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Direct integration of natural antenna structures to electrochemical cells towards novel biophotovoltaics

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Abstract

The natural photosynthetic components hold approximately the highest efficiency of quantum yields. Researchers have extracted natural complexes from photosynthetic organisms to design biohybrid photoelectrochemical systems. To this end, natural parts such as reaction center and photosystem I have been usually joined with a conductive solid environment for more effective energy conversion based on the protein–electrode charge exchange. In this minireview, we highlight the use of the most common natural components for direct solar power conversion in electrochemical vehicles and solid-state designs as well as their applications in the development of new organic solar cells.

Keywords: *Artificial Photosynthesis, Photoelectrochemical Cells, Organic Solar Cells*

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1. Introduction

Growing global energy demands, depletion of oil reserves, and increasing greenhouse gas emissions have necessitated the revision and control of our energy consumption toward sustainable and renewable energy resources. Combustion of enormous amounts of fossil fuels leads to accumulating an alarming level of CO₂ in the atmosphere thus causing global warming and climate change. Given the need to gain alternative energy reservoirs to fossil fuels and high-efficient natural energy conversion, humankind should set one of the primary global goals for our society today as achieving a complete biomimetic of natural photosynthetic systems.

Photosynthesis is a natural phenomenon responsible for solar energy capture and saving as a chemical fuel. Photosynthetic organisms are ubiquitous on the earth and have a very important role in the expansion and nourishment of whole life on the planet. All organisms use a similar fundamental mechanism: the solar light energy is initially absorbed and concentrated by an antenna complex. It is then transferred to a reaction center through an unknown efficient way where charge separation occurs, after which reactions occur that convert the absorbed light energy into a more stable form via formation of chemical compounds. The specialized compartment where the photosynthetic processes take place is the chloroplast within the cell. Each reaction is accomplished by functional light-absorbing molecules binding to specific proteins, followed by redox reactions, and charge transfer. Proteins are nano-scaled biopolymers specialized in shape and function and are organized within a phospholipid membrane. Natural light-harvesting antennas are complexes of proteins that are designed to capture light and deliver light-induced exciton to the reaction center; then the charge separation starts to occur there. They significantly increase the light absorption cross-section for photosynthetic organisms, avoiding from building an entire distinct reaction center compartment for each pigment, which would be very costly for synthesis within the living cells. Nature's solution for the low intensity of sunlight is incorporating several pigments into each antenna unit and creating supramolecular assemblies from these units, which broadly cover the photosynthetic

membrane and guarantee that photons beating any point on the surface will be absorbed. The interconnections between antenna complexes are responsible for carrying solar light energy through long-distant exciton movement to the reaction centers. Photosynthetic organisms are equipped with a large variety of light-harvesting antennas (Figure 1) containing different pigments such as chlorophylls, carotenoids, or phycobilins to organize different macro-structures [1].

Scientists have established new research and technological areas inspired by the conversion of solar energy to chemical fuels in nature, that is, through artificial photosynthesis. Photocatalytic studies are a set of efforts in this area developed in response to the pollution challenges. The term "photocatalysis" refers to reactions that require a catalyst in addition the demand to light. An important difference between photosynthetic and photocatalytic reaction is related to thermodynamics. A true photocatalytic reaction is a thermodynamically favorable process with $\Delta G < 0$, while the photosynthetic reactions are thermodynamically unfavorable processes with $\Delta G > 0$. This difference is usually disregarded in the literature [2]. Artificial photosynthesis regards all aspects of natural photosynthesis including light capture, charge separation and electron transfer, and catalysis. It can be separated into two main approaches: (1) bio-based systems which utilize the direct integration of biological parts, extracted with biochemical techniques from living organisms, (2) bio-inspired synthetic systems which imitate the biological systems using synthetic chemistry approaches or surface.

