# VALUE ADDED PRODUCTS FROM $CO_2$ CAPTURE THROUGH PHOTOSYNTHESIS

Thesis submitted towards the partial fulfilment of Master of Engineering degree in Bio-process Engineering

By

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# DECLARATION OF ORIGINALITY AND COMPLIANCE OF ACADEMIC ETHICS

I hereby declare that this thesis contains literature survey and original research work by the undersigned candidate, as part of his "***Master of Engineering in Bio-process Engineering***" studies. All information in this document have been obtained and presented in accordance with academic rules and ethical conduct.

I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to research work.

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# CERTIFICATION

This is to certify that **Mr. Shreya Ghosh**, final year student in Master of Bio-process Engineering examination in the department of Chemical Engineering, Jadavpur University, bearing Registration No: 131673 has successfully completed the thesis work entitled "**Value added products from $CO_2$ capture through photosynthesis**" under the guidance of **Dr. Raj Kumar Das** during his master degree curriculum. This work has not been reported earlier anywhere and can be approved for submission in partial fulfilment of the requirements for the Master of Engineering in Chemical Engineering.

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# CERTIFICATE OF APPROVAL

This thesis is hereby approved as creditable study of an engineering subject carried out and presented in a manner satisfactory to warrant its acceptance as prerequisite to the degree for which it has been submitted. It is understood by this approval that undersigned don't endorse or approve any statement made, opinion expressed or conclusion drawn therein but approve the thesis only for purpose of which it is submitted.

.....

Shreya Ghosh

Department of Chemical Engineering

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I would sincerely express my gratitude towards my project guides Dr. Raj Kumar Das for his valuable guidance and cooperation and for providing me the opportunity to accomplish the project. Without their guidance and assistance, I would never be able to work successfully in this area. I am greatly thankful to them for guiding me always throughout my project work.

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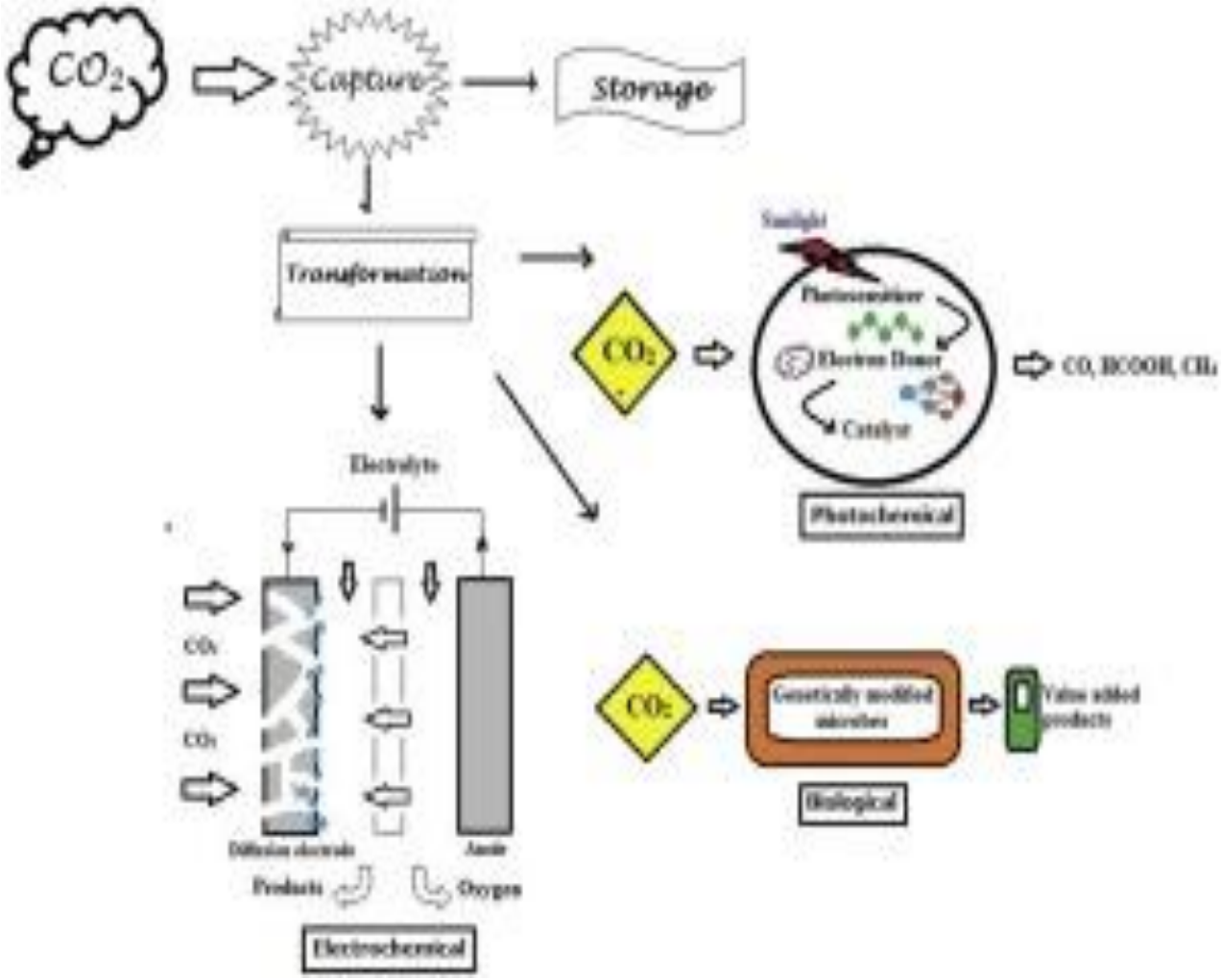
I would also like to express gratitude to HOD and all faculties of the Chemical Engineering Department, Jadavpur University.

Thanking you,
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# ABSTRACT:

Carbon dioxide ($CO_2$), a potent greenhouse gas contributing to climate change, necessitates efforts to reduce its levels in the atmosphere. Various innovative methods such as photochemical, biochemical, and electrochemical processes aim to capture, store, and utilize carbon, thereby reducing reliance on nonrenewable sources like coal and oil. Photochemical transformation involves creating charged carriers, separating them, transporting them, and ultimately using photoelectrons to reduce $CO_2$. Among these methods, photocatalytic reduction of $CO_2$ is gaining traction, with research focusing on semiconducting materials such as oxides, sulfides, and phosphides. Carbon dioxide ($CO_2$), a potent greenhouse gas contributing to climate change, necessitates efforts to reduce its levels in the atmosphere. Various innovative methods such as photochemical, biochemical, and electrochemical processes aim to capture, store, and utilize carbon, thereby reducing reliance on nonrenewable sources like coal and oil. Photochemical transformation involves creating charged carriers, separating them, transporting them, and ultimately using photoelectrons to reduce $CO_2$. Among these methods, photocatalytic reduction of $CO_2$ is gaining traction, with research focusing on semiconducting materials such as oxides, sulfides, and phosphides.

