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CO_2 sequestration by hybrid integrative photosynthesis (CO_2-SHIP): A green initiative for multi-product biorefineries

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ABSTRACT

Diversification among organisms has resulted in uniqueness and complexity between them leading to maintenance of continuous energy supply while restoring equilibrium in the environment. Photosynthetic organisms are capable of naturally converting atmospheric CO_2 in presence of sunlight and water leading to production of organic molecules whereas artificial photosynthesis yields solar fuels by directly converting light through photovoltaic cells. Therefore, hybrid integration of both photosynthetic mechanisms involving catalytic processes by converting light energy which is an unlimited source of energy leading to the production of fuels and various valuable products, will be an amicable solution for efficient CO_2 sequestration. For optimizing photosynthesis various approaches and processes need to be improvised such as light harvesting complexes, reaction centres, carbon fixation and metabolic pathways for enhancing their photosynthetic efficiencies. This review highlights enormous potential and possibility of solar energy utilization leading to a new horizon to the researchers for exploring the CO_2 sequestration by hybrid integrative photosynthesis (CO_2-SHIP) for a sustainable renewable production of energy components for multi-product biorefineries.

1. Introduction

There is an continuous increase in the atmospheric CO_2 cheifly due to various anthropogenic activities like burning of fossil fuels, approximately 87% by the combustion of fossil fuels, 9% due to the deforestation and remaining 4% could be contributed by different human activities, industrial processes and manufacturing procedures [1]. In broader terms, the major contributors of CO_2 emissions are from three sectors mainly like, transportation, industries and all other sources of fuel combustion activities [2,3]. Data suggests that nearly 80% was utilized in the transport and industrial sectors whereas remaining 20% or less in electricity sector [2].

Essentially, natural photosynthesis is a biological process, categorised broadly into two half reactions i.e., oxidation and reduction, which are very crucial for the production of fuels and other commodities. In plant systems, the first phase includes photo-oxidation of water molecules releasing oxygen and photons whereas in the second phase, which is light dependent reaction (also known as the Calvin cycle), inorganic carbon i.e., CO_2 is incorporated in the organic form and converted into carbohydrates (storage supplements) [3]. Naturally, carbohydrates are the ultimate end products of photosynthesis, which are converted chemically by reducing protons and generating oxygen from water, creating stored chemical potential [4].

One mole of photons is equivalent to $6.022*10^{23}$ light particles, as 'mole' represents light particles in sunlight. Approximately, 10 to 120 mol of photons strike the earth's surface area in about square metre per day, which are critically determined and influenced by the location and time of the year. Like in Netherlands, ~40 mol per square metre of average photon flux are observed per day [5]. On the other hand, artificial photosynthesis [1] mimics the biochemical process by chemically converting the sunlight, water and CO_2 into carbohydrates (sugars) and oxygen. The best part of the artificial photosynthesis process is that the substances obtained and formed can be assimilated, store piled and further be transported as required.

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Artificial photosynthesis also functions in the same way and almost similar to natural photosynthesis mechanisms involved namely in, the light harvesting, charge separation, water splitting and fuel production processes. Light harvesting mechanism revolves around reaction centres where the photons and/or the light particles are accumulated within the antenna molecules [6]. There is a separation of positive and negative charges in the reaction centres referred as charge separation, followed by water splitting where it splits into hydrogen ions (protons) and oxygen in the catalytic centres and simultaneously leads to the production of fuels, either as hydrogen and/or carbon-based fuels [5,7,8]. Henceforth, the final by-products generated in the artificial photosynthesis are simple molecules of carbon-based fuels such as methane, methanol and carbon monoxide rather than complex molecules like carbohydrates [9].

In the present review, our emphasis on the concept of artificial photosynthesis has been focussed as main thematic along with detailed case studies. Such context will further develop a hybrid integrative platform to sequester CO_2 (CO_2-SHIP), a stepping roadmap towards a green initiative for multi-product biorefineries.

2. Defining natural and artificial photosynthesis

Photosynthesis is a multi-step biological process by which photosynthetic organisms convert solar energy into chemical energy in the form of ATP and NAD(P)H, which is then utilized for carbon dioxide fixation [10]. This process is completed through two distinct reactions: light (light dependent) and dark (light-independent reactions) reactions. In the light-dependent mechanisms, antenna molecules absorb photons, leading to the excitation of specific chlorophyll molecules followed by splitting of water and charge separation to produce ATP and NAD(P)H. These energy rich molecules are dissipated to synthesize sugars and other large organic molecules utilising carbon dioxide in the dark reaction [11].

