



Review Paper

Photoelectrochemical cells based on photosynthetic systems: a review

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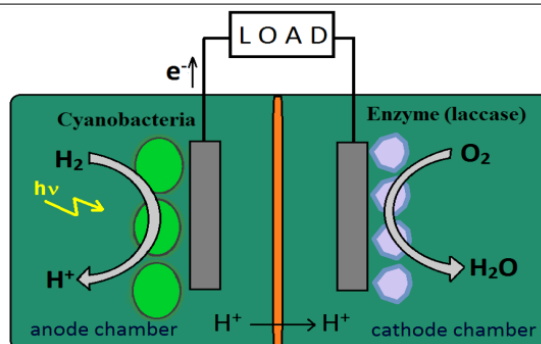
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HIGHLIGHTS

- Photobioelectrochemical photoconverters based on photosynthetic systems are discussed
- Strategies used to improve the efficiency of photobioelectrochemical cells were presented
- Advantages and disadvantages of photobioelectrochemical cells were highlighted

GRAPHICAL ABSTRACT



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ABSTRACT

Photosynthesis is a process which converts light energy into energy contained in the chemical bonds of organic compounds by photosynthetic pigments such as chlorophyll (Chl *a*, *b*, *c*, *d*, *f*) or bacteriochlorophyll. It occurs in phototrophic organisms, which include higher plants and many types of photosynthetic bacteria, including cyanobacteria. In the case of the oxygenic photosynthesis, water is a donor of both electrons and protons, and solar radiation serves as an inexhaustible source of energy. Efficiency of energy conversion in the primary processes of photosynthesis is close to 100%. Therefore, for many years photosynthesis has attracted the attention of researchers and designers looking for alternative energy systems as one of the most efficient and eco-friendly pathways of energy conversion. The latest advances in the design of optimal solar cells include the creation of converters based on thylakoid membranes, photosystems, and whole cells of cyanobacteria immobilized on nanostructured electrode (gold nanoparticles, carbon nanotubes, nanoparticles of ZnO and TiO₂). The mode of solar energy conversion in photosynthesis has a great potential as a source of renewable energy while it is sustainable and environmentally safe as well. Application of pigments such as Chl *f* and Chl *d* (unlike Chl *a* and Chl *b*), by absorbing the far-red and near infrared region of the spectrum (in the range 700-750 nm), will allow to increase the efficiency of such light transforming systems. This review article presents the last achievements in the field of energy photoconverters based on photosynthetic systems.

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Abbreviations

Asc	Ascorbic acid
BOD	Bilirubin oxidase
BQ	1,4-benzoquinone
Cyt b ₆ f	Cytochrome b ₆ f complex
Chl	Chlorophyll
CNT	Carbon nanotube
DCMU	3-(3,4-dichlorophenyl)-1,1-dimethylurea
DCIP	2,6-dichlorophenolindophenol
ETC	Electron transport chain
Fd	Ferredoxin
FNR	Ferredoxin:NADP-oxidoreductase
FTO	Fluorine tin oxide
GNP	Gold nanoparticle
HNQ	2-hydroxy-1,4-naftahinon
ITO	Indium tin oxide
MWCNT	Multi-walled carbon nanotube
OEC	Oxygen-evolving complex
PS1	Photosystem I
PS2	Photosystem II

1. Introduction

The energy crisis and environmental problems are among the most important challenges that humanity must solve in the XXI century. Many of the current investigations are focused on the development of energy sources which must be renewable, sustainable and eco-friendly. Now, the available sources of renewable energy, including solar, wind, rain, waves and geothermal heat, could generate only approximately 16% of the energy used (Sekar and Ramasamy, 2015). Sunlight is the most accessible and reliable among these renewable energy sources. One of the main pathways of solar energy conversion is photosynthesis. Higher plants, microalgae and some bacteria implement photosynthesis. In the course of photosynthesis, water or another electron donor, carbon dioxide and light are used to produce carbohydrates and other organic compounds.

On the other hand, photovoltaic semiconductor devices have also been developed that could generate electric power by converting sunlight directly into electricity. The coefficient of efficiency of the light energy conversion into the electric current by commercial silicon photovoltaic cells is typically less than 20% (Blankenship et al., 2011). Unfortunately, materials and components used in photovoltaic systems are exhaustible and cannot be fully recycled. As photosynthetic organisms operate with a quantum yield close to 100%, therefore, it is reasonable to use this natural process for energy conversion applications. Recently, experts in the field of artificial photosynthesis reviewed and critically analyzed the photosynthetic and photovoltaic energy conversion mechanisms and concluded that it is difficult to compare the conversion efficiency of the current photovoltaic cells with the living photosynthesizing cells because they are completely different systems (Blankenship et al., 2011). The efficiency of photovoltaic cells can be measured based on the output power divided by the total solar radiation spectrum. However, this method does not take into account the storage and transportation of energy. Photovoltaic energy is generally stored in the batteries, which increases their production cost while this also increases the expenses required for the maintenance of such systems. On the contrary, photosynthesis stores solar energy in the form of energy of chemical bonds, which can further be converted into electrical energy (Sekar and Ramasamy, 2015).

2. Solar cells

Solar cells are used to convert energy of solar radiations into electrical energy. Since searching for alternative energy sources is very serious, the development of effective and inexpensive solar cells is of particular interest. Currently, there are many different types of solar energy converters. The so-

called solar cells or photoelements are devices serving to convert solar energy into usable energy such as an electrical one and can be divided into two types, though maybe not very accurately. They are termed as regenerative cells and photosynthetic cells (Grätzel, 2001). In the regenerative cells, sun light is converted into electricity. This process is not accompanied with any subsequent chemical reactions while the photosynthetic cells generate hydrogen controlled by light (Grätzel, 2001).

Major general steps can be identified for all types of solar cells (Das, 2004):

A) Absorption of light by photoactive component

Photoactive component is the substance inside the cell, which absorbs photons. A semiconductor acts as a photoactive component in conventional photovoltaic solar cells while an organic pigment (photosensitizer molecule) serves as a photoactive component in dye-sensitized solar cells. Absorption of a photon leads to certain changes in the energy of the photosensitizer molecule, which is necessary for the further generation of current or activation of chemical reactions leading to the synthesis of molecular hydrogen. In photoelements based on biological systems, a photosensitizer molecule is excited by light. Excited photosensitizer molecule has a very low redox potential, thus, further charge separation is possible.

B) The charge separation.

