Photobioelectrochemistry: Solar Energy Conversion and Biofuel Production with Photosynthetic Catalysts

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Photobioelectrochemical cells are devices which have been developed over the past few decades and use photosynthetic catalysts for solar energy conversion or biofuel production. In this paper, a critical review of reported photobioelectrochemical systems is presented. The systems discussed include several types of photobioelectrocatalysts: whole cells, organelles, and enzymes. Special attention is paid to power or product generation as well as immobilization and electron transfer strategies used. The issues that need to be addressed in order for such systems to compete with current technologies are also discussed.
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As global energy consumption continues to rise, the need for renewable energy sources becomes increasingly important. The development of photovoltaic devices (PVD) which convert solar energy into electricity is of great interest because it is an abundant source of clean energy. For example, in 2002, the total amount of energy consumed in one year on Earth was roughly equal to the amount of solar energy that strikes the planet's surface in one hour, $\sim 4 \times 10^{20}$ J.[1] Several types of PVD have already been developed to take advantage of this plentiful energy source: Si-based,[2] dye-sensitized,[3] organic,[4] and multi-junction[5] solar cells. However, some of these solar cells use materials which are expensive[6] and/or toxic in the environment.[7,8]

The balance of cost and efficiency must be considered in order for photovoltaic devices to compete with fossil fuel energy. Fossil-derived fuels cost \$0.02-0.05 per kW-hr while, for example, a Si-based solar cell with 10% efficiency costs ~\$0.35 per kW-hr, which must be reduced in order for photovoltaic devices to be competitive.[1] Either the efficiency must be improved or the cost must be reduced for silicon-based systems. Dye-sensitized and organic solar cells use much lower cost materials, but their conversion efficiency is significantly lower than thin film solar cells. Multi-junction solar cells can have very high efficiencies (up to 44%),[9] but the semiconductor materials they use are very expensive.[5]

It is crucial to find a safe, inexpensive, and efficient catalyst for solar energy conversion if this type of device is going to compete with conventional methods of energy production. One option is to take advantage of photosynthesis, nature's method for solar energy conversion, which has evolved over the last 3.8 billion years to be quite efficient.[10,11]

Photosynthesis.— Photosynthesis, the conversion of solar energy into chemical energy, is an essential process for life on Earth. This process occurs in plants and certain types of bacteria (i.e. cyanobacteria, purple photosynthetic bacteria, and green sulfur bacteria). In photosynthesis, carbon dioxide in the atmosphere and water is converted into oxygen and carbohydrates, providing an energy source for the photosynthetic organism as well as food for other organisms (see Figure 1). The light-dependent reactions of photosynthesis result in the production of ATP and NADPH which are then used in the dark reactions (which do not require light) to drive the conversion of CO_2 to carbohydrates. The light reactions occur in the membrane and make up an electron transport chain similar to that in mitochondria.[12] Chlorophylls (Chl) in plants and cyanobacteria and bacteriochlorophylls (BChl) in photosynthetic bacteria act as light harvesting complexes (LHCs) where energy from absorbed photons is passed from molecule to molecule until reaching a photosynthetic reaction center (RC) containing a chlorophyll of slightly lower energy. The proton gradient across the membrane that is generated during photosynthesis is used to produce ATP by ATP synthase which is then used in the Calvin cycle. The electron transfer processes are similar in different types of photosynthetic organisms, but the initial electron donor as well as necessary components for the process varies.[13,14]

Solar energy conversion by the light-absorbing enzymes of photosynthesis is very efficient (quantum yields of ~1 and ~0.8 for photosystem I[15] and II,[16] respectively). However, the efficiency of the entire photosynthetic pathway is only ~5-10% because energy is lost in several places during the process. Photons outside of the visible spectrum cannot be used for photosynthesis which gives a 47% energy loss. Another 16% is lost by photons hitting components other than chloroplasts and 9% is lost due to wavelength-mismatches when transferring from one Chl molecule to another. Finally, 19% of the energy is lost in converting ATP and NADPH into glucose.

Purple photosynthetic bacteria.—Purple bacteria perform anoxygenic photosynthesis, meaning O_2 is not produced, because the initial electron donor for this type of bacteria is not water. Purple sulfur bacteria use either sulfide or elemental sulfur, while purple non-sulfur bacteria use organic compounds. Photosynthesis occurs via two types of LHCs (LH1 and LH2) and two protein complexes (the RC and cytochrome bc_1). Light is absorbed by LH1, transferred to LH2, and then transferred to what is referred to as the "special pair", two BChl molecules found in the RC (P870, which absorbs at 870 nm, see Figure 2). Within the RC, an electron is transferred from the special pair to bacteriopheophytin (BPh) and then to a quinone which varies depending on the species (Q_A, either menaquinone or ubiquinone). Next, the electron is transferred to ubiquinone (Q_B) which accepts two such electrons along with two protons from the cytoplasm before moving into the quinone pool (Q_P). The reduced ubiquinone, called ubiquinol, diffuses to the cytochrome bc_1 complex where it is oxidized back to ubiquinone and its protons are released outside the cell. One of the electrons from ubiquinol is passed to cytochrome c_2 which diffuses to the RC and the electron is transferred to the special pair to complete the cycle. The ubiquinol, still containing the second electron, moves back into the quinone pool. After the RC absorbs two photons, the net result is the transfer of four protons from the cytoplasm to the exterior of the cell.[14] There is another category of photosynthetic bacteria, green sulfur bacteria, which has a similar reaction pathway, except its special pair absorbs at 840 nm (P840) and it uses Fe-S proteins and ferredoxin (Fd) instead of quinones for transferring electrons (see Figure 2).[17]

Plants and cyanobacteria.—Photosynthesis in plants and cyanobacteria occurs via two RCs contained in two photosystems according