Photosynthetic organisms can be broadly classified into two groups - oxygenic photosynthetic organisms like purple bacteria, green bacteria, and helio-bacteria, which utilize inorganic reduced compounds as an electron donor and consist of one photosystem whereas the second group of organisms like cyanobacteria, algae and higher plants, uses water as an electron donor and with two different photosystems [12]. Classification can also be according to the type of photochemical reaction centres such as - type I reaction centres (RCs) where iron-sulphur act as the terminal electron acceptor for example helio-bacteria and green-sulphur bacteria, and type II RCs, where quinone act as the terminal electron acceptor (EA), for example filamentous bacteria [13]. Whereas in higher plants, algae and cyanobacteria, there are two types of RCs i.e., Photosystem I (PSI) and Photosystem II (PSII) and can undergo photosynthetic oxygen evolution (Fig. 1A.); while all other photosynthetic prokaryotes only perform anoxygenic photosynthesis [13,14].

The most critical step in photosynthesis is the effective absorption of the solar light by antenna pigments which are called as light harvesting complexes. In recent decades, the information on the crystal structure of PSII for higher plants and cyanobacteria, showed the existence of PSII in a dimeric form [15–17]. Each monomer is a complex of 19–20 protein subunits that contain core antenna pigments of approximately 35 chlorophyll *a* (Chl-a) molecules along with, 11 β-carotenes, 2 pheophytins, nearly 20 lipid molecules, two plastoquinones, one non-heme iron, two heme irons, four manganese (Mn) atoms, three or four calcium (Ca) atoms, three chloride ions [18], one bicarbonate (HCO_3) ion and 15 oxygenic detergents [16]. Furthermore, Photosystem I (PSI) consists of a monomeric form in higher plants and algae [19], however it is commonly present in a trimeric form in cyanobacteria [20].

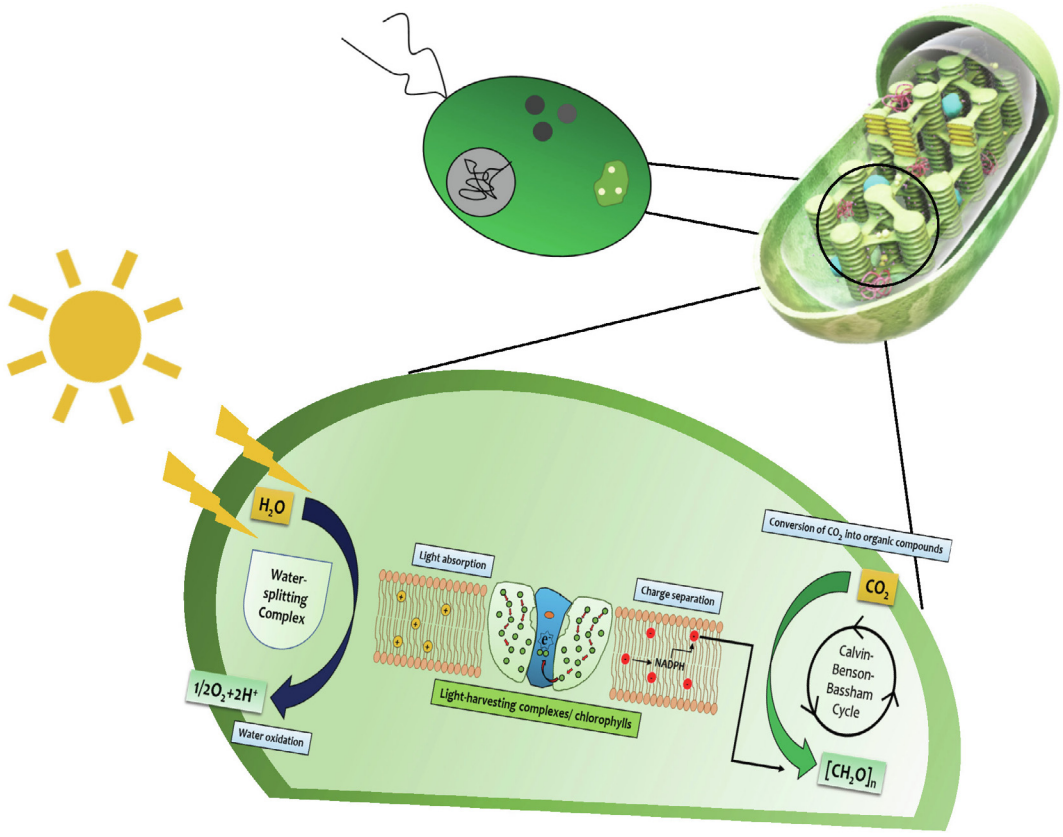

Fig. 1A. Natural photosynthesis: The charge separation is induced by the sunlight with the help of chlorophyll functioning as the antennae.

