	[64]
<i>Plectranthus amboinicus</i> extract	Dye-sensitized TiO <sub>2</sub> /FTO electrode, Pt counter electrode, I <sub>3</sub> <sup>-</sup> /I <sup>-</sup> 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 <sub>2</sub> Chl and ZnChl	Chl-based biosolar cell (ZnChl) <sub>n</sub> /TiO <sub>2</sub> -H <sub>2</sub> Chl/TiO <sub>2</sub> /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 TiO<sub>2</sub>. Amao and Kato [55] improved the chlorophyll-a anchoring to the nanocrystalline TiO<sub>2</sub> 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<sup>-2</sup> for Chl-a/Ste-TiO<sub>2</sub>, Chl-a/Myr-TiO<sub>2</sub>, and Chl-a/Cho-TiO<sub>2</sub> 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 TiO<sub>2</sub> for an improved performance of DSSCs. The adsorption of chlorophyll-a on TiO<sub>2</sub> 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  $\text{TiO}_2$ .

The proper contact of the dye with the  $\text{TiO}_2$  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  $\text{TiO}_2$  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  $\eta$  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  $\text{TiO}_2$  surface, probably caused by the presence of impurities in the dye extract [49].  $\text{TiO}_2$  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  $\text{TiO}_2$  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- $\text{TiO}_2$  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  $\text{TiO}_2$  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  $\text{TiO}_2$ , 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  $\text{TiO}_2$  surface, which is fundamental for the adequate performance of the solar cell. Promoting a good interaction between chlorophyll and  $\text{TiO}_2$  has been one of the main points affecting the process, which still requires improvements from the conversion efficiency and stability point of view.

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