Photosynthetic Energy Conversion: Recent Advances and Future Perspective

by Narendran Sekar and Ramaraja P. Ramasamy

Photosynthesis is the most important natural process on earth, which transformed the once lifeless planet into a living world. While primitive photosynthetic bacteria such as purple sulfur bacteria and green sulfur bacteria carry out anoxygenic photosynthesis, producing elemental sulfur from hydrogen sulfide with the help of sunlight, cyanobacteria, algae and plants carry out oxygenic photosynthesis to convert water and carbon dioxide to sugars with the help of sunlight and release oxygen as a byproduct. The conversion of solar energy to chemical energy via photosynthesis with the release of oxygen has an evolutionary significance on life as we know it today. In fact, photosynthesis is the only natural process known on earth to form oxygen from water. Further, fossil fuels such as coal, petroleum and natural gas are formed from the remains of the dead plants by exposure to heat and pressure in the earth's crust over millions of years. With increasing energy crisis and environmental issues lately, now is the time to revisit photosynthesis in order to address these issues. In this context, a great deal of ongoing research is focused on utilizing photosynthetic energy conversion as a renewable, self-sustainable and environment friendly source of energy. When compared to the finite reserve of fossil fuels, sunlight, the energy source for photosynthesis, is abundant around the planet and is inexhaustible.

The earth receives solar energy at the rate of about 120,000 TW, which far exceeds our current global demand of ~16 TW.[1] However the only major technology available for solar energy conversion is photovoltaics (PV). PV devices such as solar panels generate electrical power by converting solar radiation into direct current electricity using semiconductors. Solar cells include first generation conventional wafer-based cells made up of crystalline silicon (Fig. 1a), second generation thin film solar cells (Fig. 1b) made up

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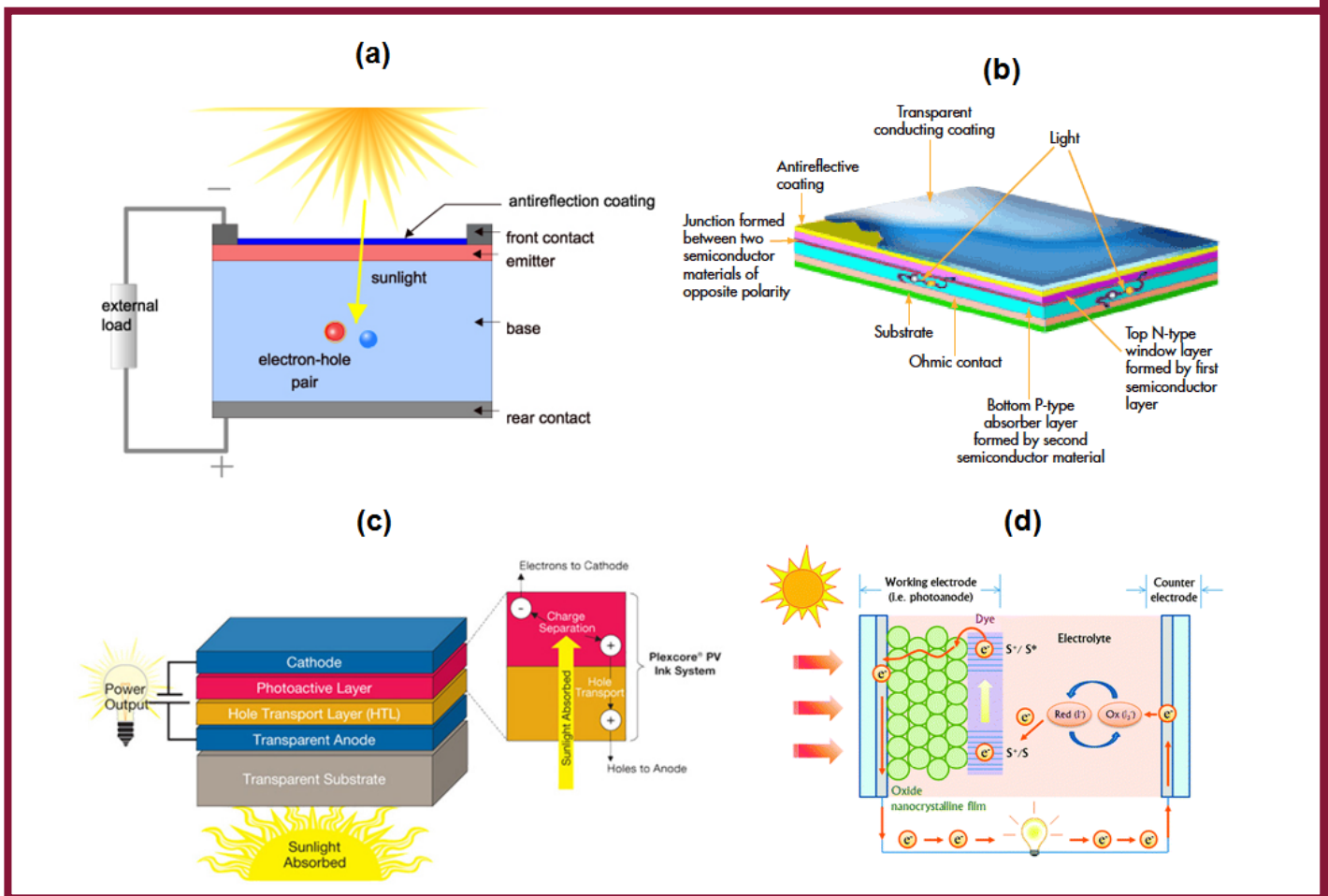

