Chapter

Artificial Photosynthesis an Alternative Source of Renewable Energy: Potential and Limitations

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Abstract

Artificial photosynthesis system (APS) uses biomimetic systems to duplicate the process of natural photosynthesis that utilizes copious resources of water, carbon dioxide and sunlight to produce oxygen and energy-rich compounds and has potential to be an alternative source of renewable energy. APS like natural photosynthesis includes the splitting of water into oxygen and hydrogen, and the reduction of carbon dioxide into various hydrocarbons such as formic acid (HCOOH), methane (CH_4) and carbon monoxide (CO), or even pure hydrogen fuel. These processes are accomplished by a handful of device designs, including photoelectrochemical cells or photovoltaic-coupled electrolyzers which are driven by energy extracted from sunlight photons as well as suitable catalysts. Researchers are trying to combine advantageous components from both natural photosynthesis and artificial photosynthesis to create a semi-artificial photosynthesis system, involving the incorporation of enzymes or even whole-cell into synthetic devices. However, there are several limitations to the advancement of this field which are mainly centered on the inability to establish a system that is cost-effective, long-term durable and has the highest efficiency. Artificial photosynthesis devices can also function as atmospheric cleansers by extracting the excess amount of carbon dioxide and releasing back oxygen into the environment. Although there is still a long way to go to empower society with energy supplied through artificial photosynthesis, at the same time it is both desirable and necessary. To date, the efforts to commercialize APS have been fruitful, and it will soon be a viable alternative fuel source.

Keywords: artificial photosynthesis system (APS), biomimicry, photocatalyst, photosynthesis, photons, water oxidation

1. Introduction

In this technological era, it has become mandatory to safeguard our natural resources and search for renewable sources of energy that can reduce the use of conventional fossil fuels. The usage of fossil fuel emits large quantities of carbon dioxide, sulfur dioxide and oxide particles as well as depletes natural resources. The International Panel on climate change recommended the urgent need to decrease

carbon dioxide emissions to zero on a global scale. To combat this grieving situation the development of sustainable and carbon-neutral energy technologies is the most compelling challenge faced by the entire humanity. Over the years, scientists have explored numerous alternatives that could possibly reduce our dependence on fossil fuels. Recently, efforts are centered toward the development of high-tech energy-generating systems inspired by nature itself. Nearly all natural resources are either depleting or getting contaminated except the solar energy which on conversion or utilization is a promising solution for energy-related problems.

One such phenomenon or reaction that takes place in plants, algae and photosynthetic bacteria to produce energy for themselves and provide energy to other organisms is photosynthesis. To mimic photosynthesis, the concept of artificial photosynthesis was introduced by Giacomo Ciamician way back in the year 1912 in a science paper entitled "The photochemistry of the future" [1]. He visualized and insisted on the use of technologies that can eliminate complete dependence on fossil fuels. Solar power stations could meet the challenges of sustainable energy more over the cost is lower than that of nuclear and thermal plants but the main bottleneck is the lack of efficient storage solution [2]. Different studies established systems to carry out photosynthesis similar to that of solar panels and convert it into electricity for direct application, as it was not possible to store energy for later use. So far, researchers have not been able to devise solar-driven catalysts for water oxidation and fuel production that are vigorous and use this abundant earth element.

Artificial photosynthesis system (APS) imitates the fundamental process of photosynthesis taking place in organisms for our societal needs. APS captures as well as stores solar energy in the form of fuel rather than glucose and is able to meet both the challenges of being carbon-negative and a source of solar fuel (**Figure 1**). Artificial photosynthesis devices involving semiconductors can absorb solar energy and store it by converting in the form of chemical energy which can be used later. Many

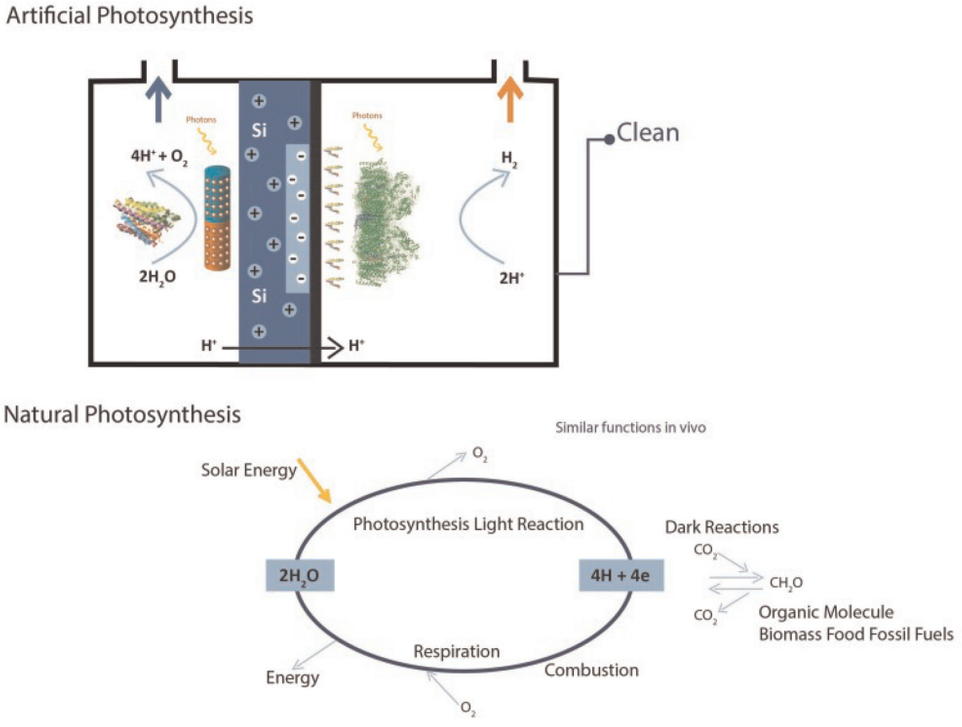

Figure 1.
An outline diagram to compare natural and artificial photosynthesis.

advancements have been achieved where artificial reaction center involving the movement of electrons (injected from a dye) into the conduction band of nanoparticles (such as titanium dioxide) on to electrode coupled with catalyst (such as platinum) or hydrogenase enzymes producing hydrogen gas. This system involves solar energy to split the water molecule into oxygen and hydrogen fuel; however, the efficiency is quite low and requires external electrical potential. The energy stored in this way is cheap and dense as compared to expensive battery storage [3]. Besides these APS is more environmentally attractive than solar panels as it absorbs excess carbon dioxide from the environment and releases oxygen back into the environment and can revolutionize the world of solar power [4]. This chapter includes a comprehensive view of the artificial photosynthesis system, its limitation, challenges and the future scope of APS as an alternate source of energy.