## Graphical Abstract



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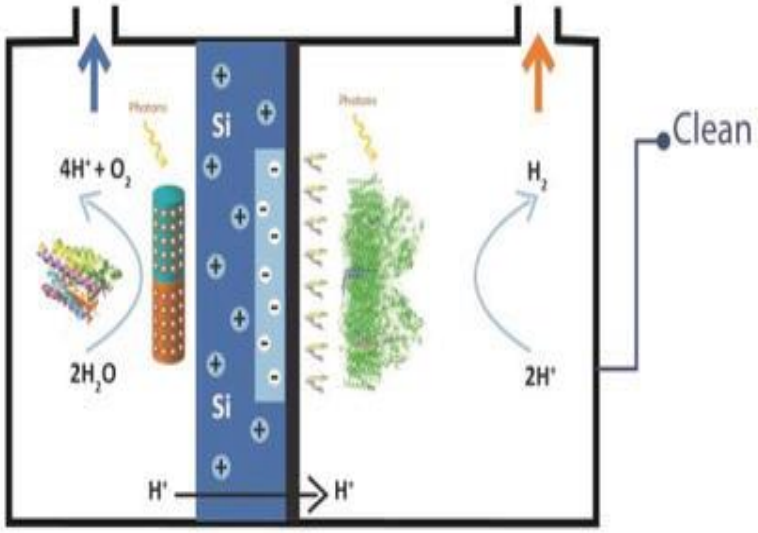
# INTRODUCTION

In today's technological age, it's imperative to protect our natural resources and seek renewable energy sources to reduce reliance on fossil fuels. Fossil fuel usage not only emits harmful gases like carbon dioxide and sulfur dioxide but also depletes precious resources. The urgent call to reduce carbon dioxide emissions globally has led to a pressing need for sustainable and carbon-neutral energy technologies. Scientists have explored various alternatives over the years, with recent focus on high-tech energy systems inspired by nature.

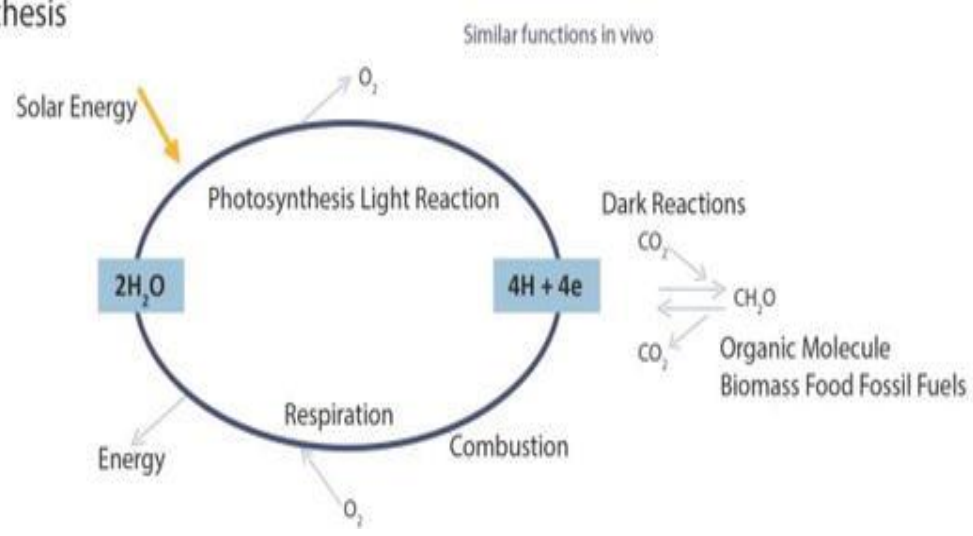
Photosynthesis, a process found in plants, algae, and photosynthetic bacteria, serves as a model for energy production. Artificial photosynthesis, first proposed by Giacomo Ciamician in 1912, aims to mimic this process to reduce fossil fuel dependency. While solar power stations offer a promising solution for sustainable energy, the challenge lies in efficient energy storage. Attempts to replicate photosynthesis for electricity generation faced hurdles in energy storage until now.

Artificial photosynthesis systems (APS) mimic natural photosynthesis by capturing and storing solar energy as fuel. APS devices utilize semiconductors to absorb solar energy and convert it into chemical energy for later use. Advances have been made in creating artificial reaction centers, where solar energy splits water molecules into oxygen and hydrogen fuel. Despite its potential, APS efficiency remains a concern, often requiring external electrical input. Nevertheless, APS offers a more environmentally friendly solution compared to traditional solar panels, as it absorbs carbon dioxide and releases oxygen. This chapter provides an overview of APS, its limitations, challenges, and future prospects as an alternative energy source.