2. Quantum coherence feature of photosynthesis

Observation of recent quantum coherence features [3, 4] in the dynamics of electronic energy transport within the biological photosynthetic systems has led to several intriguing questions even in the context of the sketching of the novel artificial light-harvesting materials. Over recent decades, intensive efforts have been made to apply biological photosynthetic processes to produce a novel generation of bioelectrochemical devices. New developments of artificial light-harvesting systems range from entire biomimetic systems to those that have only a minor

feature of natural organism just like some kind of translation of a natural function to an unnatural regime. The growth of synthesizing polymeric materials, supramolecular chemistry and self-assembly techniques over the past few decades allows us to examine a broad range of chemicals as viable platforms for artificial photosynthesis and light-harvesting phenomenon. Enormous research works on solar cells, solid-state photovoltaics, solid-liquid photoelectrochemical cells are in progress. Even some of the artificial light-harvesting arrays consisting of ordered arrangements from chromophores and proteins are expected to be potential alternatives to the current solar cell technologies.

The possibility of manual design of the molecular assembly of photoactive units can provide an additional control key to tune some structural and environmental features of chromophores that are significant to incorporate the fascinating role of quantum coherence effects within photosynthetic organisms as well as within the artificial light-harvesting devices. The capability of ordered, organized and bottom-up architectures of pigment-protein structures is achieved through tunable pigment-pigment distances and their relative orientation. The distances and orientation between chromophores, the fundamental factors in the extent of the quantum coherence effect, are determined based on inter-pigment interactions in photosynthetic systems.

It was found that natural photosynthetic systems capture visible and near-infrared light extremely effectively. Such a super-advanced mechanism for harvesting light even at low-intensity light detection suggests that a biomimetic light-harvesting platform would possess many attractive potentials including tunability, low cost, low weight, remarkable function at moderate temperatures with high quantum efficiency, and the capability to react to a wide range of wavelengths. As single-photon detection tools are restricted at present, such biomimetic devices would be very practical if they could work over an extensive range of infrared wavelengths and show a deeper sense into the infrared spectrum.

Although several efforts to date have been made to set natural light-harvesting arrangements into the solid-state environments of photodetectors, there have been no impressive attempts to mimic light-harvesting structures and take advantage of their quantum coherent properties in order to create more sensitive light sensors. Applying biomimetic synthetic structures offers further advantages over the

direct integration of natural light-harvesting complexes including extremely larger possibilities for synthetic supramolecular arrays and rapid growth of knowledge about the relationship between quantum coherence feature and architecture of light-harvesting arrays. These features now enable us to have desirable design and tune properties of artificial arrangements as well as to produce optimized and high-performance light-sensing materials.

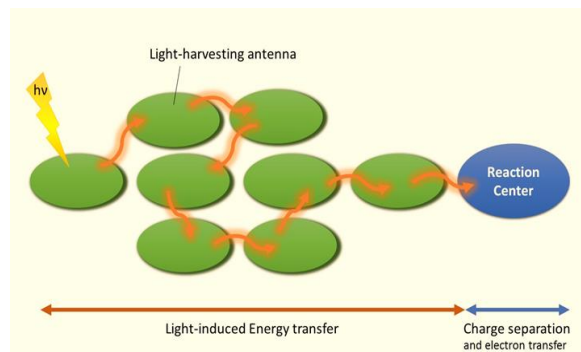


Figure 1. The schematic diagram demonstrating the concept of light-harvesting antennas in photosynthesis.

3. Stability of natural light-harvesting complex vs photovoltaics

Recently, researchers have achieved remarkable progress in constructing light-harvesting antennas using protein scaffolds of living organisms. The main purpose of this kind of research is to control nanoscale frameworks and create robust photovoltaics or light-sensing artificial systems. Engineering such structures allows tuning of the capture of light photons, excitonic energy transfer, and formation of charge carriers. Applying these strategies, researchers expect to achieve improvements via aggregation of quantum efficiency, utilized solar light, respond to a broad band of wavelengths, longer lifetime, and the production costs.

Each natural light-harvesting complex is constructed from the assembly of some pigments capturing the solar light. These amazing architectures are assembled from light-absorbing building blocks such as pigments from the chlorophyll or porphyrin families. An environment composed of protein chains provides a suitable scaffold for them when necessary. One of the most remarkable features of natural light-harvesting complexes is their high photo-stability as well as the important role in organizing light absorption and energy transfer to prevent some

chemical damages such as unwanted oxidation reactions. For natural photosynthetic living systems, it is even possible to genetically manipulate plants and enhance their ability of photoprotection. In contrast, the current organic photovoltaics generally lack the feature of photo-stability and possessing regulative processes, which is one of the significant reasons to restrict their commercial success.