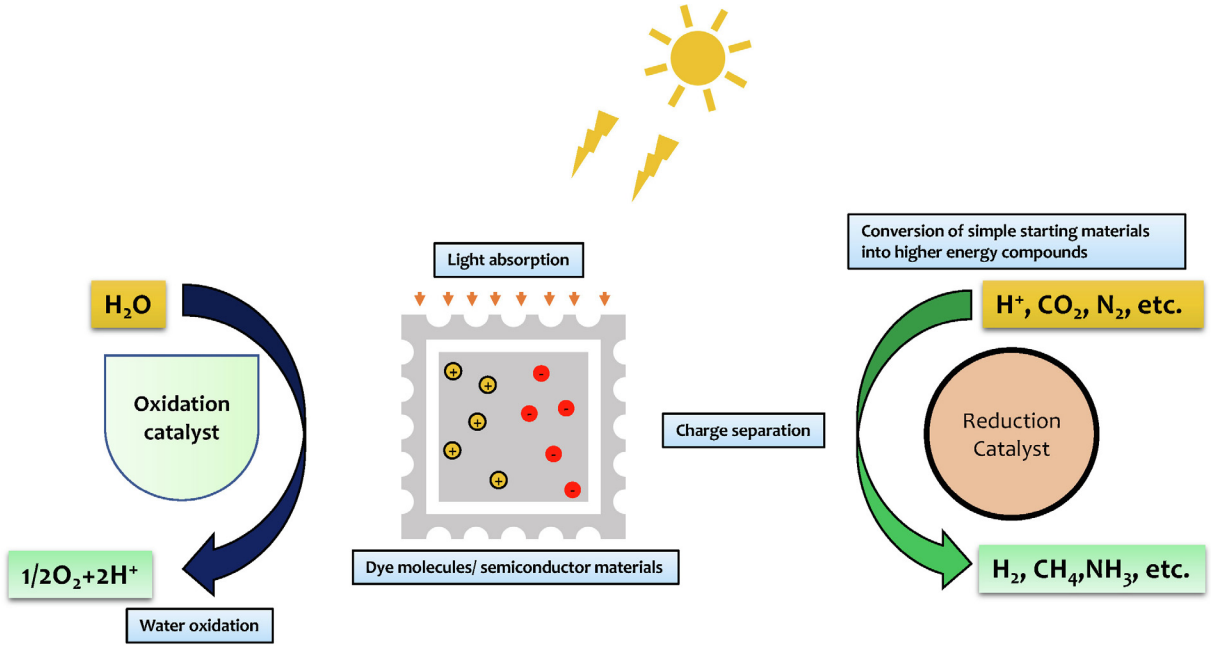

Fig. 1B. Artificial photosynthesis: charge separation induced with the help of dye molecules or light-absorbing material.

Each monomer of PSI contains 12–14 protein subunits consisting of 96 Chl-a molecules along with, 22 β-carotene, 3 (4Fe-4S) clusters, two phylloquinone molecules and 4 lipid molecules [19-23]. The efficiency of the light-dependent photosynthesis, perhaps depend upon the energy capture; therefore, algae and higher plants are equipped with antenna molecules which helps in the transfer of large quantity of solar energy to the reaction centres [16,19,23-25]. The common antenna system in PSII of higher plants and chlorophytes is confined to the LHC II complex [24,25].

There are two main photosynthetic electron transport chains, the linear and the non-linear (cyclic) electron transport chains that occurs in the thylakoid membrane of oxygen evolving organisms [4,26,27]. Photosynthetic process is followed by the photocatalytic splitting of water stimulated by the PSII in plants, algae and cyanobacteria. The electrons are transferred further through a number of co-factors within PSII and PSI to reach the final electron acceptors plastoquinone and ferredoxin [4,22]. The first phase of solar energy conversion into an electrochemical potential is completed with a maximum efficiency of about 70% that leads to the generation of a radical pair state $P680^{\bullet+}$ (Chl-a) & $Pheo^{\bullet-}$ (Pheophytin) [4]. The $P680^{\bullet+}$ generated in PSII accepts the electron generated through splitting of water molecules at oxidizing centre, simultaneously two water molecules are dissociated to generate dioxygen, four protons and four electrons [4,16]. This reaction process is proceeded by the oxidation of the quinol molecule in the presence of light, wherein the absorbed solar energy induces movement of the reducing equivalent to PSI, consequently, the reaction centre, P700, helps in generation of a reducing potential of about −1.0 V or more [4,27]. Eventually, the electrons generated in this process pass through a series of carriers reaching the final acceptor i.e., ferredoxin, allowing the reducing equivalents to be transferred to NAD(P)H.

This chemical free energy, in the form of NAD(P)H and ATP, is being utilized in the dark reaction, which occurs in the cytosol of cyanobacteria and other oxygenic photosynthetic organisms [26]. All three transmembrane protein complexes (Cytochrome b6f complex, PSI and PSII) are connected like a series in the linear electron transport reaction [26,27]. In addition to the electron-transfer pathway, an alternative cyclic electron transport pathway also exists. At low $NADP^+$ concentration in stromal side or low activity of PSII, the reduced electron carrier (ferredoxin) is directed to Cytochrome b6f and the electrons are transferred back to plastocyanin or Cyt c6 through the Cyt b6f complex. There is no evolution of O_2 as PSII is not involved and does not require any input of energy directly by PSII [28].