## Artificial Photosynthesis

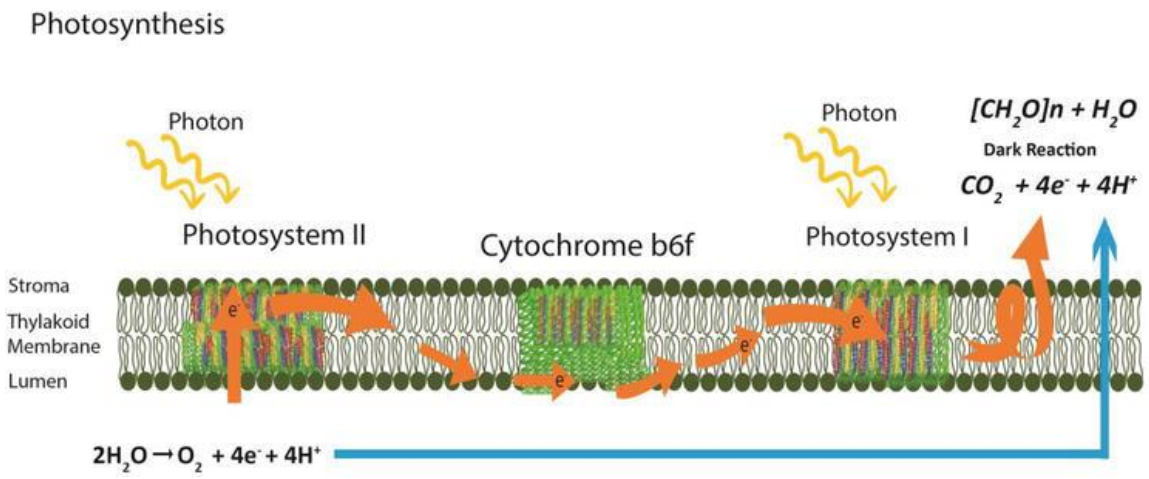



## Natural Photosynthesis



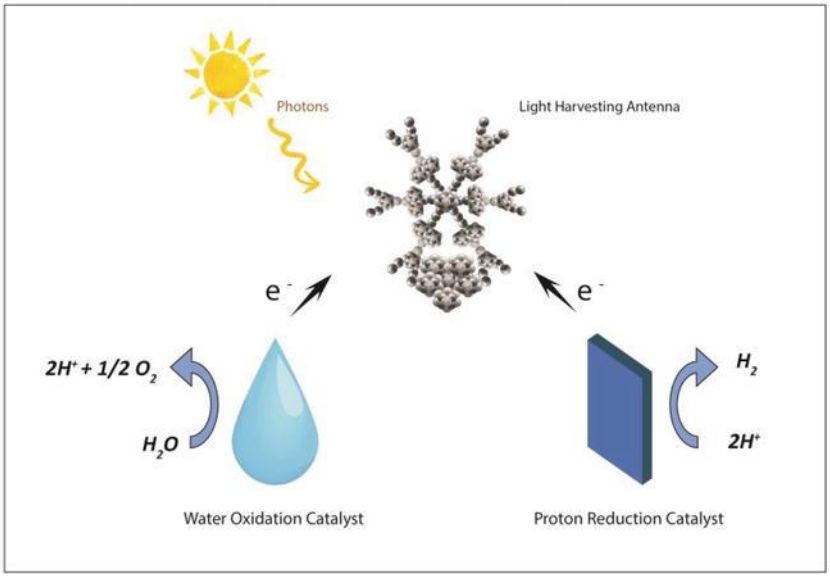
## Photosynthesis: nature’s marvel

For over a billion years, green plants, algae, and photosynthetic bacteria have engaged in photosynthesis without significant alteration, making it a crucial component of models aimed at safeguarding our planet's future. Within this process, the electron transport system operates at a pace faster than the photons of solar energy reaching the light-harvesting complexes found in chloroplast membranes. Photosynthesis unfolds in three key protein complexes within the chloroplast membrane of higher plants: two light-harvesting complexes (LHC I/PS I and LHCII/PSII) or antennae, and cytochrome b6f, linked by various electron carriers. These complexes transfer photons to reaction centers (RCs) as resonance energy, establishing charge differences across the membrane. On the donor side of PSII lies the oxygen-evolving complex (OEC), a potent oxidant that catalyzes the photolysis of water into molecular oxygen, protons, and electrons. The electrons move through the plastoquinone pool to cyt b6f, then plastocyanin to PSI, ultimately reducing NADP+ to NADPH via ferredoxin. This electron movement, coupled with proton pumping across the membrane, generates a potential and pH gradient, leading to ATP synthesis. This assimilatory power from the light reaction is harnessed for the unique process of atmospheric carbon dioxide fixation by the enzyme Rubisco, the most abundant protein on Earth. However, Rubisco's slow catalytic rate poses a significant bottleneck to increasing photosynthetic efficiency. The structural composition of RC complexes, with molecular cofactors arranged in a network held by the membrane, enables efficient light capture and electron movement, a testament to its nanoscale complexity operating flawlessly for billions of years, providing energy to all heterotrophs. Replicating the entirety of photosynthesis remains an immense challenge.(Bhatla SC, 2018)



## Artificial photosynthesis

The idea of artificial photosynthesis was proposed by an Italian chemist in 1912, but significant progress didn't occur until 1972, when Kenichi Honda and his student Akira Fujishima achieved a breakthrough. They developed a water-splitting device powered by light, known as the "Honda-Fujishima effect". This device consisted of a photoelectrochemical cell with a TiO2 photoanode and a platinum (Pt) black cathode submerged in water. When exposed to light, the TiO2 released an electron, creating a positive charge on the Ti atom. This electron hole was filled by an electron from a water molecule, oxidizing the water to produce oxygen. Simultaneously, the released electron combined with a proton from water, reducing it to form hydrogen. While this device successfully generated oxygen at the anode and hydrogen at the cathode through water photolysis, a limitation was that TiO2 only absorbed ultraviolet wavelengths and was inactive in visible light. (Dette C, Pérez-Osorio MA, Kley CS, Punke P, Patrick CE, Jacobson P, et al. $TiO_2$ anatase with a bandgap in the visible region. Nano Letters. 2014).



## Artificial photosynthesis: principle

As previously stated, artificial photosynthesis, akin to its natural counterpart, encompasses three primary stages: light absorption inducing excitation, the subsequent generation and separation of charges, and ultimately, the chemical conversion process culminating in fuel production.

## Light absorbed

In natural photosynthesis, chlorophylls and carotenoids are organized into antennae structures to capture specific wavelengths of light, primarily in the red and blue range, inducing electron excitation. These pigments have a limited absorption range, typically between 400 to 700 nm, which corresponds to less than half of the sunlight reaching Earth. Thus, a key objective is to develop photosensitizers capable of efficiently utilizing photons upon exposure and effectively aggregating light energy. Furthermore, the materials employed should possess the ability to absorb a broader spectrum of solar wavelengths to maximize energy extraction from sunlight.

Drawing inspiration from the "Honda-Fujishima effect," various materials have been explored by researchers. These include semiconductor photoanodes such as TiO2 and silicon, metal oxides like ZnO, Fe2O3, and BiVO4, metal nitrides such as Ta3N5, metal phosphides like GaP, and metal oxynitrides such as TaON. Silicon, known for its abundance and cost-effectiveness, exhibits a wider light absorption spectrum. Additionally, Gallium Nitride, another semiconductor, has been utilized in thin-film technology to produce formic acid and ethanol.

## Lysis of water

The process of water oxidation in artificial photosynthesis (APS) is energetically demanding, requiring approximately 237 kJ mol−1 of free energy and a potential of around 1.23 V to transfer 4H+ and 4e−. In natural photosynthesis, this is accomplished through the oxygen-evolving complex (OEC), typically containing manganese, which catalyzes the formation of oxygen-oxygen bonds. In APS, semiconductor nanowires absorb light, initiating water oxidation to produce oxygen, protons, and electrons. Electrons migrate while protons traverse a proton-conducting membrane, such as Nafion, ultimately being reduced to hydrogen. Thus, the photolysis of water in APS combines distinct systems tailored for their respective roles.

Water splitting entails an energy input of approximately 2.5 V, necessitating a catalyst to absorb sunlight photons and initiate the reactions. While bioinspired approaches using manganese encountered stability issues, cobalt oxide (CoO) emerged as a stable, efficient, and readily available alternative.

Various materials exhibit efficiency in certain steps of the process but inefficiency in others, prompting the use of coupled materials customized for their reactivity. Recent efforts have focused on molecular water-oxidation catalysts, typically comprising metal complexes with open coordination sites and electronic structures conducive to stabilizing metal-hydride intermediates. While noble metals like rhodium and platinum are commonly used, attempts to develop catalysts from earth-abundant metals such as cobalt, iron, molybdenum, and nickel have yielded promising results, with nickel complexes demonstrating notable stability and efficiency.

Transition metal families such as copper, nickel, and iron-based catalysts have been explored to enhance catalytic function. Additionally, cobalt and zirconium heterobimetallic complexes on porous silica, separated by nanotube membranes, have been investigated. However, the search and optimization of materials for APS applications remain ongoing endeavors.