Degradation mechanisms of a photovoltaic device have been investigated using a combination of physical and chemical analysis techniques including TOF-SIMS, AFM, SEM, interference microscopy, and fluorescence microscopy. It was found that illumination under simulated sunlight in air accelerates the degradation (or oxidation) processes. Attempts to develop artificial light-harvesting platforms that imitate the arrangement and features of natural light-harvesting complexes have increased broadly over the last decades. The significant difference between these platforms and the polymer or quantum dot based photovoltaic devices is their biomimicry requirements and their approach to using the same, or similar, building blocks present in nature. Sometimes the entire photosynthetic parts of living organisms including LHCs are directly embedded into an artificial device framework. Typically, specific features of designed devices aiming to mimic the natural light-harvesting systems are as follows:

- (1) A near-unit efficiency of energy transfers from the light absorption process to the charge separation process,
- (2) A near-unit efficiency of the charge separation process happening at the reaction center in natural photoactive complexes,
- (3) The working mechanism that mimics photo-stability and protection in natural light-harvesting complexes to an acceptable extent.

Designing synthetic systems to successfully replicate the mechanism of natural light-harvesting arrays is not very simple and many face challenges. Precise control over nanoscale structure is required to architect the novel structures and inhibit the problems such as unwanted trapping and recombination of excitons and wasted energy. These are the important challenges for the field of chemistry to synthesize and design practical supramolecular structures. Despite advances in chemical techniques for the synthesis of covalent and supramolecular structures, they are still insufficient to cover the bottom-up design of nanoscale structures and simultaneously producing large-scale molecular arrays similar to natural structures. Scientists are still struggling to

overcome the existing problems and have achieved notable developments in this field over recent decades. We will consider and mention some of these major achievements in this mini-review article.

4. Direct integration of natural antenna structures to a charge collection device

Direct integration of natural LHCs into a typical solid-state environment is a simple method to benefit from the impressive light capture, energy transfer, and conversion capabilities of the structures [5]. Ultimately, generated electrons are extracted through the charge separation process. One of the great advantages of this method is the possibility to preserve all of the superior quantum properties of the natural LHCs that are integrated into a foreign platform. However, this does not necessarily ensure that the function of the LHCs is entirely unaffected by incorporation into an alien solid-state environment. Here, we briefly introduce some prominent research works employing the direct integration of natural parts into a solid-state environment.

4.1. Reaction center

Baldo et al. through their remarkable work in 2004 demonstrated a technique for integrating photosynthetic complexes with solid-based electronics for electron collection. They extracted two natural light-harvesting components, namely the reaction center (RC) and photosystem I (PSI) from the purple bacterium species as well as from spinach, and stabilized them with a solid-state electronic device (Figure 2). This group studied preserving the light-harvesting functionality of the synthesized system. Note that the assembly process is one of the critical requirements to preserve superior natural features. In this work, two main technologies for oriented assembly of photosynthetic complexes were employed to preserve the functionality of these photosynthetic complexes outside their natural environment. To stabilize the protein complexes during device fabrication, they used two peptide surfactants, then deposited a thin layer of an amorphous organic semiconductor between the extracted complexes and the top metal (gold) contact. The thin layers of organic semiconductors by improving optical absorption may function as solid-state antennae for photosynthetic complexes. Through the fabrication, they observed that the internal quantum efficiency of the device was

approximately 12% and predicted that improving the integration method and architecting the molecular assemblies can boost this value by approximately 8%.

