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Artificial Photosynthesis: Mechanism and Recent Advancement

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Abstract:

Fossil fuel firms are gaining profit from the steady utilization of coal, oil and gas, driving global warming to dangerous levels. Additionally, with rapid population growth worldwide, energy stores aredepleting faster than nature can replenish. Replacing fossil fuels dependency by harnessing the power ofthe sun with the storability and reliability of liquid fuels is the best solution and urgent requirement today.This review addresses the current predicament of solar energy storage and CO_2 emission through recenttechnological advancements. The proposed and most promising model for the stated problems is artificialphotosynthesis which mimics the multi-step natural photosynthesis process. Rather than producing electricity, the photo-generated electrons collected can be indulged in driving chemical reactions. Thus, thechemical energy generated from solar energy is stored within the chemicals in the form of chemical bond(a solar fuel). As the inspiration suggests the working prototype bio mimics the natural process at a higher efficiency. The targeted aspect of artificial photo- synthesis is the molecular catalyst, which is essential for regulating water oxidation, CO_2 reduction or proton reduction reactions. Over the years, researchers have been trying to modify these molecular catalysts to improve working efficiency and stability and get desirable by-products. With the development of delicate and powerful catalysts, the reproduction of the significant parts of photosynthesis, water and sunlight would ultimately be the onlyneeded sources for clean energy production. The ultimate implementation of artificial photosynthesis is togenerate liquid fuels such as formic acid, methanol and ethanol by CO_2 reduction. Production of such fuels with renewable sources minimizes the carbon footprint thus decreasing the emission of greenhousegasses which ultimately aids the crisis of global warming. Many researchers are looking forward to producing ethanol by absorbing CO_2, which is widely used as domesticated transportation fuel, from factories and petrochemi- cal industries. This paper also highlights related problems associated with thecommercial implementation of the applied artificial photosynthesis.

Keywords: Artificial photosynthesis, fuels, solar energy, catalysts, oxidation, reduction

1. Introduction

The United Nations Food and Agriculture Organization assure that population growth will continue to climb and it will approach nine billion by 2050. The population of the world was estimated to be 7.2 billion in 2015. Global energy markets will be driven by emerging economies. We will eventually reach a mark where the urge for food and energy will exceed the supply as affluence expands. Additionally, it has been predicted that fossil fuels would exhaust by the end of the century. Coal will persist for 114 years, natural gas for 53 years, and oil for 50 years. Global warming must also be taken into account. Most of the world's energy needs are met by hydrocarbons (oil, coal, natural gas). Hydrocarbons produce greenhouse gases (CO_2, SO_2, CH_4) when burned, and are statistically indicative of annual CO_2 emissions Figure 2. They trap heat in the atmosphere and can have devastating effects, from rising sea levels to climate change. However, renewable energy is not widespread enough to serve as an alternative on a global scale. About 1% of the sunlight that the sun emits to the surface of the planet is total energy that can be recovered from all reserves. Additionally, the solar radiation (173,000 TW)[1] distributed to the whole surface of the earth (land & sea) is nearly 9600 fold the total amount of energy consumed globally (17.91 TW in 2017). Unquestionably, there is extensive experimental and commercial research being done into solar energy's future. This will

provide
the planetary system with all the energy it needs to function. Artificial leaves, or rather artificial photosynthesis, is a very efficient and promising technological solution to this issue. Inorder to lower anthropogenic CO_2, enhance fuel reliability, and create a sustainable global economy, artificial photosynthesis, a chemical activity that mimics natural photosynthesis hasbeen so far an evolutionary alternative [2]. The ultimate objective is to catch sunlight in orderto oxidise water molecules to produce oxygen and protons on the one hand, and reduce protons to hydrogen or CO_2 to chemicals and fuels on the other. Although the idea of using the sun‘s energy to drive CO_2 removal from water is appealing, will it be actually feasible.