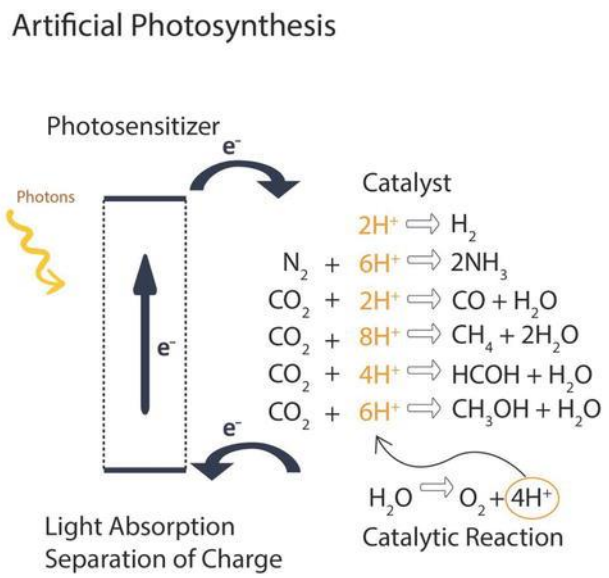
**Reduction of CO2:**

The reduction of carbon dioxide presents a significant challenge due to its linear structure and high stability, with a dissociation bond energy of approximately 750 kJ/mol. This uphill reaction necessitates a nucleophilic attack on the carbon atom. However, the carbon atom's high valence offers opportunities to create various fuels alongside the production of oxygen and hydrogen derived from water. Fuels such as formic acid (HCOOH), methanol (CH3OH), carbon monoxide (CO), and methane (CH4) can be generated, offering the advantage of easy integration into existing energy infrastructure.

Despite these advantages, the complexity arising from carbon's multi-electron nature poses a significant scientific challenge. While the exact mechanism remains unclear, it is hypothesized that the reduction of carbon dioxide in artificial photosynthesis (APS) is akin to water splitting during natural photosynthesis. In APS, carbon dioxide interacts with catalysts, facilitating electron transfer and reduction reactions, coupled with proton coupling. This process creates

an electron hole in the photosensitizer, subsequently filled by an electron, thus concluding the process.

The choice of catalyst is pivotal in APS, necessitating considerations of cost-effectiveness and durability. Researchers have explored various complexes, including rhenium-based, cobalt-based, nickel-based, iron-based, and zinc-based complexes. Innovative porous materials have been employed to enhance the adsorption of intermediates on the electrode surface. Additionally, co-catalysts such as copper, silver, and gold have shown promise in improving conversion efficiency. Nonetheless, the design of an ideal catalyst capable of significantly enhancing chemical conversion performance remains a subject of ongoing research.



**Natural photosynthesis vs artificial photosynthesis**

Photosynthesis orchestrates two pivotal reactions: the light-dependent reaction and the light-independent reaction, also known as the Calvin cycle. In the light-dependent reaction, photons are harnessed and transformed into assimilatory powers, namely NADPH and ATP, which are utilized in the subsequent fixation of carbon during the light-independent reaction. This light reaction unfolds within two photosystems, PSI and PSII, ensconced in the thylakoid membrane. These systems are replete with light-absorbing pigments like chlorophylls and carotenoids, orchestrating an intricate dance of resonance energy transfer. This culminates in the release of electrons from chlorophyll molecules, initiating a cascade through electron carriers, ultimately reducing NADP+ to NADPH and generating ATP. Concurrently, the removal of electrons from chlorophyll engenders an "electron hole," which is replenished through the photolysis of water by the oxygen-evolving complex adjacent to PSII, yielding electrons and oxygen, vital for sustaining life on our planet.The assimilatory powers engendered in the light reaction propel the reduction of carbon dioxide in the light-independent reaction, mediated by the Calvin cycle. This process, elucidated by Melvin Calvin, unfolds within the chloroplast stroma, orchestrated by an array of enzymes. Here, carbon dioxide sourced from the atmosphere is transmuted into carbohydrates, ensuring the sustenance of autotrophic organisms. In essence, photosynthesis, honed through evolutionary epochs, furnishes autotrophic organisms with the ability to synthesize their own sustenance, converting solar energy into chemical energy stored within carbohydrate bonds.Artificial photosynthesis endeavors to replicate three fundamental tenets of natural photosynthesis: light capture and electron transport, water splitting into hydrogen and oxygen, and carbon dioxide reduction. Through artificial photosynthesis, two types of fuels are synthesized: hydrocarbons like methanol and formic acid, and pristine hydrogen. Hydrogen, a pristine fuel source produced via artificial photosynthesis, boasts versatile applications spanning liquid fuel utilization, fuel cells, thermal processes, electrolysis, and biological applications, poised to supplant fossil fuels in various domains.

**Solar harvesting devices vs artificial photosynthesis**

Researchers have dedicated considerable efforts to devising devices geared towards converting solar energy into chemical energy, thereby storing it within chemical bonds. Among the most prominent of these devices are the photoelectrochemical cell and the photovoltaic-coupled electrolyzer. While they share certain similarities, they also exhibit distinct differences, each accompanied by its own array of advantages and limitations.

Both the photoelectrochemical cell and the photovoltaic-coupled electrolyzer operate based on the fundamental principle of harnessing sunlight to drive chemical reactions. In essence, they both utilize solar energy to initiate electrochemical processes. However, their operational mechanisms and configurations diverge.

In a photoelectrochemical cell, light absorption takes place directly within the device, often employing semiconductor materials. Upon exposure to sunlight, these materials generate electron-hole pairs, which then participate in electrochemical reactions at the interfaces of the electrodes. This facilitates the conversion of reactants into the desired chemical products. One notable advantage of this approach is its ability to seamlessly integrate light absorption and chemical conversion, potentially simplifying the device's architecture. Nevertheless, challenges persist, including limitations in efficiency and material stability, which remain subjects of ongoing research.

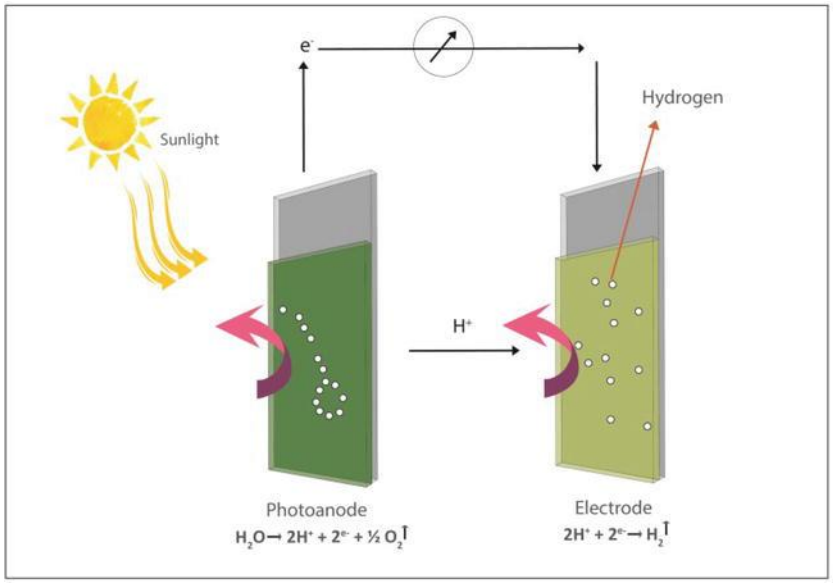
Conversely, the photovoltaic-coupled electrolyzer system segregates the processes of light absorption and chemical conversion. Here, photovoltaic cells, typically composed of semiconductor materials, absorb sunlight and convert it into electrical energy. This electrical energy is subsequently utilized to power an electrolyzer, where water undergoes electrolysis to produce hydrogen and oxygen. While this approach may offer superior efficiency and scalability compared to photoelectrochemical cells, it necessitates separate components for

light absorption and chemical conversion, resulting in increased complexity and potentially higher costs.

