Biomimetic strategies for solar energy conversion: a technical perspective

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Plants have evolved highly sophisticated light-harvesting mechanisms that allow for increased environmental tolerances and robustness, enhanced photo-efficiencies and prolonged lifetimes. These mechanisms incorporate the dynamic, cyclic self-assembly of proteins necessary for continual plant regeneration. Synthetic solar conversion devices, on the other hand, are designed to be static devices. Material and processing costs continue to be important constraints for commercial devices, and the earth abundance of requisite elements have become a recent concern. One potential solution to these problems lies in the development of biomimetic solar conversion devices that take advantage of the low material costs, negative carbon footprint, material abundance and dynamic self-assembly capabilities of photosynthetic proteins. Although research in this area is ongoing, this review is intended to give a brief overview of current biomimetic strategies incorporated into light-harvesting and energy-conversion mechanisms of synthetic solar devices, as well as self-repair and regeneration mechanisms adapted from plant-based processes.

Introduction

To become widespread for energy generation, solar cells must satisfy four essential criteria: efficiency, stability, cost-effectiveness, and material availability. Although several solar cells to date meet, or even exceed, several of these criteria, the existence of a device that meets all these criteria remains an objective for scientific research. Mono-crystalline silicon-based solar cells, for instance, demonstrate efficiencies approaching the Shockley-Queisser limits of 33.7% with stabilities on the order of decades. The abundance in material availability,
However, is offset by the relatively high processing costs affiliated with silicon purification. Thin-film technologies, which offer low-cost alternatives to silicon-based energy devices, tend to suffer from lack of material abundance and lower device efficiencies.

Ongoing research in this area focuses on not only improving existing technologies by lowering processing costs, replacing scarce, high-cost, or unstable materials and enhancing device efficiencies, but also developing devices that are entirely new to the field by utilizing new materials or alternative mechanisms for solar energy conversion. Among the most promising of these candidates is the dye-sensitized solar cell (DSSC), which incorporates a Ru-based dye reminiscent of natural dyes found in the chlorophyll of plants. Like several solar cells that seek to minimize processing costs via self-assembling mechanisms, DSSCs rely on self-assembly of the Ru dye for solar cell fabrication. Though demonstrating promising efficiencies of up to 11%, limitations in Ru availability and the replacement of unstable, liquid-based electrolytic cells are the focus of ongoing research in this field.

This brief overview in solar cell technology outlines key transitions recurring in research developments: the transition from the inorganic to the organic realm, from rigid and static to thin, flexible, dynamic technologies, and the replacement of unstable, liquid-based electrolytic cells. These transitions parallel the underlying tendency of the field towards the utilization of biomimetic strategies for solar energy conversion.

In this review, we discuss in detail solar cell technology in plants, reviewing plant physiology and discussing several key processes that occur during photosynthesis. We next provide a non-exhaustive, general overview of solar cell technologies that exploit biomimetic means of energy conversion to overcome deficiencies that currently plague leading devices in the solar technology field.

**Plant physiology**

In plants, the smallest unit of comprehensive energy conversion is the plant chloroplast (Fig. 1). The chloroplast converts solar photons into usable chemical energy via photosynthesis with an overall synthesis balance

$$6CO_2 + 6H_2O \xrightarrow{hv} C_6H_{12}O_6 + 6O_2$$

Like most organelles in the plant cell, chloroplasts are surrounded by outer and inner membranes. The inner membrane contains stacks of photoactive thylakoid membranes, or grana, surrounded by stroma fluid. Stroma lamellae serve to connect the multiple grana throughout the chloroplast. The stacks of thylakoid membranes that compose the grana are embedded with multiple protein complexes, including photosystem II (PSII), cytochrome b (cyt b6f), photosystem I (PSI) and ATP synthase. Each of the photosystems, PSII and PSI, is surrounded by light-absorbing antennas. The first stage of photosynthesis, or the light-dependent reactions, occurs within these protein complexes within the thylakoid membrane.