2. Photosynthesis: nature's marvel

Green plants, algae and photosynthetic bacteria are photosynthesizing for more than a billion years without any significant change. Photosynthesis is an integral part of simulation models to safeguard the future of our planet. The electron transport system of photosynthesis transports electrons faster than the photons of solar energy reaching light-harvesting complex present in the chloroplast membrane. The light reaction takes place in three distinct protein complexes which are an integral part of the chloroplast membrane of higher plants viz., two light-harvesting complexes or photosystem (LHC I/PS I and LHCII/PSII) or antennae and cytochrome b_6f connected by different electron carriers. Both the photosystems or light-harvesting complexes transfer photons to the reaction centers (RCs) in the form of resonance energy and create charge differences across the membrane. A strong oxidant complex commonly referred to as oxygen-evolving complex (OEC), is present on the donor side of PSII which does photolysis of water into molecular oxygen, protons and electrons. This electron moves to the plastoquinone pool to cyt b_6f followed by plastocyanin to PSI and finally via ferrodoxin reduces $NADP^+$ to NADPH. The electron movement is coupled with proton pumping from one side of the membrane to the other side of the membrane creating a potential and pH difference across the membrane ultimately leading to the formation of ATP [5]. This assimilatory power trapped in the light reaction is utilized for the unique process of fixation of atmospheric carbon dioxide by the enzyme Rubisco, the most abundant protein on this earth. The enzyme Rubisco has a very slow catalytic rate (1–3 cycles per second) creating a major bottleneck in increasing photosynthetic efficiency. The unique feature of this fundamental process of life is the structural features of RCs complexes constituting a network of molecular cofactors held by the membrane at an appropriate distance and orientation to capture maximum light and perform the movement of electrons (**Figure 2**). This mosaic structure is such a unique nanoscale complex working perfectly for billions of years and providing energy to all the heterotrophs residing on this planet. To exactly mimic the complete process of photosynthesis is definitely an undaunted task.

3. Artificial photosynthesis

The concept of artificial photosynthesis was given by an Italian chemist in 1912 but no remarkable research has been done till 1972 when Kenichi Honda and his student

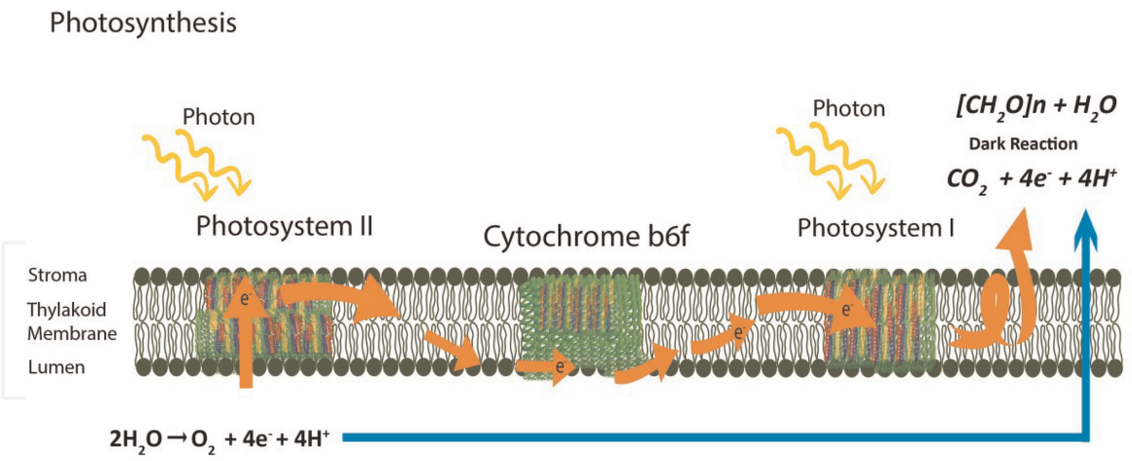

Figure 2.
The diagrammatic representation of different complexes involved in electron transfer in the Z scheme present on the membrane of thylakoid in the chloroplast. The photosystems PSI and PS II and intermediate carrier of the electron, cytochrome b_6f, sand witched between them is the key structural organization of RCs. The complete structure is present in the membrane protein scaffold at an appropriate distance to facilitate electron transfer and convert solar energy to chemical energy.

Akira Fujishima for the first time reported the successful designing of water splitting device powered by light [6], which was named as "Honda-Fujishima effect". The device includes a photoelectrochemical cell comprised of a photoanode made of TiO_2 and a black cathode made up of platinum (Pt) black cathode. Both anode and cathode were completely submerged during exposure to light, an electron was released from TiO_2 leading to the formation of an "electron hole", or positive charge on the Ti atom which was filled by an electron released from a water molecule, oxidizing the water to produce oxygen. The released electron was donated to a proton derived from water, thus reducing the proton to form hydrogen. The light of wavelength more than