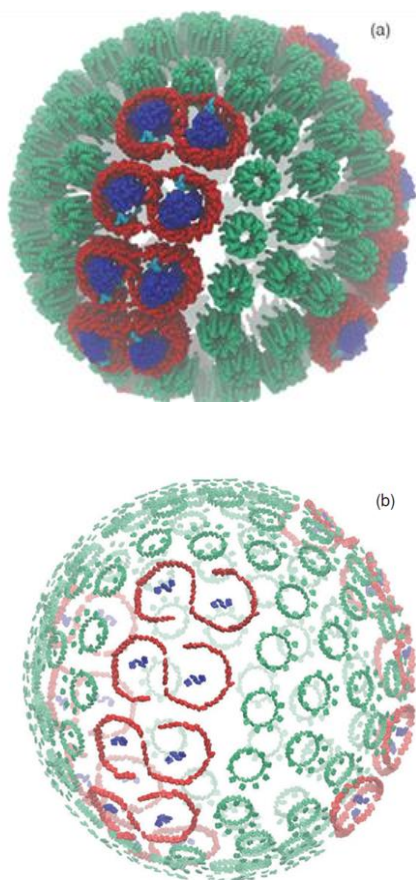


Figure 2. Supramolecular architecture of the natural chromatophore. (a) The chromatophore consist of membrane proteins including reaction centers (RC, blue) and photosystem I (PSI, red) (b) The bacteriochlorophylls are shown without protein and carotenoids. [4]

In 2005, Lu et al. used a kind of three-dimensional wormlike mesoporous metal oxide films called $\text{WO}_3\text{-TiO}_2$, with a tailored pore size to prepare novel bio-photoelectrodes by directly entrapping the bacterial photosynthetic reaction center proteins on the mesoporous surface [6]. The structure and activity of the immobilized proteins remained unaltered. The mesoporous $\text{WO}_3\text{-TiO}_2$ films showed unique features in the specific integration of reaction centers with preserved impressive activity. They also found that well-matched energy levels of $\text{WO}_3\text{-TiO}_2$ and RC have an important contribution to the photoelectric performance of the derived bio-

photoelectrodes. The procedure of manipulating the bio-photoelectrodes based on mesoporous metal oxides, owing to their attractive features and RC, has the capability of providing alternative methods to investigate the photoinduced multiple-pathway electron transfer of photosensitive chromophores and to develop new adjustable bio-photoelectric vehicles. In 2006, Dorogi et al. reported another study on the interaction of photosynthetic reaction centers extracted from a purple bacterium with single-wall carbon nanotubes [7]. Their studies confirmed the effective attachment of the reaction center protein to nanotubes. They also indicated the stabilization of the charge pair formed behind the single saturating light excitation after connection to nanotubes. The separation of photo-induced charges was accompanied by slow rearrangement of the reaction center proteins. The stabilization effect of light-initiated charge carriers by the carbon nanotubes suggests a potential path for several applications of carbon-based nanomaterials in energy conversion and electronic energy storage devices.

Understanding the mechanisms of electron transfer between the immobilized bacterial photosynthetic RC and the underlying electrode has a fundamental importance for the construction of bioinspired photo-induced energy conversion devices. Trammell and coworkers constructed a series of gold electrodes with alkanethiols self-assembled monolayers of different thicknesses and immobilized the RC on top of them with a specific protein orientation [8]. To facilitate electron transfer between the RC special pair and the electrode, a conductive protein-type wire was incorporated between them. Some significant analyses were performed regarding the dependence of the electron transfer rate on the distance to the electrode and the tunneling rate constant for the transition process from the flat gold electrode to the RC primary donor. Their obtained results would allow measuring and accurately inspecting the mechanisms of electron transfer through photosynthetic light-harvesting complexes in precisely ordered monolayers on the solid-state inorganic electrodes to achieve more effective photovoltaic devices.

In 2012, Dimonte et al. reported the design of an optoelectronic device based on the photoactive proteins in nanoscales [9]. The advantages of nanotechnology at molecular level allows adding functionalities to silicon-based electronics through naturally nanosized biological or organic molecules. The connections between the active molecules and electrodes must hold a very low resistance. To

understand metal-molecule-metal junctions, the structure of nanometric contacts should be precisely controlled. Indeed, this group used the nanoscale distances between gold electrodes to build optoelectronic devices based on photoactive proteins. Reaction centers and bacteriorhodopsin have been implanted in the nanogaps by drop-casting technology. Electrical characterizations demonstrated that the working principle of these nanosized devices is based on the charge separation process induced by employing a suitable voltage on the reaction centers whereby the photovoltage response comes from the activation of bacteriorhodopsin through illumination with proper wavelengths.