The series of light-dependent reactions are initiated in PSII, where light is initially absorbed by the P680 site to generate electron-hole pairs, with an overall half reaction of

$$2H_2O \xrightarrow{hv} O_2 + 4e^- + 4H^+$$

In addition to P680 absorption, light is also absorbed at various wavelengths by the pigments within the surrounding antenna. Electron excitation within the pigment is followed by resonance energy transfer to the P680 site, where electron-hole pairs are generated (Fig. 2a). The hole remains at the site, where it is used in the oxidation reaction of water to produce oxygen via oxygen-evolving complexes (OECs). Meanwhile, the electron is initially transferred to the pheophytin (Phe) and QA sites, resulting in the reduction of QA. The potential difference between

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the reduced QA site and the oxidized QB site drives electron transport towards QB. Upon reduction of QB, an electron transport chain is used to extract the electron from the QB site to create a proton gradient across the thylakoid membrane using cyt b6f. (This proton gradient aids in ATP synthesis via ATP synthase, as described below). Like PSII, the following protein complex, PSI, is responsible for photon absorption at the P700 site (Fig. 2b). Similarly, surrounding antennae also absorb light at various wavelengths, transferring energy to P700 through resonance transfer. Electrons gained from PSI are raised in energy \( \text{via} \) the photoelectric effect, expelling the excited electron to the ferredoxin site. From here, the electron may follow one of two possible pathways: cyclic or noncyclic phosphorylation. Under conditions where the plant produces excess NADPH relative to ATP, the cyclic phosphorylation reaction takes place, where the electron is used to pump H\(^+\) across the membrane to create a proton concentration gradient that is ultimately used to power ATP synthase. Under conditions where NADPH concentration is less sufficient, the electron enters a noncyclic phosphorylation reaction which ultimately reduces NADP\(^+\) to NADPH in the stroma according to the reaction

\[
\text{NADP}^+ + 2H^+ + 2e^- \rightarrow \text{NADPH} + H^+
\]

The final major protein complex, ATP synthase, extracts charged hydrogen atoms from previous oxidation reactions, such as water oxidation in PSII, to ultimately store energy in the form of the ATP with the addition of a phosphate group, P\(_i\)

\[\text{ADP} + P_i \rightarrow \text{ATP}\]

The energy released as protons are pumped from the interior of the thylakoid membrane to the stroma is used to carry out this reaction. Overall, the net yield of the first stage of photosynthesis becomes

\[2H_2O + 2\text{NADP}^+ + 3\text{ADP} + 3P_i \xrightarrow{hv} O_2 + 2\text{NADPH} + 3\text{ATP} + 2H^+\]

The second stage of photosynthesis, or the light-independent reactions, occurs within the stroma of the chloroplast.

Fig. 1 Chloroplast Structure. The chloroplast (left) consists of an outer membrane surrounding stacks of photoactive membranes, or granum. The thylakoid membrane contained within each of these stacks (right) is embedded with several protein complexes, including PSII, cyt b6f, PSI, and ATP synthase. Initial electron-hole separation occurs largely within PSII, with subsequent electron transport \( \text{via} \) successive redox reactions occurring in the following complexes. Synthesis of ATP, the end product of the reaction scheme, occurs within the ATP synthase of the membrane.

Fig. 2 PSII and PSI Structure. (a) Photon absorption at the P680 site in PSII results in electron-hole separation. The hole is used in the oxidation of water to produce oxygen, whereas the electron is driven to the Phe and QA sites of the complex. The potential difference between the quinone sites drives electron transport to the QB site, where it is subsequently removed to enter the electron transport chain in cyt b6f. Except for the QA site, which is located on the D2 protein, the remaining sites (P680, Phe, QB), are located on the D1 protein, which is susceptible to damage with a high turnover rate. (b) Photon absorption at the P700 site in PSI results in electron excitation and expulsion. The surrounding antenna allow for increased absorption of light at wavelengths throughout the solar spectrum. Resonance transfer from the surrounding antenna to P700 is similar to that demonstrated by PSI.
surrounding the grana. In these reactions, carbon dioxide and water are converted into glucose according to the Calvin-Benson cycle that occurs within the chloroplast, and the net yield of this subset of reactions becomes

\[6\text{CO}_2 + 12\text{NADPH} + 12\text{H}^+ + 18\text{ATP} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{H}_2\text{O} + 12\text{NADP}^+ + 18\text{ADP} + 18\text{P}_i\]