In photoelements using plant or bacterial photosystems, which include pigments, such as Chl *a*, *b*, *d*, *f* and a set of electron carriers, charge separation occurs due to a series of redox reactions. A light-excited pigment molecule quickly transfers electrons to the primary electron acceptor and is then reduced by the primary electron donor. As a result of the charge separation, some voltage is generated in the photoelement

C) The transfer of electrons to an external circuit for biofuel generation

In the case of the elements that act as a photoelectric converter - regenerative cells - this step implies an electron transfer to the electrode, and further to an external circuit. For photosynthetic cells, charge separation leads to the activation of the chain of redox pairs, resulting in the formation of molecular hydrogen.

Photoelectric cells, in which organic photoactive material act as photoactive elements, have several advantages over traditional silicon solar cells. The cost of production of such cells is less due to less strict requirements for their production, and the field of their application is wider (Das, 2004). The main disadvantage is that they do not reach the efficiency of the inorganic solar cells (Grätzel, 2001; Das, 2004). With the use of biological molecules and systems in solar cells, a great increase in the efficiency of solar energy absorption is expected.

Currently, solar cells containing inorganic semiconductors, such as mono- and polycrystalline silicon, are used for commercial applications including small devices, such as solar panels on roofs, pocket calculators, and water pumps. These traditional solar batteries can use less than 20% of the incident solar light (Blankenship et al., 2011). Production of silicon solar cells requires energy-intensive processes, high temperatures (400-1400°C) and clean vacuumed conditions, all contributing to their high cost (Das, 2004). On the contrary, production of solar cells based on biological photoactive components does not impose much cost.

3. Photosynthesis

Photosynthesis is the process by which the sunlight energy is converted into chemical energy of various organic compounds and is carried out by photosynthesizing organisms. Photosynthesis serves as the ultimate source of energy for all kinds of life on Earth. Photosynthetic organisms use the sunlight energy for synthesis of glucose and other organic compounds which in turn are sources of energy and essential metabolites for heterotrophic organisms (Blankenship, 2002; Blankenship, 2010). This process takes place in two stages: the light one is the light absorption by photosynthetic pigments and the formation of ATP and NADPH; and the dark one is the biosynthesis of carbohydrates. During the dark stage carbon dioxide (CO₂) acts as a carbon substrate, reduced form of the NADP (NADPH) molecule as a proton source, and ATP molecule as a source of energy. The electron transport chain (ETC) is an essential element of the light stage of photosynthesis. Through ETC an electron is

NADP⁺ molecule and reduces it. An external source of electrons is then required to reduce the oxidized pigment molecule. In the case when water acts as an electron source, such type of photosynthesis is named “oxygenic”, because molecular oxygen is evolved as a result of the water decomposition (Blankenship and Hartman, 1998). The key source of oxygen in the atmosphere is the oxygenic photosynthesis which manifests itself in all plants, microalgae, and cyanobacteria.

The oxygenic photosynthesis could be summarized through the following general equation (Eq. 1):



Where $h\nu$ stands for light quantum energy. Light stage processes of the oxygenic photosynthesis take place in membrane structures called thylakoids. In eukaryotic cells of green plants, thylakoids are localized in specific photosynthetic organelles - chloroplasts. Space limited by chloroplast membrane is designated stroma, and the space inside the thylakoid is designated lumen. Thus, one side of the thylakoid membrane faces the stroma, and the other side faces the lumen. In prokaryotic cells (cyanobacteria), thylakoids are located directly in the cytoplasm (Bryant, 1994). Reactions involved in the light stage of the photosynthesis occur in thylakoids.

Light energy is not immediately converted into ATP energy. In fact, it is initially stored in the form of a transmembrane electrochemical potential, which is formed due to the proton transfer by lipophilic transporters through the thylakoid membrane from the stroma into the lumen. As a result, the lumen becomes acidic and the stroma is alkalized. At the expense of the energy of the created potentials ($\Delta\mu H^+$) difference, the enzyme ATP synthase embedded in the thylakoid membrane starts functioning (Andralojc and Harris, 1992).

Light stage of photosynthesis is, in fact, a chain of enzymatic reactions. In higher plants, four transmembrane protein enzymes (Fig. 1) catalyze these reactions: photosystem I (PS1), photosystem II (PS2), cytochrome b₆f complex (Cyt b₆f) and ATP synthase (Nelson and Yocum, 2006). PS2 catalyzes the electron transfer reaction from the water molecule to plastoquinone. The Cyt b₆f takes part in the oxidation of plastoquinone and reduction of plastocyanin which mediates the transport of electrons from PS2 to PS1 as well as proton transfer from stroma into lumen (Andralojc and Harris, 1992). PS1 catalyzes the oxidation of lipophilic electron carrier, plastocyanine, and the ferredoxin reduction. The enzyme, ferredoxin:NADP-oxidoreductase (FNR) catalyses the NADP⁺ reduction at the expense of the electrons from the reduced ferredoxin.

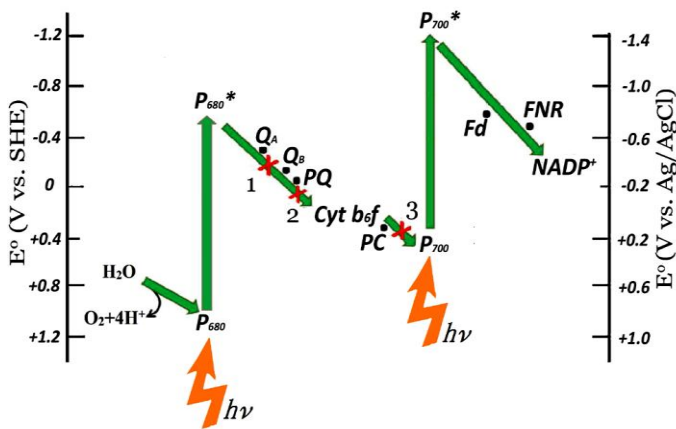
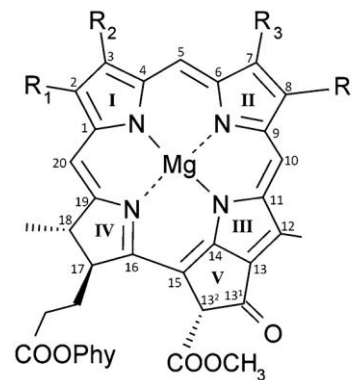


Fig.1. The scheme of the non-cyclic electron transport pathway in thylakoids of higher plants and the redox potentials of the components of electron transport chain. Redox potentials are measured vs. both the standard hydrogen electrode or SHE (left axis) and silver chloride electrode Ag/AgCl (right axis). P₆₈₀*: primary electron donor in photosystem II; P₆₈₀: singlet excited state of P₆₈₀; P₇₀₀: primary electron donor in photosystem I; P₇₀₀*: singlet excited state of P₇₀₀; Q_A and Q_B are primary and secondary quinone acceptors, respectively; PQ: mobile plastoquinone molecule which transfers electrons to the cytochrome b₆f complex (Cyt b₆f); PC: plastocyanin; Fd: ferredoxin; FNR: ferredoxin-NADP⁺ reductase; and NADP⁺: Nicotinamide adenine dinucleotide phosphate. Red crosses represent reactions that can be inhibited by a) 3-(3,4-dichlorophenyl)-1,1-dimethylurea (DCMU); b) Dibromothymoquinone (DBMIB); c) Potassium cyanide (KCN) (adapted from Sekar et al., 2014).