Fig. 1. *Schematic showing different photovoltaic technologies: (a) crystalline silicon solar cell; (b) thin film solar cell; (c) organic solar cell; and (d) dye sensitized solar cell.*

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of amorphous silicon, cadmium telluride, and copper indium gallium selenide, and third generation emerging solar cells such as organic solar cells (Fig. 1c), dye sensitized solar cells (DSSC) (Fig. 1d), and quantum dots solar cells, each with their own efficiency limits, advantages and disadvantages. Compared to the single junction solar cells (maximum efficiency of ~27% for crystalline Si cell with concentrator), gallium arsenide based multiple junction solar cells can reach efficiencies as high as 44%. However the PV-based technologies (some of which remain expensive today) are not suited for pushing the efficiency limits higher. This is main reason why alternate solar capture technologies based on natural photosynthesis are being explored. The internal quantum efficiency of the charge separation step in natural photosynthesis is ~100%. Further the charge carrier recombination time is much lower for photosynthesis-based light capture (>10^{-1} for PSII stacked membrane converter), compared to PV technologies (<10^{-3} for Si PV and <10^{-6} for organic PV) as shown in Table 1. Another remarkable feature that separates photosynthesis from traditional PV technologies is that photosynthesis contributes to global CO_2 sequestration (via the dark reaction), which can never be accomplished by any of the PV systems designed so far.

Table I. Performance comparison of natural photosynthesis versus different photovoltaic technologies (DSSC: dye sensitized solar cells; PV: photovoltaics; adopted from Pace 2005[58]).

Solar energy technology	Internal Quantum Efficiency	Theoretical Maximum Efficiency	Present Efficiency Range	Charge Recombination Duration
Silicon PV	~ 55 %	~ 25 %	18-24 %	≤ 10^{-3} s
Organic PV	10-30 %	-	2-6 %	≤ 10^{-6} s
DSSC	~ 90 %	~ 33 %	10-12 %	~ 10^{-1} s
Natural photosynthesis	~ 100 %	> 40 %	-	≥ 10^{-1} s

Mechanism of Photosynthesis

In higher plants, photosynthesis takes place in compartmentalized organelles called chloroplasts (Fig. 2). The inner matrix of chloroplast is called the stroma, in which thylakoids are organized into a structure similar to a stack of coins called granum (plural: grana) (Fig. 2). Photosynthesis consists of two reactions: (1) a light dependent reaction called the light reaction that takes place inside thylakoids (lumen); and (2) a light independent reaction called the dark reaction (Calvin cycle) that takes place in the stroma. During the light reaction, with the help of sunlight, water is oxidized to protons, electrons, and oxygen. The sequential steps of transferring the electrons from water to $NADP^+$ to generate NADPH are collectively called the photosynthetic electron transport chain (P-ETC) as shown in Fig. 3. P-ETC encompasses various protein complexes such as photosystem II (PSII), cytochrome b_6f, photosystem I (PSI) and ATP synthase, soluble proteins such as plastocyanin, ferredoxin and NADP reductase and plastoquinone that are embedded in the thylakoid membrane (Fig. 2). Both the photosystem complexes, namely PSI and PSII, contain chlorophylls at their core reaction center, where the actual charge separation happens upon light absorption thereby generating the excited electrons. When these photo-excited high energy electrons transfer down the energy gradient, the energy drop is harnessed to pump protons outside the thylakoid membrane. This generates the proton motive force necessary to generate ATP by ATP synthase. The NADPH and ATP generated in the light reactions are used in the dark reactions, during which the absorbed CO_2 is reduced to metabolites that subsequently form sugar (Fig. 4). The net reaction of photosynthesis is the synthesis of sugar using sunlight, water, and CO_2 while oxygen is released as a byproduct.

