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REVIEW

Photosynthetic reaction center-functionalized electrodes for photo-bioelectrochemical cells

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Abstract During the last few years, intensive research efforts have been directed toward the application of several highly efficient light-harvesting photosynthetic proteins, including reaction centers (RCs), photosystem I (PSI), and photosystem II (PSII), as key components in the light-triggered generation of fuels or electrical power. This review highlights recent advances for the nano-engineering of photo-bioelectrochemical cells through the assembly of the photosynthetic proteins on electrode surfaces. Various strategies to immobilize the photosynthetic complexes on conductive surfaces and different methodologies to electrically wire them with the electrode supports are presented. The different photoelectrochemical systems exhibit a wide range of photocurrent intensities and power outputs that sharply depend on the nano-engineering strategy and the electroactive components. Such cells are promising candidates for a future production of biologically-driven solar power.

Keywords Electron transfer (ET) · Energy conversion · Photocurrent · Photoelectrochemical cell · Reaction center (RC)

Abbreviations

A	Acceptor
BOD	Bilirubin oxidase
CNT	Carbon nanotube
cyt	Cytochrome
D	Donor
DCPIP	2,6-Dichlorophenolindophenol
DSSC	Dye-sensitized solar cell
ET	Electron transfer
FTO	Fluorine-doped tin oxide
ITO	Indium tin oxide
LH1	Light-harvesting 1 pigment protein
LHC	Light-harvesting complexes
MV^{2+}	*N*,*N*′-Dimethyl-4,4′-bipyridinium, methyl viologen
NC	Nanocluster
NHE	Normal hydrogen electrode
NP	Nanoparticle
NTA	Nitrilo triacetic acid
NQS	1,4-Naphthoquinone-2-sulfonate
PC	Plastocyanine
pMBQ	Poly-mercapto benzoquinone
PSI	Photosystem I
PSII	Photosystem II
RC	Reaction center
SCE	Standard calomel electrode
SWCNT	Single-walled carbon nanotube
TMPD	*N*,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine

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Introduction

Photosynthesis, the process responsible for sustaining planet life on earth, has been demonstrated, through many decades of research, to occur via the photochemical activity of unique, multi-subunit complexes termed "reaction centers" (RCs). The ability of the RC complexes to harness

light energy for transferring electrons from a primary donor (D) to an acceptor (A) exhibiting more negative electrochemical potential, conveys the uniqueness to this process. Moreover, the fact that the process occurs at 100 % quantum efficiency makes it even more special. Throughout the years, different RCs were identified in several kinds of photosynthetic organisms, but, evidently, all of them obey the same basic physical principle: upon light excitation, the RCs facilitate a charge separation process, which constitutes a crucial stage in the photosynthetic electron transfer (ET) chain. This photo-induced process is described in Eq. (1).

$$DA \xrightarrow{hv} D^{+} + A^{-} \quad (1)$$

The first RC complex which has been biochemically studied belonged to the photosynthetic purple sulfur bacteria. Following the early spectral observation of Lou Duysens, an observation that predicted the existence of the RC (Duysens 1952), Clayton and Reed, reported in 1968 on the isolation of a functional photosynthetic RC (Reed and Clayton 1968). However, the purification of these RCs to homogeneity was, indeed, carried out at George Feher's group. In the years to follow, the vast majority of biophysical characterizations of the RC photosynthetic units originated from the Feher laboratory. Through four decades of extensive biophysical/biochemical and molecular biology characterizations, the Feher–Okamura group revealed the identities of the primary donor, as well as the electron acceptors of the purple sulfur bacteria RCs (Okamura et al. 1975). Moreover, the Feher–Okamura laboratory has also revealed the identity of the RC proteins H, M, and L subunits and their amino acid sequences (Williams et al. 1983a, b, 1984). All of this important information made an indispensible contribution at the stage of revealing the structures of the purple sulfur bacteria. In the mid eighties, the structural determination, first of *Rodobacter viridis* (Deisenhofer et al. 1984; Deisenhofer et al. 1985), and later of *Rodobacter spheroidis* (Allen et al. 1987a), constituted the grounds for a comprehensive molecular understanding of the correlation between the RCs structure and their functions at the atomic level (Allen et al. 1987b), which paved the way to determining the ET as well as the proton-transfer processes occurring at the RCs (Graige et al. 1996; Okamura et al. 2000; Paddock et al. 1989). Furthermore, these studies have paved the way for major mutagenesis efforts aimed at determining the RC structures (Okamura and Feher 1992; Paddock et al. 2003). In addition to that, the seminal work on bacterial RC structures enabled the understanding of the architecture of the RCs that is responsible for their efficient photobiochemical activity, and encouraged many biochemical, molecular biology, and structural investigations on oxygenic photosynthetic RCs (Dismukes and Blankenship 2005). The first oxygenic complex whose structure was solved in the early 2000s was the cyanobacterial photosystem I (PSI) isolated from *Synechococcus elongatus* and determined at 2.5 Å resolution (Jordan et al. 2001). Following these discoveries, the structure of an eukaryotic PSI, isolated from a pea plant, was elucidated (Amunts et al. 2007; Ben-Shem et al. 2003). This study shaded light on the PSI photo-biochemical ET process, and the way by which the energy is transferred between the light-harvesting complexes (LHCs) to the pigments of the core complex, and subsequently to the dimer comprising the primary donor, P_{700} (Ben-Shem et al. 2004). Also, the existence, and the role, of the "red" and gap chlorophylls were identified. The most recent RC structure that has been solved is that of photosystem II (PSII) (Broser et al. 2010; Zouni et al. 2001), The major contribution in this case was to the understanding of the water oxidization and oxygen generation reactions (Ferreira et al. 2004; Umena et al. 2011; Yano et al. 2006).

The remarkable progress achieved by solving the structures of the different RCs has pushed forward the whole field of photosynthesis. The major questions that have to be addressed are what is the future of photosynthesis and where is this field heading to? One possible direction is artificial photosynthesis which will translate the molecular information to a blueprint of organic and inorganic syntheses (Chen et al. 2012; Gust et al. 2009; Hambourger et al. 2007; Hammarström 2003; Imahori et al. 2003; Rivalta et al. 2012; Sun et al. 2001; Sykora et al. 2000). Nonetheless, due to the complexity of the different RC structures, each composed of multiple proteins and pigments, this direction has been proven successful, until now, only for artificial pigments. A second, even more promising research direction that was discussed recently (Blankenship et al. 2011), is to employ purified natural complexes as both light-harvesting and electron transporting elements in photo-bioelectrochemical cells. This scientific direction is the subject of this review. We will highlight several recent studies which made use of the isolated and purified photosynthetic units PSI, bacterial RC, or PSII, to generate electricity upon their immobilization to electrode surfaces and illuminating the resulting photoactive assemblies. We would like to dedicate the manuscript to George Feher, who two decades ago, during a course he has been teaching at the Hebrew University of Jerusalem, said, in his unique and humoristic way: "Who knows, maybe one day the Silicon Valley will turn into the RC valley…".

PSI as a photo-biochemical source of energy

The quantum yield associated with the light-to-electrical conversion efficiency of the photosynthetic PSI unit has evolved, during the last 3.5 billion years, to the value of unity

(Brettel 1988, 1997; Brettel and Leibl 2001). This extremely high yield crowned PSI as nature's primary catalyst in the process of energy conversion, resulting in carbon dioxide fixation and the generation of fuels (Calvin 1976). The supramolecular PSI structure consists of 96 chlorophyll units that absorb sunlight photons and efficiently transfer their energy to the P_{700} center, where charge separation occurs. The excited electrons shuttle along the ET chain to the F_B iron–sulfur cluster, thus facilitating its reduction while preventing the recombination process. Concurrently with that, the photogenerated hole of the oxidized P_{700}^+ is scavenged via an ET from donor specie, such as plastocyanine or cytochrome *c* (cyt *c*). The photoexcitation of the PSI provides a considerable amount of free energy (ca. 800 mV for the electron transition between cyt *c* and F_B), which suggests the possible application of this photoactive protein as a biogenerator for producing fuels or electrical power. Indeed, during the last two decades, several research groups have been actively involved in harnessing the extraordinary capabilities of PSI for the production of fuels, such as hydrogen (Esper et al. 2006; Greenbaum 1985; Grimme et al. 2009; Iwuchukwu et al. 2010; Lubner et al. 2010; Millsaps et al. 2001; Utschig et al. 2011), electric power (Badura et al. 2011a; Carmeli et al. 2007; Ciesielski et al. 2010b; Greenbaum 1990; Terasaki et al. 2006, 2009; Yehezkeli et al. 2010b), generation of high voltage (Toporik et al. 2012), or for controlled directional (anodic or cathodic) photocurrents (Ciesielski et al. 2011; Efrati et al. 2012).