Kuang and coworkers in 2014 designed an example of nanoscale photovoltaics which could be devised using robust synthetic nanomembranes integrated with photosynthetic reaction centers [10]. The reaction centers from *Rhodobacter sphaeroides* were incorporated into well-designed polybutadiene membranes to form ordered hierarchical proteo-polymer membrane units with the reconstitution mechanism of "charge-interaction-directed". The reaction centers were reported completely active for prolonged time intervals based upon various spectroscopic measurements, while preserving their 3D pigment configuration was crucial for creation of light-induced electron current. Their result can be considered as a strategy to set solar conversion devices using structurally versatile proteo-polymer membranes with integrated RC functions to do light harvesting in a broad region of the light spectrum.

4.2. Photosystem I

Attempting to achieve the optimum mechanism of natural photosynthesis, Ciesielski et al. designed a biomimetic light energy conversion device using the Photosystem I (PSI) protein complex, immobilized on a surface of nanoporous gold leaf electrodes [11]. By constructing an electrochemical cell, they succeeded to drive a light-induced electric current. This study is another attempt to understand how the optimal functionality of the natural biological light-harvesting complexes can be preserved in integration with inorganic solid-state materials. This group demonstrated that the protein complexes would preserve their energy conversion function after stabilization on the nanoporous electrode surface. Further, nanoporous gold leaves lead to additional PSI/electrode interfacial area causing enhanced PSI-mediated electron transfer with respect to an analogous dealloying 2D system. They also reported

on this available and tunable method by which the nanoporous gold leaf electrode films used in this work were fabricated and added to glass-Au/Si platforms, and confirmed that they are widely adaptable by various modified self-assembled monolayers. These results demonstrated that the extent of the PSI-catalyzed photocurrents provided by the applied electrode was dependent upon the intensity of the light illumination on the electrodes.

PSI has attracted many further interests among researchers for usage in studies of direct integration with the solid-state environment. Faulkner and coworkers demonstrated that a critically dense monolayer of Photosystem I extracted from spinach must be immobilized on the surface of a solid-state electrode to obtain optimal photo-initiated electric currents [12]. They introduced a new rapid assembly method for fabricating these dense monolayers of PSI with a notable potential to reduce the assembly time by ~80-fold in comparison to that for the method of adsorption from solution. Through this novel method, they applied a vacuum above the aqueous solution from PSI during the assembly process to make it concentrate and precipitate it into a thick layer on the surface of several self-assembled monolayers or directly on the electrode surface such as gold electrodes.

Krassen et al. in 2009 settled a stepwise procedure of assembly of a mixture complex consisting of photosystem I and hydrogenase onto a solid surface of a gold electrode, which would result in light-initiated H_2 evolution [13]. In comparison to previous (bio)nano-electronic devices, hydrogen generation was achievable at far higher potentials and lower energy. Enzymatic reactions are crucial steps in natural energy conversion processes, for example, in photosynthesis where hydrogenases participate in the transformation of solar power to chemical energy and generating molecular hydrogen. Solar light is usually utilized to produce carbohydrates, hence, the formation of hydrogen directly from light remains an exception in nature. On the molecular level, the essential step of transforming solar energy into H_2 power is the presence of electronic coupling efficiently between photosystem I and hydrogenase. Willner's team in 2010 embedded Pt nanoparticles into photosystem I via a photochemical reaction and modified the integration with thioaniline and electropolymerized with thioaniline-functionalized Pt nanoparticles to yield a bis-aniline-cross-linked PSI/Pt nanoparticle composite [14]. The presence of PSI aligned to the Pt nanoparticles yielded effective charge separation and generated a photocurrent with

0.35% IPCE. The constructed composite exhibited a quasi-reversible redox behavior. The oxidized quinone bis-aniline state served as an electron acceptor which would bias the electrode potential. At this applied potential, approximately 10-fold higher photocurrent was achieved. Another modification was performed on thioaniline-functionalized PSI/Pt NPs composite using the ferredoxin (Fd) electron relay through the polymerization process induced by electric current. The Fd bound to the matrix facilitated the charge separation and led to increased generation of the photocurrent.