Natural Photosynthesis

The only source of inspiration and the model from which the artificial process is adapted is the natural process. Therefore, a quick look at the natural mechanism will assist in understanding how the technology is (bio) improving its efficiency Figure 1. The majority ofCO_2 in plants is typically converted into glucose via photosynthetic process. In this process, the sun‘s light is absorbed, where it transforms water (H_2O) into oxygen (O_2) and chemical energy (initially as electrons and protons). These energies are kept in the forms of adenosine triphosphate (ATP) and nicotinamide adenine dinucleotide phosphate (NADPH). These productshave long been regarded as the finest substitutes for the carbon-based fuels that are posing anincreasing ecological concern. One of the analytical methods for reducing CO2 in theenvironment is photosynthesis. It is crucial for maintaining the carbon/oxygen cycle. The light and dark responses are the first two sequential processes. During a light reaction, chlorophyll captures solar energy and converts it into chemical energy stored in ATP while simultaneously oxidising H2O into O2. Similarly, under a dark response, CO2 is gradually absorbed and reduced to form carbohydrates. This energy is stored in the form of ATP.

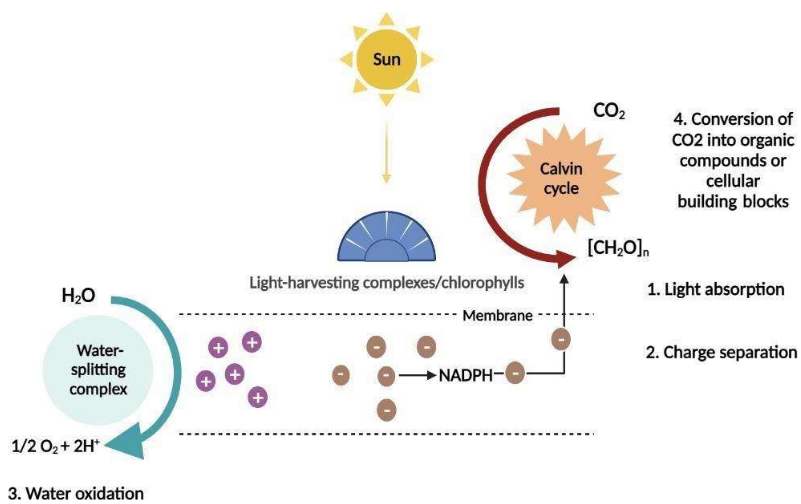

Figure 1: Schematics of natural photosynthesis

Artificial Photosynthesis

The synthetic process is explained below in a graphical manner for better understanding Figure 2. The sun is the energy source while the other most important parts of the procedure are the catalyst used for the oxidation and reduction reaction which mimics the fixative enzymes for the natural photosynthesis.

Role

Methane, methanol, and carbon monoxide are examples of simpler compounds that can be

created using artificial photosynthesis instead of complicated ones like polysaccharides Figure 3. The processes required to make these fuels are more involved than those used to produce hydrogen since reactions usually include more than four electrons, protons, and more than eight photons.Energy storage in fuels made of carbon poses a significant scientific difficulty.

Artificial leaf

A solar-powered light-harvesting device with self-assembling and self-healing catalysts is called an artificial leaf. The technology intakes water, breaking it down to release protons.

