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Thylakoid-membrane-based photobioelectrochemical systems: achievements, limitations and perspectives.

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Highlights

- Current progress on thylakoid-membrane-based photobioelectrochemical systems is presented.
- Materials, methods of fabrication and novel cell designs are reviewed.
- Perspectives for practical application are evaluated.

Summary

During the few past decades, intensive efforts have been focused towards optimizing “wiring” of thylakoid membranes (TMs) to conductive surfaces for their further application for light energy conversion and production of an electron flow. This review summarizes recent progress and current state of photobioelectrodes and systems based on TMs. We consider various electrode materials and surface modifications, mediators and setup designs reported until to now and compare achieved current and power outputs. Finally, we discuss further potentially valuable applications and perspectives of TM-based bioelectrochemical systems.

Introduction

Today solar energy is considered as one of the most promising alternative to fossil fuels. Green plants and microorganisms, possessing the natural ability to harvest solar energy, produce electrons and protons from water splitting through photosynthesis, a complex of biological light-driven reactions characterized by extreme quantum efficiencies [1] and highly efficient energy conversion yields [2]. For this reason, employment of the natural photosynthetic apparatus as light-harvesting elements in photoelectrochemical systems for solar energy conversion, application and production of ecologically clean electricity is the great scientific challenge.

Starting from the pioneering works by Allen et al., where the photoelectrochemical features of thylakoid membranes (TMs) have been measured for the first time [3] and further progress in this area was achieved by Carpentier and coworkers [4-6]. TMs have ever since been considered as perspective photosynthetic catalysts for solar energy conversion. Employment of TMs in photobioelectrochemical systems (PBESs) is commonly motivated by unexpected enhanced stability of the photosynthetic protein complexes retained within their *native* environment, availability of several alternative electron transfer pathways for optimal communication with electrode surfaces, and simple procedures for extraction and purification

[7,8]. However, photosynthetic complexes naturally are not stable, especially under strong illumination, when the lifetime of photosystem II (PSII) is limited to minutes for isolated complexes or to ca. 1 h for such complexes *in vivo* [9]. Living plants repair their PSII reaction center by exchanging photodamaged protein twice an hour, and billions of years of evolution could not optimize this process better [10]. Current trends in development of PSII-based PBESs are intended to overcome the stability limitations by interfacing the photosynthetic machinery with synthetic materials to create semi-artificial hybrids [11]. This approach can hardly be applied for TMs, where the photosynthetic machinery is embedded within the membrane (Figure 1). This makes TMs-based PBESs closer to photosynthetic microbial fuel cells and cellular bio-photovoltaic cells in terms of development of electrode materials, surface morphology and modifications, immobilization of the bioelements and the expected performance. Both TM-based and microbial PBESs produce similar photocurrent output recalculated per chlorophyll content [12], however, in terms of real power output TMs-based PBESs producing several $\mu\text{W cm}^{-2}$ are intermediate between devices employing isolated photosystems (hundreds of $\mu\text{W cm}^{-2}$) and living cells ($<1 \mu\text{W cm}^{-2}$).

In this review we aim at providing the readers a close insight into the present situation in the area of PBESs employing the photosynthetic features of TMs. We consider state of the art of such systems, progress in materials, experimental designs and setup configurations employed over recent years. Finally, we overview some future trends and directions in this research field.

Figure 1. Schematic illustration of a bioelectrochemical system comprising a TMs-based photobioanode: Cyt – cytochrome, Med_{red} and Med_{ox} – reduced and oxidized forms of a mediator, OEC - oxygen-evolving complex, PC – plastocyanin, PQ – plastoquinone, PSI and PSII – photosystem I and II, respectively, Sub_{red} and Sub_{ox} – reduced and oxidized forms of the cathodic substrate.

TMs-based systems for light energy conversion

A typical PBES is comprised of two electrodes, a photobioanode (PBA), where light capturing coupled with water splitting is performed by immobilized TMs, and a (bio)cathode, where reduction of an oxidant occurs (Figure 1). TMs can be directly wired to the anode surface or electrochemically connected through soluble or non-soluble mediators shuttling electrons between the TMs and the electrode surface.