Early attempts to utilize the PSI protein for hydrogen production were based on the use of the full thylakoid membrane (Greenbaum 1985). The thylakoid membrane, a unit which consists of the major photosynthetic complexes, PSII, cyt b_6f, PSI, and the proton ATPsynthase, has also been immobilized on an electrode surface and revealed, upon illumination, electrical currents which were attributed to the PSI protein (Lam et al. 2006). While the primary approach demonstrated in these studies has focused on the use of the entire thylakoid membrane, a further development in the generation of PSI-based systems has been achieved by the separation and purification of the PSI complex and the introduction of thermally stable PSI complexes in monomer or trimer forms (Almog 1991). Early attempts to electrically wire PSI with electrode surfaces indicated that the application of sacrificial electron-donor systems, such as ascorbic acid/2,6-dichlorophenolindophenol (DCPIP), could be implemented for reducing the photogenerated holes at the P_{700} center, which led to the efficient charge separation reflected in the generation of photocurrents (Boucher and Carpentier 1992; Erabi et al. 1997) An interesting approach that emerged from these studies involved the use of PSI/Pt nanocluster (NC) hybrid structures, in which the Pt NCs function as a catalyst for the hydrogen evolution reaction (Greenbaum 1985). In order to form the PSI/Pt NC structure, the PSI protein was illuminated in the presence of a buffer solution containing a platinum(VI) salt. The process resulted in the local photoreduction of a Pt metal NC at the photoactive F_B terminal site of the protein. The illumination of the PSI/Pt NC in acidic media containing the ascorbic acid/DCPIP (or cyt *c*/ascorbic acid) electron-donor system, allowed, then, the injection of the photo-excited electrons to the Pt NC, and the subsequent electrocatalytic reduction of protons on the surface of the cluster to yield the H_2 fuel. The soluble PSI/Pt NC nanostructure exhibits two inherent advantages that suggest its further linking to electrode surfaces: (i) The deposited Pt metal nanostructure is in an intimate contact with the photoactive F_B center, and thus, upon the illumination of the PSI, the Pt NC may effectively collect the photoexcited electrons. This process prevents recombination by increasing the charge separation at the PSI, which is essential for a high yield generation of photocurrents. (ii) A versatile surface chemistry provided by the Pt metal cluster, allows the tethering of the entire PSI/Pt NC composite to surfaces. The alignment of the PSI/Pt NC hybrid on an electrode surface in an optimal configuration, where the ET distances are minimal, was first introduced by Greenbaum (1985) and was further developed by others. In one report (Frolov et al. 2008), a genetically-engineered cysteine-functionalized PSI was irradiated in the presence of a platinum salt to form a platinized, thiolated PSI protein nanostructure. The resulting composite was, then, used to assemble a multilayer of PSIs on Au support, in which the photoactive units were crosslinked through Pt–sulfide bonds provided by the genetically-engineered cysteine mutants. The layered configuration was used for the generation of a photovoltage whose value was significantly intensified by the gradual increase in the number of PSI layers. In a follow up study, a remarkable photovoltage value of 50 V was achieved by implementing a similar approach, but with the use of crystallized PSI units (Toporik et al. 2012). An alternative method to align the photosynthetic RC of PSI on an electrode, involved the extraction of the electron acceptor unit phylloquinone A_1 from the PSI structure, and reacting the resulting apo-protein complex with an electrode surface modified by a monolayer of vitamin K molecules. Photo-excitation of the resulting PSI-reconstituted surface induced a direct ET from the A_1 site to the electrode that bypassed the natural transfer chain to the F_B site. Using this advanced methodology, a series of photoactive devices was developed (Terasaki et al. 2006, 2007, 2009). Further studies indicated that the iron–sulfur F_B cluster of PSI could also be separated from the protein structure. The F_B cluster was chemically tethered to a Pt nanoparticle (NP), and the modified composite was reconstituted back into the PSI apo-protein (Grimme et al. 2009). Upon irradiation of the

reconstituted PSI/Pt NP structure, the close proximity between the F_B site of the PSI and the metallic NP has led to an efficient photo-catalysis of proton reduction to yield hydrogen. Similarly, efficient hydrogen production was also achieved by coupling the F_B site of PSI to a [Fe–Fe]-hydrogenase through a molecular wire (Lubner et al. 2010). The versatile nature of the PSI complex to act both as an acceptor (P_{700}^{+}) and as a donor (F_B^{-}), implies that it can be used not only for the generation of anodic photocurrents (or as a reducing agent in different photosynthetic reactions), but also for the generation of cathodic photocurrents (directional flow of electrons from the electrode toward the electrolyte). This was exemplified by the construction of photo-bioelectrochemical cells that were prepared by the co-adsorption of a poly bipyridine osmium complex and the PSI protein on electrodes (Badura et al. 2011a). In these cells, the $Os^{3+/2+}$-based polymer acted as an electron mediator, receiving electrons from the electrode and directing them to scavenge the holes generated during the excitation of the PSI. Concurrently, and in the presence of the diffusional electron acceptor *N*,*N*′-dimethyl-4,4′-bipyridinium, methyl viologen (MV^{2+}), the photo-excited PSI electrons reduced the mediator to its radical form, $MV^{+\cdot}$, which, in turn, allowed the reduction of solubilized oxygen in the electrolyte. Consistent with this mechanism, cathodic photocurrents were obtained. Several illuminating examples implementing the PSI, PSII, and photosynthetic RC for the assembly of photo-bioelectrochemical cells will be discussed in detail.

PSI-based photoelectrochemical cells

Upon its immobilization onto an electrode, PSI may act either as an electron-donor or electron-acceptor, depending on the chemical environment in the cell and the potential applied on the electrode. The equilibrium potentials of the F_B/F_B^{-} and the P_{700}/P_{700}^{+} couples were estimated to be −0.585 and +0.490 V versus normal hydrogen electrode (NHE), respectively (Brettel 1997). An interesting approach to construct a multi-layered PSI assembly on electrodes was recently demonstrated (Ciesielski et al. 2010a). By the repeated layer-by-layer deposition of PSI from aqueous suspensions, followed by the subsequent removal of the solvent using vacuum, thin films of PSI proteins of controlled thicknesses were deposited on electrode surfaces. The PSI units were bound through hydrophobic interactions, and electrical communication with the surface was achieved by the use of the diffusional electron mediator couple ferricyanide/ferrocyanide, $Fe(CN)_6^{3-/4-}$, in the system, Fig. 1a. The redox potential of the $Fe(CN)_6^{3-/4-}$/ couple is ca. 0.36 V versus NHE, which thermodynamically enables the reduced ferrocyanide specie to act as a donor for P_{700}^{+}, whereas the oxidized ferricyanide specie is used as an acceptor for the reduced F_B^{-} center. Upon illumination, and by the application of a fixed constant potential, 0.1 V versus Ag/AgCl, on the PSI-modified electrode, photocurrents that followed the absorption spectrum of PSI, were generated, Fig. 1b. At this potential, the electrode reduces the ferricyanide specie to the ferrocyanide form, which, then, drifts away to the photoexcited P_{700}^{+} center and allows its reduction. The resulting ferricyanide from this process diffuses back to the electrode, where it acts as an acceptor for