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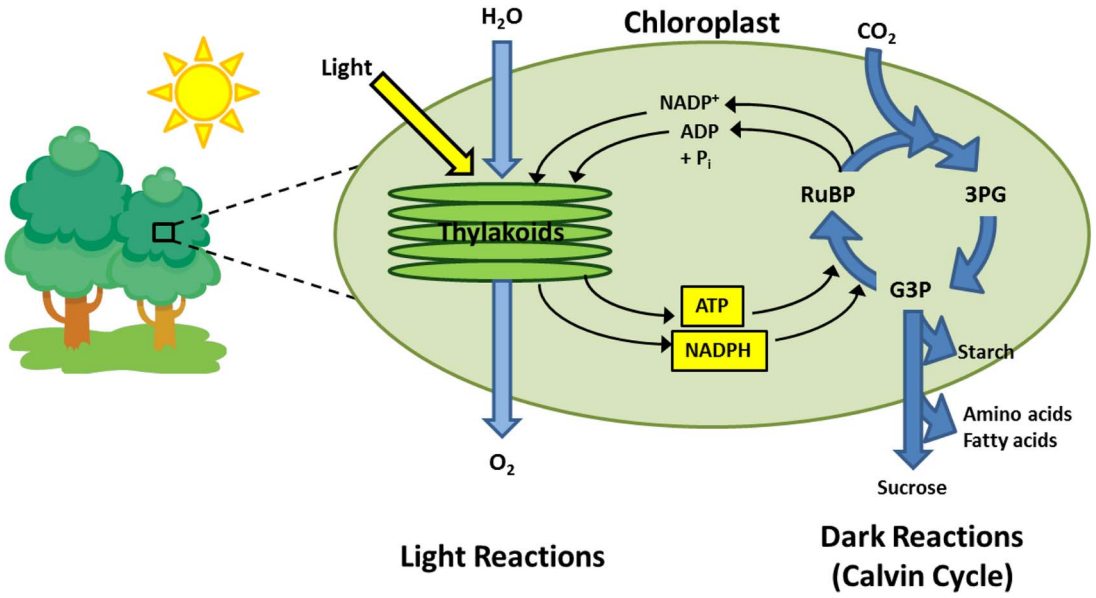

Figure 1. Photosynthesis is an energy conversion process which occurs in plants and certain types of bacteria. The light reactions of photosynthesis convert light energy into energy used in the cell in the form of ATP and NADPH. The dark reactions use the ATP and NADPH for carbon fixation, converting CO_2 into a number of organic molecules including amino acids, fatty acids, sucrose, and starch. Abbreviations: RuBP = ribulose-1,5-biphosphate; 3PG = 3-phosphoglycerate; and G3P = glyceraldehyde 3-phosphate.

to a mechanistic model called the Z-scheme. Photosystem II (PSII) is similar to the RC in purple bacteria with Chl, pheophytin (Pheo), and plastoquinone (PQ) replacing BChl, BPh, and ubiquinone (see Figure 3). PSII also contains the oxygen-evolving center (OEC), a Mn protein complex, where H_2O (the initial electron donor) is oxidized to O_2 and the resulting protons are released into the thylakoid lumen. From the OEC, an electron is transferred to the special pair of PSII, a chlorophyll dimer referred to as P680. The electron is passed from P680 to Pheo and then to a bound PQ before being transferred to a second non-bound PQ which picks up two protons from the stroma (cytosol in cyanobacteria) and moves into the quinone pool. The electron is then transferred to the cytochrome b_6f complex (analogous to cytochrome bc_1) where plastoquinol is oxidized and the protons are released into the thylakoid lumen. From the cytochrome b_6f complex, electrons are transferred to photosystem I (PSI) via plastocyanin (Pc), a Cu-containing protein free to move along the thylakoid membrane surface in the lumen. From the PSI special pair, P700, electrons are passed through several redox centers, quinones (A_0 and A_1) and Fe-S clusters, before being transferred to Fd, a small protein containing a single [2Fe-2S] center. From here the electrons can follow two different pathways. The reduced Fd is oxidized during the production of NADPH by ferredoxin-$NADP^+$ reductase (FNR). Alternatively, the reduced Fd can transfer the electrons back to the quinone pool, completing a cyclic pathway. The two photosynthetic pathways (cyclic and noncyclic) make it possible to control the relative amounts of ATP and NADPH produced. The net result of photosynthesis in plants and cyanobacteria is the transfer of ~12 protons into the thylakoid lumen per O_2 produced, including 4 from oxidation of H_2O to O_2 and 8 transferred from the stroma to the lumen via the "proton pumping" of cytochrome b_6f.[12]

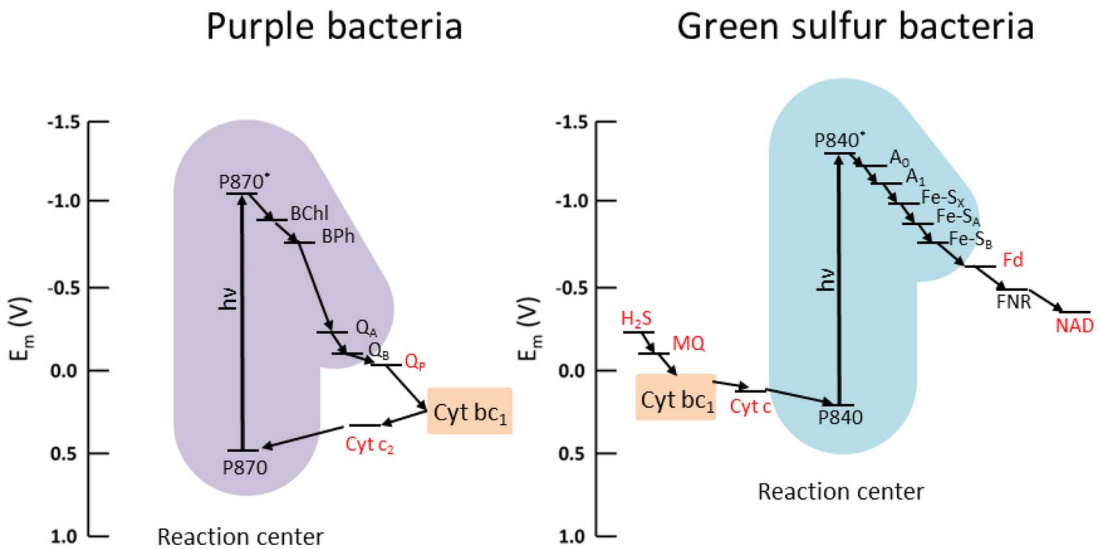

Figure 2. Electron transport chain diagrams for purple photosynthetic and green sulfur bacteria. Molecules in red are mobile electron shuttles. Protein complexes containing multiple electron transfer steps (reaction centers and cytochromes) are highlighted.[82]

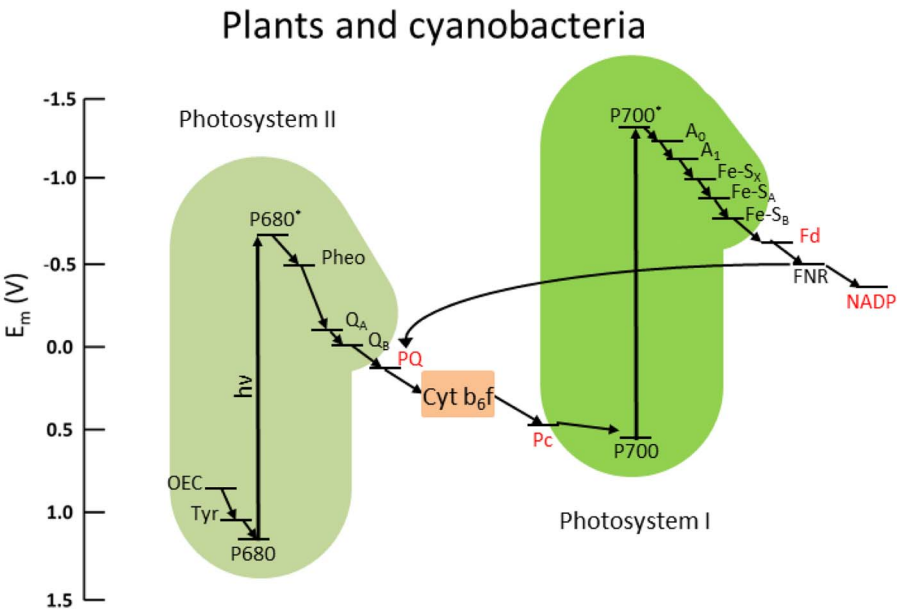

Figure 3. Electron transport chain diagrams for plants and cyanobacteria. Molecules in red are mobile electron shuttles. Protein complexes containing multiple electron transfer steps (photosystem and cytochromes) are highlighted.[82]