Using sunlight as the primary driving source of energy, artificial photosynthesis generates chemical energy reservoirs and valuable products. In this process (Fig. 1.B), chemicals such as dye molecules act as the antenna units which harvest sunlight and the excited energy is channelized to the reaction centres. The electron-transfer reactions occur in multiple stages to generate potential that can lead to chemical reactions for production of chemical energy which is stored in the organisms and finally results in formation of high-value products such as methane and hydrogen [5,28,29]. The field of artificial photosynthesis already made great advancements in the last few decades by developing chemical photosynthetic systems which are capable of transferring electrons and energy reactions faster [30–32]. The basic advantage of this system is that they are produced as renewable energy that can be stored in chemical form. Such systems are composed of organic components such as antenna, electron donor & acceptor which are similar to the natural photosynthetic complexes and show advantages by absorbing the light in a broad solar spectrum. It is not convenient to replicate the huge complex biological machinery, which seems to be unnecessary while alternative methods such as artificial photosynthesis would be sufficient to perform the process with minimal efforts.

Recently, different approaches developed for storing solar energy in form of chemical energy, the majority of which follow the general concept of artificial photosynthesis [4]. In the first step, absorption of visible light leads to charge separation, as a result, electrons are generated. These energy-rich compounds such as hydrogen, methanol or ammonia are generated from precursors namely water, carbon dioxide or nitrogen, perhaps seems to be a complex process requiring catalysts [33]. The storage of solar energy in chemical form can be differentiated into two approaches:

a. **Direct approach**: In this process, the light absorption, charge separation and reduction reactions occur in an integrated way as a single unit. Just like in artificial leaves the catalysts for producing the valuable products and oxidizing water are applied directly to the semiconductors of a solar cell are involved [34].
b. **Multistage approach**: Each individual steps are separated although they do proceed and functions at a common focal point. For example, by combining conventional solar cell technology with electrolysers [35].

The resultant products by both the approaches are either used directly or indirectly. For example, hydrogen as a fuel or, in combination with downstream reactions, is converted into energy carriers such as methane, methanol or formic acid [36]. Biological and industrial systems can also be combined into multistage hybrid systems in order to obtain higher value products, for instance; production of isopropanol bio-electrochemically from hydrogen and oxygen in presence of sunlight and CO_2 by hydrogen oxidizing bacteria [37].

3. Comparison of natural and artificial photosynthesis

3.1. Natural photosynthesis

- Biological photosynthesis is a complex catalytic process involving an ensemble of protein components with reaction centres, cofactors and pigments (chlorophylls and carotenoids) for light absorption and energy conversion.
- As a net result of multistep light and dark reactions the CO_2 is reduced into biomass and energy rich biomolecules such as carbohydrates and other renewables.
- All the reactions are performed in well-organized light harvesting components such as PS I & PS II complexes.
- The actual efficiency of light energy conversion in crop plants is typically <1% annually, while >3% achieved in microalgae strains grown in photobioreactors [38].

3.2. Artificial photosynthesis

- Artificial photosynthesis is a process that requires light absorbing chemicals or dye molecules that helps in chemically derived energy conversion.
- In the case of artificial photosynthesis, the charge separation from splitting of simple molecule results in production of high-value compounds such as hydrogen, methanol and ammonia.
- Splitting of water or CO_2 and generation of high-value products such as hydrogen is a catalyst driven complex process.
- In artificial photosynthesis, the theoretical maximum efficiency that can be achieved is nearly 10% [39].

4. Case studies

4.1. Natural photosynthesis

The energy and environmental crisis around the globe imposed a mandate to reduce the greenhouse gases (GHG) emissions and also to find renewable solution for the problem of global climate change [40]. Several countries around the world established targets for reduction of CO_2 emissions towards meeting the sustainability goals under the Kyoto Protocol, 1997. The benchmark was to reduce up to 5% of GHG emissions. Subsequently, a second commitment period signed by the member nations at the climate change convention held in Copenhagen, agreed to provide approximately US $100 billion for the mitigation of GHG emissions to at least 18% in GHG reduction by 2020 [41]. This international commitment promotes the development of new alternatives for reduction of GHG emissions.

Currently, photosynthesis underlies the production of all our food and fibers sources including biomass-based biofuels as a source of renewable fuels [42]. About 0.05% of the solar energy is captured in biomass each year through the process of photosynthesis [43-45] and combustion of fossil fuels contribute to more than 80% of the energy produced throughout the world each year [40,42]. Overall, the direct carbon combustion annually generates an amount of CO_2 that is equivalent to more than 24 gigatons contributing towards energy production [42]. The most environmentally sustainable way to reduce the GHG emissions associated with energy production is to generate energy from carbon-neutral and/or reduced carbon emission sources [46]. As a result, utilizing the capability of natural photosynthesis would help pave the way for a renewable and sustainable future.