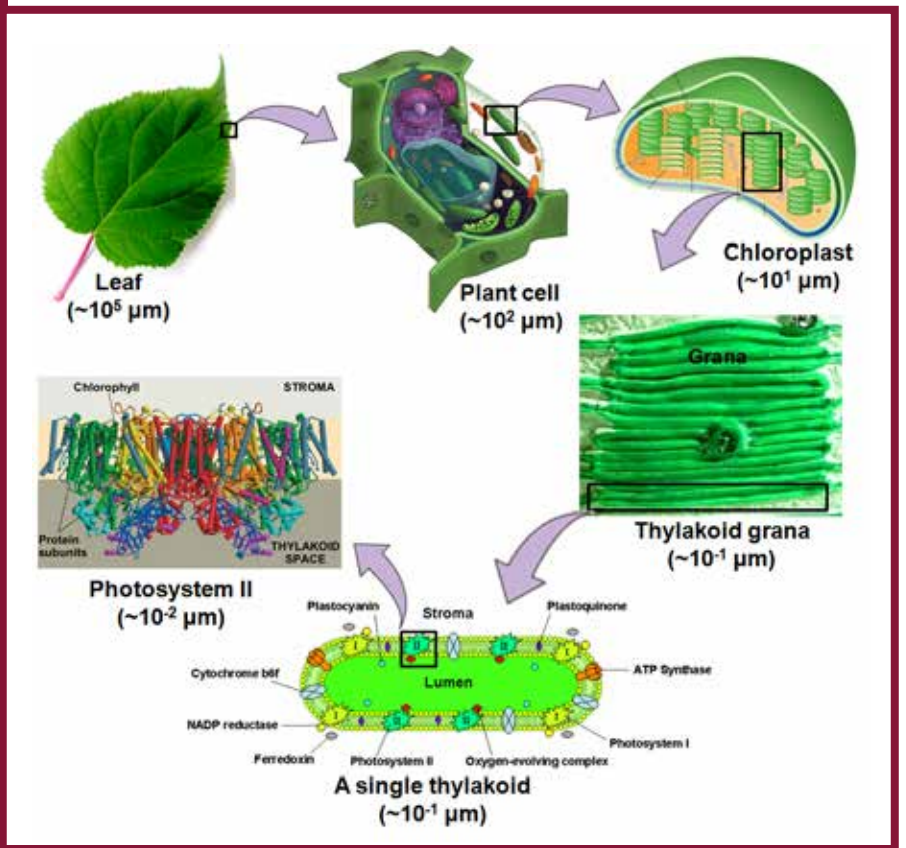

Fig. 2. *Hierarchical organization of photosynthetic machinery in thylakoids inside the chloroplast of plant cell (with relative dimensions mentioned in micrometers).*

Light energy can be harnessed in many ways using photosynthesis for either direct generation of electricity or the production of energy rich fuels like ethanol, propanol, butanol or hydrogen (Fig. 4).[2] For electricity and hydrogen generation, the light reaction is of the most concern; however, for the production of energy-rich carbon-based fuels, the dark reaction is exploited. Figure 5 shows different schemes of electricity generation in photo-bioelectrochemical cells (PBEC). The PBEC is made up of an anode containing a biocatalyst such as photosystem II (Fig. 5a), thylakoid membrane (Fig. 5b), or whole cell microorganism such as cyanobacteria (Fig. 5c) coupled with an enzymatic cathode. With the help of light, the biocatalyst on the anode transfers the electron generated from oxidation of water. On the cathode, enzymes such as laccase or bilirubin oxidase are employed that catalyze the reduction of oxygen to water. When such anodes are coupled with cathodes containing enzymes such as hydrogenase or nitrogenase, the system generates hydrogen (Fig. 5d). In either case, water and light are the only raw materials used to generate electricity and hydrogen, thereby making the system sustainable, economic, and environment friendly. On the other hand, the pathways in the Calvin cycle and the central carbon metabolism are manipulated to produce carbon based biofuels like ethanol, propanol, and butanol.

Electricity Generation

Direct conversion of light to electricity can be achieved in a photo-bioelectrochemical cell (PBEC) using natural photosynthetic machines as biocatalysts. The photosynthetic machines

include bacterial photosynthetic reaction center (RC), photosystem I and II (PSI and PSII) complexes, organelles such as thylakoids that are isolated from algae and plants, and whole cell photosynthetic microorganisms such as cyanobacteria and microalgae. When the biocatalyst used is a photosynthetic microorganism, the system is also called as photosynthetic microbial fuel cell (PMFC).[3] The PBEC systems based on the various biocatalysts (Fig. 6a) are discussed below.

Thylakoids, PSI, PSII ▸ Like any other bio-electrochemical system, the primary challenge in getting the photosynthetic machines to work on the electrode relies on the electrical communication between the biocatalyst and the electrode. The electrical communication is heavily dependent on the effectiveness of the attachment between the electrode and the biocatalyst and therefore the type of biocatalyst immobilization is of prime importance. The immobilization method determines how effectively the biocatalysts (thylakoids, PSI and PSII complexes) are tethered onto the electrode. An effective immobilization confers structural stability and retains biocatalyst activity.

Various attempts have been made to immobilize the isolated thylakoids onto different support matrices such as albumin-glutaraldehyde cross-linked matrix,[4] multi-walled carbon nanotubes,[5] encapsulating the thylakoid membrane vesicles onto conductive nanofibers by electrospinning,[6] and vapor deposition of thin layer of silica onto the thylakoid layer.[7] PSI complexes have been immobilized using several different strategies such as gold nanoparticle (GNP) modified electrode,[8] functionalized nano-porous gold leaf electrodes,[9] PSI-GNP hybrid electrode modified with 3-mercapto-1-propanesulfonic acid,[10] and via self-assembly onto zinc oxide nanomaterials.[11] The immobilization strategy is instrumental in dictating the orientation of biocatalyst on the surface as well as its proximity to the electrode. These two factors are very important for electrochemical reactions because the electron transport pathway inside the huge PSI and PSII complexes is strictly vectorial. A poly-histidine (His) tag and Ni(II)-nitrilotriacetic acid (Ni-NTA) system has been found to be profoundly useful in immobilizing PSII for its efficient photo-electrochemistry.[12-16]. Other significant improvements are witnessed by immobilizing PSII in osmium-containing redox polymer based on poly(1-vinylimidazole)[17] and a matrix of 2-mercapto-1,4-benzoquinone (MBQ), electro-polymerized on the gold surface.[18] Further, a lot of effort has been taken to maintain the activity of the isolated thylakoids and photosystems by mimicking the natural environment on the electrode[11,13] or by preventing the loss of activity through catalytic quenching of reactive oxygen species which otherwise reduces the activity of the photosynthetic machines.[19]