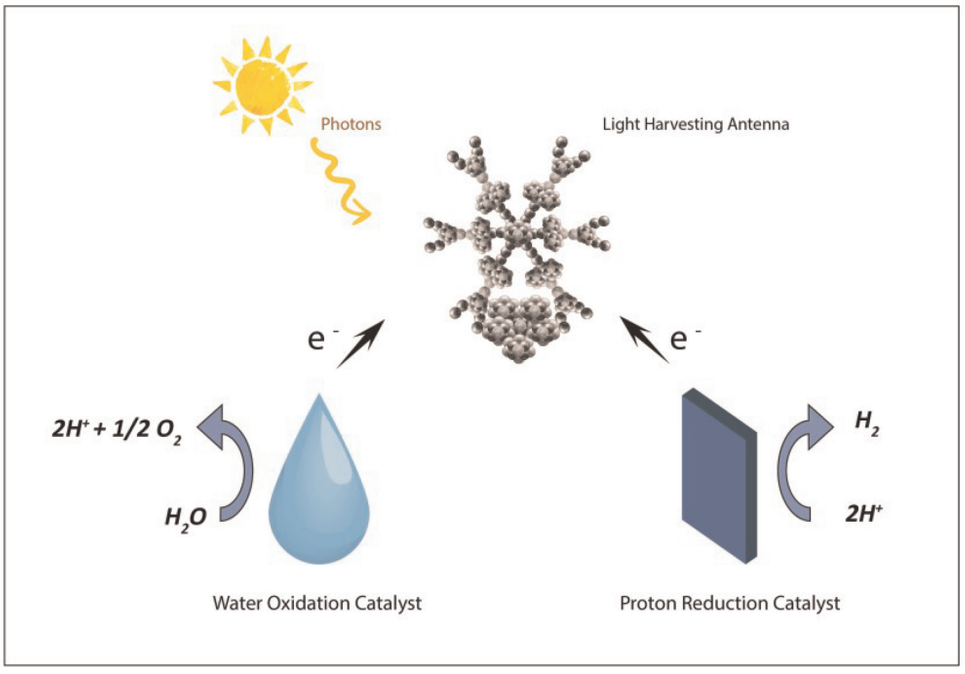

Figure 3.
The diagram representing the fundamental process of artificial photosynthesis systems having an efficient light absorber to trap sunlight and efficient water oxidation and proton reduction catalysts.

400nm was given to the photoanode and the device was able to generate oxygen at the anode while hydrogen was generated at the cathode by photolysis of water and ultimately releasing oxygen and hydrogen [7] as summarized in **Figure 3**. The major bottleneck of using the molecule TiO_2 was that it only absorbed ultraviolet wavelengths and is inactive in visible light wavelength [8].

In 1978, M. Halmann used a p-type phosphide semiconductor made of gallium phosphide as the photocathode suspended in an aqueous solution and achieved the reduction of carbon dioxide into hydrocarbons such as formic acid (HCOOH), formaldehyde (CH_2O) and methanol (CH_3OH) [9]. In 1983, William Ayers designed and patented the first visible light water-splitting device named as "artificial leaf" made up of silicon with a nafion membrane for ion transport above the cell. The entire structure is immersed in water and when illuminated results in the release of oxygen from the back of the metal surface, while hydrogen evolved on the silicon surface [10].

4. Artificial photosynthesis: principle

As mentioned above the three principle steps involved in artificial photosynthesis, similar to natural photosynthesis, are the absorption of light causing excitation, charge generation followed by charge separation and finally chemical conversion leading to the production of fuel.

4.1 Light absorption

In natural photosynthesis, chlorophylls and carotenoids are arranged in antennae to capture the maximum red and blue wavelength of light and bring about the excitation of electrons. These pigment molecules can absorb only a limited range of wavelengths ranging from about 400 to 700 nm which makes less than 50% of the sunlight that reaches earth [11]. The first major task is to design photosensitizers that can optimally use photons on exposure and are capable of aggregating light energy. In addition, the materials used should be capable of absorbing a wider wavelength of the solar spectrum so as to extract maximum energy falling on the earth.

Inspired by the "Honda-Fujishima effect", many materials such as TiO_2 photoanode semiconductors like silicon, metal oxides such as ZnO, Fe_2O_3 and $BiVO_4$, metal nitrides such as Ta_3N_5, metal phosphides such as GaP, metal oxynitrides such as TaON etc., have been tried by a different group of researchers [12]. Silicon, an abundant and cheap source, can absorb a wider spectrum of light. Another semiconductor Gallium Nitride has been used to produce formic acid and ethanol using thin film technology [13].

4.2 Lysis of water

Water oxidation is a thermodynamically uphill process and requires free energy of $\Delta G \approx 237$ kJ mol^{-1} and potential $E0 \approx 1.23$ V to transfer $4H^+$ and $4e^-$. In natural photosynthesis, water splitting is achieved through the involvement of an oxygen-evolving complex (OEC) which has manganese (Mn), a tetrameric high valent oxo species, that catalyzes oxygen-oxygen bond formation. Semiconductor nanowires are used to absorb light resulting in the oxidation of water producing oxygen, proton and electrons. The electrons move toward other ends while protons move through a proton-conducting membrane made up of Nafion, ultimately reduced to hydrogen.

Thus, photolysis of water in APS is achieved through the combination of two different customized systems for their respective purpose [12].

The redox equations involved in water splitting are as follows:

$$\text{Oxidation reaction} : 2H_2O \rightarrow 4e^- + 4H^+ + O_2$$

$$\text{Reduction reaction} : 4H^+ + 4e^- \rightarrow 2H_2$$

$$\text{Redox reaction} : 2H_2O \rightarrow 2H_2 + O_2$$

The splitting of water needs an energy of approximately 2.5 V, hence a catalyst is essential to absorb photons of sunlight and set off the reactions [14]. The bioinspired approach of using manganese as a catalyst resulted in instability due to short-term and inefficient function [15]. In comparison, cobalt oxide (CoO) found to be stable, efficient and is easily available [16].

Different materials tested show efficiency in some steps and inefficiency in other steps leading to the use of coupled materials, which are customized for their respective reactivity. Recently, molecular water-oxidation catalysts are designed for splitting water and evolution of oxygen. These catalysts generally comprise a metal complex with wide open coordination sites as well as an electronic structure to stabilize a metal-hydride intermediate. The most common materials used are noble metals such as rhodium and platinum-based complexes. To develop catalysts from earth-abundant metals such as cobalt, iron, molybdenum, and nickel have also been tried by various scientists. The most stable and efficient catalyst out of many tried and tested is Nickel complexes. Ruthenium and iridium-based catalysts showed good reactivity and stability but are scarce and expensive [17]. The transition metal family such as copper, nickel and iron-based were tested in order to improve the catalytic function. Cobalt and Zirconium heterobimetallic on porous silica separated by nanotube separation membranes was also used by researchers [18]. However, the search and optimization of materials to be used in APS are still under investigation.