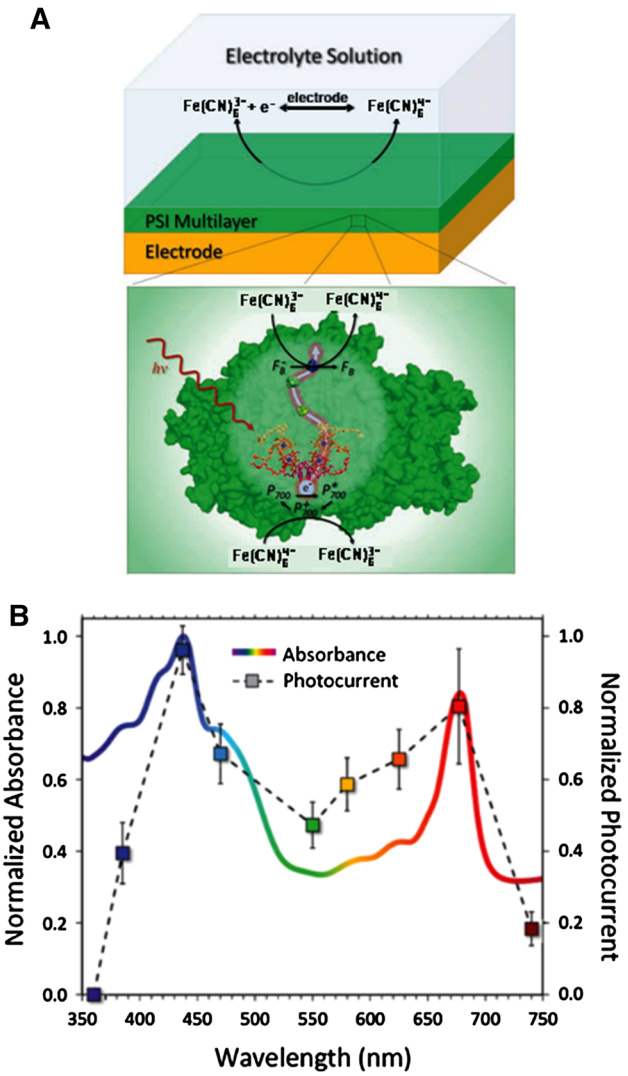


Fig. 1 **a** ET pathways across the photoexcited PSI multi-layer deposited on an electrode surface. **b** Normalized absorption spectrum of PSI (*full line curve*), and photocurrent action spectrum (*dotted curve*), corresponding to the PSI multilayer assembly on an electrode surface. The photocurrent was measured in the presence of a $Fe(CN)_6^{3-/4-}$ redox couple as a diffusional charge mediator. Reproduced with permission from Ciesielski et al. (2010a). Copyright Wiley-VCH Verlag GmbH & Co. KGaA

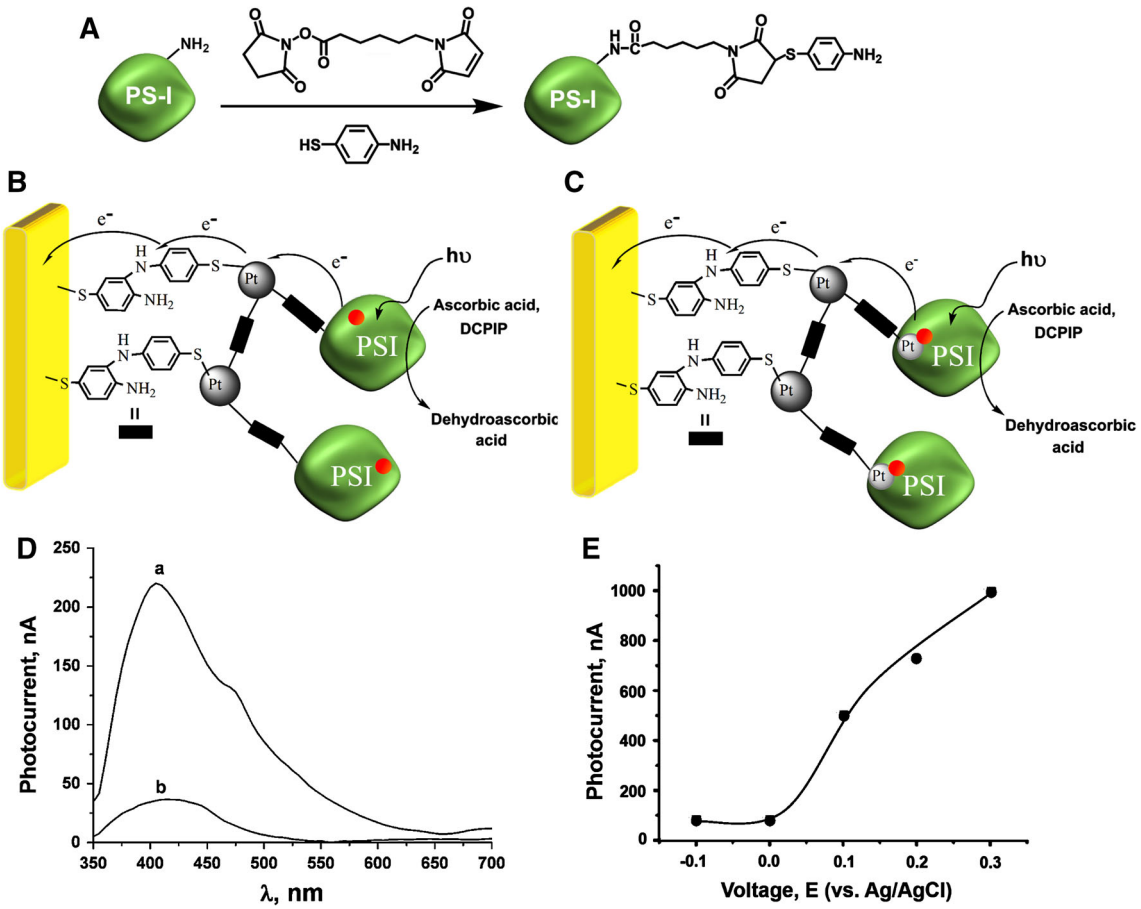
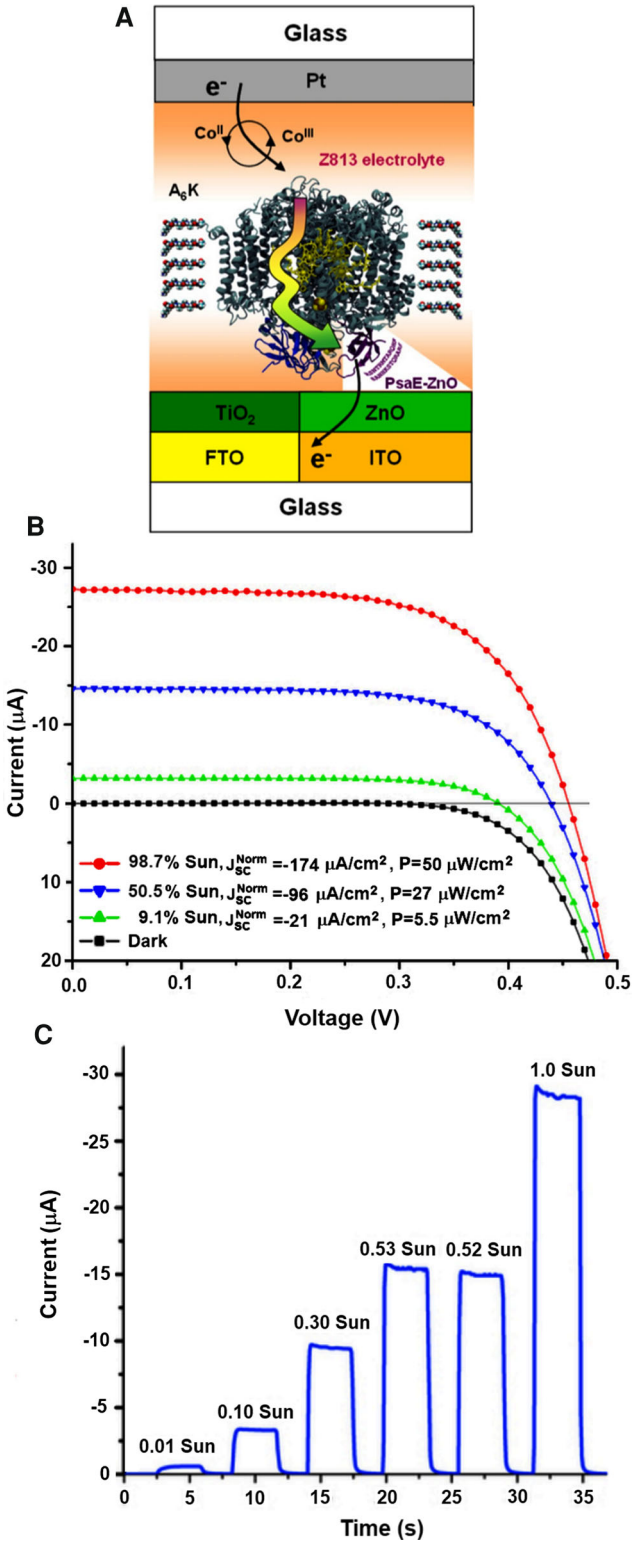