The primary charge separation, which involves photosynthetic pigments, occurs in the photosynthetic RC. In the RC, the primary electron donor is at the inner luminal side of thylakoid membrane whereas the primary electron acceptor is closer to the outer stromal side of the membrane. Thus, an electron captured from the molecules of the primary electron donor moves onto the opposite side of the thylakoid membrane (Andralojc and Harris, 1992). As a result of the charge separation an electric charge on the membrane is generated.

The electron transport chain is activated by light. The photon excites the primary electron donor - a special pair. Chlorophyll is the pigment molecule that can be excited by light of a certain wavelength (Fig. 2). The basis of the chlorophyll structure is a heterocyclic ring consisting of four pyrrole rings, connected by methine bridges (Scheer, 2006). Four nitrogen atoms within the chlorine ring are associated with magnesium ion (Mg²⁺). A long hydrophobic phytol tail is attached to the fourth pyrrole ring, while a pigment molecule is attached to the membrane and is correctly oriented. There are several forms of chlorophyll with Chl *a* and Chl *b* as two main forms which are the most widespread in nature.



Name	R ₁	R ₂	R ₃	R ₄
Chlorophyll <i>a</i>	CH ₃	CH=CH ₂	CH ₃	CH ₂ -CH ₃
Chlorophyll <i>b</i>	CH ₃	CH=CH ₂	CHO	CH ₂ -CH ₃
Chlorophyll <i>d</i>	CH ₃	CHO	CH ₃	CH ₂ -CH ₃
Chlorophyll <i>f</i>	CHO	CH=CH ₂	CH ₃	CH ₂ -CH ₃

Fig.2. The structural formula of chlorophylls: Chl *a*, Chl *b*, Chl *d*, and Chl *f* (adapted from Loughlin et al., 2013).

Chl *a* serves as the primary electron donor in the RC, and Chl *b* is the accessory pigment of the antenna complexes. A free Chl *a* molecule absorbs light preferably in the wavelength ranges of 400-500 nm and 600-700 nm. Due to the use of other pigments, such as carotenoids, the absorption spectrum of the photosystems is much broader (Sandman, 2009). In addition to Chl *a* and Chl *b*, other forms of chlorophyll, Chl *d* and Chl *f* could also be found in antenna complexes of phototrophic organisms, such as cyanobacteria. Chl *d* is also present in the photosynthetic RC (Tomo et al., 2008, Tomo et al., 2014). The chemical difference between the Chl *b*, Chl *d*, Chl *f* and the Chl *a* is that methyl or vinyl group are substituted by formyl one (Fig. 2). The absorption spectra of the chlorophylls also differ from each other. More specifically, the long-wavelength maximum in the absorption spectrum of Chl *d* and Chl *f* markedly shifts towards longer wavelengths compared to that of the Chl *a* (shift up to 40 nm). The energy region (i.e. 380-710 nm) consists of photosynthetically-active radiations which constitutes about 40% of the total solar radiation reaching the Earth's surface (Blankenship and Chen, 2013). However, further expansion in the region ranging from 700 to 750 nm, leads to an increase in the overall energy intensity by about 19%,

the creation of solar cells based on the use of photosynthetic components looks very attractive.

4. The use of components/systems of the photosynthetic apparatus to generate electricity

4.1. Thylakoids as photobiocatalysts

Thylakoid membranes can be isolated from plants and immobilized on the electrode surface to generate a photocurrent. A team of researchers led by Robert Carpenter (1999) was the first to begin using thylakoid membranes isolated from spinach leaves as a photosensitizer. In their work, a platinum electrode was used as a final acceptor. Studies were carried out in the light and in the dark, in the presence and in the absence of potassium ferrocyanide as a mediator. Native thylakoids generated a photocurrent reaching 6-9 μA without a mediator, and by 4 times more current in the presence of potassium ferrocyanide. It was concluded that the photocurrent generation without any mediators is associated with direct transfer of electrons from the membrane proteins to the electrode surface or through the presence of molecules in the electrolyte that can function as mediators. Oxygen, capable of producing the superoxide radical, may be viewed as a mediator. In 2011, Bedford et al., immobilized thylakoids on conductive nanofibers. They used the electrospinning technique, important for the stabilization of the thylakoid membranes, for immobilizing the thylakoids on the conductive nanofibers. Upon illumination by red light with a wavelength of 625 nm, the maximum electric power generated by the cell surface (1 cm^2) was 24 mW.

It is possible to create a stable solar cell by combining the photosynthetic anode and biocatalytic cathode. The idea is to use photosynthetic organisms/organelle/photosystems for the water oxidation at the anode and the oxygen reduction to water at the cathode.

Calkins and colleagues (2013) created photobioelectrochemical cells using thylakoids isolated from spinach. Thylakoids were immobilized on the anode modified with multi-walled carbon nanotubes (MWCNT). Glass electrode modified by laccase/MWCNT system was used as the cathode (Fig. 3a). The work demonstrated maximum current density of 68 mA/cm^2 and the maximum power density of 5.3 mW/cm^2 (Fig. 3b). Composite electrode based on thylakoid-MWCNT produced a current density of 38 mA/cm^2 , which was by two orders higher than the predicted density.

The main advantage of the use of membrane thylakoids for photocurrent is that during the isolation process, the integral membrane protein complexes remain in their native state. This leads to greater stability and greater power output as compared to the results that may be achieved by using isolated protein complexes or RCs.

4.2. Photosystem I as photobiocatalyst

Beside the thylakoid membrane preparations, some researchers have conducted studies to generate photocurrent by cells based on isolated photosystems. There are two major benefits of using photosystems as a photosensitizers compared to thylakoids as follows:

A) There is less influence exerted by the other redox systems on the electron transfer in the photosystem chain.