4.3 Reduction of carbon dioxide

Carbon dioxide is a linear, highly stable molecule having very low electron affinity. Conversion of carbon dioxide is an uphill reaction and requires a nucleophilic attack on the carbon atom, the dissociation bond energy of C═O is ~750 kJ/mol. The carbon atom has the highest valence due to which different fuels can be created in addition to the production of oxygen and hydrogen derived from water. The different fuel compounds that can be generated are formic acid (HCOOH), methanol (CH_3OH), carbon monoxide (CO) and methane (CH_4) as given in these equations:

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$$

The generation of these liquid hydrocarbons has added advantage of being easily integrated into energy infrastructure. Nevertheless, the greatest scientific challenge due to carbon's multi-electron nature imposes additional complexity [19]. The exact

mechanism is not clearly established but it is predicted that the reduction of carbon dioxide is similar to water splitting during the process of photosynthesis. In APS, carbon dioxide interacts with catalyst along with the transfer of electrons resulting in a reduction reaction followed by proton coupling creating an electron hole in the photosensitizer which is filled by an electron leading to the end of the process [20]. A co-catalysts and photoelectrode material break carbon and oxygen bonds and form carbon and hydrogen bond i.e., C—H bond. The choice of catalyst is very critical in APS which includes low cost and durability. Researchers have tried various combinations of complexes viz., rhenium-based, cobalt-based, nickel-based, iron-based and zinc-based complexes [21]. With the use of innovative porous materials adsorption of intermediates at the surface of the electrode is significantly enhanced. In another trial, co-catalyst such as copper, silver and gold were found to be very effective in enhancing conserving efficiency. However, an ideal catalyst is yet to design which can improve the performance of chemical conversion (**Figure 4**).

5. Natural photosynthesis vs artificial photosynthesis

Photosynthesis involves two reactions viz, light-dependent (light reaction) harnessing light photons and converting it in assimilatory powers in the form NADPH (nicotinamide adenine dinucleotide phosphate) and ATP (adenosine triphosphate) which are utilized to fix carbon in light-independent reaction (dark reaction). The light reaction involves two photosystems, viz., PSI and PSII (photosystem I and II) consisting of light-absorbing pigments in the form of antennae system involving chlorophylls and carotenoids and have a reaction center having chlorophyll a molecule. The two photosystems are present in the thylakoid membrane along with other electron carriers, absorb light photons and transfer the energy to the reaction center through resonance energy transfer and release an electron from chlorophyll molecule

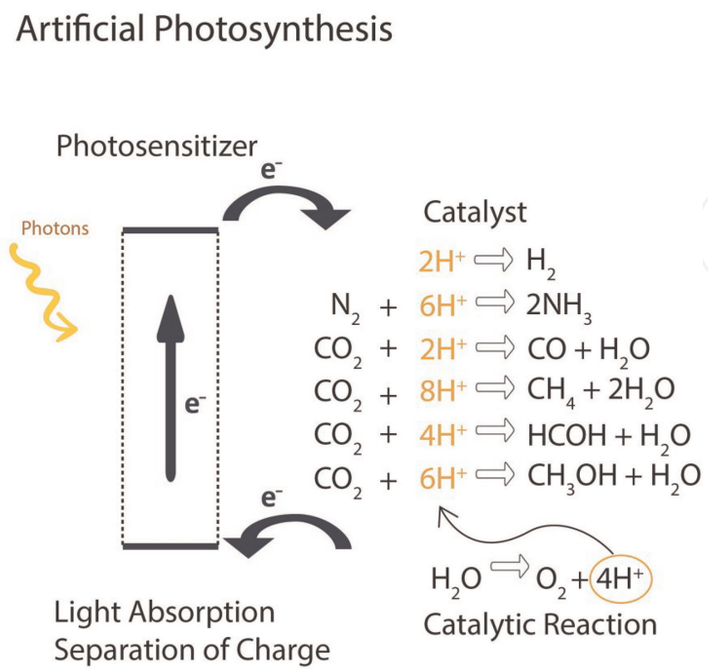

Figure 4.
The formation of different end products due to the reduction of carbon dioxide catalyzed by different catalysts in artificial photosynthesis.

from the reaction center. This electron moves through a series of electron carriers and finally reduces NADP into NADPH and the formation of ATP. The removal of electrons from chlorophyll results in the formation of "electron hole" in the chlorophyll pigment which is filled by photolysis of water by oxygen-evolving complex present next to PSII releasing an electron and oxygen as a waste product for the plants and the most valuable by-product for the survival of life on this biosphere. This light-dependent reaction also involves a complex array of enzymes such as the photosystems themselves, as well as hydrogenases which interact with hydrogen derived from water molecules, is known as photophosphorylation; a unique system of generation of chemical energy present only in photosynthesizing organisms [4, 5].

The assimilatory powers being generated during light reaction then bring about a reduction of carbon through the light-independent reaction or dark reaction involving the Calvin cycle. The dark reaction, discovered by Malvin Calvin, occurs in the stroma of chloroplast through a series of reactions catalyzed by different enzymes to transform carbon dioxide from the atmosphere into carbohydrates. The carbon dioxide is absorbed by the stomata present on the leaves and ultimately converted into carbohydrates, the overall reaction of photosynthesis is

$$6\,H_2O + 6\,CO_2 \xrightarrow[\text{Chlorophyll}]{\text{Sunlight}} C_6H_{12}O_6 + 6O_2$$

Thus, photosynthesis is ingeniously designed through series evolution to provide autotrophic organisms to produce their own food by converting solar energy into chemical energy stored in the energy-rich bonds of a carbohydrate.

Three major components of natural photosynthesis that need to be imitated by artificial photosynthesis are (i) light capture and electron transport (ii) water splitting (into hydrogen and oxygen) and (iii) reduction of carbon dioxide. Two types of fuel are being generated through APS viz., hydrocarbons (methanol and formic acid) and pure hydrogen. Hydrogen is a clean option generated via APS and can be used directly as liquid fuel, consumed in the fuel cell, thermal processes, electrolysis, biological processes and other application to substitute fossil fuel [2, 22].

6. Solar harvesting devices vs artificial photosynthesis

Various efforts have been made to design the devices with the aim to convert solar energy into chemical energy which is stored in chemical bonds. The two most powerful devices designed by researchers are the photoelectrochemical cell and photovoltaic-coupled electrolyzer. Both the systems are designed on certain similarities and differences as well as having advantages and limitations which are discussed here.