Photosynthetic Microorganism ▸ While relatively higher power densities were achieved using isolated photosynthetic machines such as RC, PSI, PSII or thylakoids, they are not practical for energy conversion systems due to: (1) requirement of laborious, skillful isolation procedures; (2) requirement of specific environmental conditions (pH, temperature, ionic concentration of surrounding media etc.,); (3) instability caused by photo damage; and (4) inability to self-repair upon photo damage, since they are present in an artificial environment devoid of their natural counterparts. All the above caveats can be overcome by employing the whole cell photosynthetic microorganisms in PBEC/PMFC. The whole cells retain all their native biological functions and therefore possess superior stability upon immobilization on electrode surfaces. Cyanobacteria such as *Synechococcus elongatus*,[20] *Synechocystis* sp.,[21,22] *Nostoc* sp.,[23] *Anabaena variabilis*,[24] and *Spirulina platensis*[25] and green algae such as *Chlamydomonas reinhardtii*,[26] *Chlorella vulgaris*,[27] and *Ulva lactuca*[27]are employed in the PMFC for light induced electric current generation. Compared to growing the culture of cyanobacteria in PMFCs with bare untreated electrodes,[22] growing cyanobacterial biofilm or immobilizing the cyanobacterial cells onto electrodes modified with nanostructure based support matrix such as polyaniline,[28] polypyrrole,[29] multi-walled carbon nanotubes,[23] and electrodes modified with osmium redox polymer,[30] indium tin oxide[31] have been shown to significantly improve the power density. When such an anode is combined with an oxygen reducing cathode, the oxygen evolved in photosynthesis would be subsequently reduced at the cathode and the entire system would be completely sustainable, environment friendly and requires only water and light for the generation of electricity.[23] However, the extracellular electron transport flux from P-ETC of the photosynthetic microorganisms to the electrode is fairly low compared to the extracellular electron transport flux of dissimilatory metal reducing bacteria (DMRB) such as *Geobacter* and *Shewanella* in microbial fuel cells (MFC).[32,33]. One way to address this is through the use of redox mediators such as 1,4-benzoquinone,[23,34] 2,6-dimethyl-1,4-benzoquinone,[34,35] 2-hydroxy-

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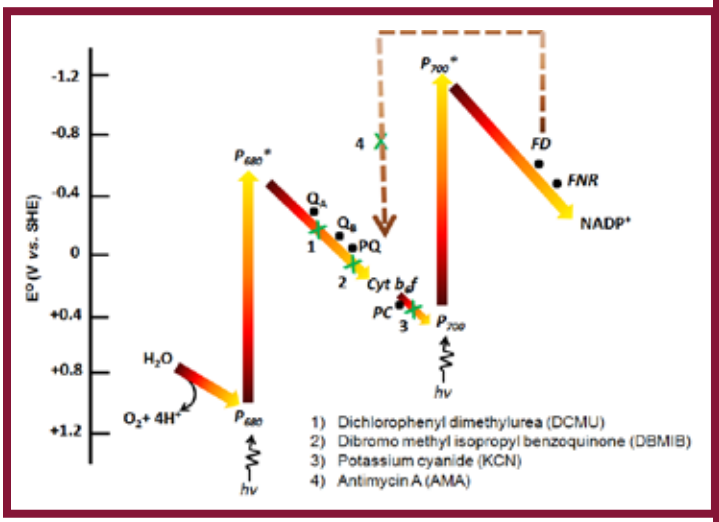

Fig. 3. *Z- scheme of linear photosynthetic electron transport chain (solid arrow) and cyclic electron transport chain around PSI (broken arrow) with all the components expressed along the redox potential scale; the green cross marks (1-4) represent the specific sites inhibited by the photosynthesis inhibitors such as DCMU, DBMIB, KCN and AMA. (P_{680}: photosystem II; P_{680}*: excited photosystem II; Q_A: Q_A site of photosystem II; Q_B: Q_B site of photosystem II; PQ: plastoquinone; Cyt b_6f: cytochrome b_6f complex; PC: plastocyanin; P_{700}: photosystem I; P_{700}*: excited photosystem I; FD: ferredoxin; FNR: ferredoxin NADPH reductase; $NADP^+$: oxidised form of NADPH; Adopted from Sekar et al. 2015[3]).*