Fig. 2 **A** Modification of the PSI protein with a thioaniline electropolymerizable unit. **B** Photocurrent generation scheme for a non-aligned bis aniline-crosslinked Pt NPs/PSI composite-modified electrode. **C** Photocurrent generation scheme for the bis aniline-crosslinked Pt NPs/PSI–Pt NC composite-modified electrode in which the PSI is aligned toward the electrode by means of the Pt NC. **D** Photocurrent action spectra generated by: *a* the non-aligned Pt NPs/PSI composite, and *b* the aligned Pt NPs/PSI–Pt NC composite. **E** Photocurrent responses upon the application of variable potentials on the aligned Pt NPs/PSI–Pt NC composite. Reproduced with permission from Yehezkeli et al. (2010b). Copyright 2010 American Chemical Society

the electrons generated by the F_B^- unit. Following this route, the generation of the photocurrent was sustained.

An alternative approach to form integrated PSI assemblies on electrodes was introduced by the Willner laboratory (Yehezkeli et al. 2010b). In this study, PSI was covalently modified with electopolymerizable *p*-aminothiophenol (thioaniline) molecules, Fig. 2A, and was electropolymerized, in the presence of thioaniline-capped Pt NPs, onto a thioaniline-modified Au surface, Fig. 2B. The resulting bis aniline-crosslinked Pt NPs/PSI composite films exhibited, under illumination and in the presence of the electron-donor system DCPIP/ascorbic acid, photocurrents of ca. 30 nA (for an effective illuminated area of ca. 0.25 cm^2). In this system, the bis aniline bridging units, which are the building blocks of the composite film, and are thus highly prevalent in the system, act as electron-acceptors for the photoexcited electrons. The method was further improved by the photo-reduction of a Pt salt at the F_B^- site of the thioaniline-functionalized PSI, and the subsequent electropolymerization of the resulting PSI/Pt NC composite to yield an aligned bis aniline-crosslinked Pt NPs/PSI–Pt NC matrix, Fig. 2C. As expected, the aligned configuration, in which the F_B^- site was oriented at a close proximity with the Pt NC, thus shortening the ET distance, supported a sevenfold increase in the photocurrents as compared to the non-aligned configuration that lacked the Pt NCs, Fig. 2D. A further increase in the photocurrents to above 1,000 nA was evident upon the application of an external potential, $E = 0.3$ V versus Ag/AgCl, on the PSI–Pt NC/Pt NPs composite electrode, Fig. 2E. This observation can be attributed to the fact that at potentials higher than 0.05 V (the equilibrium potential of the bis aniline bridging units at pH 7.0), the bis aniline bridges are oxidized to the quinoide state, which is a good acceptor for the photoexcited electrons. Furthermore, by negatively shifting the applied potential below 0.05 V versus Ag/AgCl, a decrease in the photocurrent is evident, consistent with the increase in the population of the reduced



◀ **Fig. 3** **a** Schematic illustration of the photo-bioelectrochemical cell composed of a nano-engineered PSI protein with a ZnO-binding peptide-modified psaE subunit linked to a ZnO surface and a Pt cathode. A regenerative $[Co(dbbip)_2]^{2+/3+}$ redox couple is used to mediate the charge transfer in the cell. **b** Polarization *i*/*V* curves corresponding to the discharge of the photo-bioelectrochemical cell under variable illumination intensities. **c** Time-dependant photocurrents obtained by the discharge of the cell under variable illumination intensities. Adopted with permission from Mershin et al. (2012). Copyright Nature Publishing Group, 2012

bis-aniline units, which do not posses acceptor properties. Evidently, at potentials lower than ca. 0.0 V versus Ag/AgCl, the majority of the bridging units exist in the reduced state, and hence only diminished photocurrents could be observed.

A recent promising application of the isolated PSI component is its integration in dye-sensitized solar cells (DSSCs). DSSCs have been highlighted as an emerging technology for alternative energy production (Gratzel 2001, 2003, 2011; Hagfeldt et al. 2010; Oregan and Gratzel 1991) and their combination with biomaterials is an especially promising field. In a recent study, a high throughput PSI-based bio-photovolatic cell was introduced (Mershin et al. 2012). The cell demonstrated the capability of PSI to function both as a light-harvesting element, as well as a charge separator unit. The cell consisted of a PSI protein whose native psaE subunit was replaced with a bioengineered psaE subunit, containing a ZnO-binding peptide. Following the interaction of the modified PSI with a ZnO surface in the presence of the stabilizing surfactant A6k, the PSI protein was aligned on the surface in a favorable configuration, providing a direct path for ET between the electrode and the F_B site of the PSI, Fig. 3a. Upon excitation, and using the solution phase cobalt(II/III)-bis [2,6-bis(1′-butylbenzimidazol-2′-yl)pyridine] mediator, $[Co(dbbip)_2]^{2+/3+}$, the photogenerated P_{700}^{+} hole was scavenged by the reduced cobalt complex, which, in turn, was regenerated at the Pt cathode. The discharge curves of the cell are shown in Fig. 3b, indicating an open circuit voltage of ca. 0.5 V. The dependence of the photocurrent produced in the cell upon its exposure to different light intensities is demonstrated in Fig. 3c.

Photo-bioelectrochemical cells based on the purple bacteria RC

The purple bacteria RC protein was identified, isolated, and characterized more than 20 years ago (Allen et al. 1987b; Feher et al. 1989; Okamura et al. 1975; Okamura and Feher 1992; Stowell et al. 1997), and its photochemical mechanism has been intensively investigated (Kirmaier and Holten 1987; Parson and Warshel 2009). The studies indicated that the bacterial RC is capable of powering a special photo-induced ET chain, a process which occurs in conjunction to the pumping and transfer of protons across a membrane, to produce ATP. Due to the unique photochemical properties of the bacterial RC, it has been