**Chloroplast generation and repair machinery**

In addition to carrying out the carbon-fixation processes in the form of the Calvin-Benson cycle, the stroma of the chloroplast also contains genetic material needed to reproduce itself and synthesize necessary proteins, along with the necessary machinery to continually repair photodamaged proteins that accumulate during the first stage of photosynthesis. The D1 protein in particular, which contains the P680 site required for light absorption, and the Phe and Q<sub>B</sub> sites required for electron separation, demonstrates the highest turnover rate. The self-repair cycle associated with photosynthesis is an evolutionary adaptation allowing plants and photosynthetic organisms a wide range of adaptability. These self-repair processes enable plants, for example, to not only adapt in a manner that minimizes damage, but also fully recover from a state of excessive protein denaturation. Without these self-repair processes, plants would produce less than 5% of their typical photosynthetic yields with lifetimes on the order of minutes under intense illumination.

Upon continuous illumination, the D1 protein in PSII becomes photo-damaged, resulting in the total photo-inactivation of the protein complex. Upon photo-inactivation, PSII partially disassembles to release the damaged protein. The damaged D1 protein is replaced with a newly biosynthesized D1 protein and PSII spontaneously re-assembles, incorporating the new protein to create a fully functional PSII. In the meantime, the damaged D1 protein undergoes protease degradation.

Under non-saturating light conditions, this D1 degradation and synthesis occurs at the same rate as D1 protein damage, which is determined by light intensity, among other factors. Thus, the D1 turnover rate increases with increasing light intensity. However, under excessive light intensities, the damage rate is too large for the repair rate to match, resulting in the overall inhibition in PSII activity. When stressed plant cells are returned to moderate, non-saturating conditions, they recover their photosynthetic activity via replacement of the photodamaged D1 protein. However, after prolonged stress conditions, the cells reach an inactive, irreversible state from which there is no recovery, which is in part due to damage to the transcriptional and translational machinery used to synthesize D1 proteins, as well as other proteins involved in the cell cycle.

Although the exact nature of the cause behind PSII photodamage and repair are still under investigation, several key players in the process have been identified. For instance, it is known that toxic oxygen radicals are produced under excessive light intensities. These radicals are not only responsible for protein cleavage and denaturation, but also for bleaching light-harvesting antennas that surround the photosystem and for general damage to the gene expression machinery used to synthesize new proteins. It is hypothesized that the production of the above reactive species is limited when cells are exposed to saturating light conditions for only limited periods of time, since the cells initially demonstrate virtually no decrease in photosynthetic activity. This limitation may be due to the inherent presence of scavengers such as xanthophylls, carotenes, and specific enzymes that work to deactivate the oxygen radicals, until they are no longer sufficient to buffer against prolonged exposure to saturating light intensities. Further evidence also suggests that radical occupancy of the Q<sub>B</sub> site of the D1 protein is specifically linked to photo-inhibition sensitivity and that it is the first target of high light stress. The D1 protein, which contains an abundance of proline, glutamine, serine, and threonine, is hypothesized to undergo cleavage at the Arg-238 or Phe-239 site upon photodamage. Degradation at Q<sub>B</sub> would account for the
decrease in the electron transport from the Q$_A$ to the Q$_B$ site observed upon photo-inactivation, where Q$_A$ remains in the reduced state.

Not only does the exact cause of photo-damage remain unclear, but also the precise mechanism by which the plant initiates protein degradation and synthesis is elusive. It has been suggested that phosphorylation may play an active role in regulating D1 degradation and synthesis. The steady-state level of D1 phosphorylation increases with increasing D1 protein photodamage, and degradation of the phosphorylated form of the protein is reduced. Several studies have examined protein self-assembly by artificially inducing phosphorylation at decreased temperatures and monitoring re-assembly at elevated temperatures. However, nothing is known about the D1 protein phosphorylation when PSII is under repair and new photosynthetic reaction centers (RCs) have been formed. Regardless of the details of the molecular mechanism, one fact remains certain: for plant regeneration, both D1 protein degradation and synthesis must occur at a rate sufficient to match that of protein damage.