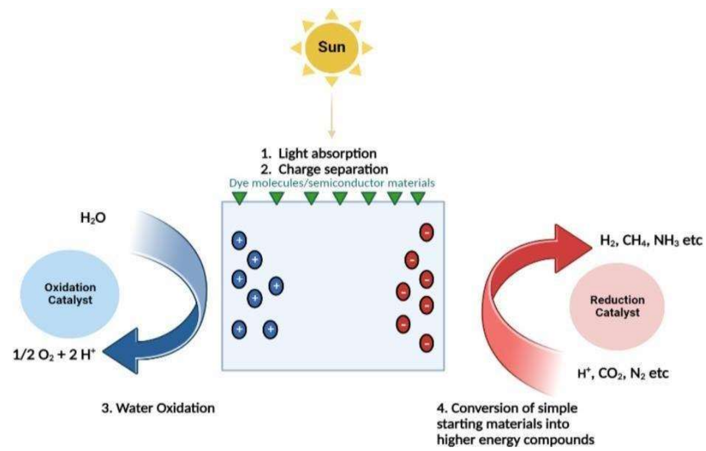

Figure 2: Artificial photosynthesis prototype schematics

and electrons that can be used to create hydrogen or other renewable fuels for a sustainable future. Through photosynthesis, the leaf divides water molecules to produce O_2 and H_2 molecules in the form of protons and electrons, which is used to turn solar energy into chem- ical energy. Three-dimensional (3D) nanomaterials have excellent mechanical and optical qualities as well as a generous capacity for mass transfer. As a result, creating a 3D artificial photosynthesis system that looks like real leaves (also known as hierarchical design) is an important step in storing and converting solar energy (CO_2 reduction) Figure 4.

Related Chemical Equations

The Chemical Reactions involved in breaking down water and producing fuels are as follows:

Water (H_2O) is split into oxygen, hydrogen ion and electrons, shown in Equation 1

$$2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4e^- \quad (1)$$

Carbohydrates (H_2CO) are made from CO_2 and the hydrogen ions and electrons released during splitting of water, shown in Equation 2:

$$CO_2 + 4\,H^+ + 4\,e^- \longrightarrow H_2CO + H_2O \quad (2)$$

Light initiates the aforementioned reactions. Four photons are needed for each half-reaction. The full photosynthesis reaction is formed by the combination of these two half-reactions (Equation 1 and Equation 2). Eight photons—two photons for each electron—are used while transferring four electrons, as shown in Equation 3.

$$CO_2 + H_2O \longrightarrow H_2CO + O_2 \quad (3)$$

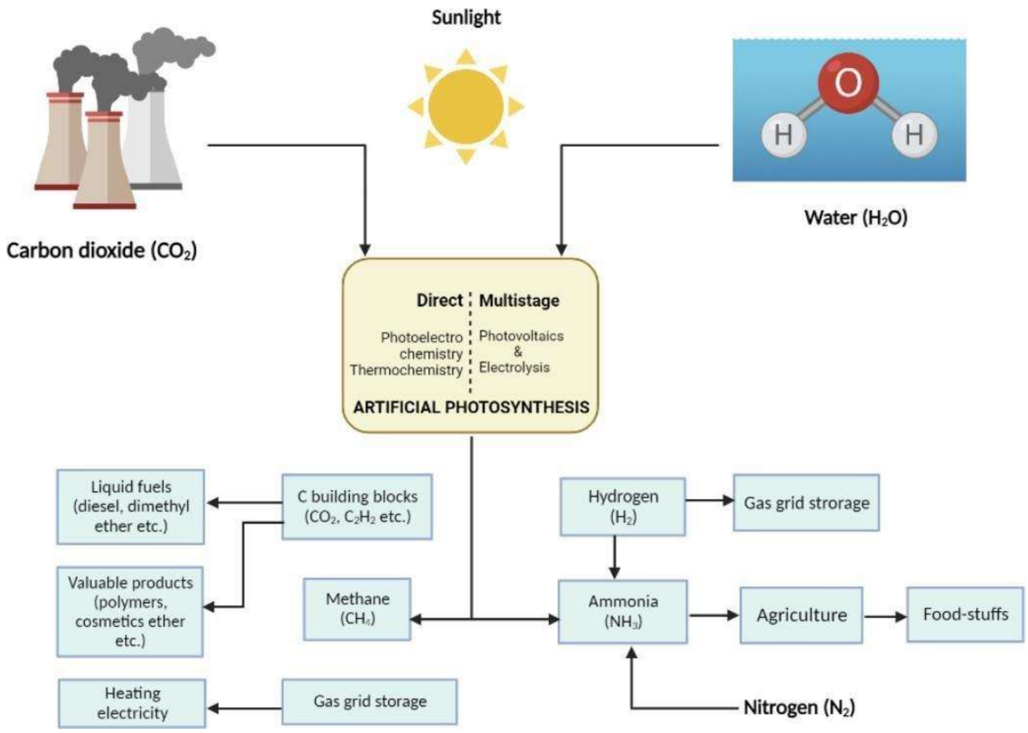

Figure 3: Possible role of artificial photosynthesis in the global energy and natural resource system

In comparison to the production of carbon-based fuels, the chemical processes used to pro- duce hydrogen are simpler. The energy of four extra photons is used to form two hydrogen molecules from the four protons and four electrons that are released during the splitting of water, as shown in Equation 4.