By integrating nanocrystalline quantum dots as artificial light-harvesting antennas with the photosystem I, Jung et al. in 2010 intended to boost the spectral range of their photoresponse [15]. They performed some optical and electronic measurements including photoluminescence and ultrafast time-resolved absorption techniques to investigate this process. Photoluminescence experiments revealed that emission from the quantum dots disappeared, and the fluorescence from photosystem I increased. Current measurements versus voltage on the synthesized composites proved a clear photoresponse.

For their biohybrid photoelectrochemical cell constructed from immobilized Photosystem I on a gold nanoslit electrode surface, Zeng and coworkers presented new achievements on the produced photocurrent [16]. Regarding the relationship between the efficiency of surface plasmon generation by nanoslits and the photocurrent obtained by immobilized gold nanoslit electrode, they found that the photocurrent can be enhanced with the increment of surface plasmon generation efficiency. They attributed this result to the coupling effect between plasmon and exciton on the Photosystem I in the nanoslits.

In multichromophore photosynthetic proteins such as photosystem I, one strategy to change the photoexcitation path is to produce plasmonic effects based on the interactions between metal nanostructures and fluorophores [17]. This strategy results in the concurrence between the photocurrent-enhancement spectra from protein assemblies and the plasmonic resonances for the nanoscaled ordered substrates, as well as broadband light-induced current enhancements due to plasmon-coupled photoactivation. Hence, these findings will be important for the rational design of novel generation of biohybrid structures composed of natural light-harvesting complexes and metal nanostructures with a plasmonic effect.

Note that a mediated approach to protein–electrode charge exchange and biophotovoltaic devices based on Photosystem I was reviewed by Robinson et al. in 2017 through their minireview article [18]. They proposed that employing both solution-based and solid-state film mediated electron transfer via solution-solubilized molecules and a fabricated conductive platform would respectively improve the charge separation for boosting the cell performance.

It has been demonstrated that integrating photosystem I into many liquid-based photoelectrochemical cells enhances their performance remarkably. Recent studies suggest that use of hydrogel as an electrolyte enables the fabrication of more durable solar cells and more manageable in comparison to liquid-based systems. Passantino and coworkers in 2020 reported a gel-based bio-dye-sensitized solar cell via integrated photosystem I with the proven capability of improving the cell performance. The photoelectrodes were comprised of TiO₂-coated FTO slides, dyed by blackberry anthocyanin, as an anode, and a layer of photosystem I immobilized onto copper comprises the photocathode, where ascorbic acid (AscH) and 2,6-dichlorophenolindophenol (DCPIP) were the redox mediator pair inside the hydrogel [19]. The results showed that the performance for such a device fabricated out of AscH/DCPIP couple was pH-dependent. Devices at pH=7 had a better function than those at lower pH. The photosystem I provided enhancement in photovoltage, concentration-dependent photocurrent, photocurrent, and energy conversion efficiency in comparison to the devices without photosystem I.

Apart from application of photosynthetic components, notable studies have been conducted using isolated natural chlorosomes as light-harvesting antennas. Sridharan et al. studied the distinctive antenna structure from *Chloroflexus aurantiacus* for potential exploitation in novel biohybrid optoelectronic devices [20]. Electrochemical characterization of photosynthetic apparatus comprised of perfect chlorosomes demonstrated an increase in the charge density which stored around the working electrode upon light induction. This implied that chlorosomes claim a notable fraction of the overall photo-induced current. The results reported in this work were the first to prove that isolated chlorosomes, without additional photosynthetic components such as reaction centers, biochemical mediators directly transform light energy electrochemically. Applying these individual bacterial chlorosomes with such as potential

photoresponders suggests an alternative, biomimetic manner for devising interfacial sensors in biofuel cells and biomedical tools.