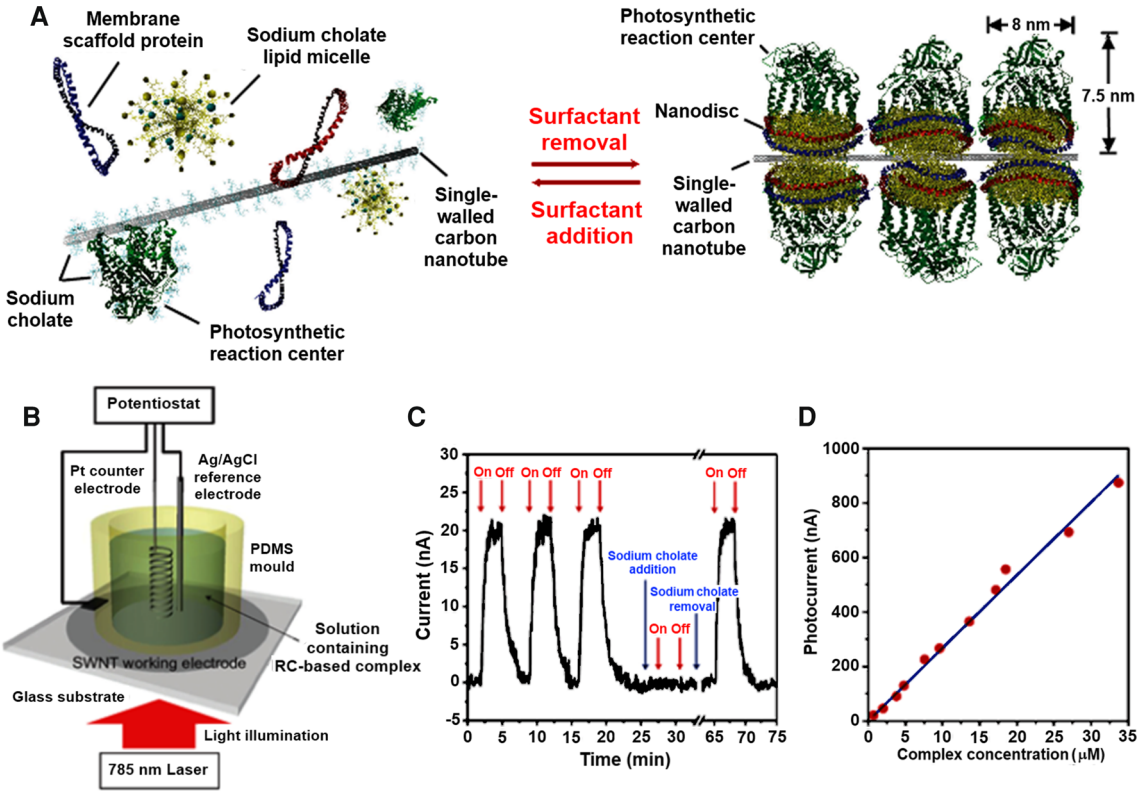


Fig. 4 **a** Self assembly (or disintegration) of the RC/lipid bilayer nanodisc/SWCNTs photoactive complex in the absence (or the presence) of the sodium cholate surfactant. **b** Schematic presentation of the RC/lipid bilayer nanodisc/SWCNTs-based photoelectrochemical cell. **c** Photocurrent responses of the photoelectrochemical cell in the presence of 700 nM RC/lipid bilayer nanodisc/SWCNTs complex, and ferrocyanide/ubiquinone, to intermittent light irradiation, and to the incorporation, and removal, of the sodium cholate surfactant. **d** Dependence of the photocurrent on the concentration of the RC/lipid bilayer nanodisc/SWCNTs photoactive complex in the electrolyte. Adopted with permission from Ham et al. (2010). Copyright Nature Publishing Group, 2010

integrated in several photo-bioelectrochemical cells applications, with the primary focus on the immobilization of the protein on the electrode and its electrical contacting with the surface (Hollander et al. 2011; Kondo et al. 2012; Trammell et al. 2004). These efforts included, for example, an interesting approach in which cyt *c* was adsorbed on an electrode surface and was further attached to the bacterial RC through complexation with the His-tag ligand. This configuration led, upon excitation of the RC complex, to efficient photoinduced ET from the RC to the electrode (Lebedev et al. 2006). The Lebedev group was also the first to introduce arrays composed of carbon nanotubes (CNTs) and RCs, linked together through a pyrene-functionalized Ni–Nitrilo triacetic acid (NTA), and their application for generating photocurrents (Lebedev et al. 2008).

An elegant approach to switch ON and OFF photocurrents using RC-modified CNTs was recently presented (Ham et al. 2010). The system utilized nanodisc structures composed of lipid bilayers, which were formed through the dialysis of phospholipids (i.e. 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine) in the presence of an amphipathic apolipoprotein as binding interfaces between single-walled carbon nanotubes (SWCNTs) and RC complexes. Upon mixing the components in the electrochemical cell, the lipid nanodics assembled onto the CNTs and provided a platform for the tethering of the photoactive RC membrane protein. The formation of this spontaneous self assembly process was highly dependent on the presence of the sodium cholate surfactant, whose presence disintegrated the RC/lipid bilayer nanodisc/SWCNTs composite, and its removal allowed the reassembly of the structure, over a large number of cycles, Fig. 4a. The photoactive assembly was, then, used for the controlled generation of photocurrents. By the light irradiation of a CNTs-modified glass electrode in an electrolyte solution that included the photoactive complex (composed of the RC protein, the lipid bilayer nanodisc structures, and the SWCNTs), and ferrocyanide/ubiquinone as a diffusional double mediator system, Fig. 4b, steady-state photocurrents of ca. 20 nA were obtained, and these were shown to depend on the light-modulated ON/OFF switching of the laser source, Fig. 4c. A further control over the photocurrent was achieved by the introduction, or elimination, of the sodium cholate surfactant to/from the electrolyte solution. In the presence

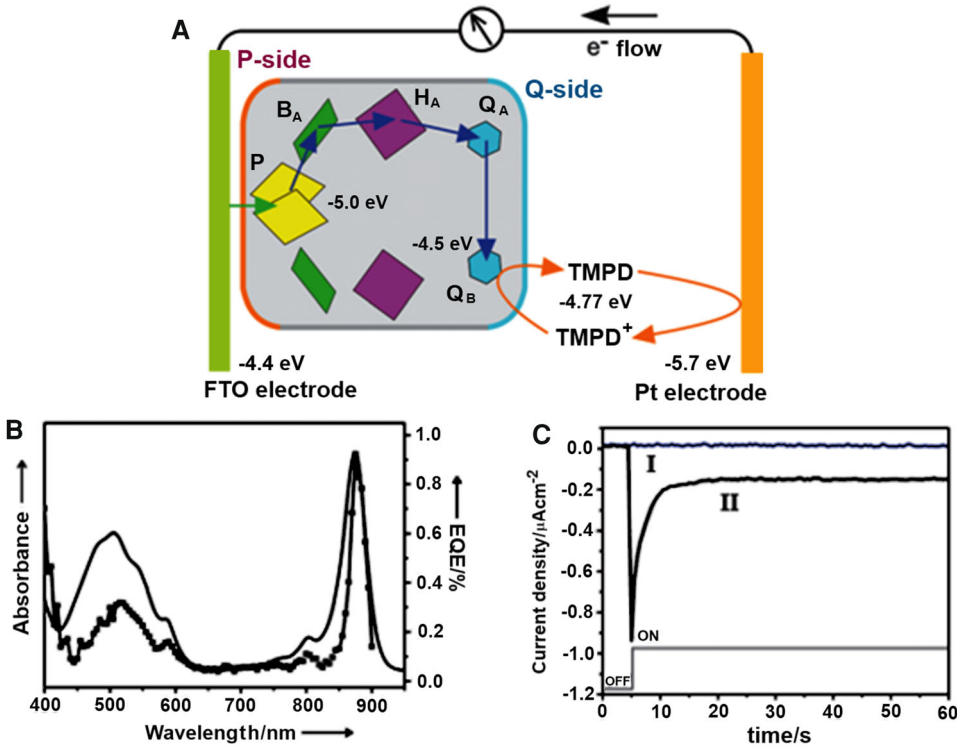


Fig. 5 **a** Operation scheme corresponding to the TMPD-mediated, RC (or RC–LH1)–FTO/Pt photoelectrochemical cell. **b** Absorption spectrum (*full line*) of solubilized RC–LH1 complex and the external quantum efficiency action spectrum (*squares*) obtained by the TMPD-mediated RC–LH1/FTO cell. **c** Time-dependant short-circuit current density measured for: *I* the TMPD-mediated, RC–LH1–FTO/Pt photoelectrochemical cell, and *II* a control cell in the absence of the RC–LH1 protein. Illumination of the cells started after 5 s, as indicated by the lower curve. Adopted with permission from Tan et al. (2012). Copyright Wiley-VCH Verlag GmbH & Co. KGaA

of the surfactant, the photoactive assembly disintegrated, and no photocurrents were observed. The photocurrents were fully restored through the removal of the surfactant from the cell, and almost no degradation in their values was observed, Fig. 4c. Also, a linear relationship was demonstrated between the photocurrent intensity and the concentration of the photoactive complex in the electrolyte solution, Fig. 4d. These results suggest that by substance exchange methodologies, and by the frequent renewing of the content of the degradable biological components in the system, photo-bioelectrochemical cells of extended lifetimes could be generated.