Basic Mechanism

$$4\,H^+ + 4\,e^- \longrightarrow 2\,H_2 \qquad (4)$$

Two light-absorbing minerals which can utilize the conversion of CO_2 and H_2O into a chemical form of energy storage are required to replicate natural photosynthesis. Perovskite and bismuth vanadate were utilized by certain researchers from Cambridge University to perform synthetic photosynthesis. In contrast to Bismuth Vanadate, which mostly absorbs blue light and also releases electrons, Perovskite is a mineral that absorbs light from the red end of the spectrum. This is how the mechanism

- Light absorber perovskite and a catalyst altogether were used for CO_2 reduction. On one side there was the perovskite layer and on the other side was the molecular catalyst.
- To connect these two a thin metal was used which can melt at a lower temp. So, the metal was first heated up and cooled down fast in order to attach the perovskite to the molecular catalyst together forming a layer. This layer was then wired and encapsulated.
- Thereafter another light absorber Bismuth Vanadate was used. First light will come and pass-through bismuth and create oxygen. Then a part of the light will reach the perovskite and drive the reduction of CO_2 into CO and H_2O into H_2 which are the key ingredients of liquid fuels.

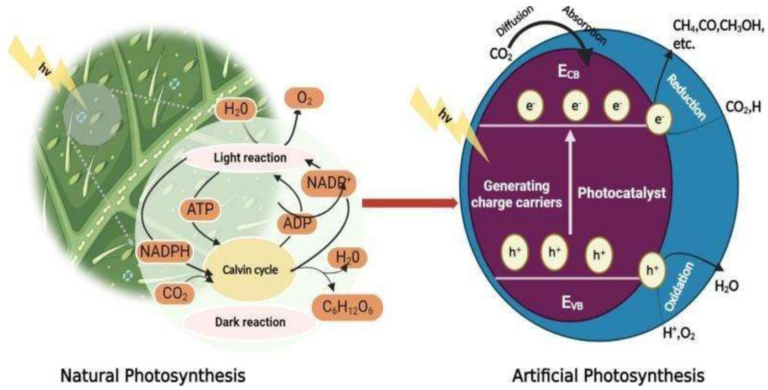

Figure 4: Comparison of the processes

Utilizing various semiconductor and bio-catalytic materials, there has been a sharp increase in the photo-catalytic and photo-electro-catalytic conversion of CO_2 to date. The intricacy of the low quantum yield, multi-electron reduction process, the photo-stability of material, and selective creation of products still necessitate state-of-the-art developments in this sector despite the substantial advancements in photo/electro-catalytic CO_2 conversion. Defect, interface, and crystal facet engineering, as well as the insertion of co-catalysts through the creation of hetero-structures, are just a few of the modification strategies that have been developed to solve the aforementioned CO_2 photo-conversion difficulties. Additionally, creating 3D hierarchical ‗1fake leaf' structures by imitating the procedure is a successful technique to capture light and convert CO_2 [3].

Progresses in the Structure and Mechanism of the Technology

The functioning of a semiconductor-based photocatalytic system is more advantageous technologically and economically, because a PEC (Photoelectrochemical) system needs a 25% STH (solar to hydrogen) conversion efficiency. The cost-competitiveness of photocat- alytic reactors would decrease with a STH efficiency of 5–10% [4]. The goal of the ongoing researches is to better understand how PEC cells function, in order to clarify the reaction processes. They anticipate the development of the PEC systems' use of earth-abundant light absorbers. In order to efficiently capture solar energy to split H_2O and decrease atmospheric CO_2 to enriched hydrocarbon compounds, a number of possible studies have so far analyzed the idea and building of artificial leaves.