B) RCs are closer to the electrode which facilitates direct electron transfer to the electrode.

Formond et al. (2007) developed a photobioelectrochemical system with PS1 as the main photocatalytic subunit, cytochrome C_6 and ferredoxin as electron carriers and ferredoxin:NADP-oxidoreductase (FNR) as an electron acceptor (Fig. 1). In that experiment, a gold electrode was used. In an earlier investigation, Frolov et al. (2005) created a photobioelectrochemical cell that could generate a voltage of $0.498 \pm 0.02\text{ V}$. They used the PS1 preparations isolated from the cyanobacteria *Synechocystis sp.* PCC 6803. These systems are more stable than plant systems because in the preparations, the antenna pigment molecules (chlorophylls and carotenoids) are integrated into the nuclear subunits. More specifically, unlike in plant systems, the antenna pigments are associated with chlorophyll-protein complex only, which the latter is coupled to nuclear subunits. To stabilize such PS1, surfactant peptides, which are necessary for the stabilization of other plant and bacterial RCs, were not required (Das et al., 2004). Another important factor in their work was the mutation-based replacement of specific amino acids of the PS1 by cysteines. Stable, properly oriented monolayer of PS1 was formed through

the formation of Au-S bonds between the thiol group of cysteine and purified hydrophilic gold surface. The procedure for creating the corresponding gold electrode included thermal treatment at 350°C .

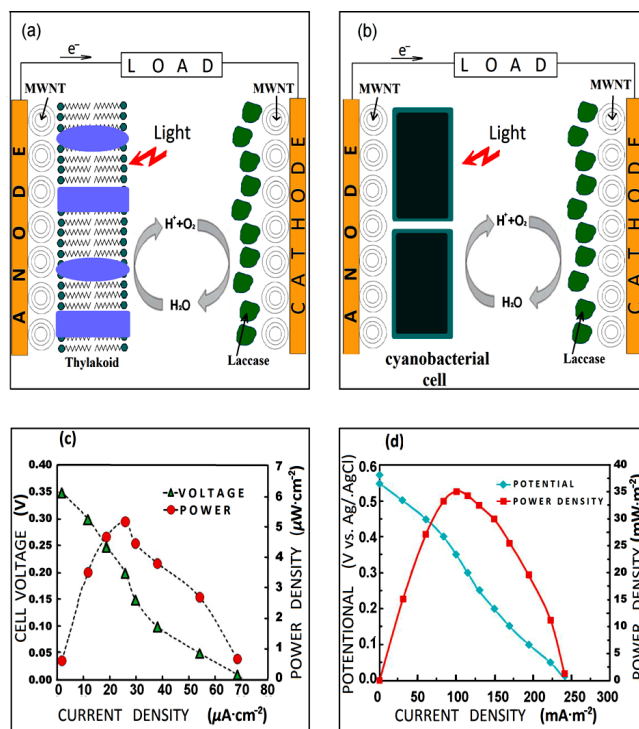


Fig.3. Schematic representation of the functioning photobioelectrochemical cells based on, a) the thylakoid-multi-walled carbon nanotubes (MWCNT) and, b) cyanobacteria *Nostoc sp.*-MWCNT. The graphs c) and d) present the dependences of the voltage and the flux density of the received energy on the current density for each of the cells shown (adapted from Calkins et al., 2013; Sekar et al., 2014).

In a different study, Faulkner et al. (2008) reported a fast way for creating a dense monolayer of PS1, isolated from spinach leaves, on a gold electrode. This method of the monolayer creation requiring vacuum conditions was 80 times faster than monolayer creation by method of photosystem precipitation from a solution. More specifically, PS1 was immobilized on the electrode modified with gold nanoparticles (GNP). In the presence of suitable mediators, the cell generated a photocurrent of 100 nA/cm^2 (Fig. 4).

However, photobioelectrochemical elements based on the PS1 monolayer were not sufficiently effective in cases when a large cross-sectional area of light absorption was required. In the same year, a photobioelectrochemical cell based on multilayer structures of PS1 was created (Frolov et al., 2008). To form the multilayer structures, PS1 complexes were platinized. The platinum ions facilitated the binding of the luminal side of PS1 and the platinized stromal side resulting in the electrically connected multilayer. The first PS1 monolayer was attached to the gold surface through the bonds between the cysteine's thiol groups in the mutant PS1 and the gold atoms. The next layer was then formed through the connection between the photosystem donor side of the next layer and the platinum atoms (Fig. 4c). The devices developed based on the two and three layers generated photovoltage outputs of 0.330 and 0.386 V, respectively (Frolov et al., 2008). Hereafter, work on the development of solar cells based on multilayer structures of PS1 was continued (Ciesielski et al., 2010; Mershin et al., 2012). The suggested method did not require the use of photosystems isolated from mutated cyanobacteria, nor the use of a high vacuum, making it more economical and less time-consuming. In this work, a plate of gold (thickness of about 125 nm) immobilized on a silicon substrate and a working surface of transparent plastic plate coated with lead oxide doped with indium served as cathode and anode of the photoelement, respectively. A cavity

remaining between them, was half-filled with an electrolyte composed of 5 mM 2,6-dichlorophenolindophenol (DCIP), 100 mM ascorbic acid (Asc), and 100 mM NaCl in 5 mM phosphate buffer, pH 7.0. The other half was filled with a buffer solution containing PS1 complexes (about 9 μM), Triton-X100 (0.05% w/v), 0.14 M in 0.2 M NaH₂PO₄ at pH 7.0. The PS1 complexes were precipitated on a gold electrode for 7 d. As a result, a multi-layered structure of the PS1 complexes with a thickness of 1-2 μm was obtained. The obtained solar cell generated a photocurrent at a density of about 2 mA/cm² under illumination by a standard light intensity (clear sky at noon). The device demonstrated a considerable stability and retained activity under ambient conditions for at least 280 d (Ciesielski et al., 2010).