It should be noticed that the source of TMs is a significant factor effecting the performance of TM-based electrodes. It was shown that the photobiocurrent generated by using stroma TMs was up to 4-fold higher compared to that for PBA employing grana TMs in DET conditions [13]. A comparative study of thylakoids from higher plants made by Rasmussen et al. demonstrated that the largest photocurrent among investigated sources (80 μA per mg protein, 430 μA per mg chlorophyll at 0.45 V vs. Ag|AgCl and illumination of 5200 lumen) was achieved for TMs from *Spinacia oleracea* [14]. Nowadays it is the most commonly used source of TMs in the laboratory; most of the photobioanodes and PBES described in this review are based on TMs extracted from this plant.

Mediators, electrode materials and modifications

Early examples of electrochemical communication between TMs and conductive surfaces involved planar metal electrodes as current collectors and support for immobilization of the photosynthetic membranes. Such studies were mainly focused on investigation of fundamental principles of photosynthetic reactions and extracellular electron transfer pathways in TMs [15,16]. Later utilization of carbon-based materials with extended surface area and suitable morphology allowed higher photocurrent outputs and improved the performance of TMs-based PBAs by a much enhanced loading of the bioelement.

One of the first examples is the work by Calkins et al., who immobilized TMs onto multi-walled carbon nanotubes (CNTs) and achieved a maximum and a steady state photobiocurrent density of 68 and 38 $\mu\text{A cm}^{-2}$, respectively, at 0.2 V vs Ag|AgCl and a light intensity of 800 W m^{-2} using $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as mediator. A biosolar cell constructed by coupling this TMs/CNTs anode and a laccase/CNTs cathode delivered a maximum power density as high as 5.3 mW cm^{-2} at ca. 0.2 V, which was the highest value reported for the PBESs at that moment. Recently, Takeuchi et al. achieved a photobiocurrent density of ca. 100 $\mu\text{A cm}^{-2}$ from a TMs/CNTs PBA at 0.2 V vs. Ag|AgCl_{sat} and a light intensity of 1500 $\mu\text{mol m}^{-2} \text{s}^{-1}$ using 1,2-naphthoquinone as mediator [17]. Bunea et al. demonstrated micropatterned carbon-on-quartz electrode chips with a varying degree of transparency for immobilization of TMs in the presence of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ as soluble mediator; a maximum current density of 71 $\mu\text{A cm}^{-2}$ was obtained for the optimized electrode design under a light intensity of 1000 W m^{-2} [18].

Pankratova et al. employed a 3D matrix of electrochemically reduced graphene oxide (rGO) with an amidated surface for immobilization of TMs [19]. A maximum photocurrent output of 5.2 $\mu\text{A cm}^{-2}$ was obtained at 0.6 V vs. standard hydrogen electrode (SHE) and at an illumination intensity of 400 W m^{-2} in the absence of any mediator, which was more than a 2.5-fold greater current density compared to results obtained for TMs directly wired to amide-modified MWCNTs [20]. Introduction of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as mediator in this TMs/rGO PBA configuration resulted in a photobiocurrent output of ca. 20 $\mu\text{A cm}^{-2}$ at potentials >0.44 V vs. SHE under illumination of 1000 W m^{-2} [21].

Employment of Os-complex modified redox polymers (OsRPs) as an alternative to common soluble redox mediators received considerable attention due to the stability of OsRPs, a relatively fast electron transfer rate through the polymer matrix, the ability to form strong electrostatic interactions with negatively charged biomembranes including TMs and simplification of the design for a complete PBES. Hamidi et al. tested four different OsRPs for immobilization of TMs on graphite electrodes and achieved a maximum current output of ca. $22 \mu\text{A cm}^{-2}$ (0.5 V vs. SHE, light intensity of 800 W m^{-2}) in case of $[\text{Os}(2,2'\text{-bipyridine})_2(\text{polyvinylimidazole})_{10}\text{Cl}]^{+/2+}$ [22]. Recently, the photobiocurrent density was increased up to $62.5 \mu\text{A cm}^{-2}$ (+0.4 V vs. Ag pseudoreference, 400 W m^{-2} illumination) by enhancing the electrode surface area using gold nanoparticles [23] and up to $97 \mu\text{A cm}^{-2}$ (0.6 V vs. SHE, 400 W m^{-2} illumination) using CNTs synthesized by pyrolysis of polymeric precursors [24].