Another interesting example for a photoelectrochemical cell based on the RC protein (or the RC with the light harvesting 1 pigment protein, RC-LH1) was recently reported (Tan et al. 2012). In this system, the RC was adsorbed onto an fluorine-doped tin oxide (FTO) surface. Presumably, due to the existence of hydrophilic interactions between the FTO support and the positive (*P*) side of the RC (or RC-LH1) protein, an oriented configuration was formed, Fig. 5a. By illuminating the RC-modified FTO electrode in the presence of the regenerative *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) electron acceptor, electrical current was produced. This photocurrent (presented in the form of external quantum efficiency, Fig. 5b) overlapped the absorption spectrum of the RC (or RC-LH1) protein, indicating that the origin of the current was, indeed, the excitation of the photoactive unit.

A photocurrent transient, corresponding to the RC-LH1-modified FTO surface under continuous illumination, is depicted in Fig. 5c. The short-circuit photocurrent density decayed for approximately 20 s, until a steady-state value of ca. 0.15 μA cm^{-2} was reached, Fig. 5c. Through the regeneration of the TMPD mediator, a fully operating RC-based photoelectrochemical cell was obtained, one of the very few known to date.

PSII-based photo-bioelectrochemical cells

Oxygenic photosynthesis has opened the route for different forms of life on earth as we know them today. The ability of several cyanobacteria to harness sunlight and sustain the photosynthetic process was transferred, through the evolution process, into the plant life, and became one of the most challenging mechanisms which have ever been investigated. Throughout the years, along with the exploration of the photosynthetic mechanisms and the rapid development of nanotechnology, a call for clean and renewable energy resources has emerged. Moreover, ongoing advances in surface chemistry, and specifically in the electrical wiring of biomaterials (e.g., enzymes) with electrodes (Heller 2006; Willner et al. 2006; Yehezkeli et al. 2009, 2010a). Such methods facilitated the immobilization of photoactive proteins on electrodes for the construction of efficient photoelectrochemical devices (Badura

et al. 2008, 2011b; Lavan and Cha 2006; Wang et al. 2012) that may eventually provide a solution to the main global energy concerns. Of the more promising biomaterials for this eminent goal is the PSII protein. The importance of this biological unit stems from its ability to invoke the effective process of photo-oxidation of water, which initiates the entire photochemical transfer chain, and, from a more practical point of view, due to the fact that it can be used as an advanced replacement for the diffusional/sacrificial electron-donor substances, presented in most of the photoelectrochemical cells. There are, yet, several major challenges that hinder the integration of PSII in photoelectrochemical devices. For example, the need for an efficient electrical contacting between the PSII protein and the electrode requires the Q_A or Q_B electron-acceptor terminal sites to be wired with the surface. Moreover, this requirement must be fulfilled with only a minimal steric perturbation to the structure of the PSII protein, in order to fully preserve its functionality. Despite these challenges, intensive efforts are currently being made in this field.

The use of chelating agents, such as His-tag, is a well-known biochemical method to attach proteins to surfaces (Terpe 2003). In one of the studies (Terasaki et al. 2008), the carboxy terminal associated with the CP43 subunit of PSII was linked to a Au electrode by its primary modification with His-tag, and the subsequent attachment to the surface using Ni^{2+}–NTA–thiosuccinamide ester, to form a His-tag/PSII-modified Au electrode, Fig. 6a. By following this methodology, the PSII protein was immobilized on the surface in a favorable orientation for injecting the photoexcited electrons to the electrode, and thus for the generation of anodic photocurrents. Furthermore, by the deposition of increasing quantities of Au NPs on the Au support, Fig. 6b, a gradual increase in the surface roughness of the electrode was obtained. Following the modification of the roughened surfaces with the PSII assembly, enhanced photocurrents that correlated with the amount of Au NPs deposited, were revealed, Fig. 6c.

Immobilization of PSII on electrode surfaces could also be achieved by means of entrapment of the photosynthetic protein in polymeric layers. In one of the studies (Badura et al. 2008), osmium-containing redox polymers based on poly(vinyl)imidazol were used both to entrap, and mediate, PSII photoactive units, Fig. 7a. Through the deposition of a mixture containing PSII, the redox polymer, and the crosslinking agent poly(ethylene glycol)diglycidyl ether on the surface of Au electrodes, a photoactive matrix was created. In this matrix the PSII proteins were firmly attached to the polymeric backbone, while small molecules were still allowed to diffuse to the photosynthetic units due to the hydrogel nature of the polymer. Upon the PSII-driven splitting of water, the Os^{2+}/Os^{3+}-based polymer mediated the charge transport of electrons from the PSII to the electrode surface, generating a light-triggered anodic photocurrent, Fig. 7b. Due to the higher amount of PSII entrapped in the polymeric matrix (in comparison to PSII monolayer configurations), and due to the relative close proximity between the active sites of the photoactive protein units and the osmium redox centers, an efficient charge transfer was obtained, as evident by the relatively high photocurrent density, 45 μA cm^{-2}, compared to the other photosynthetic elements-based photo-bioelectrochemical cells, Table 1.

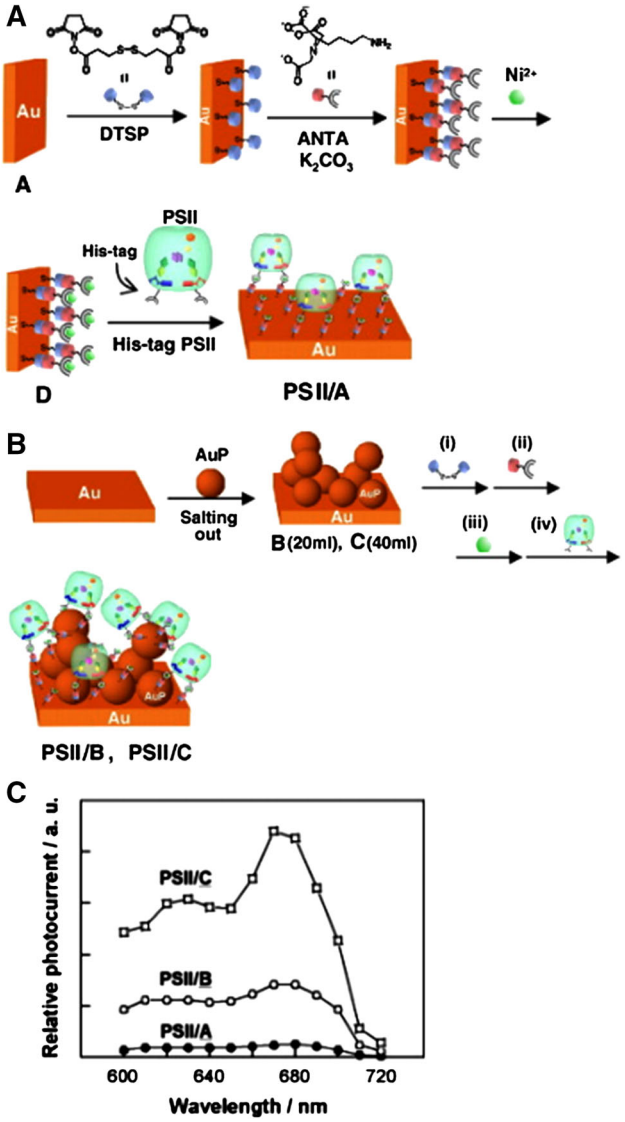


Fig. 6 **a** Synthesis of the His-tag/PSII photoactive assembly on a planar Au electrode. **b** Synthesis of the His-tag/PSII photoactive assembly on a Au NPs-roughened Au electrode. Electrodes *B* and *C* correspond to different loading of Au NPs on the electrode surface. **c** Photocurrent action spectra corresponding to the His-tag/PSII-modified planar Au electrode (*full circles*), and the His-tag/PSII-modified Au NPs-roughened Au electrodes *B* (*open circles*), and *C* (*open squares*). Adapted with permission from Terasaki et al. (2008). Copyright Elsevier, 2008