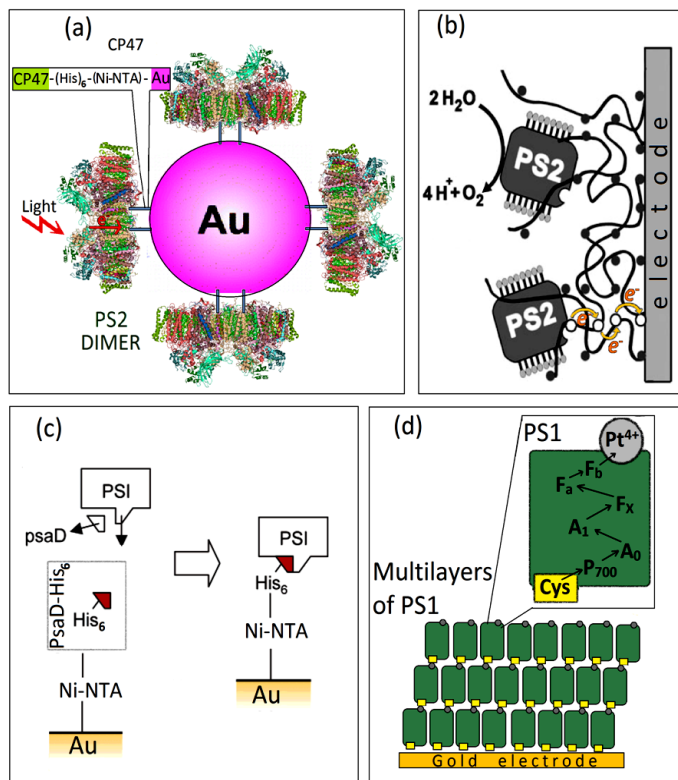


Fig.4. Models used for immobilizing photosystems on the electrode. a) connection of PS2 through gold nanoparticle (GNP; Au) histidine tag with Ni-nitrilotriacetic acid (Ni-NTA) attached to the C-terminus of the CP47 protein (adapted from Noji et al., 2011). b) PS2 associated with an osmium redox polymer containing a mediator network (adapted from Badura et al., 2008). Osmium complexes are represented by gray circles. Yellow arrows depict the electron transfer pathway by a hopping mechanism. c) Native PsaD subunit of PS1 replaced by PsaD-His which clings to the histidine tag and the entire structure is associated with the gold electrode through a Ni-NTA (adapted from Das et al., 2004), and d) the scheme of the cysteine mutants of the PS1 with Pt ion and the multilayer structure of such PS1 on a gold substrate (adapted from Frolov et al., 2008).

Sekar and Ramasamy (2015) recently reviewed the recent advances in photosynthetic energy conversion and stated that to date the highest current density of 362 mA/cm² and the energy flux density of 81 mW/cm² using PS1 were obtained by Merishina et al. (2012). In their work, measurements were carried out under normal sunlight and the efficiency of solar cells with different semiconductor substrates i.e. nanocrystalline titanium dioxide TiO₂ and nanowires of zinc oxide (ZnO) were compared (Fig. 5). The PS1 complexes were adsorbed on each of these two substrates. Stability of the isolated PS1 complexes was increased by the treatment with surface-active peptides. Peptide Ac-AAAAAAK-NH₂ - a sequence of six alanines and one lysine was used as the surfactant. This also promoted the selective adsorption of the PS1 on the substrates and increased the absorption of light. Such approach improved the photovoltaic performance. In this artificial system, cobalt electrolyte Z813 performed the role of plastocyanine, and ferredoxin

was replaced by nanocrystalline TiO₂, or nanofiber ZnO (Merishin et al., 2012).

Overall, PS1 is a good photobiocatalyst, but has several disadvantages as a photosensitizer. Firstly, the process of the complex isolation is more laborious compared to the isolation of thylakoid membranes. Secondly, the isolated PS1 complex is less stable. Thirdly, for getting a continuous electron transfer, the RC of the PS1, P₇₀₀, requires an external electron donor with a redox potential approximately equal to the redox potential of plastocyanin and thus, the photosystem depends on other electron sources.

4.3. Photosystem II as photobiocatalyst

The main advantage of PS2 vs. PS1 is the fact that the electron source, which is required to activate the electron transfer, is water, which is abundant in the environment (Sekar and Ramasamy, 2015). Unlike the PS1, which requires an electron donor, PS2 has an internal oxygen-evolving complex (OEC), also known as water-splitting complex, and depends on the availability of water and light. Here, electrons from P₆₈₀ are transferred to pheophytin, then to plastoquinone and further to the other ETC components (Nelson and Yocum, 2006). Reduction of plastoquinone in Q_B-site of PS2 by two electrons from plastoquinone in Q_A-site of PS2 and diffusion of the double reduced quinone (PQH₂) inside membrane are the major rate-limiting steps (Nelson and Yocum, 2006). Therefore, it is assumed that the water oxidation in PS2 should be accelerated if electrons from Q_A⁻ could be efficiently transferred to an external electron acceptor (Ulas and Brudvig, 2011). Thus, in order for the electrons from PS2 to be transferred onto the electrode, the complex should

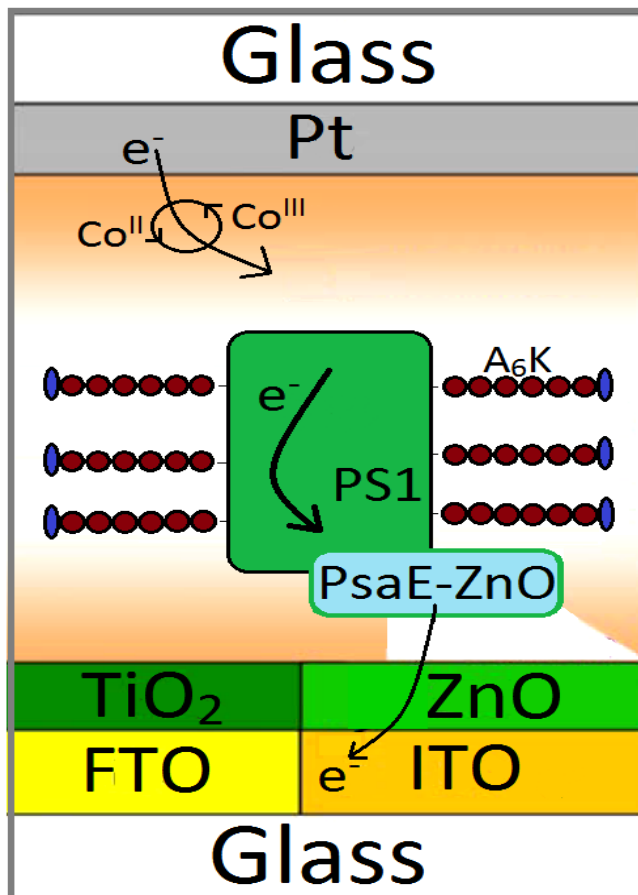


Fig.5. Schematic presentation of two Merishina's cells with zinc oxide and titanium dioxide. FTO - a layer of fluorine doped with tin oxide and, ITO - a layer of indium doped with tin oxide (adapted from Merishin et al., 2012). A₆K - designed peptide detergents, acetyl-AAAAAAK.

come in contact with the surface of the electrode, or a mediator should carry out the electron transfer. In fact, it is difficult to achieve direct electron transfer from the PS2 to the electrode because the site of Pheo-PQ is localized deeply inside the PS2 (Badura et al., 2008).