It has also been demonstrated that nanomaterials with a low particle size may penetrate into the membranes close to the photosynthetic reaction center and serve as electronic bridges between the TMs and the electrode surface enhancing the current output and improving the longterm electrochemical stability. In such a way, implementation of carbon nanoparticles (nanodots) in a TMs-based PBA demonstrated 2-fold enhancement in photocurrent output compared to the PBA with only TMs [25]. Furthermore, the recently reported employment of dual-emissive carbon dots on the surface of extracted chloroplasts and into green plants showed a 2.8 times increase in the production of adenosine triphosphate and a 25% increase in electron transport rate of photosynthesis in living plants [26], which can potentially be utilized for TMs-based systems.

The Bazan group investigated the influence of various organic compounds on the efficiency of electrochemical communication between TMs and electrode surfaces. Utilization of conjugated oligoelectrolytes with a systematic progression of chemical structures results in a 2.3-fold increase in photocurrent density for the best oligoelectrolyte [27]. Incorporation of a cationic poly(fluorene-co-phenylene) conducting polymer containing positively charged side chains facilitated the electrostatic binding with TMs and accelerated the rate of photosynthetic water splitting by a factor of 2 and resulted in a 4-fold enhancement of the photocurrent density [28].

Electrospray deposition may be considered as a future perspective approach for fabricating stable and uniform films of photobiocatalysts in terms of possible scalable fabrication of mediator-free TMs-based PBAs. Kavadiya et al. reported a notable example of a hybrid PBA fabricated by electrospray deposition of TMs on a 1-D single crystal nanostructured TiO_2 and exhibiting a photocurrent density of $12 \mu\text{A cm}^{-2}$ at <0.5 V vs. SHE under visible light illumination. Since both photosystem I and II alone cannot work on TiO_2 , it can be expected that the whole Z-scheme works is utilized in this design [29]. Shi et al. fabricated a PBA based on TMs/graphene oxide films electrosprayed on a metal support or on flexible indium tin oxide-coated polyethylene naphthalate films. A maximum photobiocurrent of $2.5 \mu\text{A cm}^{-2}$ was obtained for this design at 0.6 V vs. SHE under illumination of 1000 W m^{-2} [30].

As can be seen in Figure 2, the maximum photobiocurrent from TM-based opaque anodes can be expected to be between ~ 10 and $\sim 100 \mu\text{A cm}^{-2}$ for direct electron transfer and mediated approach, respectively, regardless on the nature of the mediator. A higher loading of a photosynthetic material leads to a weak electrochemical communication between the multilayers of the TMs, losses of charge and faster photodamage, whereas an increase in porosity and thickness of the electrode material limits the access of the light into the more deep

layers of the TMs [19]. Introduction of transparent microporous 3D materials may significantly enhance the photocurrent output and stability of TMs-based PBAs and can be considered as one of the most urgent directions in this field.

Device configuration and design

Aside from the influence of the material employed, the overall configuration and design of a built-up PBES is a highly relevant aspect for systematic optimization of the system. Utilization of a TMs suspension was proposed as an alternative to the immobilization procedures to increase the active concentration of TMs in the presence of dissolved charge carriers. Pinhassi et al. conducted a comparative study of crude TMs suspension from the cyanobacterium (*Synechocystis*) and from higher plants (spinach and tobacco) in DET mode with graphite electrodes or using 2,6-dichloro-1,4-benzoquinone (DCBQ) as soluble mediator. A large amount of loaded TMs suspension allowed the achievement of *ca.* 100 $\mu\text{A cm}^{-2}$ for spinach TMs in the presence of DCBQ and a mediator-less photocurrent of 35 $\mu\text{A cm}^{-2}$ for *Synechocystis* TMs at 0.24 V vs Ag|AgCl and a light intensity of 1000 W m^{-2} [31]. Based on this early work an elegant example of a hybrid PBES for water splitting was developed employing TMs suspension [32]. This device produced a photocurrent density of 0.5 mA cm^{-2} and exhibited a Faradaic efficiency of hydrogen and oxygen production up to 69% demonstrating the perspective of a real practical application of TMs-based systems.