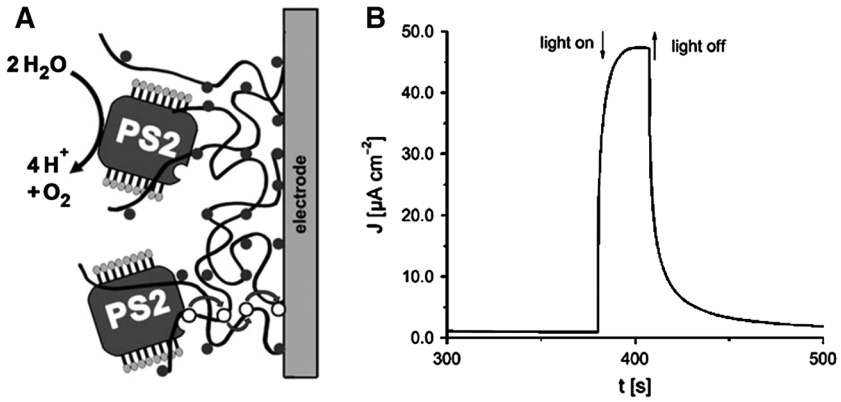


Fig. 7 **a** Entrapment of PSII units in an Os^{2+}/Os^{3+} polymer for the generation of photocurrent. The *black dots* represent osmium complexes. **b** Light-triggered photocurrent upon the pulsed illumination of the PSII/$Os(bipy)_2Cl$ polymer/PEGDGE-modified Au electrode. Potential applied 0.3 V versus Ag/AgCl. Reproduced with permission from Badura et al. (2008). Copyright Wiley-VCH Verlag GmbH & Co. KGaA

Table 1 Photocurrent density values generated by the different photosynthetic elements-based photo-bioelectrochemical cells

Reference	Photosynthetic element employed	Photocurrent density (μA cm^{-2})	Presence of diffusional mediator	Irradiation power (mW cm^{-2})	Applied potential (V)
Ham et al. (2010)	RC	1	+	20	Not reported
Tan et al. (2012)	RC	0.15	+	10	OCV
Yehezkeli et al. (2010a, b)	PSI	4	−	1.13	0.3 (vs. Ag/AgCl)
Ciesielski et al. (2010a, b)	PSI	7.9	+	95	0.1 (vs. Ag/AgCl)
Badura et al. (2008)	PSII	45	−	2.65	0.3 (vs. Ag/AgCl)
Terasaki et al. (2008)	PSII	2.4	−	3.3	0.3 (vs. Ag/AgCl)
Kato et al. (2012)	PSII	1.6	−	8	0.3 (vs. Ag/AgCl)
		12	+		

In a further study, mercapto benzoquinone was electropolymerized on a Au surface to yield a poly-mercapto benzoquinone (pMBQ) film, on which PSII could be adsorbed (Maly et al. 2005). This method was further developed by the Willner group (Yehezkeli et al. 2012) for the construction of a water/O_2-powered photo-bioelectrochemical cell, Fig. 8a. The anode was assembled by chemically tethering the PSII protein to a pMBQ layer electrochemically deposited on Au surface. The cathode was composed of a glassy carbon surface on which SWCNTs, chemically modified with the oxygen-reducing-enzyme bilirubin oxidase (BOD), were adsorbed. Upon the irradiation of the PSII-modified anode in a pure buffer solution, water was oxidized to O_2, concomitantly with the transfer of electrons from the Q_B center of PSII to the pMBQ polymer (acting as a charge carrier for the photo-excited electrons). The formation of O_2 was simultaneously accompanied by a four electron reduction of this specie to water at the cathode by the electrically wired BOD enzyme. The fully balanced set of electrochemical reactions operating in the integrated photo-bioelectrochemical cell suggested that, unlike in most of the other reported cells, no sacrificial electron- donor was required, and a water/O_2-powered generation of photocurrents might be achieved by renewable biological means. Figure 8b demonstrates the effect of the irradiation intensity on the resulting photocurrents.

The current transients obtained upon the intermittent irradiation ON/OFF of the anode under variable illumination power intensities, indicate that the origin of the current produced in the cell is in the photo-excitation of the PSII protein, and that enhanced photocurrent responses are obtained by increasing the irradiation intensity. The photo-bioelectrochemical cell performance was further investigated by performing discharge measurements under variable external resistances, Fig. 8c, from which a maximum power output of ca. 18 μW cm^{-2} was achieved.

Another example for an integrated PSII assembly exhibiting electrical communication between the photo-active unit and an electrode, was recently reported (Kato et al. 2012), and is shown in Fig. 9A. In this study, the PSII protein was adsorbed onto a mesoporous indium tin oxide (ITO) surface. Presumably, due to the comparable dimensions of the PSII and the ITO pores, the protein could be entrapped inside the matrix. Furthermore, the high surface area provided by the mesoporous structure of the ITO, allowed the entrapment of considerable amounts of PSII, thus leading to several favorable orientations that