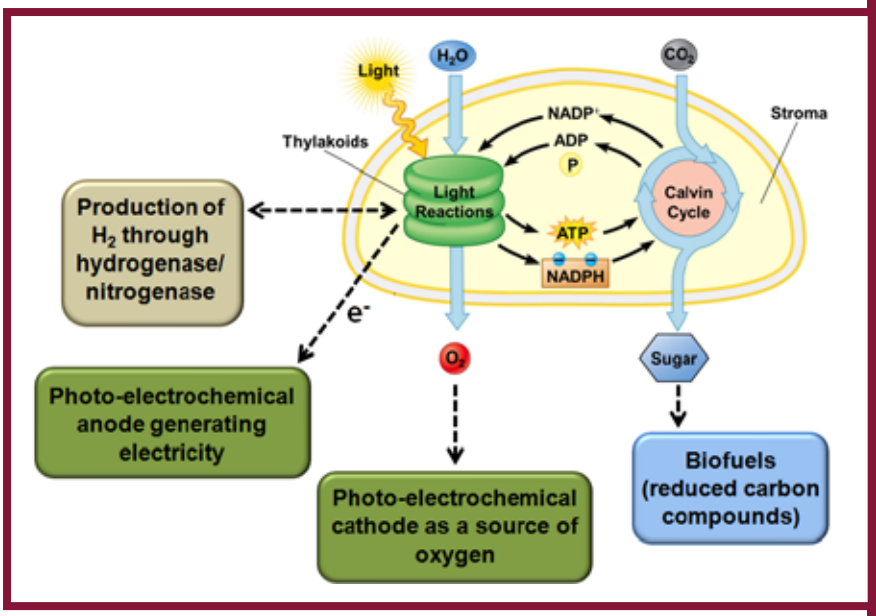

Fig. 4. *Chloroplast showing light reaction in thylakoid and dark reaction in stroma and utilization of these reactions for various applications such as generation of electricity, hydrogen and carbon based biofuels.*

1,4-napthaquinone,[20] or phenazine methosulfate[36] that are permeable through the outer membrane of the living cell and greatly enhance the power density. However, from an energy conversion standpoint, the use of redox mediators decreases the overall cell voltage and therefore is not attractive. Moreover, mediators must be regenerated constantly, which introduces additional complexity to the system and hence is not attractive from a design standpoint. High power density can also be achieved by engineering a novel miniaturized systems such as microfluidic bio-photovoltaic devices[37] and micro-sized bio-solar cells,[38] however these systems are only suited for ultra-low power applications.

Genetic Engineering ▸ Regardless of the mode of extracellular electron transport (direct or mediated), the PMFC generally suffers from low electron flux because the electrons must be diverted from their native routes to alternate pathways to reach the electrode. These alternate electron-harvesting pathway are very difficult to achieve. A robust approach to efficiently collect more electrons from the P-ETC without using the redox mediators would be a welcome strategy to improve the performance of PMFC on par with that of MFC.[1,39] The photosynthetic microorganisms such as cyanobacteria have been performing photosynthesis for over 3.5 billion years. However they have not evolved for extracellular electron transport. Nonetheless, with the advancement of genetic engineering and molecular biology, these smart microorganisms can be made smarter to benefit our needs to generate more electricity. Analyses of electron transfer pathways from the P-ETC to the electrode leading to photocurrent generation on the PMFC anode would greatly help in understanding the mechanism of extracellular electron transfer as well as other bottlenecks which facilitates further optimization for enhancing photocurrent. This can be accomplished with the help of site-specific photosynthesis inhibitors that block a specific pathway in P-ETC as shown in Fig. 3. Using these inhibitors both individually as well in certain combinations, more precise source of photocurrent can be ascertained[5,23,40,41] and is very useful to engineer appropriate strategy to improve the photocurrent. For example, diverting electrons from earlier steps in P-ETC, say from PSII complex, contributes to more photocurrent and the conversion efficiency can be further increased (Table 1). Accordingly various efforts have been undertaken to collect more electrons from PSII.[42]

Certain genetic engineering approaches have been used to redirect the electrons from the photosystem complexes, thereby manipulating P-ETC for generating higher photocurrent. Electrons from Q_A^- in PSII were redirected to engineered collection sites approximately 13 Å away on the stromal side of the thylakoid membrane.[42] The positively charged amino acid lysine (Lys, K) at position 238 of D1 protein in PSII is important for the insulation of the PSII electron flow from external oxidation by soluble species and is also highly conserved in PSII of higher plants and algae. Modification of this lysine to glutamate (Glu, E), i.e., K238E resulted in alternative electron transfer pathway to soluble electron acceptor protein (cytochrome c) near the Q_A^- site.[42] This redirection along with the addition of an herbicide that blocks the electron flow at Q_B site resulted in decreased oxidative damage. In another attempt, cationic redox-active metal complexes