Both systems possess their unique advantages and limitations. Photoelectrochemical cells offer the advantage of directly integrating light absorption and chemical conversion, potentially simplifying device design and operation. Conversely, photovoltaic-coupled electrolyzers may deliver higher efficiency and scalability, albeit at the expense of increased complexity and cost. Ultimately, the choice between these approaches hinges on factors such as desired efficiency, scalability, cost-effectiveness, and specific application requirements.

**Photoelectrochemical cell**

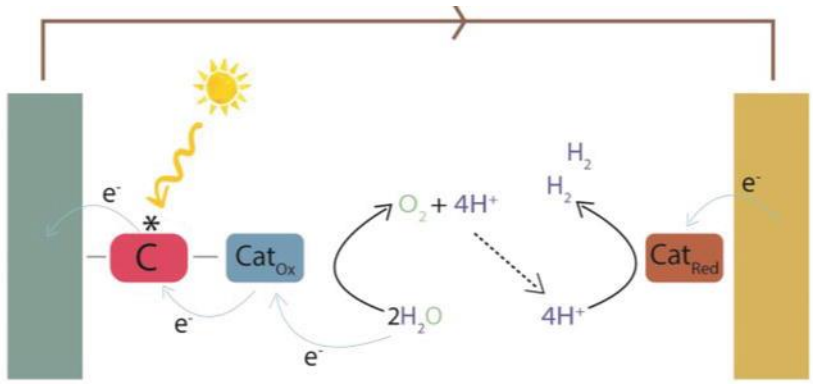
The photoelectrochemical cells (PEC) consist of two electrodes, a photoanode and a photocathode immersed in an electrolyte and an external wire . One of the variants designed comprises a single electrode evolving mixture of oxygen and hydrogen which entails contamination which is an additional step of 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 . 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 .




The choice of material for the photoanode plays a pivotal role in determining the efficiency, stability, and light absorption capabilities of water-splitting processes in aqueous solutions. While semiconductors have been explored, they often exhibit low efficiency, instability, and limited absorption of visible light. Consequently, the focus has shifted towards alternative materials such as carbon-based substances, transition metals, and nanostructured photoanodes.

Carbon-based materials like graphene, carbon nanotubes, carbon dots, and carbon quantum dots have demonstrated remarkable stability and photocurrent generation capabilities. Transition metals such as germanium-doped hematite, cadmium sulfide, zinc oxide, copper sulfide, and molybdenum exhibit high performance owing to their excellent electrical conduction and electrochemical stability. Furthermore, nanomaterials like nanowires, nanotapers, and nanorods have shown promising results, particularly in achieving high hydrogen evolution rates at the photocathode.

Recent advancements have led to the development of serially coupled photoelectrochemical cells (PECs) incorporating both Photosystem II (PSII) and Photosystem I (PSI) along with an Au electrode. This semi-artificial setup mimics the Z scheme of natural photosynthesis, wherein two types of redox osmium complexes embedded in a hydrogel facilitate electron transfer between the photosystems. This innovative approach has demonstrated the production of photocurrent in PECs, further advancing the field of artificial photosynthesis.



**Photovoltaic-coupled electrolyzer**

The operational principle of a photovoltaic-coupled electrolyzer hinges on the synergy between solar and electrochemical cells. In this setup, the photovoltaic cell serves as the primary component responsible for both light absorption and charge separation. Solar radiation is initially captured and converted into electricity within the photovoltaic cell, which subsequently channels this energy potential to an electrolyzer for redox reactions.

The process unfolds in two main steps:

1. Solar radiation is first converted into electricity through the photovoltaic cell.

2. This electricity is then utilized for the oxidation and reduction reactions of water or carbon dioxide within the electrolyzer cell.

This system boasts an efficient strategy, yielding remarkable solar-to-hydrogen efficiencies ranging from 10% to 15%, and in some instances reaching as high as 30%. To achieve such high efficiencies, an ultra-efficient photovoltaic-coupled electrolyzer system is employed, typically featuring a triple-junction solar cell comprising three subcells made of indium gallium phosphide (InGaP), gallium arsenide (GaAs), and gallium indium nitrogen arsenic antimonide (GaInNAs(Sb)).

The setup incorporates two polymer electrolyte membranes: one coated with Pt black catalyst at the cathode and another with Ir black catalyst at the anode. The power generated by the triple-junction cell pumps water into the anode of the first electrolyzer. The effluent, consisting of water and oxygen, is then transferred to the second electrolyzer, where hydrogen from the first electrolyzer's cathode is conveyed to the second electrolyzer's cathode. This process yields hydrogen and oxygen at the cathode and anode of the second electrolyzer, respectively. The remaining water is recycled for subsequent cycles without interruption, enabling continuous operation for nearly 48 hours. The system achieves a solar-to-hydrogen conversion efficiency of 30%.

In summary, the photovoltaic-coupled electrolyzer system represents an innovative approach that harnesses solar energy to efficiently produce hydrogen through electrochemical processes, offering a sustainable and renewable energy source.

**Semi-artificial photosynthesis**

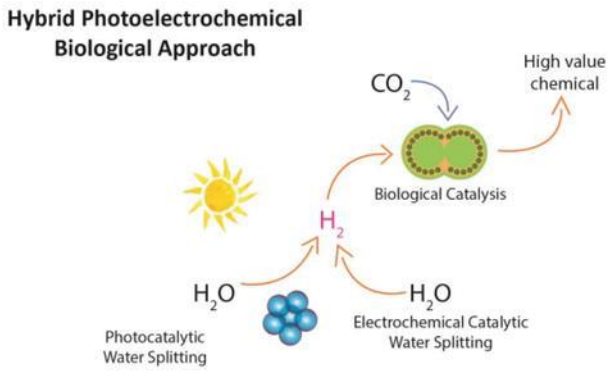
"Semi-artificial photosynthesis" refers to a fascinating approach that combines elements of both natural and artificial photosynthesis to enhance efficiency and overcome limitations. By integrating the advantageous features of natural photosynthesis, such as high quantum efficiency, selectivity, specificity, and self-repair mechanisms, with synthetic materials and modified molecular chemistries, researchers aim to create more efficient and versatile systems.