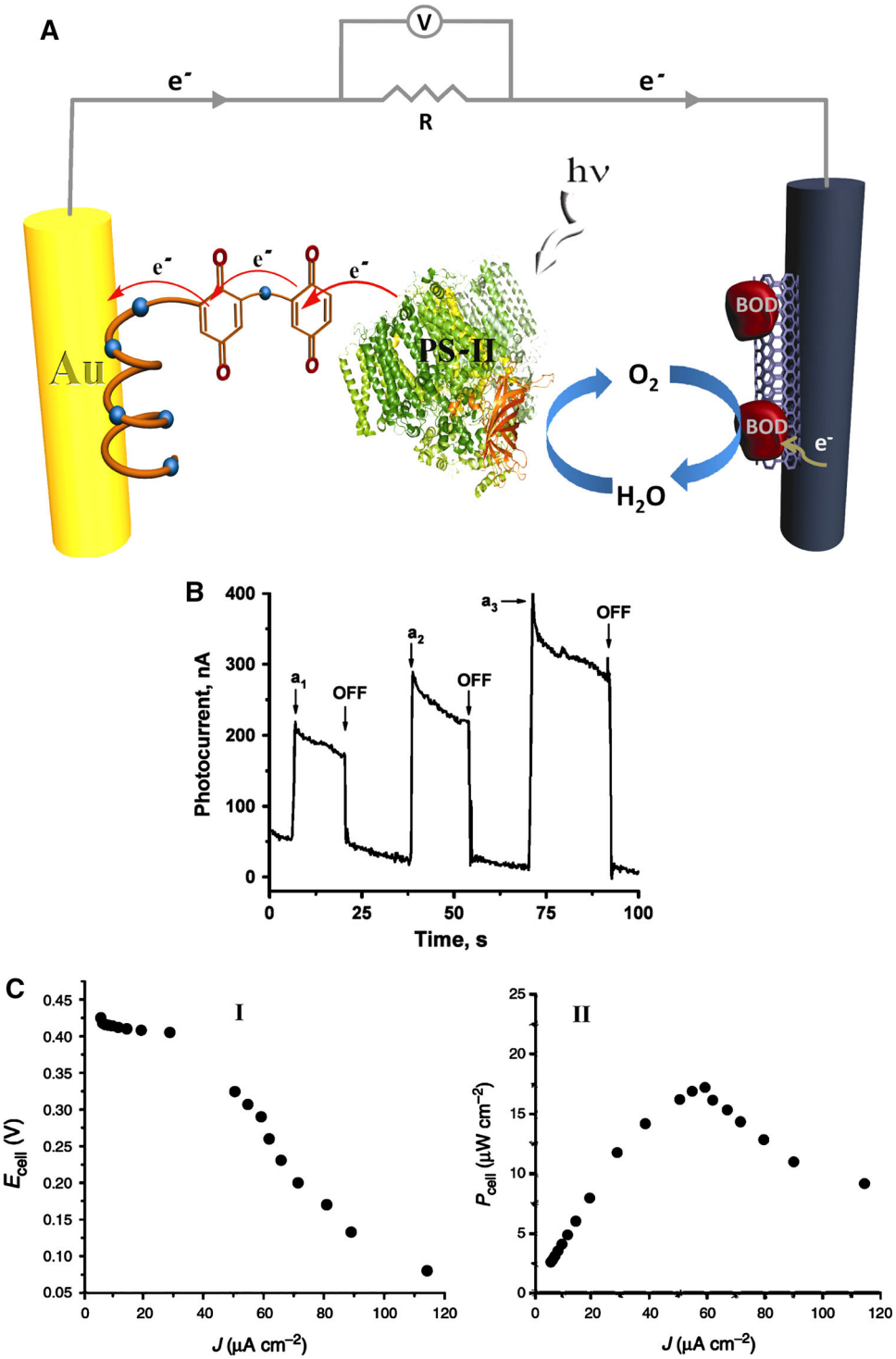


Fig. 8 **a** Schematic presentation of the pMBQ/PSII//BOD/CNTs photo-biofuel cell. **b** Photocurrent responses of the pMBQ/PSII anode upon the application of variable external potentials on the electrode. **c** Photocurrent responses of the pMBQ/PSII anode upon the application of intermittent light illumination at variable irradiation intensities: a_1 $P = 0.04$, a_2 $P = 0.07$ and a_3 $P = 0.10$ W. **d** Polarization curve (*panel I*), and power output (*panel II*) corresponding to the discharge of the pMBQ/PSII//BOD/CNTs photo-biofuel cell at variable resistances. In all measurements the electrolyte was a phosphate buffer (pH 7.4, 0.1 M). Reproduced with permission from Yehezkeli et al. (2012). Copyright Nature Publishing Group, 2012

support a direct electrical contacting between the Q_A site of the protein and the electrode surface. Upon the light triggering of the PSII and the application of an external potential, 0.5 V versus NHE, on the electrode, and in the absence of any diffusional mediator, high photocurrents, 1.6 μA cm^{-2}, were obtained, Fig. 9B, curve (b). A further introduction of a solution phase quinone mediator, potassium 1,4-naphthoquinone-2-sulfonate (NQS) allowed a larger number of PSII units to communicate with the electrode, thus leading to an expected enhancement in the photocurrent intensities, Fig. 9B, curve (a). It should be noted that control experiments performed on bare mesoporous ITO, curve (a), or on a [Mn_4Ca] cluster-depleted PSII-modified mesoporous ITO surface, curve (b),

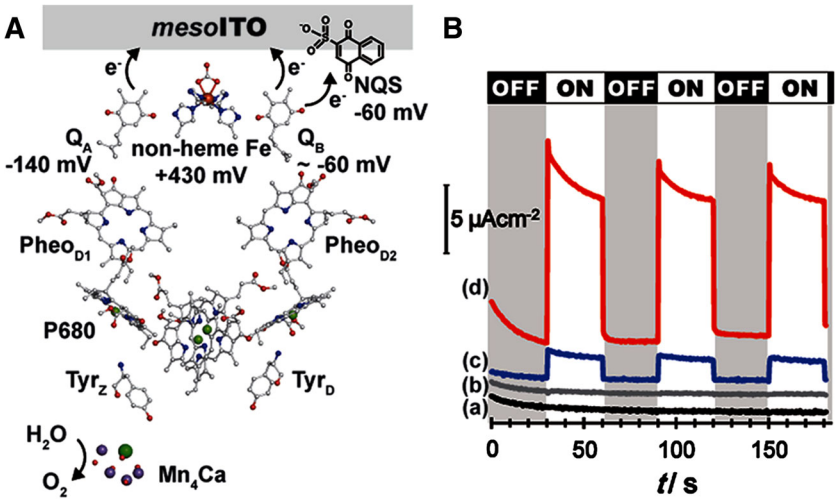


Fig. 9 **A** Schematic illustration of the aligned components involved in the light-triggered ET chain corresponding to the PSII-adsorbed mesoporous ITO surface. **B** Photocurrent responses to intermittent light irradiation on: *a* a mesoporous ITO surface, *b* a [Mn_4Ca] cluster-depleted PSII-modified mesoporous ITO surface, *c* a PSII-modified mesoporous ITO surface, and *d* a PSII-modified mesoporous ITO surface, in the presence of 1 mM NQS. Measurements were performed at a bias potential of 0.5 V versus NHE, and using a MES buffer (pH 6.5, 40 mM) containing 50 mM KCl, 15 mM $CaCl_2$, and 15 mM $MgCl_2$. Reproduced with permission from Kato et al. (2012). Copyright 2012 American Chemical Society

Table 2 Output power density values generated by the different photosynthetic elements-based photo-bioelectrochemical cells

Reference	Photosynthetic element employed	Power output density ($\mu W\ cm^{-2}$)	Presence of diffusional mediator	Irradiation power ($mW\ cm^{-2}$)
Mershin et al. (2012)	PSI	81	+	100
Yehezkeli et al. (2012)	PSII	17	–	280

revealed no photocurrents under similar experimental conditions.

Concluding remarks

Different approaches of using natural photosynthetic complexes as light-harvesting elements in photo-bioelectrochemical cells were highlighted. The different photocurrents and power output values obtained for the various systems described are highlighted in Tables 1 and 2, respectively. While the tables reflect the large diversity in the performances of the different photo-bioelectrochemical cells, employing the different photosynthetic units and using different strategies for wiring them to the supporting electrodes, it seems that the use of redox active polymer hydrogels might be a promising approach for future development mainly due to the improved electrical contacting, high content of photoactive proteins, and protective features associated with such systems.

Albeit the progress achieved in this novel and promising field, there are still several scientific challenges ahead. One main concern that needs to be addressed is the stability of the photo-bioelectrochemical cells. Whereas this problem poses a technological obstacle that might hinder the development of the cells, the long-term experience in the stabilization of other biological substances, e.g., enzymes, on electrode surfaces, suggests that finding the optimal stabilizing conditions is only a matter of time. The application of protective polymer (or bio-polymer) membrane-alike layers might hinder the gradual degradation in the activity of the photosynthetic active units through serving as mechanical shields, preventing changes in the protein tertiary structures. Furthermore, the application of hydrogels and conjugated polymers, may play an important role in concentrating the photosynthetic units, as well as dissipating the excess energy associated with the photochemical processes. These will, hopefully, increase heat dissipation and will minimize the generation of radical specie known to cause structural changes affecting the activity of the photosynthetic units

(for example, the D_1 unit of the PSII protein is known to be highly susceptible to damages caused by free radicals). The use of porous matrices is another promising direction expected to greatly increase the surface coverage of the photosynthetic units, thus facilitating the generation of enhanced photocurrents. Interestingly, the incorporation of the protein units inside the pores might also stabilize the photochemical activity of the cells by preventing their disintegration from the surface, preserving their three dimensional structure, and might even reduce direct effects of photo-bleaching. Another challenge relates to broadening the absorption range of the photoactive layers in the cells for exploiting a wider region of the solar irradiation spectrum. This is especially critical for the photosystem proteins that exhibit low absorptivity at the green–blue regions of the visible range. Combined with the stabilization strategies described above, this goal might be achieved by introducing different light-absorbing biological antenna-like units, such as LHCs or phycobilisomes, which, along with the photosynthetic complexes, are expected to adsorb, and convert to electricity, a broader range of the visible light. Finally, the application of nanoengineering techniques and advanced surface chemistry are expected to yield more efficient electrochemical configurations in which the RCs or photosystem proteins will be tethered to the electrode surface in an optimal manner, where the ET distances between the photosynthetic units and the electrodes are minimized, thus increasing the charge transfer rate. Whereas such a method was described in this review (Terasaki et al. 2009) for the PSI protein, no analog approach has yet been developed for PSII. With recent advances in bioelectronics and nanoengineering, including, for example, the use of reconstitution of photoactive centers on electrode surfaces or on relay units, and the application of genetically modified proteins, one may envisage a rapid progress in the photocurrent intensities, power outputs, and conversion efficiencies.

In view of the recent advancements to the rapidly evolving field of photo-biofuel cells and the promise it holds for the generation of ecologically benign electricity, it seems that George Feher's statement from 20 years ago is becoming a reality.

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