Electron transfer with biological catalysts.— The multiple electron transfer steps in photosynthesis make it an attractive prospect for incorporation into photobioelectrochemical cells. In order to generate photocurrent, electron transfer from the biological catalyst to the electrode must be possible. This is typically achieved through one of two methods: direct electron transfer (DET) and mediated electron transfer (MET). DET is the simpler method, where electrons are transferred directly from the biocatalyst to the electrode surface. There is no voltage loss or added instability or mediator leaching with DET, but this method requires that the active site where the electrons are transferred must be close to the surface (<1 nm) in order for tunneling to occur.[18] Addition of metallic conductors (such as nanoparticles and nanotubes) to increase surface area as well as selective orientation of catalysts are methods used to achieve larger DET bioelectrocatalytic currents.[19,20]

For biological catalysts unable to perform DET, a mediator must be incorporated into the system. The mediator is a species able to exist in multiple redox states and can donate or accept electrons from the catalyst to carry the electrons to or from the electrode surface.[21] Mediators can be incorporated in a number of ways. The simplest method is to add a mediator to the electrolyte solution. However, this requires the mediator to diffuse to and from the electrode surface and catalyst active site and therefore is not the most efficient method for electron transfer.[21] Immobilizing the mediator on the electrode surface greatly increases the electron transfer kinetics. Redox polymers, where the mediator is covalently bound to a polymer backbone, are commonly used for immobilizing biological catalysts.[22–26] The redox species can be tailored to have a redox potential close to that of the active site of the catalyst in order to reduce the amount of voltage loss.[27,28]

Photobioelectrocatalysts.— There are several types of photosynthetic biological catalysts that can be adapted for solar energy conversion. One option is to incorporate whole photosynthetic microbes such as cyanobacteria or purple sulfur bacteria. A major advantage to using microbes is that they contain all the necessary enzymes and cofactors for photosynthesis. Additionally, they have less loss of activity during normal operating conditions because damaged or destroyed components will be removed and replaced by normal cell mechanisms. However, the electrons produced by photosynthesis are inside the cell and need to be transferred through the outer membrane in order to reach the electrode surface. Typically, for microbial systems, a mediator is required to overcome this issue. This generally leads to a voltage loss and also limits the locations in the photosynthesis pathway where electrons can be obtained because electrons will only be transferred to the mediator when it is thermodynamically favorable. In addition to solar energy conversion capabilities, these organisms can also be incorporated into hybrid systems where biomass produced during photosynthesis is used as fuel to generate electricity. This type of system will also be discussed in this review.

A second photosynthetic biological catalyst is the thylakoid membrane. Similar to a microbial system, thylakoids contain all the necessary components, but they do not have the outer membrane so electron transfer to the electrode surface is less limited and a mediator is not required[29] but may still be incorporated.[30] However, the system is still quite large, so methods for increasing the number of active sites close enough to the surface to undergo DET are necessary. Thylakoid systems also have decreased stability, because there is no longer a mechanism for repairing or replacing damaged or destroyed components caused by production of reactive oxygen species, a normal method of regulation within this sytem.[31]

Finally, a third choice for biological catalysts capable of solar energy conversion are the photosystems. A major advantage to these catalysts is their small size and lack of membrane allows them to get quite close to the surface which makes DET possible. If MET is used instead, there is no loss of electrons due to mediator choice as long as the chosen mediator has a redox potential close to that of the specific photosystem being used. However, similar to the thylakoid membrane, there is no repair mechanism for damaged or destroyed components so there will be a decrease in activity over time.

Device design.— The cell design of devices for solar energy conversion or biofuel production can vary greatly depending on several variables such as the biological catalyst and how it is used (immobilized or in solution), the cathode, and the application. However, the general operating principles are the same. In such devices, the photosynthetic catalyst is used at the anode. The oxidation reactions performed by the catalysts produce electrons which are then transferred to the electrode. The cathode in these systems can vary, but for most of the examples to be discussed, the cathode reduces either oxygen or ferricyanide. Depending on the cathode reactant and the biological catalyst choice, a membrane separator may be required; this separator is most commonly a Nafion proton exchange membrane which allows for the transfer of protons from the anode compartment to the cathode compartment.

Microbial/bacterial Systems

The development of microbial solar cells (MSCs) began in the 1960s and significant progress with these systems has been made since then. For a more comprehensive overview of MSC research, the authors recommend several reviews[32–34] which cover this topic in

greater detail. Microbial solar cells can be divided into two types of systems. The first type uses photosynthetic bacteria at the anode as the biocatalyst where electrons are transferred from the microorganism to the electrode surface. The second type functions as a hybrid of a fuel cell and solar cell. The products of photosynthesis in the microorganism (either hydrogen or organic compounds such as carbohydrates) are used as a fuel for power generation at the anode.

Solar cell with photosynthetic bacteria.— The first bio-solar cell incorporating a microorganism was reported by Tanaka et al. in 1985. Their system used the cyanobacterium *Anabaena variabilis* along with 2-hydroxy-1,4-naphthoquinone (HNQ) as the mediator in solution in the anode compartment, while the cathode compartment contained a N_2-purged solution containing ferricyanide which is reduced during cell operation. They showed that the O_2 produced photosynthetically reacted with the reduced form of HNQ and short-circuited the system unless N_2 was vigorously bubbled into the compartment to displace the O_2. This cell initially had a voltage close to 0.8 V which decreased to 0 V in 24 hours with current output on the order of 1.25 $\mu A/cm^2$.[35]

A similar solar cell was reported by Yagishita et al. which used *Synechocystis* sp. PCC6714 along with HNQ as the mediator. They showed that the addition of glucose to the anode compartment greatly increased the current output, from 8 $\mu A/cm^2$ up to 18.75 $\mu A/cm^2$. However, similar to the *A. variabilis* cell, the current generated by this system was limited due to the reaction of the mediator with O_2.[36]