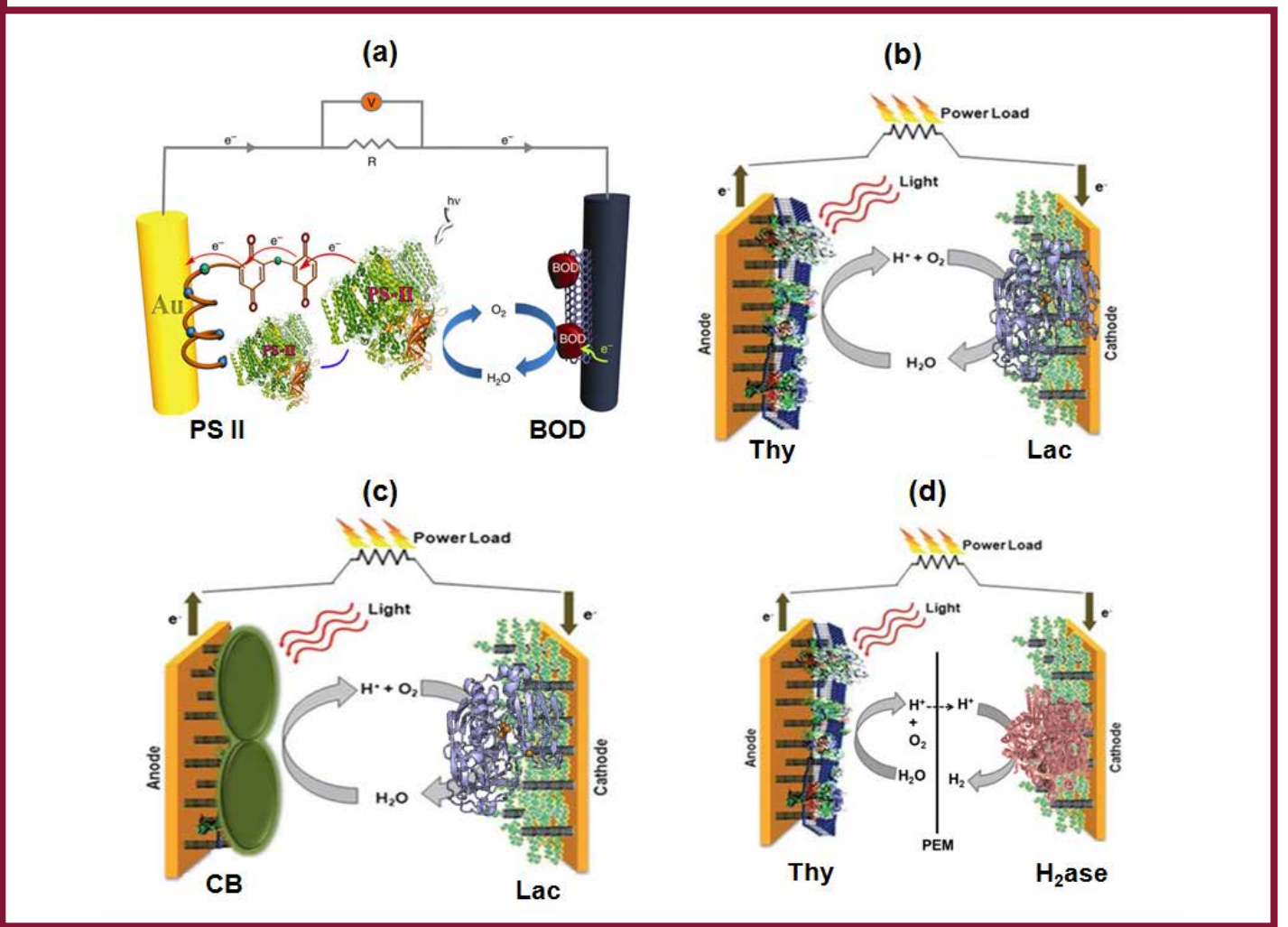

Fig. 5. *Schematic showing different photo-bioelectrochemical cell architectures for photosynthesis based electricity generation using biocatalysts such as (a) photosystem II (PSII);[18] (b) thylakoid (Thy);[5] (c) whole cell photosynthetic microorganisms like cyanobacteria (CB)[2] on the anode and enzymatic cathode employing laccase (Lac) and bilirubin oxidase (BOD); (d) hydrogen generation using thylakoid (Thy) on the anode and hydrogenase (H_2ase) on the cathode (PEM: proton exchange membrane).*