**Biomimetic solar energy conversion devices**

Although plants have evolved highly sophisticated, dynamic mechanisms that allow them to replace photo-damaged proteins to prolong lifetime and enhance efficiencies, as well as structures that seek to optimize light absorption, man-made energy devices lack this capability of dynamic assembly, repair and possible self-replication. Several studies have made progress towards applying energy conversion and self-repair processes used by plants to synthetic devices.

**Artificial photosynthesis via water-splitting catalysis**

As discussed, photosynthesis ultimately results in the formation of an electron-hole pair upon absorption of sunlight. The electron is captured and shuttled to PSI, whereas the hole is used by the OEC for the oxidation of water, resulting in the formation of hydrogen. In an effort to duplicate photosynthesis, researchers have sought the creation of a device capable of electron-hole separation upon light absorption where the hole is used in water oxidation such that solar energy is stored chemically in the bond formation of H$_2$ and O$_2$. For decades, researchers have focused on mimicking the OEC near PSII by creating catalysts capable of converting water, carbon dioxide and light into carbohydrates, releasing hydrogen as a source of fuel. A synthetic, non-protein based form of catalysis that can oxidize water as efficiently as the OEC is the ruthenium “blue dimer”, which requires activation via a strong oxidizing agent (Fig. 4a).

\[
4\text{Ce}(IV) + 2\text{H}_2\text{O} \rightarrow 4\text{Ce}(III) + \text{O}_2 + 4\text{H}^+
\]

**Fig. 4** Key Contributions in Artificial Photosynthesis. (a) The ruthenium “blue dimer” catalyzes the oxidation of water into oxygen and hydrogen with efficiencies approaching those of the OEC. (Ref. 119 Reproduced by permission of The Royal Society of Chemistry). (b) Iridium-based catalyst demonstrates larger turnover frequencies for the catalysis of the oxidation of water. (Reprinted with permission from ref. 88. Copyright 2008 American Chemical Society).

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**Catalysts**

**Coupling artificial photosynthesis with hydrogenases**

An extension of the bio-inspired systems for hydrogen production interfaces natural photosystems for hydrogen production with synthetic hydrogenases. Like plants, cyanobacteria and green algae synthesize glycogen and starches from CO$_2$ when under illumination. Under anaerobic conditions, hydrogenases catalyze the recombination of hydrogen ions with electrons to produce hydrogen gas according to the reaction

\[
2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2
\]

To couple the water-splitting reactions during photosynthesis with hydrogenases that remain active under aerobic conditions, a synthetic PSI-hydrogenase hybrid was assembled onto a gold electrode using a genetically engineered, cyanobacteria-derived PSI and a soil bacterium-derived hydrogenase. Light-activated hydrogen production in these biomimetic devices occurs at higher potential and lower energies than synthetic (bio)nanoelectronic devices that did not implement a photosynthetic apparatus. Although the high costs affiliated with protein isolation make future prospects of PS-based hybrid systems infeasible...
for solving the global energy crisis, cellular-based systems still hold promise in this field. In this sense, the future of this field will tend towards devices consisting of photosynthetic organisms and mechanisms, rather than just protein complexes. In fact, several recent studies have taken steps in this direction with the development of nanoprobes capable of direct electron extraction from intact algal cells. Some studies have even advocated for the development of biofuel cells that utilize algal cells, as well as living plants and bacteria.

**Biomimetic systems utilizing plant-derived photosystems**

Conventional technology cannot equal the molecular circuitry found in photosynthetic complexes. PSI, for example, which has yet to be synthesized synthetically, has external quantum efficiencies of approximately 100% and energy yields of 58%. Several studies have focused on the assembly of monolayers of PSI onto various substrates, including Au. One such study examined the adsorption of PSI extracted from commercial spinach leaves onto gold surfaces coated with various amine groups. Based on the result of these studies, PSI adsorption was conducted onto a hydroxyl-coated Au electrode surface. To fill in the electrode-exposed areas between the adsorbed PSIs, the interstitial, shorter hydroxyl chains were replaced with longer thiol chains, confining the protein layer between hydrocarbon chains. This incorporation of the PSI amongst long, hydrocarbon chains closely resembles the natural environment in the thylakoid membrane, thus stabilizing the PSI and conserving secondary structure upon exposure to various solvents.