The first microbial photosynthetic bioelectrochemical cell using biological catalysts at both the anode and cathode was reported in 2001. This system contained *Synechococcus* sp. PCC 7942 in the anode compartment with either 2,6-dimethyl-1,4-benzoquinone (DMBQ) or diaminodurene (DAD) as the mediator. The cathode compartment consisted of bilirubin oxidase (BOD), an enzyme which reduces O_2 to H_2O, in solution with 2,2'-azinobis(3-ethylbenzothiazolin-6-sulfonate (ABTS) as the mediator. The maximum power generated by this cell was 0.29 mW/m^2 and the open circuit voltage (OCV) was 0.6 V. The current output increased linearly with increasing chlorophyll concentration (by adding more cyanobacteria). However, eventually the current reached a plateau as the increased cell concentration leads to light scattering, preventing the light from reaching the bacteria near the electrode surface.[37]

More recently, the first microbial photo-bioelectrochemical cell capable of DET was reported. The cyanobacteria *Nostoc* sp. were immobilized onto carbon nanotube (CNT) modified carbon paper for the anode instead of being free in solution like the previously reported systems. The cathode consisted of laccase covalently bound to CNTs for oxygen reduction. This system was able to perform DET due to the overlap of the photosynthetic and respiratory electron transport chains. When exposed to high intensity light, the plastoquinone pool is mostly in its reduced form which leads to photo-damage of PSII. In cyanobacteria, the reduced plastoquinone can be oxidized by bd-quinol oxidase which is found in the cell membrane and can transfer electrons directly to the CNTs. The *Nostoc* bio-solar cell generated a maximum current density of 24 $\mu A/cm^2$ when illuminated and an OCV of 0.57 V. When 1,4-benzoquinone was added as a mediator, the maximum current density increased to 233 $\mu A/cm^2$ with an OCV of 0.45 V.[38]

Fuel cell/solar cell hybrids.— In 2005, Rosenbaum et al. reported a microbial system that generates current from the oxidation of hydrogen produced by *Chlamydomonas reinhardtii*. They used a platinum mesh coated with a conductive polymer, polytetrafluoroaniline, as a catalyst to increase the hydrogen oxidation at the anode by reducing the amount of fouling of the electrode. This electrode was able to generate a maximum current of 9 mA with a hydrogen production rate of 4.1 mL/h. The current decreased over 40 hours and stabilized at 1.6 mA.[39]

In 2002, Tender et al. reported a system which takes advantage of the benthic voltage gradients at sediment surfaces in coastal marine environments. In their fuel cell, the anode was placed in the marine sediment while the cathode was suspended in the water. Polarization data and power curves for the two fuel cells can be seen in Figure 4. They tested one of their fuel cells for one year and, at a cell voltage of 0.27 V, the power output remained stable at ~28 mW/m^2 for four months.[40] A study of the microorganisms that attach to the anode showed that the majority of the bacteria were related to *Desulfuromonas acetoxidans*, a species which can oxidize acetate while reducing sulfur.[41] However, long-term current generation is limited by diffusion of the reactants (the organic compounds such as acetate as well as sulfide) to the anode which is quite slow through sediment.[40] In 2009, they added cyanobacteria to the overlying water which could regenerate the acetate used at the anode to reduce the amount of depletion. The power output of this system did not change significantly with the added cyanobacteria, but this did remove the necessity of continually adding acetate.[42]

Vascular plant bio-photovoltaics are an interesting and somewhat recent technology in which plants are used to harvest solar energy and produce organic compounds through normal metabolic activity. These organic compounds can then be consumed by microorganisms in the plant rhizosphere, the small area of soil near the roots, to generate electricity at the anode. De Schamphelaire et al. tested a cell with an anode embedded in the rhizosphere of rice plants. The presence of the plants gave a 7-fold increase in current output of the cell because the plant continuously generates biomass near the anode.[43] Bombelli et al. used a carbon fiber network for their anode which was able to conform to the shape and size of the root system for greater surface area. They also incorporated two plant species, rice plants (*Oryza sativa*) and a competing weed (*Echinochloa glabrescens*). The rice plants showed much larger power and current densities than the weed but the overall

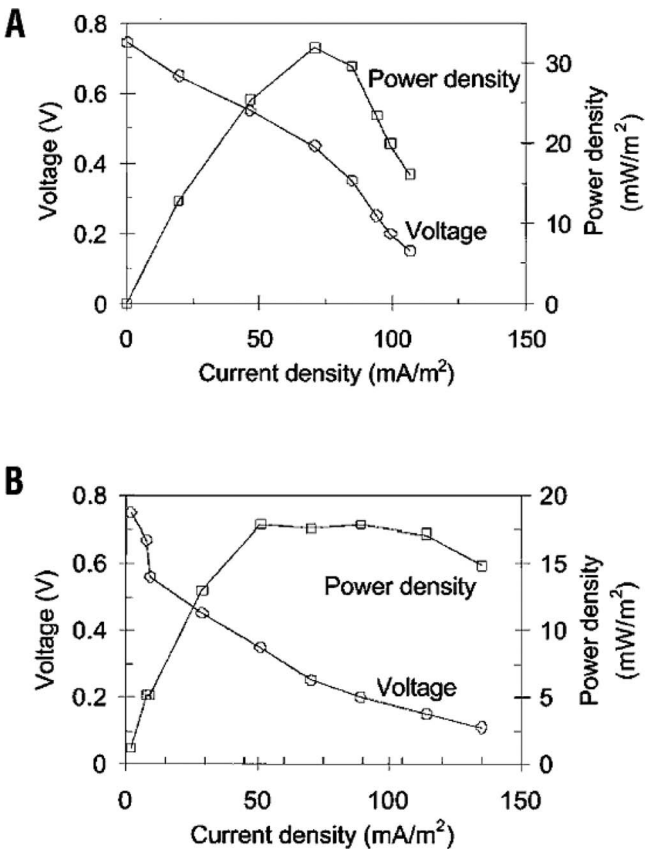

Figure 4. Voltage and power density vs. current density characterization of fuel cells deployed at two different marine environments. Data was obtained by stepwise reduction of cell voltage followed by measurement of current through the external circuit after sufficient time elapsed for current to stabilize (>10 min). Current density (mA/m^2) was calculated by normalization of current to the electrode footprint area (0.183 m^2). Reproduced with permission from *Nat. Biotechnol.*, **20** (2002) 821-825. Copyright 2002, Nature Publishing Group.

output of the cell was much lower (~1.6 mW/m^2) than other reported systems. However, most systems require the continuous addition of organic nutrients whereas the electricity produced by this cell only depends on illumination.[44]