6.1 Photoelectrochemical cell

The photoelectrochemical cells (PEC) consist of two electrodes, a photoanode and a photocathode immersed in an electrolyte and an external wire [19, 22]. One of the variants designed comprises a single electrode evolving mixture of oxygen and hydrogen which entails contamination which is an additional step of separating hydrogen and oxygen. The reduction of carbon dioxide by PEC is the most efficient method involving the amalgamation of photo and electrocatalysis, an addition of

biocatalysts enhanced its efficiency further. The photoelectrodes are constructed using either a molecular electrode or a light-absorbing semiconductor [23]. At the photoanode, water splits to get oxidized to form oxygen while it is reduced to form hydrogen at the photocathode. On exposure to solar energy excitation at the photoanode releases an electron which is donated to water leading to the reduction of hydrogen molecules at the photocathode. The "electron hole" created at the photoanode is filled by an electron donated by water molecule oxidation ultimately leading to the production of oxygen (**Figure 5**).

The material of the photoanode has a tremendous effect on water-splitting efficiency, stability and absorption of visible light in an aqueous solution (**Figure 6**). A membrane composed of Nafion, having proton-conductive and separation properties, has also been tried in some photoelectrochemical cells. Even semiconductors have also been tried but found to be having low efficiency, instability and only narrow visible light can be adsorbed. Therefore, the criteria of selection shifted toward carbon-based, transition metals, and nanostructured photoanodes e.g., carbon-based materials, graphene, carbon nanotubes, carbon dots and carbon quantum dots all demonstrated stability as well as photocurrent generation. In addition, transition metals such as germanium-doped hematite, cadmium sulfide, zinc oxide, copper sulfide and molybdenum exhibited high performance due to their high electrical conduction and electrochemical stability. Nanomaterials such as nanowires, nanotapers and nanorods also exhibited excellent performance in terms of high hydrogen evolution at photocathode [24]. A serially coupled PSII and PSI along with an Au electrode has been developed recently where semi-artificial PECs produced photocurrent and imitated Z scheme of natural photosynthesis, interfaced by two types of redox osmium complex hydrogel for the transfer of electrons [23].

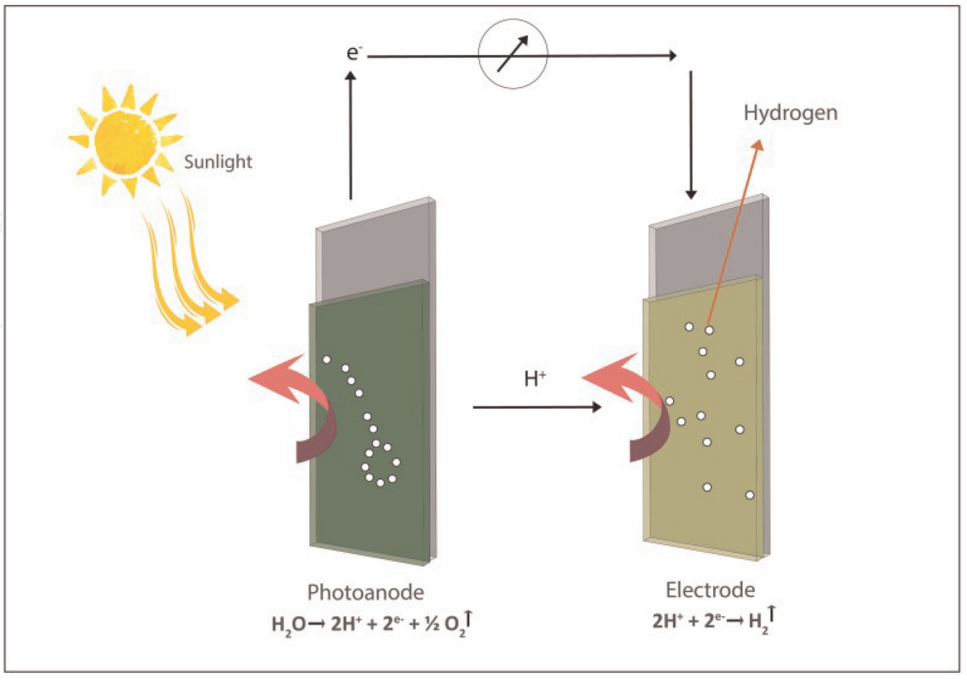

Figure 5.
The working principle of a photoelectrochemical cell where the charge separation is induced by light which leads to water splitting releasing molecular oxygen, proton and electrons. The protons move to the cathode where it is reduced to molecular hydrogen and electrons.

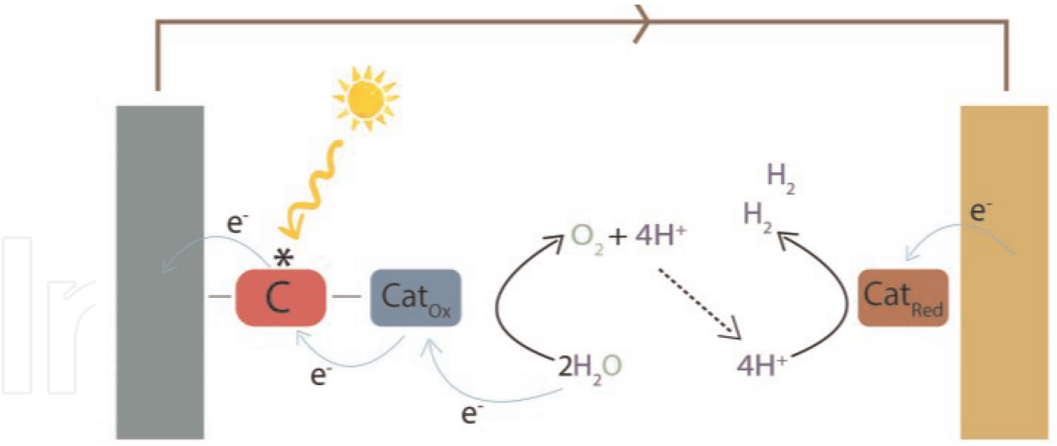

Figure 6.
A modified photoelectrochemical cell having a molecular chromophore and catalyst for water splitting. C is excited chromophore C which transfers electrons and leads to water splitting.*