Evidently, photosynthesis in course of time emerged as an energy generating mechanism and its accumulation for the synthesis of biomass since sunlight, water and CO_2 are inexhaustibly available in nature [4]. Microalgae are such sunlight-driven cell factories capable of converting atmospheric CO_2 into raw materials for producing biofuels, animal food, chemical feedstocks and high-value bioactive compounds [47]. The concentration of CO_2 with the help of microalgal photosynthesis is a potential and promising resource for the capture and storage of CO_2. These organisms are capable of combining the process of photosynthetic CO_2 fixation with the production of the value-added bioactive molecules, thereby offsetting the mitigation costs towards economic sustainability [48,49]. As a result of the faster growth rate, photosynthetic CO_2 fixation efficiency of microalgae is ten times higher than any of terrestrial plants facilitating the channelization of captured solar energy and to synthesize high-energy storage molecules i.e., lipids, carbohydrates and others [50]. Henceforth, the application of microalgae can be considered as a sustainable and efficient way of photosynthetic biofixation of CO_2 [51,52].

A number of reports showed enhanced CO_2 fixation by microalgae representing the capability of these photosynthetic cell factories in the process of mitigating the GHG emission [53]. Light plays a major role in the growth kinetics of microalgae and there is a huge lacuna in the understanding of the optical behaviour of microalgae, which fundamentally hinders their design innovation [54]. In 2019, Cho et al., revealed the optical inefficiency of microalgal photosynthesis through advanced modelling studies based on both microscopic 3D tomography and macroscopic photosynthesis profiling patterns [55]. This study demonstrates that by making photons penetrate longer distance into the bioreactors, the biomass productivity can be increased to >100 g m^{-2} day^{-1}, eventually, increasing the photosynthetic carbon fixation. Similarly, the influence of various light intensities was studied to mimic illumination variations in *Nannochloropsis salina*, that the cells are capable of utilizing very intense light, provided that dark cycles occur for re-oxidation of the electron transporters in the photosynthetic apparatus [56]. Recently, studies reported the positive impact on microalgal growth under high concentrations of inorganic carbon (Ci) in the form of gaseous CO_2, flue gas, or bicarbonate, increasing overall photosynthetic carbon bio-fixation and biomass productivities [57]. Kuo et al. (2017), treated an alkali-tolerant *Chlorella* sp. AT1 mutant strain generated by N-methyl-N'-nitro-N-nitrosoguanidine (NTG) mutagenesis showed an improved photosynthetic CO_2 bio-fixation and increased CO_2 utilization efficiency [58]. Studies also demonstrated the use of flue gases to substantially increase the biomass productivities upto 30% [40]. The efficiency of CO_2 capture by microalgae can vary according to the cellular physiology of the algal strains, media

composition, light and temperature, whereas the photosynthetic CO_2 capture efficiencies are achievable as high as to 80–99% [59,60]. The use of natural photosynthesis via microalgae facilitates a long-term prognosis of sustenance with a biorefinery-approach for the mitigation of GHG emissions and concomitant production of biofuels and high-value renewables.

4.2. Artificial photosynthesis

The primary aspect of artificial photosynthesis is to develop integrated systems where light absorption, charge separation and conversion of chemical energy into fuels or valuable products are confined within a single functional unit. Perhaps, large devices of this type do not exist, yet there are reports of small-scale devices being developed by eminent scientific groups [33]. Most of these are for splitting water to produce H_2 [61], some for reducing CO_2 [62] or combinations of the two, for example to produce higher alcohols [63,64]. Few examples of such devices are discussed in this review with an increasing degree of integration as:

4.2.1. Photovoltaic (PV) driven electrolysis:

The simplest structure for demonstrating the artificial photosynthesis system is by representing a solar cell which is driven by electrolysis. Under typical operating conditions, any silicon-based solar cells generate a voltage between 0.5 and 0.7 V [63,64]. In such context, at least three silicon cells are required to be connected in series mode for generating the voltage of nearly 2 V which is conventionally required for electrocatalytic splitting of water [65]. Alternatively, electronic voltage converters will be used to raise the voltage of the solar cells to the level required by the electrolyser.

Similarly, another approach uses multiple stacked absorber materials, namely tandem solar cells which are capable of generating voltages up to 2 V, thus driving electrolysers for hydrogen production [36]. For instance, development of solar-based water splitting system with three-layer semiconductors and two electrolysers made up of polymer electrolyte successfully demonstrated [66,67]. The solar cell when irradiated with (48 times) concentrated sunlight generates nearly 3 V, which are able to drive at least two series-connected electrolysers. The system achieves an average efficiency of 30% over a period of 48 h, thus the highest value so far reported for photoelectrochemical splitting of water molecules [67]. The crucial challenge to be addressed by the PV-driven electrolysis with production and operation of the system is the overall cost associated with the assembly of all the components [68]. Another major technical challenge is heat dissipation from the solar absorber to the electrolysis modules making it suitable for generation of the electrochemical reactions within the cells.