Thylakoids

An alternative photosynthetic catalyst for solar energy conversion is the thylakoid membrane. Isolated thylakoids are small (0.1-1 μm in length)[45] compared to whole bacteria cells (on the order of several micrometers in length)[46] which allows for greater loading of active material on the electrode while maintaining the photosynthetic pathway. Carpentier and Mimeault studied the photobioelectrocatalysis of thylakoids in solution in a three electrode set-up with a calomel reference electrode. Without the addition of mediators, the thylakoids generated a photocurrent of 5-6 μA/cm^2. They showed that electrons could be accepted from either PSI or PSII based on the redox mediator added to the solution. The best results they obtained were with the addition of PSII mediators which led to photocurrents that were twice as large compared to the DET system. They also showed that the photocurrent significantly decreased with the addition of photosynthesis inhibitors such as 3-(3,4-dichlorophenyl)-1,1-dimethylurea (DCMU) and 2,5-dichlorobenzoquinone (DCBQ).[47]

Lam et al. designed a microelectromechanical system (MEMS) which incorporated thylakoid membranes for solar energy conversion along with the redox mediator phenazine methosulfate (PMS) in the anode compartment. The cathode compartment contained ferricyanide which is reduced to ferrocyanide during operation of the cell. The ferrocyanide reacts with O_2 in the solution to regenerate the ferricyanide. While theoretical calculations showed this cell should be capable of producing a maximum current density of 9.6 mA/cm^2, their experimental results were only 1.0 μA/cm^2 due to mass transport limitations of the mediator.[48]

In 2012, the Minteer research group developed a bioanode with immobilized thylakoids capable of DET. As seen in Figure 5, they showed that addition of catalase to the electrode was necessary to prevent the degradation of the thylakoids from reactive oxygen species that are naturally produced during light exposure.[29] Their thylakoid bioanode was able to generate 2.46 μA/cm^2 when connected with a Pt air-breathing cathode[29] and 14.0 μA/cm^2 with a laccase oxygen reduction biocathode.[49] The OCVs for these cells were 0.46 V and 0.73 V, respectively. They also showed that this system could be used as a self-powered herbicide biosensor which allows for the determination of herbicide in solution based on the decrease in power output when the photobioelectrocatalysis is inhibited,[50] and the different sources of thylakoids have different sensitivities for herbicide detection.[51] The limits of detection for three different herbicides were below 0.5 μg/L which is below the EPA limits for acceptable concentrations in water. In order to improve photocurrent generation and increase the amount of the solar spectrum being used by the bio-solar cell, they incorporated fluorescent carbon quantum dots in the thylakoid bioanode which gave more than twice the current compared to just thylakoids.[52]

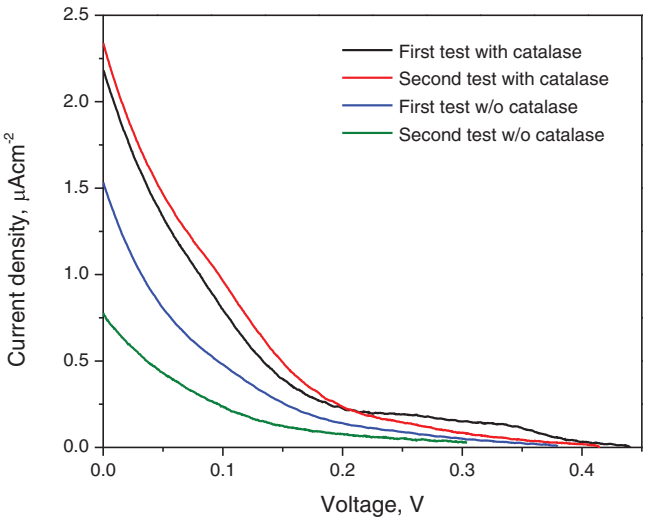

Figure 5. Current-voltage plots for a thylakoid bio-solar cell. Each cell was tested twice while exposed to light. Anodes containing no catalase and anodes with catalase are compared. Reproduced with permission from *ECS Electrochem. Lett.*, **1**, 5 (2012) G7-G9. Copyright 2012, The Electrochemical Society.

Calkins et al. tethered thylakoids to multiwalled carbon nanotubes for a bioanode which generated a steady-state current density of 38 μA/cm^2 with ferricyanide as the mediator. When connected with a laccase biocathode, their bio-solar cell produced a power output of 5.3 μW/cm^2 and an OCV of ~0.4 V. They also used inhibitors to show that the measured photocurrents were produced by PSII.[30] The Gorton research group tested thylakoids in solution with a series of quinone mediators with different structures and redox potentials. They showed that *p*-benzoquinone (PBQ) gave the largest photocurrent, 127 μA/cm^2. They also determined the optimum chlorophyll concentration of the system to be 100 μg/mL. Below this concentration the photocurrent decreases with decreasing concentration, while above this concentration the high thylakoid concentration prevents light from reaching enough of the active sites and the photocurrent decreases with increasing concentration.[53]

Photosystems and Reaction Centers

The smallest biological catalyst capable of solar energy conversion is the individual photosystems or reaction centers. The photobioelectrocatalytic abilities of these complexes have been studied by a number of groups. One major advantage to these catalysts is their small size which allows for increased loading on the electrode surface and increased electron transfer due to improved access to active sites.

Reaction centers.— The first enzymatic biological catalysts for solar energy conversion to be evaluated electrochemically are the RCs of photosynthetic bacteria. Katz isolated RC from the purple sulfur bacteria *Rhodobacter sphaeroides R-26*. The RCs were then immobilized by covalently bonding to a compound with pyrenyl groups which bind to the surface of a graphite electrode. The orientation of the RCs could be controlled by binding through either a lysine or cysteine residue as seen in Figure 6. When binding through a lysine residue, the RC showed only a small DET photocurrent; the addition of a ubiquinone-50 as the electron acceptor increased the current more than 10-fold. The cysteine-oriented binding generated a DET photocurrent of 300 nA/cm^2 and the addition of a mediator showed little to no effect.[54]

Trammell et al. isolated histidine-tagged RCs from the same bacteria, which they then tethered to a Au electrode modified with a Ni-terminated SAM. With ubiquinone-10 as the electron accepted, the measured photocurrent was ~30 nA/cm^2. They also evaluated the photocurrent in the presence of atrazine, an herbicide which inhibits photosynthesis by binding to the quinone (Q_b) binding site, preventing electron transfer from the RC. As the atrazine concentration was increased, the photocurrent decreased due to photosynthesis inhibition.[55]

Photosystem II.— PSII is the first protein complex in the light-dependent reactions of photosynthesis. It is a transmembrane complex (MW 350 kDa) containing 20 subunits (17 transmembrane and 3 peripheral) along with numerous cofactors including 35 chlorophylls.[56] Oxidation of water to produce O_2 takes place at the OEC, a Mn_4CaO_5 cluster. This cluster can exist in several oxidation states and cycles between them during the extraction of four protons and four electrons from two H_2O molecules to produce one molecule of O_2.[57]