6.2 Photovoltaic-coupled electrolyzer

A photovoltaic-coupled electrolyzer working principle is based on the working of both solar and electrochemical cells [13, 25]. The photovoltaic cell includes absorption of light as well as charge separation. The energy potential generated by the photovoltaic cell is transferred to an electrolyzer for redox reaction [26]. Thus, in the first step solar radiation is converted into electricity, which is further used for the oxidation and reduction of water or carbon dioxide in the electrolyzer cell. This system has the more efficient strategy and has remarkable solar-to-hydrogen efficiencies of 10–15%, reaching as high as 30%. This ultra-efficient photovoltaic-coupled electrolyzer system utilizes a triple-junction solar cell which is made of three subcells having indium gallium phosphide (InGaP), gallium arsenide (GaAs) and gallium indium nitrogen arsenic antimonideGaInNAs(Sb), respectively. This solar cell involved two polymer electrolyte membranes consisting of a Nafion membrane coated with Pt black catalyst at the cathode and an Ir black catalyst at the anode [27]. The power generated at the triple-junction cell pumped water into the anode of the first electrolyzer and effluent having water and oxygen is further pumped into the second electrolyzer where hydrogen is transferred from the first electrolyzer cathode to the second electrolyzer cathode. As a result, hydrogen and oxygen are collected from the cathode and anode, respectively, at the second electrolyzer, the leftover water is recycled back for the next cycle without any disruption for almost 48 hours with solar to hydrogen conversion efficiency of 30% [27].

7. Semi-artificial photosynthesis

It involves the merging of unique features of both natural and artificial photosynthesis such as high quantum efficiency (100%), selectivity, specificity and self-repair mechanisms of natural photosynthesis [28]. At the same time, the ability to use synthetic material with a wider light absorption spectrum as well as modified molecular chemistries thus minimizing the limitations. The photocatalytic properties of two photosystems PSI and PSII viz., generation of reducing power and photolysis of water, respectively are used for the creation of semi-artificial devices which convert light energy into molecular hydrogen and carbon-based fuels [29].

7.1 Enzyme hybrids

Enzymes have high molecular, chiral and substrate specificity along with high turnover and biodegradability. Enzymes utilization is limited due to their thermal instability, limited optimum pH range, denaturation by organic solvents and inhibition by metal ions. To fully utilize their potentiality as biocatalyst researchers have used porous matrices to elevate their stability *in vivo* (**Figure 7**). Different network materials such as metal-organic frameworks (MOFs) and metal-phenolic networks (MPNs) have been utilized to hold biocatalysts for enhancing their stability. A hundred percent efficiency has been achieved using artificial light absorbers and biological catalysts where photocurrents through electrode-wired enzymes generate kinetically and thermodynamically efficient products at very fast rates. Photosystem II enzymes along with semiconductors and mesoporous opal indium tin oxide (ITO) electrodes are well-studied examples of an inorganic collector with a biological catalyst creating efficient systems [30].

7.2 Cell hybrids

Biological unicellular systems are more efficient in terms of specificity as compared to isolated enzymes from living organisms. The use of microorganisms along with inorganic semiconductors or metal nanoparticles has been investigated by researchers (**Figure 8**) [31]. In one of the studies, the anaerobe *Methanosarcina barkeri*, bacteria, was used along with a materials catalyst, nickel sulfide electrode, a material inspired by naturally occurring nickel-dependent hydrogenases. The bacterial culture was added to the cathode and was exposed to visible light which resulted in the reduction of carbon dioxide to methane with no net loss in performance efficiency [32]. In another study, an acetogenic bacterium *Moorella thermoacetica* was treated with water-soluble gold nanoclusters AuNCs (mainly Au22(SG)18) and illuminated with light of 532 nm wavelength. The cytoplasm mediators in bacteria selectively pick up photo-generated electrons (bypassing cell membrane) and produce acetic acid from carbon dioxide for six days [20]. Another hybrid system was reported where light harvesting indium phosphide (InP) nanoparticles were introduced in genetically engineered yeast cells where photoexcited electrons produced from InP activate nicotinamide adenine dinucleotide phosphate regeneration [33] .

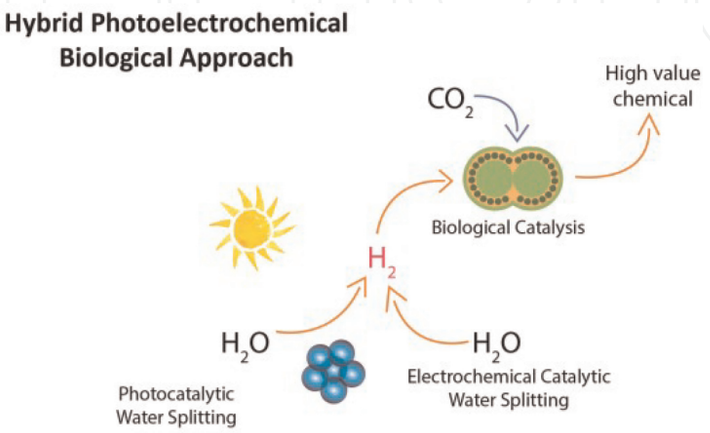

Figure 7.
An outline diagram of a hybrid of photoelectrochemical and biological approach where the biological catalyst is utilized to catalyze the reaction for the production of high-value products.