Gorton and coworkers proposed a concept composed of double-featured supercapacitive photobioanodes and biosolar cells for simultaneous solar energy conversion and storage in the form of electric charge as a possible opportunity to overcome the low power output for TM-based systems [19,33,34]. To investigate the influence of the capacitive unit on the overall photobiocurrent output, additional charge-storing electrodes with a variable capacitance were connected to the TMs-based photobioanode and a bilirubin oxidase-based biocathode demonstrating up to a 2.5-fold rise in photocurrent density from a separate PBA and 5 times higher maximum power output from complete PBES [33].

Figure 2. Recent progress in biophotovoltaics based on immobilized TMs represented by maximum photocurrent density of the bioanodes (left scale, spheres) and power output of the assembled biosolar cells (right scale, stars) achieved at a light intensity below 1000 W m^{-2} also indicating the year of the reports. The results achieved for TMs directly immobilized onto the electrode surface and in the presence of soluble mediators or redox polymers are marked in black, blue and red, respectively. The references cited in this figure are [8,17-24,29,30,33,35].

TMs-based systems for biosensing

Along with employment in energy converting systems, TMs-based systems can potentially be employed for detection of various pesticides or other soluble analytes affecting the photosynthetic processes.

Minteer's group proposed a self-powered herbicide sensor incorporating a TMs-bioanode for direct photoelectrocatalysis [36] based on a previously developed design of a thylakoid biosolar cell using laccase based biocathodes [37]. A linear response up to concentrations of $\sim 15 \mu\text{g L}^{-1}$ and limits of detection below $0.4 \mu\text{g L}^{-1}$ were obtained for atrazine, bromacil, and diuron by measuring the current response at 0 V (short circuit current), which is below the permissible level set by the United States Environmental Protection Agency. A comparative study of TMs from different sources displayed different sensitivities of the TMs from various sources to the inhibition by diuron and a better sensitivity when using the TMs from spinach [14].

Obviously, this approach can hardly be utilized for quantitative detection of specific compounds or for continuous monitoring of water quality (due to the low stability of the PBAs) and requires high reproducibility of the fabricated PBES. But employment of cheap abundant materials for a fast preliminary screening for water pollutants may be a good option in places with limited access to advanced analytical techniques.

Future directions and concluding remarks

Fabrication of scalable, stable PBESs based on immobilized TMs for delivery of a remarkable power on a long-term basis for real-life applications is currently limited by such properties of the biocatalyst as lack of internal stability, absence of a self-repairing machinery of the photosynthetic apparatus and the relatively low content of photosensitizers. This can be also be illustrated by the very limited number of reported assembled PBESs employing PBA-anodes (Figure 2).

Though TMs keep a number of drawbacks, they possess a good mechanical stability, high loading of photosynthetic proteins compared to living cells and fast and cheap isolation and purification procedures. This enables the employment of TMs in bioelectrochemical systems operating under low-intensity illumination, where the operational stability in the immobilized state is not a crucial factor. Promising examples of PBESs employing stable TMs suspensions constitute a possible niche, where the performance of the TMs can be an ideal option. Their employment as anodic photobioelements in transparent disposable wearable biomedical devices for continuous health care monitoring may help to overcome the limitations of conventional enzymatic fuel cells related to a low concentration of fuels and provide sufficient power supply for miniature self-powered biosensing platforms [38,39].

Furthermore, the similar size of plane TMs and whole microbial photosynthetic living cells allows conducting representative experiments, which do not require a long time for growing microbial cells and formation of a stable biofilm but provide comparative results for choosing optimal conditions for electrochemical communication between a photobiocatalyst and various conductive surfaces. This trend can be observed in the development of microbial PBESs following the principles successfully employed in TM-based devices. For example, recently reported examples of a self-charging cyanobacterial supercapacitor [40] and photosynthetic cyanobacterial [41] and algal [42] biosensors successfully utilized the concepts previously disclosed for the TM-based systems [20,36]. Another example, TMs became a model object in a detailed investigation of the relationship between the transparent area available for photosynthesis and the opaque area of a carbon current collector [18]. TMs-based technologies may therefore be considered as a fundamental research field for screening electrode materials, surface modifications and novel design concepts for further employment in photosynthetic energy converting systems employing cyanobacteria or algae.

Until now, various proof of concepts for TMs-based PBESs have been proposed demonstrating broad capabilities of their utilization. Further successful development in this field is related to a cross-disciplinary mindset with close relationship between academia and industry, which is necessary for efficient use of existing knowledge and critical evaluation of possible directions and perspectives.

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- Paper of special interest
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