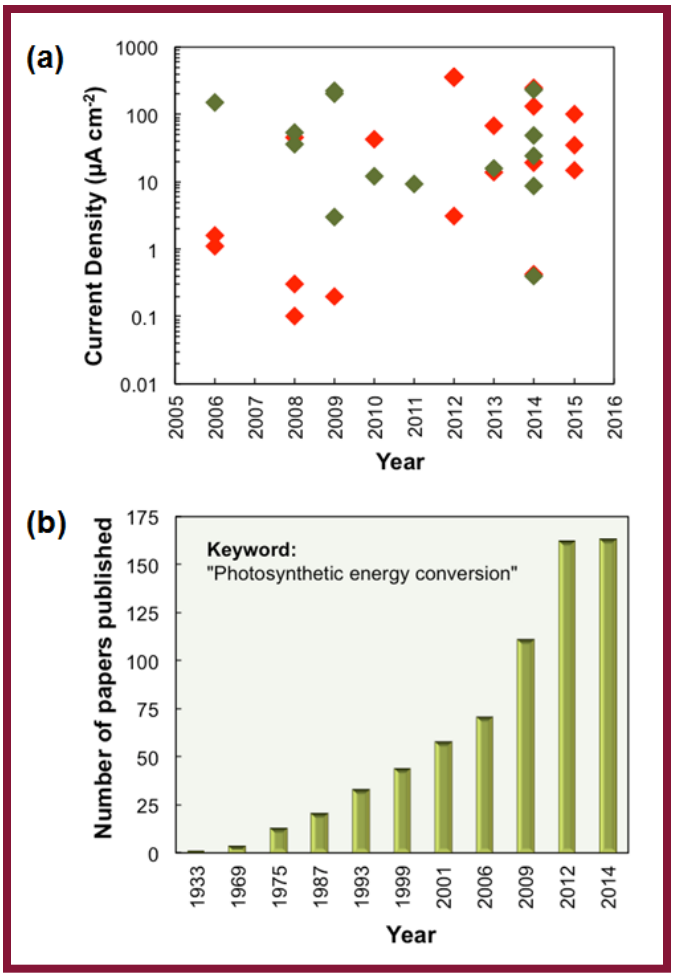

Fig. 6. *(a) Current density achieved in photo-bioelectrochemical cells in the last decade using thylakoids or photosystems (red filled marker) and whole cell microorganisms such as cyanobacteria or microalgae (green filled marker) as a biocatalyst on the anode; (b) Number of papers published in the research area of photosynthetic energy conversion (data collected from Web of Science database using the keyword "photosynthetic energy conversion").*

like Co^{III} complexes, small enough to fit in a 5 Å diameter negatively charged patch along the stromal side of the membrane were also used to redirect electrons from Q_A^- site.[43]

Cyanobacteria, algae and green plants contain chlorophyll-a (Chl-a) as the primary photosynthetic pigment in their PSI and PSII complexes. Chl-a strongly absorbs only blue (430 nm) and red (670-680 nm) lights. Light harvesting complexes in algae and green plants and phycobilins in cyanobacteria contain accessory pigments that absorb visible light in the range of wavelengths neglected by the Chl-a, thereby increasing the action spectrum of photosynthesis. In any case, they cannot absorb light beyond the red end of visible spectrum. However, another class of photosynthetic bacteria such as green bacteria and purple bacteria contain bacteriochlorophylls (BChl) that absorb strongly in near infrared region spectrum (705–1040 nm range). Further, Chl-a present in both PSI and PSII compete for the same light which theoretically reduces the efficiency by half. Replacing one of these Chl-a in the photosystems with BChl could effectively enhance the existing efficiency by a factor of two, similar to the multi-junction solar cell with different bandgaps and greatly broadens the action spectrum of photosynthesis to the near infra-red region.[1] Besides the recommendation and discussion of the prospects this genetic modification could bring, no attempts have been made yet in this pursuit.

An interesting feature unique to cyanobacteria is that both P-ETC and R-ETC are functional in their thylakoid membrane. The photosynthesis and respiration reactions share certain components such as plastoquinone pool, cytochrome b_6f complex and cytochrome c_6 or plastocyanin.[44] This peculiar organization in cyanobacteria is the primary reason for its capability to generate electricity under both light and dark conditions[23] unlike PBEC based on isolated thylakoids, PSI and PSII, which can generate electricity only in light. The light-induced generation of electrons in P-ETC can be used up by either quinol oxidase or cytochrome oxidase in R-ETC and vice versa. Indeed the overlapping of photosynthesis and respiration is a protective mechanism evolved to handle excess electrons.[40,45] The photocurrent generated by live cyanobacteria can be attributed to the overflow of the excess electrons from the P-ETC on excessive light absorption.[40] From a PMFC perspective, the R-ETC can be considered as a competitive pathway for electron transport that decreases the electron flux to the electrode thereby decreasing the photocurrent generation. Some or all of the competing oxidases in R-ETC were knocked out of cyanobacteria through genetic manipulations that resulted in more electrons being available for photocurrent generation.[46] Further, the superior electron transfer ability of DMRB such as *Geobacter* and *Shewanella* can be predominantly attributed to the cytochromes present in their outer membrane collectively called as outer membrane cytochromes (OMC). Imparting these efficient extracellular electron transfer ability of DMRB to cyanobacteria through genetic manipulations can be a ground breaking and remarkable milestone in cyanobacterial photosynthetic energy conversion. Recently, one such novel and innovative manipulation has been successfully carried out by our group.[47]