For creation of efficient converters based on PS2, it is important to improve its stability and increase electron transport efficiency. To achieve that, Vittadello et al. (2010) reported the application of histidine-tagged protein complex of PS2 from *S. elongatus* covalently bound to a gold electrode treated with Ni(2+)-nitrilotriacetic acid (Ni-NTA). The current density of the resulting photobioelectrochemical cell reached 43 mA/cm². On the other hand, while the photochemical energy conversion efficiency of the freshly isolated PS2 was 0.7, the same parameter for the PS2 immobilized on Au was 0.53. This clearly indicated that the PS2 complexes were photochemically stable even after immobilization, but long-term stability was not discussed by the authors (Vittadello et al., 2010).

Utilization of osmium-containing redox polymer based on poly-1-vinylimidazole is also an effective immobilization method, which could help maintain the stability as well as enhance the coating degree of the electrode by the PS2 complexes (Fig. 4b) (Badura et al., 2008). The polymer works as an immobilization matrix and a mediator. Such a system could facilitate the electron transfer from the PS2 complex to the electrode. The correct orientation of the immobilized complex could also facilitate the electron transfer. Recently, Noji and colleagues developed a nanodevice for the artificial water decomposition controlled by light, using a conjugates of PS2-GNP (Noji et al., 2011). The core of the PS2 complex, comprising a histidine tag on the C-terminal of CP47 protein, was immobilized on a GNP by Ni-NTA (Fig. 4a). GNPs used in this work were about 20 nm in diameter, and were able to bind four to five PS2 complexes. The efficiency of oxygen evolution by the developed PS2-GNP was comparable to that of the unbound PS2 (Noji et al., 2011).

Israeli scientists developed the photocell which was based on bacterial PS2 complexes isolated from the thermophilic bacterium *Mastigocladus laminosus*. The photoanode consisting of a matrix of 2-mercapto-1,4-benzoquinone (MBQ) was electro-polymerized on the gold surface. Then, PS2 complexes were immobilized on the surface. The anode was electrically connected to the cathode by a composite based on bilirubin oxidase/carbon nanotube (BOD/CNT). They claimed that photo-induced quinone-mediated electron transfer led to the generation of photocurrent with an output power of 0.1 W (Yehezkeili et al., 2012).

Both photosystems (PS1 and PS2) are highly sensitive to photoinhibition and are effectively protected by protective compounds present inside the chloroplast (Sekar and Ramasamy, 2015). It is evident that the stability of isolated photosystems will be impaired after their isolation from native environments. It should be noted that isolated PS2 is more unstable compared to PS1 and photocurrents of high density could be achieved in cells using PS1 complexes. Thus, the use of thylakoids as a photosensitizer should be more preferable as compared to isolated photosystems.

4.4. The bacterial cell as photobiocatalyst

Photocells in which isolated photosynthetic structures such as thylakoids, PS1 and PS2 are used suffer from significant disadvantages. The components of these cells are quite expensive, have a short running time, require laboratory procedures such as isolation/purification and are relatively unstable. These limitations could be overcome if whole cells of photosynthetic microorganisms would be used as a biocatalyst or/and sensitizer.

In the last few years, some studies have been conducted to construct a photosynthetic microbial fuel cell (PMFC) based on whole cells of photosynthetic organisms such as cyanobacteria (Sekar and Ramasamy, 2015). In the anode chamber of PMFCs, photosynthetic organisms are used which could oxidize water using light. Only sunlight and water are required for a PMFC to function, whereas traditional MFCs based on bacteria such as *Gejibacter*, *Shewanella*, etc. require organic carbon sources such as glucose/lactate, and they produce CO₂ as final product. The general scheme of the combined cell is shown in Figure 6, which demonstrates (a) a hydrogen fuel cell with a platinum catalyst on the anode and the cathode, and (b) photobioelectrochemical photoelements based on cyanobacterial cell at the anode and the laccase enzyme at the cathode.

Various cyanobacteria were used in most effective PMFCs reported (Yagishita et al., 1993; Torimura et al., 2001; Pisciotta et al., 2010). In particular, the ability of the cyanobacteria *Nostoc sp.* in generating a photocurrent was investigated using various electrochemical methods. In a recent study, using the site-specific photosynthetic inhibitors (Fig. 1), the mechanism of direct electron transfer from *Nostoc sp.* ETC on electrode was studied (Sekar et al., 2014). It was shown that the photobioelectrochemical cell with *Nostoc sp.* immobilized on the MWCNT-modified carbon electrode as an anode and laccase/MWCNT-modified cathode (Fig. 3c) generated a current with a maximum density of 25 mA/cm², while the maximum energy flux density achieved without mediators was only at 3.5 mW/cm² (Fig. 3d). While the cell based on thylakoids (Fig. 3a) generated a current with a maximum density of 10 mA/cm², and the maximum energy flux density achieved without mediators was recorded at 5 mW/cm² (Fig. 3b). Overall, the maximum current density by the photobioelectrochemical element based on the native photosynthetic cells was higher than that of the photoelement based on thylakoids.

One of the main advantages of cyanobacteria vs. individual components of the photosynthetic apparatus is that they are considerably less susceptible to dehydration. Currently, the power which could be generated by PMFCs is less than those achieved by the biofuel cell (Sekar and Ramasamy, 2015). However, their many advantages such as simplicity of operation, the utilization of available substrates e.g. water, as well as stress-resistance of PMFCs in comparison with the other biofuel cells mark them as promising options for the future.