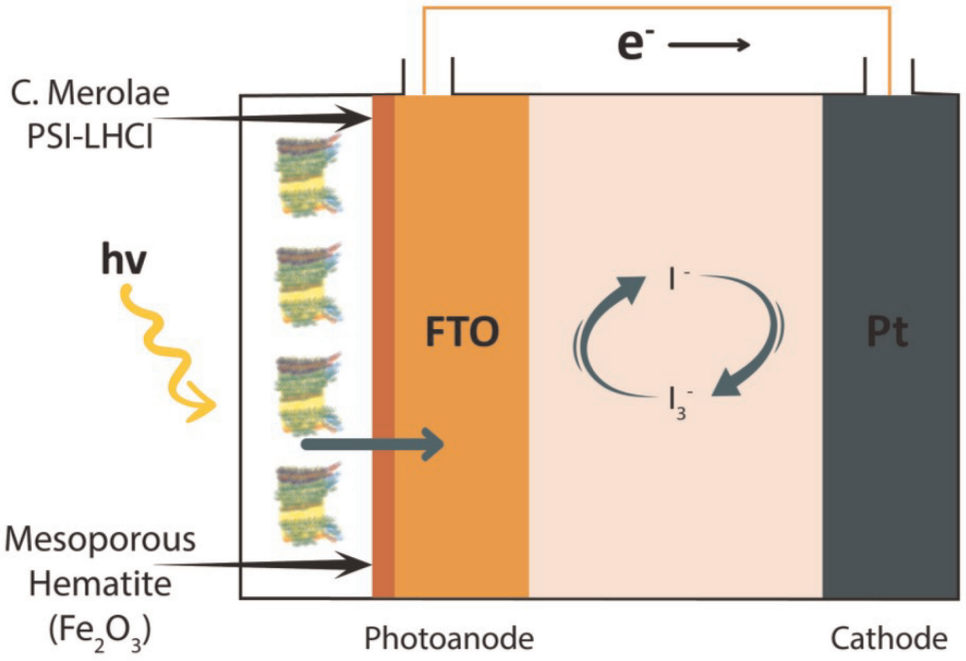

Figure 8.
A biohybrid made by PS-I photosystem I from a red microalga Cyanidioschyzon merolae *nanostructured present on multilayer hematite/FTO electrode.*

7.3 Artificial leaf

The imitation of the Z-scheme and designing of the artificial leaf is another important benchmark in the quest for foolproof operational systems using a biohybrid approach. American chemist Daniel G. Nocera and colleagues (2011) developed a

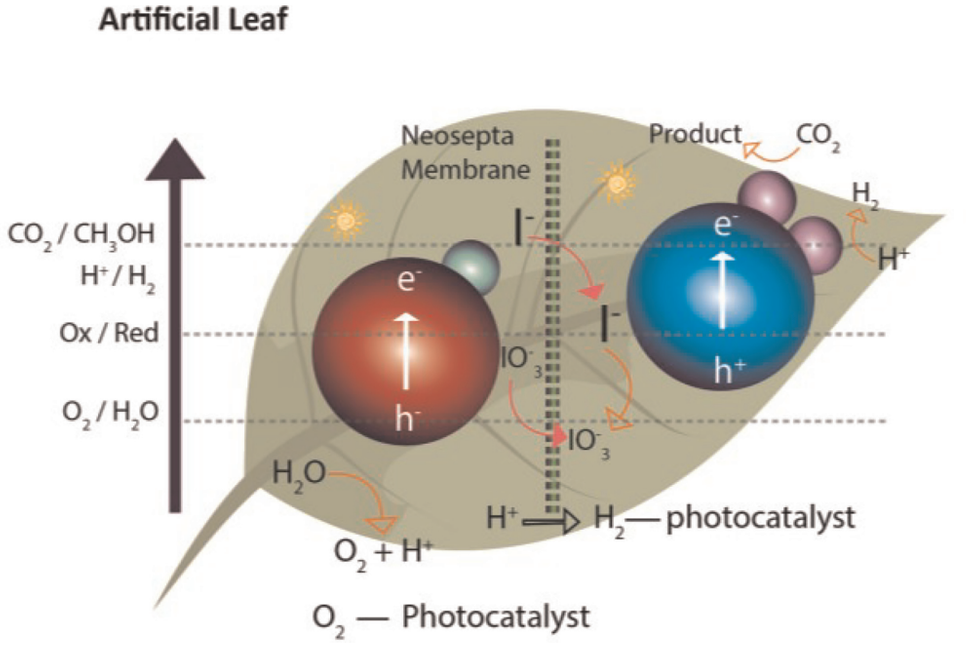

Figure 9.
The artificial leaf designed with a silicon chip coated with a chemical catalyst to speed up the water-splitting reaction on exposure to sunlight. The separated electrons and protons are captured to form hydrogen gas which can be used for the generation of electricity.

silicon-based device that can produce hydrogen and oxygen using solar energy without adding any pollutants was named as artificial leaf [34]. The artificial leaf has a silicon chip coated with a chemical catalyst which on exposure to sunlight speed up the water-splitting reaction and captures separated electrons and protons to form hydrogen gas which can be used for the generation of electricity (**Figure 9**). Artificial leaf still faces significant challenges and focused research is needed to increase hydrogen fuel efficiencies which is very low at about 5% of the total possible fuel availability in solar energy. The technology is highly expensive and the safety of hydrogen fuel generated is negligible limiting the use of artificial leaves for commercial purposes. An artificial leaf was designed using cuprous oxide to produce methanol and oxygen from carbon dioxide and sunlight [35].

8. Improvement strategies

The advancement in nanotechnology (in the area of imaging and modification of nanomaterial) and molecular manipulation such as adding impurities to semiconductors resulted in an increase in light absorption capability, efficient catalyst performance and selectivity [36]. Researchers have created highly efficient antennae complex mimicking light-harvesting complex involved in natural photosynthesis. The antennae reaction center has a hexad nanoparticle having four zinc tetraarylporphyrin molecules, (PZP)3-PZC coupled to a free-base porphyrin-fullerene molecule, P-C60 to form a hexad structured nanoparticle (PZP)3−PZC−P−C60 [37] The nanoscale materials and devices have been developed by "bottom-up" nanofabrication creating "molecular-lego" which are then used in manufacturing new devices. The creation of supramolecular and their usage in the construction of devices based on molecular components have enhanced the efficiency of catalysts by creating supramolecular cages and hence preventing degradation [17]. The development of single photoelectrode, photovoltaic-coupled electrolyzer, use of nanostructure materials can influence the functioning and efficiency of the device to a greater extent [13, 30]. The physical factors such as temperature, pressure and ion concentration of the environment hold significant leeway.

Wastewater treatment (WWT) leads to the emission of a huge amount of carbon dioxide which is harvested as a source of renewable energy. To tackle the waste-energy-carbon challenge, an integrated approach has been adopted which involves hybrid microbial photoelectrochemical (MPEC) integrated with microbial electrochemical system WWT with artificial photosynthesis. The energy released during WWT aids in achieving carbon neutrality goal side by side assist in solar harvesting, conversion and storage [38].