In addition to PSI assembly, monolayer assembly has also been extended to RCs in photoelectrochemical cells. Immobilization of His-tagged RCs onto an electrode was demonstrated using a nickel-nitrilotriacetic acid (Ni-NTA) terminated substrate. To enhance device efficiency, RC configuration was altered to more closely mimic the native orientation of the protein complex with cytochrome such that the primary donor is facing the electrode surface. Photoelectrochemical measurements were obtained with the immersion of the decorated electrode into a ubiquinone-contained redox solution, as the redox potential of ubiquinone closely matches that of the Q_b site for electron extraction.

The effect of varying orientations of PSI monolayers was studied by Greenbaum and co-workers. Au electrodes were coated with negative, positive and hydrophilic surfaces and incubated with spinach-extracted PSIs for adsorption. Depending on the hydrophobicity and charge of the electrode surface, the PSI would orientate itself horizontally, upwards, or downwards, with I–V characteristics similar to semiconducting and diode-like behaviors. Monodispersion of PSI onto chemically treated Au surfaces allowed for the first single PSI photoelectric measurements using Kelvin force probe microscopy (KPFM). Covalent attachment of spinach-derived PSI through imine binding with lysine residues upon vacuum-assisted solution evaporation was also used in device fabrication. Upon evaporation, the decreased solubility of PSI and selective precipitation out of solution was used to create highly dense layers on a functionalized Au substrate. Using this fabrication, the PSI is orientated such that its electron transfer vector is directed away from the Au surface. Photoelectrochemical measurements reveal that such dense monolayers of PSI yield enhanced photocurrents of ~100mA/cm².

Alternative approaches for monolayer assembly have focused on obtaining covalent attachment of PSI in specific orientations. An approach to directly tether PSIs as a monolayer onto a gold surface required genetic mutation at various cysteine sites in the vicinity of P700. Since the PSIs were isolated from the cyanobacteria *Synechocystis sp.*, they require no stabilizing agents, since the antenna chlorophylls are integrated within the core subunits of the photosystem rather than as a peripheral attachment as in plants (Fig. 1). Although the fundamental optoelectronic properties of PSI remain conserved upon attachment to gold, attached PSI demonstrated an increase in spectral range and a loss in photopotential.

Dry multilayers of PSI onto gold substrates were also achieved to fabricate bio-inspired solid-state devices. As with the monolayer devices developed by Carmeli and co-workers in 2005, genetically-altered, cysteine mutants were attached via sulfide binding in the stacked configured shown in Fig. 5, with binding events occurring on the Au substrate for the first monolayer, and on sequentially depositing Pt for the subsequent layers. Such high-density devices resulted in enhanced absorption and increased device efficiencies.

A more direct attempt at reconstructing leaf-like structures using PSI was obtained using similar lysine-binding chemistries onto a nanoporous gold leaf (NPGL), wherein PSI was immobilized onto structured, rather than planar, electrodes for increased surface area. Greater control in layer assembling mechanisms was shown to enhance photoelectrochemical efficiency. This surface enhancement quadrupled photocurrents, producing photocurrents of ~400 nA/cm².

Another attempt at enhancing surface area coverage of PSI onto electrode surfaces was made using nanoparticle-PSI hybrid systems. Gold nanoparticles were deposited onto a planar gold electrode through sedimentation. Electrostatic deposition of cyanobacteria-isolated PSI onto the negatively charged gold nanoparticles to create a bio-nanohybrid material with photoelectrochemical currents exceeding analogous planar-based electrodes.

As opposed to non-covalent deposition, direct tethering of PSI to a functionalized surface is another approach used by research scientists to extract photoelectrical output. In one such study, Au nanoparticles were decorated with artificial vitamin K1 tethers, and native vitamin K1 tethers were removed from bacteria-extracted PSIs. Incubation of the modified PSI complexes with the functionalized nanoparticles creates synthetically tethered PSIs with direct electron extraction from the quinine pocket. In a similar study, planar gold electrodes were coated with electrostatically adsorbed, synthetic vitamin K1 wires. Incubation of the adsorbed wires with PSI where natural vitamin K1 tethers have been removed covalently attaches the photoactive protein complex to the Au electrode surface.