One key aspect involves utilizing synthetic materials with broader light absorption spectra, allowing for more efficient energy capture across different wavelengths of light. Additionally, modified molecular chemistries can enhance the functionality and stability of the system, minimizing limitations encountered in natural photosynthesis.

The process typically involves leveraging the photocatalytic properties of photosystems PSI and PSII, which are responsible for generating reducing power and facilitating the photolysis of water, respectively. By harnessing these mechanisms, semi-artificial devices can convert light energy into molecular hydrogen and carbon-based fuels, offering a promising avenue for sustainable energy production.

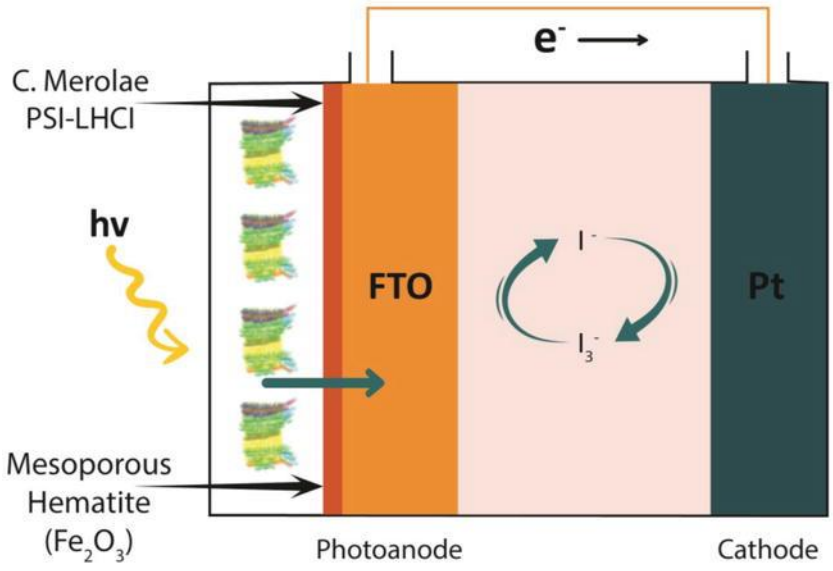
**Enzyme hybrids**

This paragraph outlines the characteristics, limitations, and strategies for enhancing the utilization of enzymes as biocatalysts. It emphasizes the specificity, turnover rate, and biodegradability of enzymes, while also acknowledging their limitations including thermal instability, pH sensitivity, susceptibility to organic solvents, and inhibition by metal ions.To overcome these limitations and fully exploit the potential of enzymes, researchers have turned to porous matrices such as metal-organic frameworks (MOFs) and metal-phenolic networks (MPNs). These matrices provide a stable environment for enzymes, thereby enhancing their stability and efficacy.Moreover, the paragraph highlights the achievement of 100% efficiency through the combination of artificial light absorbers and biological catalysts. By utilizing photocurrents through electrode-wired enzymes, researchers have been able to generate products with high efficiency, both kinetically and thermodynamically, at rapid rates.Examples such as Photosystem II enzymes, semiconductors, and mesoporous opal indium tin oxide (ITO) electrodes are cited to illustrate successful integration of inorganic collectors with biological catalysts, resulting in highly efficient systems.



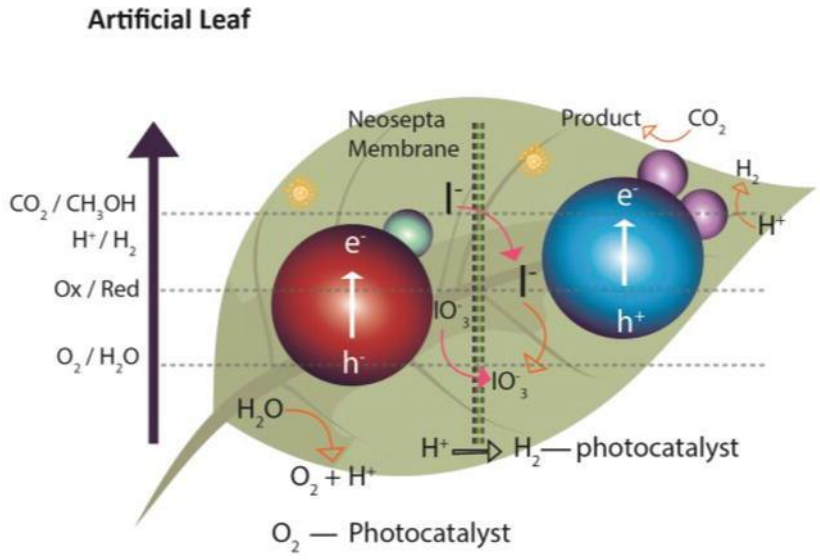
**Cell hybrids**

It seems like you've provided another paragraph discussing the utilization of biological systems, specifically unicellular organisms, in combination with inorganic materials to enhance efficiency. This paragraph highlights the investigation of cell hybrids, where microorganisms are paired with inorganic semiconductors or metal nanoparticles.For instance, one study involved the use of the anaerobe Methanosarcina barkeri bacteria along with a nickel sulfide electrode, inspired by naturally occurring nickel-dependent hydrogenases. Exposure to visible light resulted in the reduction of carbon dioxide to methane without a net loss in performance efficiency.In another study, an acetogenic bacterium Moorella thermoacetica was treated with water-soluble gold nanoclusters (AuNCs) and illuminated with light at a wavelength of 532 nm. The bacteria's cytoplasm mediators selectively picked up photo-generated electrons, bypassing the cell membrane, and produced acetic acid from carbon dioxide over six days.Another hybrid system involved introducing light-harvesting indium phosphide (InP) nanoparticles into genetically engineered yeast cells. The photoexcited electrons produced from InP activated nicotinamide adenine dinucleotide phosphate regeneration.



**Artificial leaf**

The paragraph discusses the development of an artificial leaf, inspired by the Z-scheme, as a significant advancement in biohybrid systems. Daniel G. Nocera and colleagues introduced a silicon-based device capable of producing hydrogen and oxygen using solar energy without emitting pollutants. This artificial leaf consists of a silicon chip coated with a chemical catalyst that accelerates the water-splitting reaction upon exposure to sunlight, capturing separated electrons and protons to form hydrogen gas. However, despite its potential, the artificial leaf still faces challenges, including low hydrogen fuel efficiencies and high costs. Safety concerns regarding the generated hydrogen fuel also limit its commercial use.