Maly et al. isolated histidine-tagged PSII from *Synechococcus elongatus*. The enzymes were covalently bound to a Ni-modified self-assembled monolayer (SAM) on with a Au electrode by chelating the

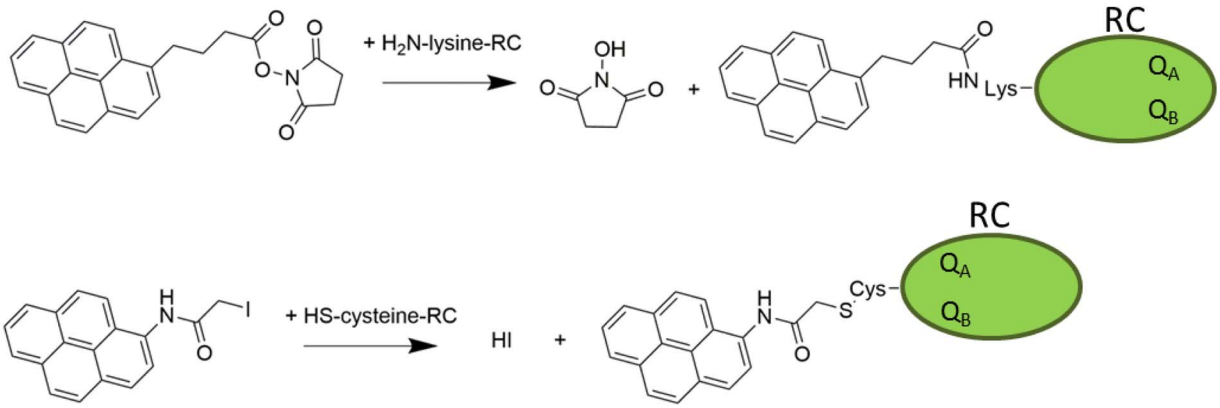

Figure 6. Idealized scheme for the covalent immobilization of RCs via (a) a lysine residue and (b) a cysteine residue.[54]

histidine tag. They found that the PSII electrodes, with duroquinone (DQ) as mediator, generated a photocurrent of 11.3 nA/cm^2. The dense packing of the enzyme on the electrode surface limited the mass transport of the mediator. When they included bovine serum albumin (BSA) in the enzyme mixture during immobilization, the photocurrent increased to 108 nA/cm^2 after the BSA (which is only adsorbed) is washed away from the surface.[58] In 2008, researchers in Japan used the same immobilization technique on nanostructured Au electrodes and reported a photocurrent of 2.44 μA/cm^2 with no added mediator.[59]

A very commonly used method for enzymatic electrodes is tethering with a redox polymer.[22–26] The polymer acts as an immobilization matrix as well as a redox mediator for the enzyme. One well-studied polymer contains osmium centers with a redox potential of 190 mV vs. Ag/AgCl. Schumann and Rögner used this polymer, [Os(bipy)$_2$Cl$_2$], to immobilize PSII onto Au electrodes.[60] They confirmed photobioelectrocatalysis by cyclic voltammetry which showed the osmium oxidation peak increasing while the reduction peak decreased as the light intensity increased. The photocurrent generated during amperometric studies was 45 μA/cm^2, significantly higher than other reported PSII results.[61,62]

The Willner research group reported the first PSII bio-solar cell. The bioanode consisted of a Au electrode with a layer of electropolymerized poly(mercapto-*p*-benzoquinone) over which PSII isolated from *Mastigocladus laminosus* was adsorbed. The cathode contained BOD and carbon nanotubes on a glassy carbon surface. This bio-solar cell had maximum power and current outputs of ∼17 μW/cm^2 and ∼120 μA/cm^2, respectively, with an OCV of 425 mV.[63]

Photosystem I.— PSI is the second photosystem in the light-dependent reactions of photosynthesis in plants and cyanobacteria. It is a membrane-bound protein complex consisting of 12 subunits and a large number of cofactors, including close to 100 chorophyll molecules.[64] Its role in photosynthesis is to harvest energy from light which is then used to drive the reduction of NADP$^+$ by ferredoxin-NADP$^+$ reductase.[65]

PSI's photodiode-like properties make it a promising candidate for use in solar energy conversion devices. The Rusling research group studied the redox properties of a PSI film on a lipid layer on graphite using cyclic voltammetry. While the purpose of their experiments was not to evaluate the photobioelectrocatalysis of the PSI electrodes, they showed that DET was possible. The oxidation peak they observed with PSI decreased when ferredoxin was added to the solution. Their results show that the electrode can act as an electron acceptor for PSI when the natural acceptor, ferredoxin, is not present.[66]

The Cliffel research group has done extensive studies on photocurrent production with PSI electrodes.[67–71] Initially they immobilized PSI onto Au electrode surfaces using a SAM with terminal hydroxyl groups. However, this electrode only generated photocurrents of ∼7 nA/cm^2 with methyl viologen in solution as the electron acceptor.[67] As seen in Figure 7a, by applying PSI to a Au surface in multiple layers, the photocurrent increased to 7.9 μA/cm^2. Figure 7b shows the results of applying several different potentials. When a positive overpotential is applied, the oxidation of $[Fe(CN)_6]^{4-}$ generated by reaction with F_B^- is favored. At negative overpotentials, the reduction of $[Fe(CN)_6]^{3-}$ produced by reaction with P_{700}^+ occurs. Small overpotentials lead to a photocurrent with contributions from both reactions. As seen from the results, this cell generates larger photocurrent with positive overpotentials.[68] The Cliffel group used the same multilayer technique on graphene to construct a transparent PSI electrode with methylene blue as the mediator. While the photocurrent was smaller with this electrode (∼550 nA/cm^2),[70] the transparency makes the electrode more practical for use in a solar energy conversion device. Finally, they compared the photocurrent production with 14 different redox mediators, either electron donors or acceptors, and showed that ferricyanide gave the best results (900 nA/cm^2). They also evaluated mixed mediator systems to mimic the natural reaction pathway in nature where plastocyanin donates electrons to PSI and ferredoxin accepts them from PSI. By using both methyl viologen (with a redox potential similar to ferredoxin) and ferrocyanide (with a similar redox potential to plastocyanin), the photocurrent showed at least twice the current compared to the individual mediators.[71]

Recently, Mershin et al. reported a PSI biophotovoltaic device.[72] The system used a Co-containing electrolyte for the electron donor and either a TiO_2 surface or ZnO nanowires for the electron acceptor. They also genetically altered the electron acceptor subunit PsaE of PSI by adding a sequence with high affinity for ZnO. As seen in Figure 8a, this bio-solar cell was able to generate current and power outputs of 362 μA/cm^2 and 81 μW/cm^2 with an OCV of 0.5 V. The fill factor was ∼70% which is similar to conventional solar cells and illustrates the high efficiency of this cell. Filtering out the ultraviolet light led to a decrease in photocurrent and OCV (see Figure 8b) which shows that approximately 80% of the current is generated by PSI. The photocurrent increased with increasing light intensity as expected (Figure 8c). Finally, Figure 8d and 8e compare the result with and without the genetically modified PsaE, respectively. The modification leads to an increase in both the photocurrent and OCV.