- The artificial leaf structures for solar-driven water splitting and CO_2 reduction, for example, were the subject of a mini-review. The systematic comparison of artificial and natural leaf, analogues for applications such as CO_2 conversion and water splitting were also covered.
- Another study presents a thorough presentation of the design and engineering of an artificial leaf structure with special emphasis on the various operational factors involved in solar water splitting.
- The development of artificial leaf structure has improved CO_2 conversion, however a current in-depth analysis that emphasizes and elaborates this advancement is still lacking.

Significance of the Catalyst

The development of inorganic semiconductor photo-catalysts, whose electronic structures drive the CO_2 reduction process, is crucial for the possibilities of photo-catalytic artificial leaf techniques. Chlorophyll P680 and P700, which were modeled after the natural photosyn- thetic

system, display absorption at 680 nm and 700 nm as dual concentrators, respectively, with an optical band gap of 1.8 eV [5]. The reduction potential of the photo-generated elec- trons in the

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CB (conduction band) is very necessary for the CO_2 photo-reduction process [6]. Artificial sheets made of semiconductors are created for heterogeneous photo-catalysis with conduction bands that are more negative than the redox potential of CO2 reduction. Inorganic semiconductor photo-catalysts with corresponding band gaps of 2.2 eV, 1.5 eV, 2.3 eV, 2.0 eV, 2.7 eV, and 2.3 eV, such as Fe_2O_3, CdTe, GaP, InP, Cu_2O, ZnSe, and ZnTe, have all been used to reduce CO_2 to date. The following steps are involved in photo-catalytic CO_2 reduction with the help of an artificial leaf-based semiconductor: Solar photons are absorbed by semiconductors, creating charge carriers and then photo-excited electrons. Contiguous hole and electron separation and migration to the appropriate photo-catalytic surface take place. The essential thermodynamic step in this process is CO2 adsorption on the photo- catalyst surface, which may produce partly charged species of $CO_2^{\delta-}$ that are later converted into bent CO_2^{-} anion radicals. There is no such semiconductor that can generate CO_2 owing to the greater potential of 1.9 V vs NHE (Normal Hydrogen Electrode). Hence, this single electron transfer activity is regarded as the rate determination step as shown on Equation 5.

$$CO_2 + e^- \longrightarrow CO_2^-, E^0 = -1.90 \quad \text{V vs NHE} \qquad (5)$$
$$CO_2 + 8\,H^+ + 8\,e^- \longrightarrow CH_4 + H_2O,\ E^0 = -0.24 \text{ V vs NHE} \qquad (6)$$
$$CO_2 + 6\,H^+ + 6\,e^- \longrightarrow CH_3OH + H_2O,\ E^0 = -0.38 \text{ V vs NH} \qquad (7)$$
$$CO_2 + 4\,H^+ + 4\,e^- \longrightarrow HCHO_2 + H_2O,\ E^0 = -0.48 \text{ V vs NHE} \qquad (8)$$
$$CO_2 + 2\,H^+ + 2\,e^- \longrightarrow CO + H_2O,\ E^0 = -0.53 \text{ V vs NHE} \qquad (9)$$
$$CO_2 + 2\,H^+ + 2\,e^- \longrightarrow HCOOH,\ E^0 = -0.61 \text{ V vs NHE} \qquad (10)$$