**CO2 Capture:**

The escalating concern over CO2 capture arises from the pressing need to address the environmental crisis fueled by the greenhouse effect and to purify CO2-involved gaseous products. Researchers and industries are actively pursuing materials with highly efficient CO2 absorption capabilities. While aqueous alkaline solutions are commonly used for CO2 capture, they often lead to severe corrosion of equipment and energy-intensive treatment of waste solutions, posing secondary pollution risks. Recent advancements highlight the promise of green sorbents like zeolites, metal organic frameworks, and carbon-based materials for CO2 capture without environmental harm. However, the regeneration of these sorbents typically involves energy-intensive processes reliant on fossil fuels, necessitating a focus on reducing regeneration costs and secondary CO2 emissions. Natural photosynthesis serves as a model for sustainable CO2 capture and conversion, utilizing sunlight to convert CO2 into organic compounds efficiently and without pollution. Inspired by this process, researchers have developed systems combining CO2 capture with conversion through special catalysis. Yet, achieving a breakthrough akin to photosynthesis, driven by light, remains a challenge. This requires the development of light-sensitive sorbents capable of reversibly switching CO2 capture and release. Proposed here is a cost-effective and versatile system for light-triggered CO2 capture, release, and conversion. This system employs porous polymeric particles as CO2 sorbents, a dark material for triggering CO2 release under light irradiation, and catalytic elements for CO2 conversion into storable chemical compounds. Through a one-step double emulsion process, porous particles composed of polylactic acid and polyethyleneimine (PLA-PEI) are synthesized without surfactants, enabling high throughput production. Carbon nanotubes, capable of photothermal conversion, are incorporated into the particle matrix, allowing for CO2 absorption in the dark and release under light irradiation. This light-triggered CO2 capture system, coupled with CO2 catalysis, enables direct collection of CO2 from the air and conversion into organic compounds. **(prf. Yapei Yang,2017) .**

## Comparison and analysis of $CO_2$ capture technologies:

(L.X. Hao, G.J. Zhang, Y. Jia, J.W. Qu, Q.T. Su,2016)

(A.A. Olajire,2010)(Y. Cao, E. Yang, W. Wang,2015)

| Capture technology | Advantages | Limitations | Future outlooks |
|---|---|---|---|
| **Chemical absorption** | Superior $CO_2$ capture performance; excellent $CO_2$ selectivity; relatively mature technology | High corrosion rate of equipment; high energy consumption and high operating costs; discharge of absorbed solvents will cause environmental pollution | Develop new absorbent solvents with good absorption performance and low corrosion; Develop equipment and absorption processes with low desorption energy consumption |
| **Solid adsorption** | Low energy consumption for regeneration; almost non-corrosive; suitable for low-concentration $CO_2$ capture; relatively simple operation; multiple adsorption technologies (TSA, PSA, ESA) | The capture capacity is smaller than chemical absorption; the capture of industrial flue gas needs to improve the cycle stability | In order to further improve the $CO_2$ capture performance, it is necessary to modify the adsorption material; optimization and combination of several adsorption technologies |
| **Membrane separation** | Low cost; low energy consumption; simple operation process; high separation purity ；be friendly to environment | Most membranes are easily damaged and has a short service life; the separation purity is not high; moisture has a greater impact on the permeability of the polymer membrane; industrial applications require a larger membrane area | Develop advanced new membrane materials to improve $CO_2$ separation efficiency; more industrial pilot research needs to be invested |
| **Cryogenic separation** | It is suitable for the capture of $CO_2$ with high concentration and high partial pressure, and the separation purity is very high | High operating cost and complex process; the solidification of $CO_2$ at low temperature leads to pipeline blockage; not suitable for the capture of low $CO_2$ volume fraction | It is necessary to design and optimize a more effective, simple low-temperature process, and solve the problem of $CO_2$ solidification blocking the pipeline |
| **Hydrate method** | Low energy consumption; non-corrosive and non-polluting; simple process flow | Few practical applications and immature technology; high requirements for equipment selection; $CO_2$ separation efficiency is affected by the hydrate formation method in a specific pressure vessel | More in-depth research is needed to improve $CO_2$ separation efficiency and develop new equipment and processes |

| Capture technology | Advantages | Limitations | Future outlooks |
|---|---|---|---|
| **Microbiological method** | No pollution; low cost; high return value; no complicated process required, can directly convert $CO_2$ into organic matter | There are few related researches and it is still in the theoretical stage | More experimental studies are needed to promote the development of microbiological methods for $CO_2$ capture |

## CATALYSTS

A catalyst is a material that enhances the speed of a chemical reaction without undergoing any permanent change itself. It achieves this by offering an alternative route for the reaction to take place, usually by reducing the amount of energy needed to initiate the reaction, known as activation energy. Catalysts facilitate reactions to happen faster or at lower temperatures, which is critical in numerous industrial operations and biochemical processes.

**Catalysts can be divided into two main types:**

Homogeneous catalysts: Homogeneous catalysts operate within the same phase as the reactants, often dissolved in the same solvent. For instance, in the reaction converting hydrogen peroxide ($H_2O_2$) and iodide ions ($I^-$) into water and iodine, the iodide ions serve as a homogeneous catalyst, as they are dissolved alongside the reactants.

Heterogeneous catalysts: Heterogeneous catalysts are present in a distinct phase from the reactants, typically as solid materials with which the reactants come into contact. A notable example is found in catalytic converters installed in cars, where solid metal catalysts like platinum, palladium, and rhodium facilitate the transformation of harmful pollutants into less harmful compounds.

Catalysts are indispensable in a wide array of industrial operations, encompassing the manufacture of fuels, chemicals, and pharmaceuticals, and are pivotal in environmental preservation through pollutant remediation. Moreover, in biological contexts, enzymes serve as catalysts, driving vital biochemical reactions essential for sustaining life.

### Nano Catalysts

Nano catalysts, also referred to as nanoparticle catalysts, are catalysts composed of nanoparticles typically ranging from 1 to 100 nanometers in size. These catalysts offer distinct advantages and properties compared to bulk catalysts due to their small dimensions and high surface area-to-volume ratio.

Key characteristics and benefits of nano catalysts include:

Enhanced surface area: Nano catalysts exhibit a significantly higher surface area-to-volume ratio compared to bulk catalysts. This expanded surface area provides more active sites for catalytic reactions, thereby enhancing catalytic activity.

Enhanced reactivity: The unique surface structures and high surface area of nano catalysts contribute to improved reactivity and selectivity in catalytic reactions. This can lead to increased reaction rates, improved product yields, and greater control over reaction pathways.

Tailorable properties: Nano catalysts offer the advantage of tunable properties such as composition, size, shape, and surface chemistry. These properties can be finely adjusted and controlled during synthesis, enabling optimization of catalyst performance for specific reactions and applications.Decreased catalyst usage: Nano catalysts typically necessitate less catalyst loading than bulk catalysts, yet still deliver robust catalytic performance. This reduction in catalyst usage can yield cost efficiencies and minimize environmental footprints in industrial operations.

Innovative catalytic pathways: Nano catalysts might unveil distinctive catalytic mechanisms, distinct from those observed in bulk catalysts, owing to quantum size effects and confinement phenomena at the nano level. These innovative pathways hold promise for pioneering advancements in catalytic processes and materials.