Biofuel Production

In addition to photobioelectrocatalysis for electricity and power production, biofuel production is another application which can take advantage of the photosynthetic properties of these biological catalysts. For a more thorough discussion of this topic, the reader may be interested in a review by Hankamer et al.[73] Photosynthetic production of hydrogen, or bio-H_2, is particularly promising because it is a clean, sustainable, and renewable source of hydrogen compared to conventional methods.[73]

A group in Germany developed a nanodevice which used PSI and a hydrogenase for H_2 production. Electrons transfer from the

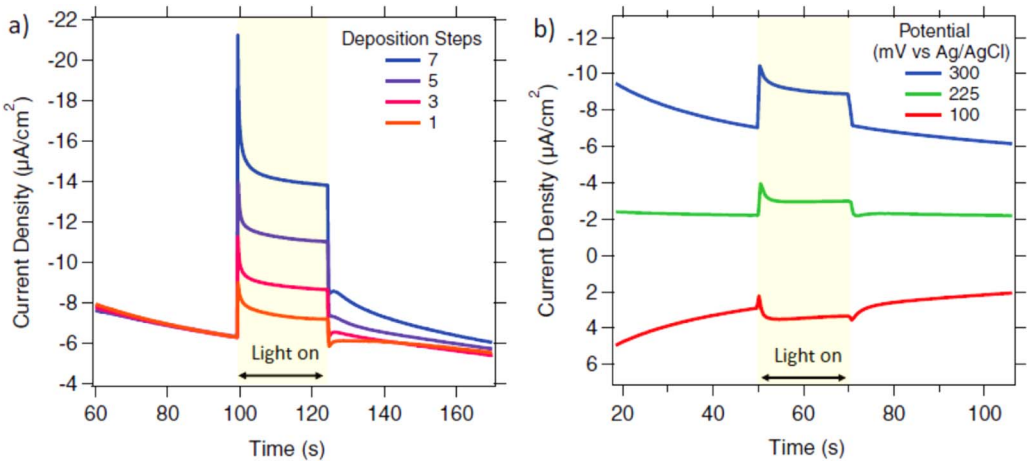

Figure 7. (a) In dark conditions, an anodic baseline current is observed in response to the + 0.1 V overpotential at which the data were collected. In response to irradiation, charge separation occurs within PSI complexes in the multilayer assembly, and these charges can then be transported through the film by the redox couple and collected at the electrode to produce a photocurrent. Thicker films produce larger photocurrents because they provide more sites at which charge separation may occur. (b) Photo-induced increases in current are observed at both anodic and cathodic overpotentials. These photocurrent responses were generated with polychromatic white light at an intensity of 95 mW/cm^2, and a PSI multilayer film fabricated by three deposition steps was used for the experiments shown in (b). Reproduced with permission from *Adv. Funct. Mater.*, **20** (2010) 4048-4054. Copyright 2010, Wiley-VCH.

Au electrode to PMS in solution which becomes reduced and is able to pass electrons to PSI tethered to the surface. PSI can then pass electrons to the hydrogenase which uses them to produce H_2. This device was able to generate H_2 at a rate of 120 pmol s^{-1} cm^{-2} or 4500 mol H_2 min^{-1} mol^{-1} PSI-hydrogenase complex.[74]

A more common method of H_2 production is to use a two-phase process as seen in the device reported by McCormick et al.[75] The cyanobacterium *Synechocystis* sp. PCC 6803 was used in the fueling phase to reduce ferricyanide while illuminated with the circuit open. During the H_2 production (in the dark), the circuit is closed and a voltage is applied to generate H_2 at the cathode. The maximum H_2 production rate they observed with their system was 2.23 mL H_2 L^{-1} h^{-1}.

Future Directions and Outlook

In order for photobioelectrochemical cells to be competitive with current technologies, there are several issues that need to be addressed. Efficiency is commonly reported for conventional solar cells. However, efficiency is rarely reported for bio-solar cells. Current photovoltaic devices operate at an efficiency of almost 30%.[76] The low cost of biological catalysts will make up for lower efficiency, but bio-solar cell efficiency must be at least 10% in order to be competitive. In order to make this comparison, the cost of fabricating bio-solar cells must be evaluated.

Stability is the most important issue that needs to be addressed to make photobioelectrocatalytic devices for solar energy conversion practical for real-life applications. While some microbial systems have been shown to operate for at least one year,[40] almost no stability testing has been performed for other reported solar systems. This is particularly important for thylakoid and photosystem electrodes because photodamage induced by oxidizing species leads to high turnover rates, specifically for PSII. One of the protein subunits of PSII, the D1 protein, where P680 is bound,[56] is replaced roughly every hour. Overall, the half-life of the entire PSII complex is <11 hours, while PSI's half-life has been shown to be >30 hours.[77]

Improving DET photocurrent production is also crucial because a commercial product will need to use DET rather than MET. By removing the necessity of a mediator, there is less voltage loss and possibly increased stability of the electrode. However, most of the reported DET systems produced significantly less photocurrent than mediated systems. One method that has been used to increase DET with non-photocatalytic enzymatic electrodes is oriented immobilization[28,78–81] which should also work for photosynthetic systems. Because the most important factor for efficient DET is distance from the surface, orienting the catalyst so that the active site or redox cofactors are near the electrode surface can lead to a significant increase in current.

An alternative method to improve DET is to modify the surface with a molecule similar in structure to the enzyme's substrate which the enzyme will then bind to and transfer its electrons to the electrode.[28] Increasing the surface area by using porous materials or by incorporating conductive materials is another common way of increasing DET. However, when incorporating materials with biological catalysts, it is important to evaluate the surface properties such as hydrophobicity, conductivity, and specific area to ensure that the catalyst activity is not negatively affected. Tailoring the design of incorporated materials in such a way that they increase the activity would lead to enhanced photocurrents as seen in the bio-solar cell reported by Mershin et al. which used a surfactant designed to stabilize the system.[72]

For most of the reported systems, the cell design has not been optimized. It may be possible to see significant photocurrent enhancement just by altering the cell construction. One major advantage to using biological catalysts on both the anode and cathode is that they tend to be very specific which removes the necessity of a separator which would add resistance to the cell. Additionally, because light is the "fuel" for photosynthetic systems, the volume of the electrolyte can be very small, allowing the two electrodes to be very close together, similar to the cell used by Lam et al.[48] Choosing the correct pH for the electrolyte is also important, but most of the systems reported have not been evaluated in this manner. An optimized small cell with a biocathode close to the anode including the proper electrolyte with no separator should lead to significant enhancements in power generation. However, the design or containment of the cell will also contribute to the cost. Development of a containment system that is able to withstand potentially extreme conditions, such as heat, cold, or wet conditions, is necessary for use in practical applications.