4.2.2. Integrated photovoltaics/electrolysis devices:

By combining both light harvesting and electrolysis as a single unit, the challenge of separate PV-driven electrolysis can be addressed. Due to the spatial vicinity of light absorption and electrolysis, the heat evolved by the photoactive material could be utilised for increasing reaction rates to maximum. Recently, Turan et al, (2016) reported a new system developed on an integrated electrolysis system with nickel catalysts for forming H_2 (or) O_2 based on two series-connected silicon-based thin-filmed tandem solar cells [69]. An efficiency of approximately 4% could be achieved by such systems within 40 h without any loss of activity, which could be further scaled up for higher efficiency. The major disadvantages associated with this process is requirement of membranes for separating two sub-processes and the larger active area for assimilation of the products [33].

4.2.3. Semiconductor surfaces assisted photo-electro catalysis:

Light absorption and electrochemistry can be combined by processing electrochemical reactions on the surface of the semiconductor i.e. titanium dioxide (TiO_2), similar to the efficiency of a photovoltaic cell [70]. The semiconductor electrolyte contacts are formed by immersing the semiconductor into the solution. Although, photo-electrocatalyst such as titanium dioxide absorbs only UV range of solar spectrum, the requirement for alternative compounds with smaller band gap are relevant. A combination of two semiconductors arranged together, known as tandem cells will be able to achieve required voltage [71]. The low catalytic activity of the semiconductors can be improved by functionalizing and depositing them as nanoparticles (or) covalently bonded molecules on the surface in the form of thin layers [72]. Another alternative is adaptive interfaces that differ fundamentally both from conventional semiconductor electrolyte interfaces and from packaged photovoltaic contacts [73].

4.2.4. Artificial leaves

Currently, the most highly integrated systems available are artificial leaves (Fig. 2) which combine all the light-absorbing materials and catalytic centres in a single, sometimes paper-thin unit without external wires. The artificial leaf is a silicon solar cell with different catalytic materials bonded onto its two sides which do not need external wires (or) control circuits in the whole process. These are simply placed in a container of water followed by exposure to sunlight, thus quickly begins to generate streams of bubbles i.e., oxygen bubbles from one side and hydrogen bubbles from the other [74]. Alternatively, placed in a container with a barrier separating both sides, where two streams of bubbles are assimilated and later can be used to deliver the energy.

The cells are arranged in triple layers with amorphous silicon-based photovoltaic systems interfaced to H_2 and O_2 evolving catalysts (OEC). In the Co-OEC, where cobalt catalyst is used as the O_2-evolving catalyst [75], upon oxidation of Co^{2+} it is capable of self-assemble [76], with self-healing property [77], and capable of operating at room temperature in buffered electrolyte with pure or natural water [78,79]. The Co-OEC when interfaced with semiconductors, enhances the efficiency of solar-assisted water splitting [80,81]. However, the H_2 evolving catalyst are made up of ternary alloy (NiMoZn) [74] and the leaves can redirect nearly about 2.5% of the energy from sunlight for production of H_2 (as wireless form). Although, there is studies available that connecting the catalysts to the solar cells using wires can lead to an increase in the efficiency up to 4.7% [74]. Although the concept of artificial leaves seems to be attractive but with few disadvantages. For instance, the molecules participating in the reactions need to pass from one side to the other of the leaf, so there is an decline in the rate of overall reaction. Due to such consequences, the leaf achieves approximately half the system's efficiency than the wired variant [74]. An amicable solution for proton transport is introducing ion-permeable membranes within light absorbers and catalytic centres [75], but the practical implementation of such similar systems, are very complicated and are yet to be studied and explored [82].

5. Advantages and drawbacks of natural and artificial photosynthesis

The goal of artificial photosynthesis is to develop modular systems integrated into a functional unit in which the three essential processes of light absorption followed by separation of charges eventually leading to the formation of fuel reservoirs occur. Artificial photosynthetic systems capability to achieve higher solar energy efficiencies and already successfully attained an average