9. Limitations and challenges

Natural photosynthesis has high quantum efficiency leading to efficient charge separation but the overall conversion of solar energy to chemical energy is quite low nearly about 1%. Using APS, efficiency up to 10% or even higher is demonstrated [12]. One of the most significant bottlenecks in APS is attaining a cost-effective, efficient and stable catalyst material. The organic-based catalyst has the tendency to lose its stability on multiple uses and shows corroding or obstructing the working of system equipment. Many metal-based catalysts have been tried and the search for cost-

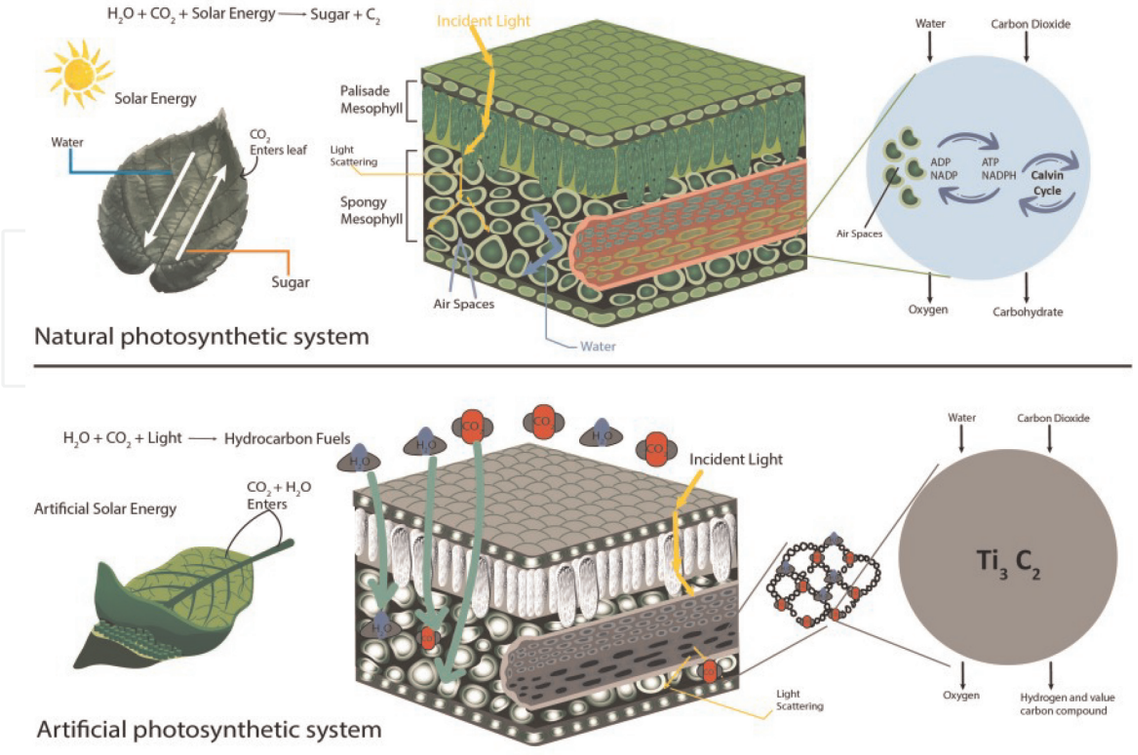

Figure 10.
The comparison of the processes in the natural and artificial photosynthetic system at the leaf, chloroplast and molecular levels.

effective and stability for at least ten years is still under process. To mimic a complex process like photosynthesis is very challenging.

Another notable challenge within the area of mimicking a natural process is the complex molecular geometry found in photosynthesizing organisms. Researchers are having a great deal of trouble replicating the level of intricacy that it entails (**Figure 10**). Many catalysts have been synthesized in the past few decades; however, these catalysts are unstable. Nevertheless, with the help of supramolecular strategies and nanotechnology, scientists are able to easily manipulate the workings of their devices through structural and molecular composition. Studies related to molecular catalyst heterogeneity are limited as it is difficult to match the details present in natural photosynthesis. The development of efficient molecular catalysts will allow the field of APS to advance toward a viable system [15].

10. Future impact and concluding remarks

The top priority of researchers is to search sources of renewable energy that can be used to get some relief from the current state of crisis all over the world [28]. The airplane was created inspired by the flight of the bird, in a similar manner natural photosynthesis serves as a model to mimic the functions of self-sustaining photo-autotroph organisms which hopefully one day create a self-sustaining world. APS already working efficiently and outperforms natural catalytic systems with respect to simplicity, charge transport and light absorption spectral range. Moreover, just as solar panels can be installed onto roofs, providing a secondary source of electricity,

future artificial photosynthesis devices can also be applied to power homes as it offers a way to store energy for later use. More than 60% of oil depletion globally is because of its usage in transportation. Electric cars are an excellent alternative but recently new models of cars powered by hydrogen, the byproduct of APS claimed to revolutionize the vehicle industry. These hydrogen-powered vehicles require a very short refueling time and are environmentally friendly.

Natural photosynthesis is solely responsible for all the energy that is required to survive on this planet. In addition, photosynthesis adds energy stored in fossil fuels. It took a billions of years for evolution to make protobiont to evolve into multicellular photosynthesizing systems. To mimic, natural photosynthesis may take more than a decade of extensive research before APS is fully equipped for industrial utilization [11]. Therefore, it is imperative to try and extract energy from a biomimetic approach to this natural process. The endeavor for creating a self-sustained system using APS is still in its infancy. Many successful versions of APS has been devised but not all models are infallible and have drawback related to efficiency, instability or financial expenses. The search for a cost-effective, robust and scalable APS continues in organizations viz., Liquid Sunlight Alliance (LiSA) and Center for Hybrid Approaches in Solar Energy to Liquid Fuels (CHASE). The various attempts to practically apply APS fall short of many efficiencies but still solar fuel production by natural photosynthesis is achievable in the laboratory. The scientific community is well versed in terms and working principles of solar fuel, artificial leaf and artificial photosynthesis and working hard to provide energy using clean, green alternatives globally.

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