For the photo-reduction process to continue after reducing CO_2, the resulting product must be desorption.The advantages of photo-catalysis and electro-catalysis are combined in photo-electro-catalytic technology, which is another possible design for an artificial leaf [7]. A PEC (Photo-electrochemical) cell, which includes photo-electrodes and flowing photo- induced electrons over the external circuit, makes up the photo-electro-catalytic artificial leaf. Incredible advancements have occurred since the first experiments on gallium phos- phide PEC CO_2 reduction cells [8]. They recognized the PEC mechanism for solar-driven chemical fuel production from CO_2 reduction at the solid-liquid interface [9]. The p-typesemiconductor photocathodes are realized in theory and give a directing channel to charge carriers for CO_2 reduction on a generation of photo-voltage [10]. Three electrodes make up the PEC configuration, including a photo-anode for simultaneous oxygen evolution reaction, a reference electrode, and a photocathode for CO_2 reduction [11]. When a p-type semicon- ductor photo-cathode is submerged in an aqueous electrolyte, a semiconductor-electrolyte interface is created [6]. Photo-catalytic splitting of water using two-step photo-excitation using two different semiconductor powders and a reversible donor/acceptor pair is one of the potential approaches of artificial photosynthesis (referred to as shuttle redox mediator). The ―Z-scheme‖ is a system that emerged as a result of green plants' organic photosynthesis. The photosynthetic light processes' oxidation or reduction changes are described by the Z scheme. The transmission of one electron in this instance involves both photo-systems and has the appearance of a Z shape. Choosing a material with practical band edge potentials is typically the most important step in developing a Z-scheme based PEC system. The material's photo (electro) stability, which allows it to effectively absorb CO_2 and convert it only to useful hydrocarbon fuels, is also crucial. The performance of CO_2 reduction by bio-catalytic systems with related photo-electrodes is high even at low over-potential values, making them asuperior class of bias-free PEC devices. As an effective electro enzymatic catalyst, formaldehyde dehydrogenase from *Clostridium ijungdahlii* (ClFDH) was used in experiments with minimal over potential and significant CO_2 to formaldehyde conversion effectiveness. The ClFDH was further annealed

with a TiO_2-adorned $CuFeO_2$ and CuO- mixed electrode (ClFDH-TiO_2|CFO) because to the negative CB (conduction band) edge potential [12]. A
wireless Z-schematic bio-catalytic PEC system was produced by integrating the FeOOH|$BiVO_4$ photoanode and the ClFDH-TiO_2|CFO photocathode in a semi-artificial FeOOH|$BiVO_4$||ClFDH-TiO_2|CFO device. The semi-artificial bio-catalytic device's component pieces, each of which has a specific role, increased the selective PEC conversion of CO_2 into formaldehyde. For example, the addition of TiO_2 layer on CFO served as a protective layer and stopped PEC corrosion of the CFO.

Efficiency

Figure 5 depicts a tandem artificial photosynthesis apparatus in schematic form along with its related light-absorbing characteristics. For the best energy efficiency, the energy levels and other chemical characteristics of the photosystems must be adjusted so that, within the two steps, the entering photon flux is (nearly) fully utilised in the transformation to fuel.

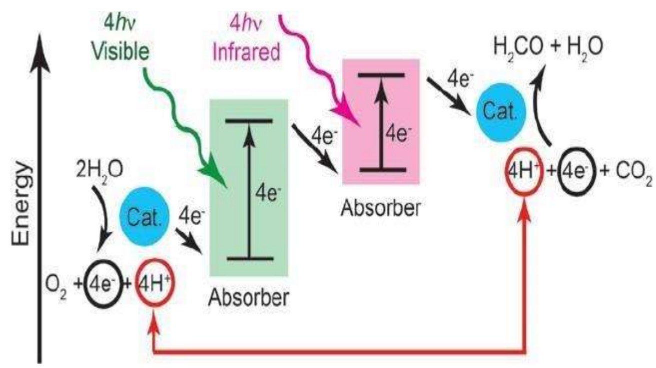

Figure 5: Tandem system for artificial photosynthesis and utilization of flux [13]

Conclusions

Researchers and experts from all around the world are attempting to create hydrogen along with carbon-based fuels using sunlight, carbon dioxide, and water. These fuels put forward the engaging proposal of sanctioning solar energy to be conserved as well as trans- ported, so that this solar energy is easily available when needed. Besides supplying the sustainable transportation fuel, we require, artificial photosynthesis can also replace the fossilraw materials currently used in industry. This review mainly focused on the use of ar- tificialphotosynthesis to turn solar energy into fuels, their mechanism and current progress in this particular research. Despite all the substantial research breakthroughs, there are still limitations of using appropriate photo electrode materials. The actual functioning of artificial photosynthesis, particularly on a large scale, is still difficult due to the requirement of externalbias and kinetic barriers to CO_2 conversion.

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