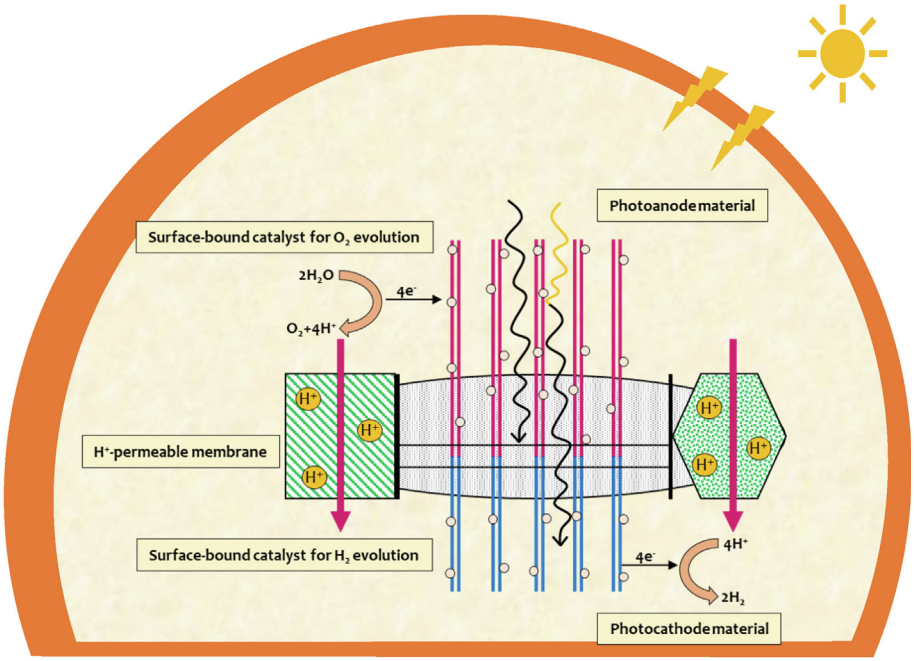

Fig. 2. Artificial leaf is demonstrated with the concept of light-harvesting nanowires embedded in a proton-conducting membrane.

efficiency of 30% via the process of photoelectrochemical water splitting [83]. The major advantage of artificial photosynthesis is that these systems are easily monitored and controllable i.e., natural and engineered photosystem proteins are immobilized on electrodes for photocurrent generation in an oriented manner [29]. In artificial photosynthesis, the raw materials (such as noble metals for catalysis) and manufacturing methods (i.e., multi-layer artificial leaves) are very expensive. Although, more effective and usable routes for obtaining carbon-based products (CH_3OH, C_2H_4, CO etc.) are known but still not feasible as energy-efficient due to non-availability of CO_2 as raw material at ease [33].

On the other hand, in natural photosynthesis, the systems are capable of repairing and replicating themselves over a period of time in evolution. The major advantage of natural photosynthesis over artificial systems is the ability of the cells to store the energy from sunlight in the long term by reducing atmospheric CO_2. Such conversion of atmospheric CO_2 into high energy carbon compounds are not yet achieved in the case of artificial photosynthesis. This involves the development of stable, inexpensive and environmentally compatible catalysts similar to the biological systems able to fix the low concentrations of CO_2 (even 0.03%) and assimilate them to higher quality products with an elevated specificity and conversion rates. In addition to the conversion of CO_2 by the Calvin cycle in plants, algae and bacteria, new metabolic pathways involved in CO_2 assimilation in microorganisms elucidated for improving their photosynthetic efficiencies [84-86]. Consequently, these CO_2 conversion processes can also be introduced in the process of artificial photosynthesis from the newly discovered unknown catalytic principles of CO_2 binding and reduction mechanisms.

In terms of the use of sunlight, biological systems are characterised by a relatively low conversion efficiency of light into chemical energy, the theoretical maximum efficiency of the light reaction is around 10%, the actual efficiency in crop plants on an annual average basis is typically less than 1%, whereas nearly 3% efficiency achieved for microalgal strains in a photobioreactor [87]. Another biotechnological application of utilizing the solar energy in natural photosynthesis is primarily stored in the form of biomass [66,88], i.e., chemically complex mixture of distinct entities which are suitable for nutrition need to be processed for use in industrial products. Moreover, the proportion of captured CO_2 is lost in the dark reaction in the chloroplasts, which results in a loss of nearly up to 30% of the energy assimilated within the cells [89]. Efforts to improve strategies for modifying these photosynthesis processes (or) creating hybrid systems, which are more efficient, capable to selectively produce the desired fuels and valuable products within these cell factories are in progress [33].

6. Integrative hybrid photosynthesis – A green initiative for multi-product biorefineries

A combination of non-biological and biological components tends to form hybrid system of photosynthesis, which aims to reduce CO_2 in presence of light. These hybrid systems operates by combining the photovoltaic process with a biological dark reaction, for example, the reduction of water and carbon dioxide to hydrogen (H_2), carbon monoxide (CO) (or) formic acid by electrolysis generated by a photovoltaic cell, which can be used by microorganisms for synthesising value-added products [90].

The chemical catalyst-based reduction of CO_2 has several limitation and therefore microbial catalysts appeared to be a suitable alternative. Microbial catalysts integrated with photovoltaics represents a novel platform for an artificial photosynthesis process that can transform solar energy to chemical products more efficiently than conventional techniques [91].