Overall, the use of photobioelectrocatalysts shows great promise for solar energy conversion devices. While stability and low photocurrent generation may currently prevent these systems from competing with conventional methods, there are several advantages which could make them a good choice for specific applications. The potential low cost of most of these catalysts is a major advantage because, while the electrodes may have low stability, they could be disposable and easily replaced. This type of disposable electrode may be very useful in portable solar energy conversion devices. Additionally, these devices are a source of clean energy without any significant negative impact on the environment.

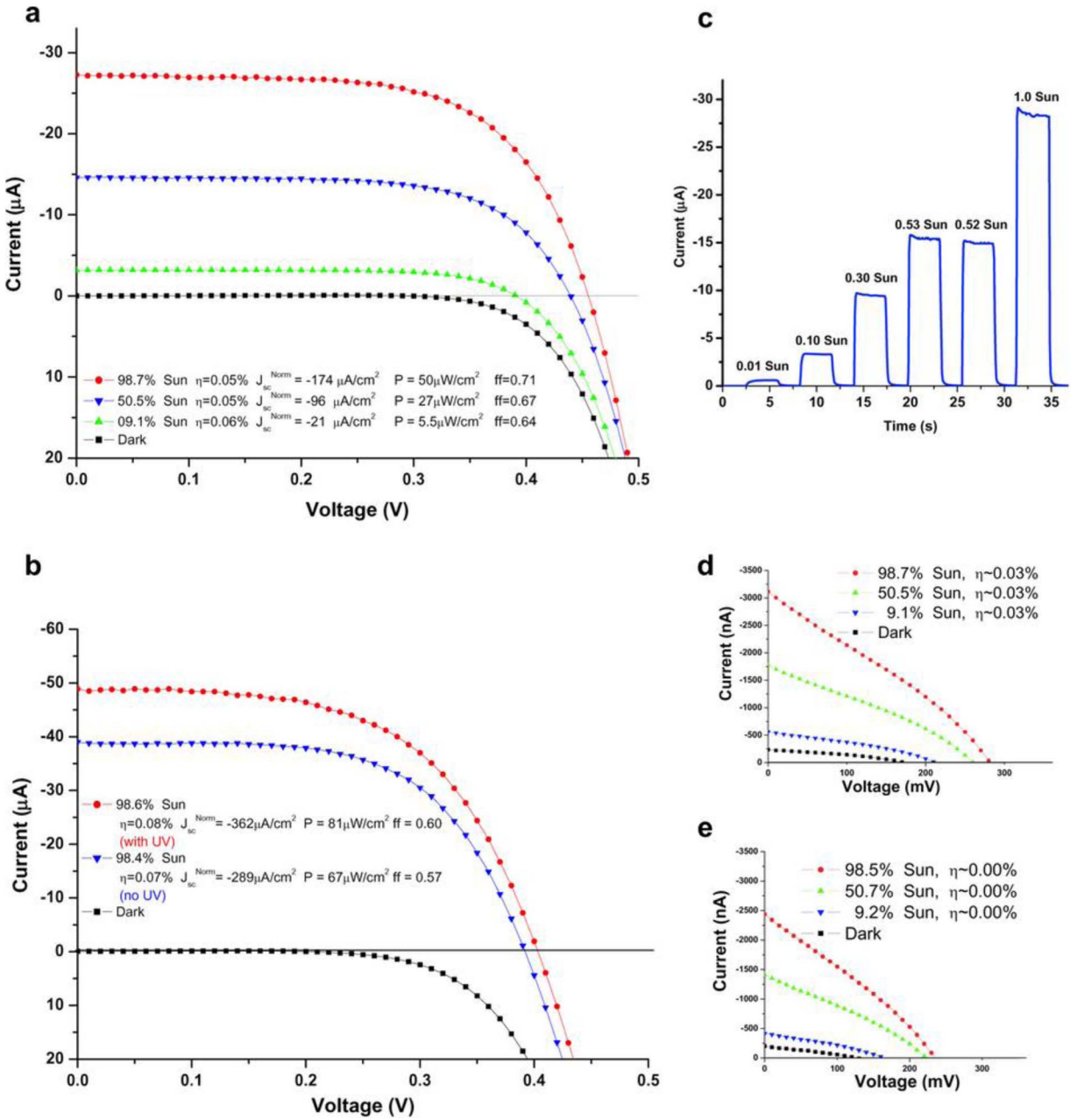

Figure 8. Photocurrent measurements of PS-I biophotovoltaic devices under AM1.5 simulated insolation at 298 K. Illuminated surface 0.159 cm^2 (a) 40 μL of PS-I (0.2 mg/mL) stabilized by 1:1 0.1%w/v designer surfactant peptide A_6K (resulting in a total of 8 μg of protein) dried on a 3.8 μm thick layer of 60 nm-pore TiO_2 produces an IV curve typical of a DSSC. Fill factor (ff) ranged from 64% to 71%. (b) Eliminating ultraviolet (UV) wavelengths below 350 nm resulted in a ∼20% reduction in the normalized short circuit current (J_{SC}^{Norm}) and a ∼10% reduction in the open circuit voltage (OCV) indicating that 80% of the total electrical power generated is due to PS-I (the rest due to UV photovoltaic response of TiO_2). These photocurrents cannot be attributed to sensitization of TiO_2 by leached chlorophyll derivatives. A blank control containing A_6K generated no power when exposed to UV-less sunlight of any intensity, neither did controls built with PS-I denatured by boiling for 10 minutes, nor devices built with PS-I not treated with A_6K (data not shown). Total incident-light to electrical external power conversion efficiency η was 0.08% with UV, 0.07% without. (c) Linearity test of PS-I photocurrent at intensities from 0.01x to 1.0x AM1.5 shows behavior typical of a dye-sensitized solar cell (DSSC). (d) IV of PS-I self-assembled in the presence of an overabundance of PsaE-ZnO electron-accepting subunit yields a total power conversion efficiency, η = 0.03%. (e) Control: IV of PS-I self-assembled with an overabundance of non-ZnO specific histidine-tag containing PsaE subunit yields lower OCV, J_{SC}^{Norm} and η = 0.00% as expected, suggesting that the PsaE-ZnO tag either enhanced binding of PS-I to the ZnO nanowires or favored the optimal orientation, or both. Z813 Co(II)/Co(III) electrolyte and platinized glass were used to complete all devices. Reproduced with permission from *Sci. Rep.*, **2** (2012). Copyright 2012, Nature Publishing Group.

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