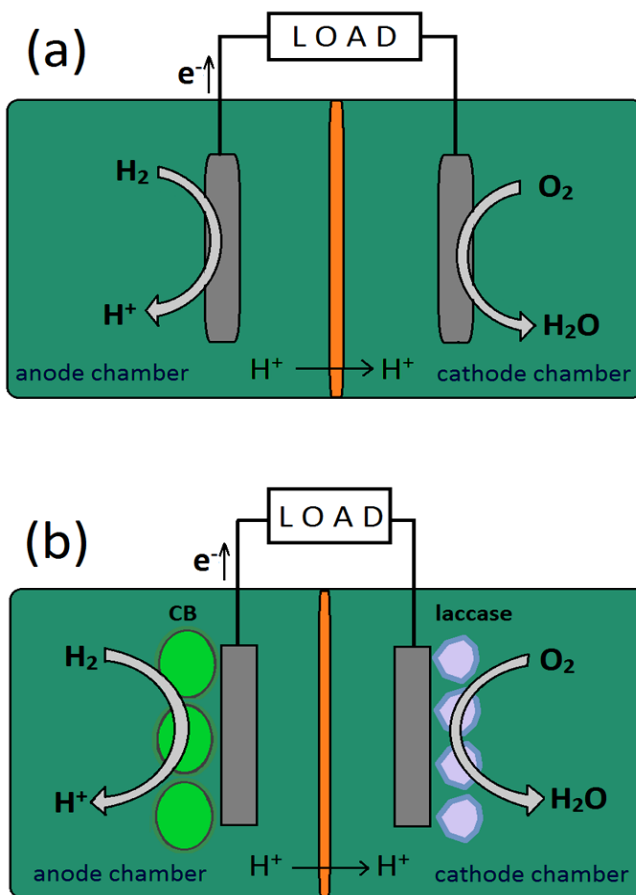


Fig. 6. Schematic representation of the different forms of fuel cells: a) hydrogen fuel cell with a platinum catalyst on the anode and the cathode, and b) photobioelectrochemical elements based on cyanobacterial cell (CB) on the anode and laccase enzyme on the cathode (adapted from Sekar and Ramasamy, 2015).

5. Improving the efficiency of solar cells

5.1. The redox-active components: changing the direction of the electron flow

Various redox-active components accept electrons from specific sites of ETC in accordance with their redox potential. Redox active sites of metalloproteins are usually hidden inside the PS2 complex (Badura et al., 2008), therefore, the electron transfer from immobilized photosystems onto the electrode may be limited. This limitation can be overcome by redirecting the electrons from the inner part of the protein to the surface (Sekar and Ramasamy, 2015). For instance, Larom et al. (2010) successfully used an artificial mediator to redirect electrons from Q_A^- to an artificial acceptor at a distance of about 1.3 nm from the stromal side of the membrane. This change in the direction of electron flow along with additional blocking of Q_B led to a reduction of oxidative damages at the expense of reducing the time of the intermediate electron transfer at the stage of Q_A/Q_B . In another study, Secar et al. (2014) used whole cells of cyanobacteria as photobiocatalysts in a photobioelectrochemical cell. They achieved a power density of about $10 \mu\text{W}/\text{cm}^2$ by adding 1,4-benzoquinone (BQ) as a mediator which was three times higher vs. transferring electrons without a mediator using the systems *Nostoc*/MWCNT and laccase/MWCNT. Since the structure of the BQ is similar to that of PQ, the addition facilitated electron transfer from the PS2 to the MWCNT (Sekar et al., 2014). Previously, mediators such as BQ, 2,6-dimethyl-1-benzoquinone (DMBIB), and 2-hydroxy-1,4-naftahinon (HNQ) were also used for accepting the electrons from the cyanobacterial photosynthetic ETC (Yagishita et al., 1993; Torimura et al., 2001).

5.2. Bioengineering of photosynthetic RCs

Primary processes of photosynthesis have high quantum yield reaching almost 100%, but the energy storage efficiency can reach as high as about 27% under ideal conditions, and much less under non-ideal ones (Fultz and Durst, 1982). This value is comparable to the efficiency of the modern silicon-based solar panels operating with an efficiency of approximately less than 20%. Note that some laboratory models demonstrated an effectiveness of 40% (Blankenship and Hartman, 1998; Grätzel, 2001; Sekar and Ramasamy, 2015). Moreover, the photosynthetic pigments usually absorb only light from the visible region of the spectrum (from 400 to 700 nm) (Blankenship and Hartman, 1998) unlike photovoltaic cells capable of absorbing light from the UV and near infrared regions as well. Thus, photosynthetic organisms utilize only about half of the incident solar energy. Nevertheless, photosynthetic efficiency can be improved by expanding the region of photosynthetic absorption by using bioengineering techniques. Since photosynthesis uses two photosystems which absorb light under the same conditions, the variation of band gaps could increase the efficiency. This approach could be feasible by using photoelements on a base of RC containing far-red and infra-red absorbing pigments similar to bacteriochlorophyll that absorbs light in the region up to 900 nm (Hanna and Nozik, 2006) or Chl *d* or Chl *f*, absorbing light in the region 400-750 nm (Blankenship and Chen, 2013). As a result, the absorption region may be significantly increased.

5.3. Biomimetics

Biomimetic approach is aimed at constructing artificial systems mimicking the natural photosynthesis for the production of electricity or hydrogen. Synthetic sensitizers and catalysts are considered as a suitable alternative to unstable native systems. As a first-line strategy, porphyrins, phthalocyanines and their metal complexes which absorb light in the same optical region as the native molecules of chlorophyll are considered as such synthetic RCs. Covalently-linked cyclic porphyrins are more durable, but they are difficult to synthesize (Sanders, 2000). Non-covalently associated porphyrins easily degrade due to their sensitivity to changing environmental conditions (Iengo et al., 2003). The advantages of utilizing the porphyrin structures include stability of the RCs and accessibility compared to synthetic products while their disadvantage is the short lifetime in their excited state. Polypyridines containing transition metals have a longer lifetime in their high energy excited states (Krassen et al., 2011). However, they generally require more expensive metals (Pisciotta et al., 2010). It is worth noting that the biomimetic-based semiconductor materials mimicking the PS2's OEC were designed to create energy devices during the early 1970's (Fujishima and Honda, 1972).

6. Improving the efficiency of solar cells

6.1. Methods of immobilization and orientation of biocatalysts

For optimum functioning of a photobioelectrochemical cell, it is necessary to immobilize photoactive molecules on a conductive substrate. Most photobioelectrochemical cells require peptides for immobilization of pigments on the electrode surface. Another important question is the correct orientation of pigment molecules. The studies conducted at Stanford (Goldsmith and Boxer, 1996) were focused on the orientation of photosynthetic RCs with respect to the electrode surface. The essence of the construction was that a poly-histidine tag was attached to the C-terminus of the M-subunit of the *Rhodospira rubra* RC. With help of the tag, the construction was immobilized on a gold electrode containing self-assembling layer of alkanethiols with a head part as Ni-NTA. It was shown experimentally that the proximity of RCs to the electrode is important for the cell effective operation (Kincaid et al., 2006).