An extension of this work also resulted in a similar, direct binding of PSI to carbon nanotubes and a tethered, indirect binding to a GaAs substrate. To improve the efficiency, Lebedev and co-workers used arrayed carbon nanotube electrodes. The RCs were encapsulated inside carbon nanotube arrays and bound to the inner tube walls in a unidirectional orientation using organic molecular linkers. The efficiency was
Bio-inspired light-harvesting antennas for enhanced efficiencies

As discussed above, enhancing biomimetic photovoltaic efficiency remains an active area of research. In addition to maximizing surface area exposure and synthesizing high-density arrays, researchers have also developed enhanced light-absorption antennas that mimic the light-harvesting antennas used by both PSI and PSII. These antennas absorb light at a broader range of wavelengths. The energy absorbed by the antenna complexes is directed to the RCs which absorb photons at a specific wavelength, where the electron-hole pairs are generated using the absorbed energy, and the electrons are...
Fig. 6 Biomimetic Regeneration for Cell Efficiency Enhancement. (a) A solution consisting of RC-lipid bilayer-nanotube complexes and a dual mediator system comprised ferrocyanide/ferricyanide and ubiquinone/ubiquinol redox couples is illuminated at 785 nm. Photoresponse is measured using a SWCNT working electrode and a Pt counter-electrode. Surfactant removal is used for complex assembly (left dialyzer), and surfactant addition is used for complex disassembly (right dialyzer). (b) Photocurrent is measured under continuous illumination as photoresponse decreases over time. When approximately 25% of the initial photoactivity is achieved, surfactant is introduced into the system to initiate complex disassembly. The photodamaged proteins are replaced, and surfactant is once more removed from the system to re-assemble the complex, incorporating the photoactive proteins. This regeneration cycle is applied over 168 h, increasing overall cell efficiency by over 300% relative to efficiencies demonstrated in the absence of regeneration. (Reprinted with permission from ref. 83. Copyright 2010 Nature Publishing Group).

Fig. 7 Nanotube-based Exciton Antenna. (a) An optical image of core-shell antenna (left, scale bar 2 μm) and a corresponding schematic (right). (b) A cross-sectional view of the antenna illustrates an outer layer consisting of larger bandgap, (6,5) nanotubes and an inner core consisting of smaller bandgap nanotubes. Light is absorbed by the outer shell tubes. This energy is transferred to the inner core tubes via electron energy transfer (EET), as indicated by the black arrows. (Reprinted with permission from ref. 118. Copyright 2010 Nature Publishing Group).
transferred to electron acceptors. In another recent report from our group, carbon nanotubes were used to synthesize multi-shell, one-dimensional optical antennas with different bandgap energies which consist of smaller bandgap nanotubes inside and (6,5) nanotubes outside (Fig. 7). This core-shell nanofiber funnels excitation to the photon energy of the smallest bandgap nanotubes in the core of the antenna, which is analogous to energy transfer mechanisms from antenna complexes surrounding PSI and PSII.

Conclusions and outlook
As it stands, the high costs affiliated with protein isolation and purification undermines the development of a low-cost, bio-based solar conversion device for both hydrogen generation and photoelectrochemical/photovoltaic applications. These high costs are partially offset by advancements that boost solar conversion efficiencies, whether it be via textured surfaces that resemble leaf-life porosity in plants, stacked arrays with densities that approach that of the stacked grana in chloroplasts, regeneration cycles that rival the self-repair mechanisms used by plants, or solar concentrators that funnel energy to photoactive complexes analogous to light-harvesting antennae found in plants. Regardless of the device (water-splitting, photovoltaic, etc.), and regardless of the approach used to enhance device efficiency, the solution scientists converge to is consistently something already addressed in nature. As researchers continue to venture out of the realm of rigid, inorganic, pricey photovoltaics and into the realm of thin, flexible, organic, quasi-fluidic devices, one thing remains certain; the tendency towards biomimetic devices is a recurring theme in this field that will continue to sculpt the fabrication of solar cells for the future.

References