Liu et al, (2016) developed a hybrid water splitting system based on biocompatible inorganic catalyst system involved in electrolysis of water to yield H_2 and O_2 at low voltages. These products are then utilised by the hydrogen-oxidising bacterium *Ralstonia eutropha* to reduce CO_2 into valuable products such as isopropanol in the same reaction vessel [64]. The reaction vessel consists of a ROS-resistant cobalt-phosphorus (Co-P) alloy cathode, which drives the hydrogen evolution reaction while the self-healing Co-P anode drives the oxygen evolution reaction (OER). The electrode pair works in concert to maintain extraneous cobalt ions at low concentration and to deliver low applied voltage that splits water to generate H_2, which supports CO_2 reduction into complex organic

molecules at high efficiency. Similar studies utilizing biocatalyst *Methanosarcina barkeri* for the CO_2 fixation and reduction to methane was achieved with 86% Faradaic efficiency [92]. Furthermore, in another study, the electrons produced from water were directed to the microbial cells of *Sporomusa ovata*, an acetogenic bacteria for the reduction process of CO_2 to organic compounds [93].

Another approach is the electrochemical reduction of CO_2 and water to syngas which is a mixture of CO, CO_2 and H_2, followed by fermentation [94]. Hass et al, (2018) described the production of butanol and hexanol from CO_2, H_2O and renewable energy using a commercially available silver-based gas diffusion electrode (used in industrial-scale chlorine–alkaline electrolysis) as cathode in the CO_2 electrolyser [95]. Electric current densities up to 300 mA cm^{-2} exhibited for continuous functioning more than 1200 h. At higher voltages, H_2 proportion rises and energy conversion efficiency declines. The gases CO and H_2 formed in the CO_2 electrolyser are passed, together with unreacted CO_2, into a separate fermenter. This syngas mixture is converted to 100% efficiency by the bacterium producing acetic acid and ethanol [95]. Furthermore, after 22 h, addition of *Clostridium kluyveri* converts acetate and ethanol into butyrate and hexanoate which further gets converted to butanol and hexanol by the action of bacteria *C. autoethanogenum*. This process highlights several advantages than others, for example, a significant portion of the electrons might end up in water, whereas aerobic microorganisms involved with generation of bioelectricity and fermentable products.

This concept of photocatalytic biomass valorization emerged as a promising application termed as photobiorefinery that requires less energy and potentially could utilize process of artificial photosynthesis to enhance selectivity. Biorefinery is the process of converting biomass into a multitude of high-value products that can be commercialized. Utilization of biomass from municipal and agriculture waste (complex molecules) as raw material coupled to artificial photosynthesis to generate renewable fuels and value-added chemicals can be a promising factor for technoeconomic feasibility of this process [96]. By utilizing the process of depolymerization, oxidation–reduction and chemical modification the derivatives of lignin, cellulose, hemicellulose, phenol and triglycerides can be reduced to simpler molecules such as adipic acid, xylitol, vanillin and sorbitol which are of industrial importance and are used in pharmaceutical sectors [97–100].

7. Conclusions

Constant combustion of fossil fuels led to catastrophic change within the environment and also depleted oil reserves, henceforth, it is necessary to explore advancements in scientific technologies to produce energy efficiently with no (or) low GHG emissions. There are reports relating to the reduction and separation of CO_2, using several state-of-the-art technologies and methods including absorption of CO_2 using water-based nanofluids and Adaptive Neuro-Fuzzy Inference System (ANFIS) modelling [101–104]. Photosynthetic organisms, however, are capable of capturing and fixing atmospheric CO_2 into simple organic molecules in the presence of sunlight and water. The concept of artificial photosynthesis nurtures from the fact that most of the human activities are able to bio-mimic some of the natural processes. This review focus on combining different aspects of sequestering CO_2 naturally in combination with artificial photosynthesis, hence known as 'CO_2 Sequestration by Hybrid Integrative Photosynthesis (CO_2-SHIP)'. Consequently, the concept of integrative hybrid photosynthetic designs are highlighted, wherein the light capturing process is coupled with the biological dark reactions to obtain value-added products such as butanol and isopropanol which will be an amicable solution for efficient CO_2 sequestration. For optimizing photosynthesis various approaches and processes need to be improvised such as light harvesting complexes, reaction centres, carbon fixation and metabolic pathways for enhancing the photosynthetic efficiencies. In conclusion, this review highlights enormous potential and possibility of solar energy utilization leading a new horizon to the researchers for exploring the CO_2 sequestration by hybrid integrative photosynthesis (CO_2-SHIP) for a sustainable renewable production of energy components for multi-product biorefineries.

8. Author's contributions

MSK and IM contributed equally to write this manuscript. AAN and PPJ conceptualized and finalized the review. All authors read and approved the final manuscript.

CRediT authorship contribution statement

Mukul Suresh Kareya: Conceptualization, Data curation. **Iqra Mariam:** Conceptualization, Data curation. **Asha Arumugam Nesamma:** Conceptualization, Data curation. **Pannaga Pavan Jutur:** Conceptualization, Supervision.

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Competing interests

The authors declare that they have no competing interests.

Availability of data and materials

All data presented in this review from the published data are included in the references.

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