Many techniques were used for immobilization of photosynthetic complexes, including in particular, bioelectrocatalytic self-assembling monolayers (bio-SAMs) (Nakamura et al., 2000; Kincaid et al., 2006; Frolov, et al., 2008; Mershin et al., 2012); Ni-NTA was attached to poly-histidine tagged PS1 complexes (Fig. 4d) (Das, 2004; Sekar et al., 2014); the redox-active hydrogels (Badura et al., 2008); and fixation on CNTs by means of molecular binding reagents (Das et al., 2004). Each of these techniques provides various beneficial properties, including increasing the electrode surface area, increasing the rate of electron transfer between the electrode and photobiocatalyst and/or orientation of specific enzymes on the electrode. Unfortunately, enzyme immobilization reduces their activity compared to their native state. Therefore, the correct methods of immobilization should retain enzyme activity for a long time. Meunier, et al. (2009) conducted a study in which thylakoids were adsorbed on a silicon matrix, thereby the stability of the native thylakoid suspension increased and it remained active for 30 d (Meunier et al., 2009). Immobilization should provide an optimum rate of electron transfer from the protein to the electrode, with minimal resistance. This can be achieved by correct orientation of proteins vs. the electrode surface or by use of intermediate carriers. Many studies showed that the correct orientation of a photosystem on the electrode results in an improved electron transport (Frolov, et al., 2008). In many studies, the correct orientation of the photosystems on a gold electrode provides specific binding of a histidine-tagged protein complex with Ni-NTA molecule anchored to a gold electrode (Noji et al., 2011; Das et al., 2004). Badura et al. (2008) used the osmium-containing polymer of polyvinyl-imidazole as modified electrode which worked as an immobilization device and a mediator (Fig. 4b). The immobilized PS2 in these modified systems were capable of generating a current density of $45 \text{ mA}/\text{cm}^2$ at light intensity of $2.65 \text{ mW}/\text{cm}^2$ (maximum wavelength at 675 nm) (Badura et al., 2008).

6.2. The stability of the isolated proteins

The main problem associated with the use of isolated proteins as photosensitizers in photovoltaic cells is their very low stability. The main reason for protein destruction is photoinhibition of photosystems, especially in case of the PS 2. Photoinhibition caused by an excessive amount of radiation may damage the photosynthetic apparatus and hence destroy the chloroplast proteins. Photosystems are provided with some protective mechanisms *in vivo* which include antioxidants (Sekar and Ramasamy, 2015). However, once the proteins are isolated, natural self-healing mechanisms do not work. Thus, isolated proteins are more susceptible to damage and have a short lifetime. One of the methods to stabilize the photosynthetic complexes is through the simulation of the natural states of proteins. Surfactant peptides can be used to imitate the lipid membrane naturally stabilizing photosynthetic complexes. Such surfactants are designed as molecular nanomaterial to study the membrane proteins stability (Mershin et al., 2012) and consist of hydrophilic amino acids (aspartate or lysine) as the head of the chain and hydrophobic amino acids (alanine) as the tail. Das and colleagues (2004) used the peptides A6K (AAAAAAK) and V6D (VVVVVVD) as cationic and anionic surfactant peptides, respectively, for the stabilization of the photosynthetic

complex during construction of a solid electrical device (Fig. 4d) and showed a short-circuit current density of 0.12 mA/cm² at the excitation light intensity of 10 W/cm² with a wavelength of 808 nm. Presumably, this direction is promising.

6.3. Increase of surface area

Increase of the electrode surface area is a traditionally used method for improving the efficiency of functioning photobioelectrochemical cells. In many cases, the electrode itself is initially flat, and its geometry cannot be changed without destroying it. However, the electrode can be modified via nanomaterials, which could increase the real surface area due to the formation of nanostructures on the electrode surface with no planar topology. In this case, the working electrode area is larger than the area of the original flat surface, and it may adsorb more pigment molecules. These approaches include the use of GNPs (Noji et al., 2011), nanoporous gold electrodes (Ciesielski et al., 2010), and redox hydrogels (Badura et al., 2008). In a study carried out by Mershin et al. (2012), two different forms of electrode modification by using nanocrystals of titanium dioxide and zinc oxide nanowires were compared (Fig. 5). Compared to the flat electrodes of the same size, the electrodes with the TiO₂ and ZnO had 200 and 30 times larger active areas, respectively. In fact, the samples based on ZnO were less effective due to the smaller coefficient of roughness. On the other hand, ZnO was found to be more conductive and less expensive compared to the TiO₂ (Mershin et al., 2012).

6.4. Direct or mediated transfer of electrons

Another way to achieve the maximum current density in the cells on the basis of photosynthetic photosensitizers is to create a system that uses direct electron transfer from photosystem to electrode without using a mediator. As mentioned earlier, the mediators have lower redox potential, required for the efficient transfer of electrons, compared to the real electron source. The electrons lose some of their energy if they are transferred to the mediator, in contrast to transfer from the real source. The distance between redox site and electrode should also be minimized in order to ensure efficient transfer of electrons. The main disadvantage of direct electron transfer is the difficulty in ensuring continuous contact between the electron source and the electrode.

Furukawa and colleagues (2006) developed a photosynthetic biofuel cell using polyaniline as an electronic catalyst instead of mediators. Polyaniline has a good electrical conductivity and is compatible with the photosystem. Polyaniline also increases the surface area due to its nanostructure. During their experiment, a good efficiency was achieved for the developed cell: peak current density was about 150 mA/cm² and power density was measured at 5.3 mW/cm². In another study conducted by Sekar et al. (2014), MWCNTs were successfully used for direct transfer of electrons, both in isolated spinach thylakoids and cyanobacteria *Nostoc sp.* (Fig. 6b).

6.5. Extension of the spectral range of the light absorption by photosystems

Such extension is possible using Chl *d* or *f* (Allakhverdiev et al., 2010; Chen et al., 2010; Chen and Blankenship, 2011; Chen and Scheer, 2013; Loughlin et al., 2013; Tomo et al., 2011, 2014). However, the creation of artificial solar cells based on these chlorophylls is still in its early stages of development. Overall, designing solar cells using these chlorophylls seems to hold great promises.

7. Conclusion

Researchers in the field of artificial photosynthesis have focused on the development of systems that could effectively produce a sustainable energy from sunlight without requiring external fuels. These systems must have a high quantum yield and generate energy fluxes of high density in order to meet the energy demands. The more we learn about the nature, the closer we come to the creation of efficient energy solar cells using the photosynthetic apparatus and its components. Using systems mimicking the photosynthetic apparatus and the elements of photosynthetic systems in current energy generators and fuel cells is a quite promising direction (Marshall, 2014). However, lot of changes and improvements are needed before such photovoltaics could be widely used.

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