4.3 Direct Integration of Natural Light-Harvesting Components to Solar Cells and Other Applications

In addition to direct integration of natural components to electrical vehicles, the bio-based materials are accepted as promising candidates for usage in solar cells. Georgios Charalambidis et al. in 2011 synthesized a new kind of materials by coupling a series of protected phenylalanine and diphenylalanine derivatives to a monoaminoporphyrin through a peptide bond. In this study, parallel investigations were performed in solution and solid-state medium. The comparison of the results confirmed some novel interesting properties for the self-assembled hybrid materials while conserving the electronic features of the chromophore [21]. They suggested that such materials are powerful candidates for use in dye-sensitized solar cells.

Ruthenium (II) complexes including 2,2'-bipyridine ligands have confirmed to be another notable component of artificial photosynthetic devices. For instance, Ruthenium (II)-polypyridyl-based Diads and triads have shown reasonable results for developing models of the photosynthetic reaction center due to their highly efficient electron transfer and increased charge separation lifetimes [22]. Further, dye compounds based on Ruthenium (II)-phenanthrolines have been known as great candidates for light harvesting. In 2013, Perera et al. synthesized a novel Ruthenium (II) aminophenanthroline-viologen with a maleimide group to attach the cysteines Diad to explore their capability for application in solar cells, and integrated them to the A96C mutant of the mycobacterial channel protein MspA13. The nanostructured layer composed of this Ruthenium-based compound at the TiO₂ electrode indicated a reasonable photochemical response. The obtained "protein nano solar cell" offered 1% photon conversion efficiency at 400 nm wavelength. These results confirmed that sturdily built proteins can be successfully collected into the design of solar cells.

In addition to the practical studies in this field, investigations using computational techniques have undergone great developments over the last decades. For example, the study of electron transfer in biological macromolecules including proteins through such techniques, in particular, understanding

detailed mechanisms in complex biological systems at the atomic level currently has been possible with different *in silico* modeling tools. Saen-Oon et al. in 2013 reviewed some of the previous major theories and work for progress in this area [23]. They also reported some of their main achievements, focusing on long-range and protein-protein electron transfer, and gave an outlook for future studies. Note that the use of such basic knowledge of electron transfer has a great impact on medical and bioengineering applications, including the amazing mitochondrial therapeutic goals, bioengineering for clean energy, and biosensors for environmental applications.

In 2014, Renugopalakrishnan and coworkers engineered a robust photovoltaic device using quantum dots and protein bacteriorhodopsin [23]. They presented a new bio-sensitized solar cell design consisting of two components, which would carry out the energy transfer process. Indeed, it was a hybrid material engineered from bacteriorhodopsin and quantum dots for harvesting light energy, as well as a thin layer of gold to create charge transfer and reproduce the retinol in the protein. The main targets of this work were controlled assembly of bacteriorhodopsin/quantum dot complexes and their highly ordered deposition on a solid electrolyte layer; replacement of the liquid electrolyte by the gold solid surface, and use of the Forster resonance energy transfer coupling between the components to achieve an efficient absorbing layer for dye-sensitized solar cells. Indeed, they proposed this method to benefit from the unique optical characteristics of quantum dots, photovoltaic properties of the protein to empower nanobioengineering technologies, thereby managing hybrid material components on the nanoscale. This method was an approach taken to boost the efficiency of dye-sensitized solar cells to practical levels.

In addition to the electrochemical application of RCs mentioned earlier in section 3.1, the light-induced current of immobilized reaction centers on solid-state electrodes has been of interest for bio-solar cell purposes. In 2015, Caterino et al. reported the use of novel electrodes based on functional conductive nanoscaled crystalline diamond onto which bacterial reaction centers were collected [24]. A three-dimensional conductive polymer framework integrated with the crystalline electrodes enabled an efficient trap rate of photoactive reaction center proteins. They demonstrated that use of a ferrocene-based electron mediator optimized the electron transfer through the functional diamond electrodes. This kind of electron mediator would offer notable

advantages, including fast and highly efficient electron transfer. This work presented useful guidelines that could serve to improve the performance of similar systems based on different materials and organizations.