Hydrogen and Other Biofuels

Hydrogen is one of the most attractive alternate energy carriers that are expected to replace fossil fuels for transportation applications. Currently, the production of hydrogen is carried out through conventional steam reforming, electrolysis and thermolysis. All these three methods are expensive and operate at high temperatures and pressures. Steam reforming uses hydrocarbons, which are non-sustainable, and generates CO_2 as byproduct. On the contrary, photosynthesis based hydrogen production is carried out at ambient temperature using photosynthetic microorganisms which generates hydrogen as part of their metabolism by simultaneously sequestering CO_2 in a photobioreactor.[48] Further, cyanobacteria such as *Synechocystis* are employed in bio-photoelectrolysis cells[49] for generating hydrogen. In vivo, hydrogen is produced with the help of metallo-enzyme complex called hydrogenases, which catalyze the reversible oxidation of hydrogen to protons and electrons. Hydrogen is also produced as a by-product during nitrogen fixation by other enzyme complexes called nitrogenases in nitrogen fixing cyanobacteria such as *Cyanothece* and *Anabaena*. The ferredoxin in the P-ETC is the electron donor for both nitrogenases and hydrogenases. In vitro, the photosynthetic route for hydrogen production would involve an electrochemical full cell with photosynthetic machinery such as PSII as biocatalyst on the anode and enzyme that can catalyze the reduction of protons such as hydrogenase on the cathode as shown in Fig. 7. To date, the highest production rate was achieved by Melnicki et al. (2012), who witnessed sustained H_2 production by a unicellular cyanobacterium *Cyanothece* through photosynthetic process in an electrochemical cell. Under continuous illumination and a nitrogen-deprived environment, cyanobacteria cells in the photo-bioreactor generated H_2 at the rate of 400 μmol/mgChl/h.[50] Though the production of H_2 through photosynthetic means is quite inspiring and challenging, a huge leap in productivity is required for this technology to supersede the conventional production of H_2. With the advancement of metabolic engineering and synthetic biology, attempts are being carried out in cyanobacteria namely *Synechococcus elongatus* PCC 7942 and *Synechocystis* sp. PCC 6803 to synthesize complex biofuels and biofuel precursors such as ethanol,[51,52] 1,2-propanediol,[53] 1-butanol,[54] 2-methyl-1-butanol,[55] isobutyraldehyde and isobutanol.[56] More literature for biofuel production in cyanobacteria has been found in reviews such as those by Machado and Atsumi (2012).[57]

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Concluding Remarks

Photosynthetic energy conversion is a sustainable, renewable, clean and environment-friendly process. It has an enormous potential to be an alternative energy technology that could effectively replace the finite fossil energy. The field of research has already witnessed major breakthroughs towards generating electricity, hydrogen and other chemical fuels (Fig. 6b). However the technology is still primitive and the performance parameters such as power density, biocatalyst stability, and output require huge improvements before the technology can be considered for any practical application. Modern genetic engineering tools offer prospects for engineering the biology towards enhanced energy conversion. There have been a few endeavors towards this outlook, but more interdisciplinary research work encompassing molecular biology, protein engineering and metabolic engineering along with electrochemistry is required to reach a paradigm shift towards realizing a true biological solar cell based on natural photosynthesis as an alternative power source.

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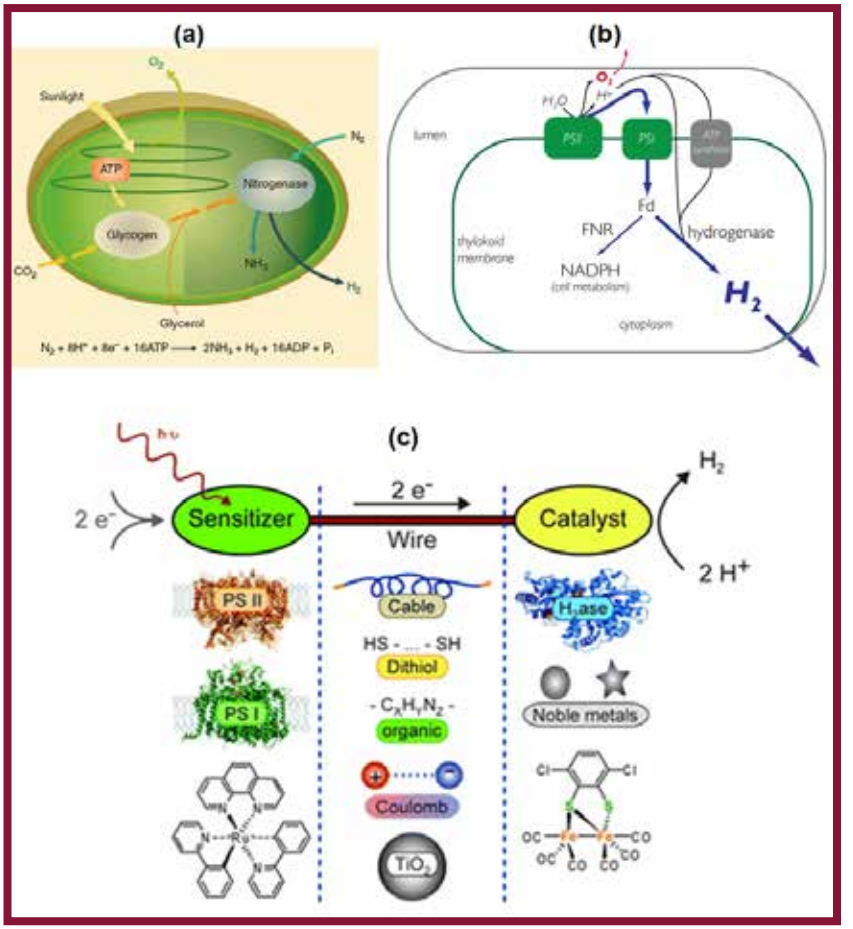

Fig. 7. *Photosynthesis based hydrogen generation in vivo using (a) nitrogenase; (b) hydrogenase; and (c) in vitro by combining photosystem (PSII/PSI) and hydrogenase (H_2ase).*[59]

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