Szabo et al. in 2015 fabricated another optoelectronic device using reaction center proteins of the photosynthetic eukaryote organism, called purple bacterium *Rhodobacter sphaeroides* R-26, applicable in the structure of the dye-sensitized organic solar cells [25]. They created a three-electrode electrochemical cell for this measurement. The working electrode were constructed from the ternary composition indium tin oxide covered with the complex of multi-wall nanotubes and reaction centers as well as the counter and the reference electrodes were platinum and Ag\AgCl, respectively. In some experiments, the presence of the RCs in the active layer under dried conditions caused tunable wavelength sensitivity in the visible light spectrum, especially in the near-infrared spectral range. The lifetime of the primary charge separation was in the order of ps and charge stabilization could be modulated between ps and seconds, at least at theoretical level. In summary, they presented a successful combination of reaction center protein with a solar energy convertor in a spectro-electrochemical cell and in a dried multilayer structure.

Several research groups have noted integrating these natural photosynthetic systems including several dyes such as carotenoids or chlorophylls into organic solar cell devices with power conversion efficiencies (PCEs) up to 0.99%. Most studies demonstrated that the functionalized derivatives of natural pigments can considerably boost their PCEs. For example, functionalized chlorophyll leads to elevation of PCEs by up to 2.1%. Also, polymers produced with amid-based isoindigo as an organic acceptor in combination with fullerene C₇₀ based electron acceptors in the active layer of the organic solar cells produce high PCEs up 8%. Another approach to integrating natural dye into the structure of organic solar cells is to immobilize the light-harvesting complexes at the border between the active layer and the charge collecting layers in photovoltaic devices. Incorporating the antennas as interlayers generates a great PCE with a growth of around 35% regarding the organic solar cells missing the interlayer. Further, combining the natural antennas with nanoparticles as interlayers adds surface plasmon effect leading to high performance of this kind of organic solar cells [26].

Guzel et al. applied a kind of bionanoferritin-based nanocage containing Fe and Mn, FeMnFBNC's, immobilized onto a graphene surface via electrostatic interactions to create their photoelectrochemical device [27]. Thanks to the robust structure of this kind of nanocages, the electron transfer performance between the FeMnFBNC containing layer and graphene surface improved. This compound consisted of some tyrosine and ferritin amino acid residues with electronic connections and photonic crosslinking between Fe and Mn in the visible light spectrum fitting for electron transfer and devising light-harvesting systems. They also developed a novel production of dye-sensitized solar cells based on bionanoferritin/graphene/TiO₂ molecules that could serve as a good candidate for replacing the traditional materials employed in dye-sensitized solar cells.

Another application of combining natural photosynthetic membranes and man-made photovoltaic vehicles is to convert solar power not to the electron current but into hydrogen fuel. The photoelectrochemical water splitting technique uses light energy to dissociate water into hydrogen and oxygen, which can be interpreted as artificial photosynthesis. Pinhassi et al. investigated the photocatalytic activity of thylakoid membranes, whose results confirmed it leads to water splitting in a bio-photo-electro-chemical cell through a simple process [28]. Thylakoids derived from spinach were incorporated into the cell occupied with a buffer solution of ferricyanide. Upon artificial solar illumination, water oxidation reaction began to occur and electrons were transferred by the ferri/ferrocyanide redox couple from the thylakoids to a transparent electrode as an anode. Hydrogen evolution occurred at the cathode at voltages as low as 0.8 V. A cell comprising the bio-photo-electro-chemical cell and a crystalline silicon photovoltaics reached solar to hydrogen efficiency conversion of 0.3%.

5. Conclusion

Incorporating the high power-conversion efficiencies of natural photosynthetic components into devices has resulted in notable improvement in biophotovoltaic performances. Key developments in expansion of biophotovoltaic utilizing various types of complexes were described in this minireview. The various methodologies applied to immobilize natural components on electrodes were also reviewed here. A natural leaf constitutes different, well-defined

nanometric systems that are precisely tuned to carry out a specific task and to interconnect with each other. On the other hand, the term ‘artificial photosynthesis’ or ‘artificial leaves’ is used to describe artificial photosynthetic devices assembled from interacting bio-based or bio-inspired components. In this study, we briefly described the design of natural photosynthesis and how its principles have inspired the design of artificial photosynthetic devices. Furthermore, integrating natural components in artificial devices as well as current progress in the design of bio-inspired light-harvesting parts and charge separation systems. This work also gives a short outlook for the design of bio-inspired electrochemical devices.

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