**Chemical Precipitation:**

In this technique, a solution containing metal salts or similar compounds is combined with a reducing agent or precipitating agent under controlled conditions such as temperature, pH, and stirring rate. This process leads to the generation of nanoparticles as the precursor compounds undergo reduction or precipitation from the solution. Illustrative instances encompass the production of metal nanoparticles such as gold, silver, and platinum.

**Sol-Gel Synthesis:**

Sol-gel synthesis entails the hydrolysis and condensation of metal alkoxides or similar precursors, culminating in the creation of a colloidal suspension or gel. Subsequently, the formed gel undergoes drying and calcination processes to yield nanoparticles. This approach finds widespread application in the fabrication of metal oxide nanoparticles like silica, titania, and alumina.

**Chemical Vapor Deposition (CVD):**

Chemical Vapor Deposition (CVD) entails the decomposition of volatile precursor molecules in the gaseous phase to deposit nanoparticles onto a substrate. Within a reactor chamber, the precursor molecules are introduced along with a carrier gas and subsequently decomposed via heat or plasma. Depending on the precise conditions, nanoparticles are deposited either on the surface of the substrate or within the reactor chamber itself. This technique is frequently employed in the production of semiconductor nanoparticles such as quantum dots and carbon nanotubes.

**Physical Vapor Deposition (PVD):**

Physical Vapor Deposition (PVD) methods, including sputtering and evaporation, entail the deposition of material from a solid source onto a substrate through physical means. By regulating deposition parameters such as temperature, pressure, and deposition rate, nanoparticles can be synthesized. This technique is frequently employed for the production of metallic nanoparticles and thin films.

**Microemulsion Synthesis:**

In microemulsion synthesis, surfactant-stabilized microemulsions serve as reaction media for nanoparticle synthesis. Precursor compounds dissolve within the water-in-oil microemulsion, where chemical reactions take place within the confined spaces of the micelles. As the reaction progresses, nanoparticles form and are stabilized by the surfactant molecules. This technique enables the production of nanoparticles with precise control over size, shape, and surface properties.

**Biosynthesis:**

Biosynthesis employs biological organisms such as bacteria, fungi, or plants as natural templates or reducing agents for nanoparticle synthesis. Biological systems produce nanoparticles through enzymatic reactions or extracellular processes. This method presents environmentally friendly and sustainable approaches to nanoparticle synthesis.

**Nanoparticle from plant extract:**

Creating nanoparticles from plant extracts involves utilizing the phytochemicals present in plants as reducing agents and stabilizers for nanoparticle synthesis. Here's a simplified explanation of the process:

**Selection of Plant Extract:**

Plants contain various bioactive compounds, such as polyphenols, flavonoids, and alkaloids, which can act as reducing and stabilizing agents for nanoparticle synthesis.

Different plant extracts may contain different types and concentrations of phytochemicals, leading to variations in the properties of the synthesized nanoparticles.

Preparation of Plant Extract: The selected plant material, such as leaves, seeds, or roots, is collected and processed to extract the bioactive compounds.

**Nanoparticle Synthesis**:

The plant extract is mixed with an aqueous solution containing metal salts (e.g., silver nitrate, gold chloride) or other precursor compounds. Phytochemicals in the plant extract act as reducing agents, converting the metal ions into nanoparticles. At the same time, phytochemicals may also act as stabilizing agents, preventing the nanoparticles from agglomerating or undergoing further growth.

Characterization: The synthesized nanoparticles are characterized using analytical techniques to determine their size, shape, composition, and surface properties. Common characterization

techniques include transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), and UV-visible spectroscopy.

**Applications:**

Nanoparticles synthesized from plant extracts have various potential applications in biomedicine, agriculture, environmental remediation, and nanotechnology. For example, silver nanoparticles synthesized using plant extracts have antimicrobial properties and can be used in wound dressings, food packaging, and water purification.

**Advantages:**

Utilizing plant extracts for nanoparticle synthesis offers several advantages, including sustainability, biocompatibility, and cost-effectiveness. Plant-based synthesis methods are environmentally friendly and do not require harsh chemicals, making them suitable for green chemistry applications.

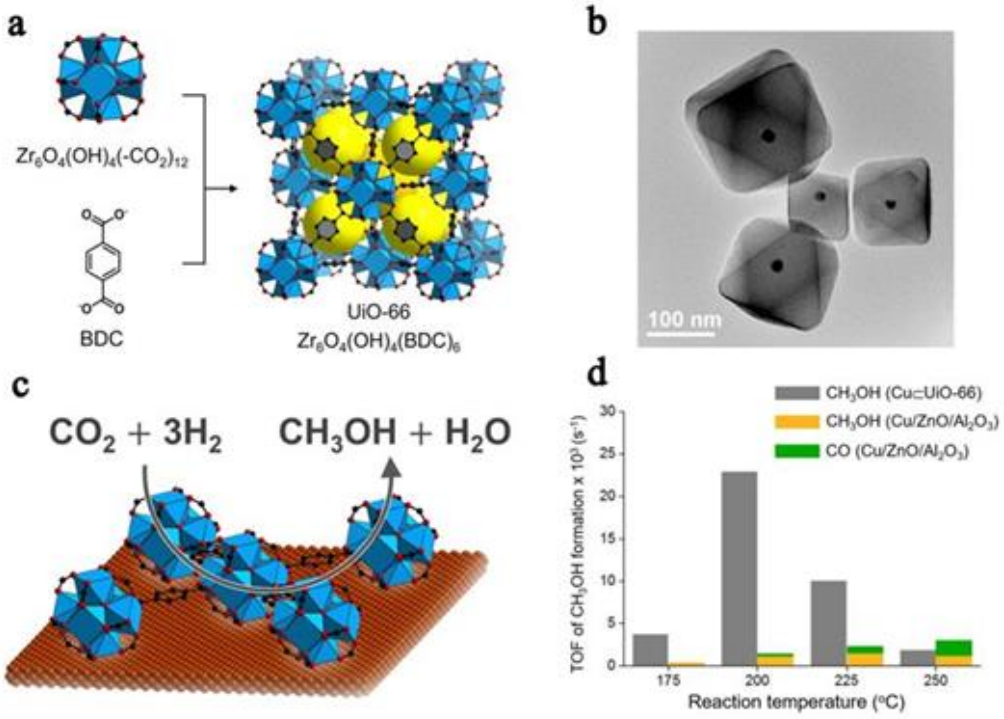
## Catalytic reduction of co2:

### Thermal catalytic:

Many thermal catalytic processes for converting CO2 involve hydrogenation reactions at relatively low temperatures, typically 523 K or lower, to produce valuable fuels like CO, methane, and methanol. However, due to the thermodynamic and chemical stability of CO2 molecules, significant energy input is usually needed when using CO2 alone as a reactant. Introducing other substances with higher Gibbs free energy, such as H2, as co-reactants can facilitate the thermodynamic process. Over the past few decades, extensive research has been devoted to thermal catalysis of CO2, leading to substantial advancements. Various catalysts, including metals like Cu and Co, metal oxides like ZnO2 and InO2, as well as novel nano-sized catalysts like metal-organic frameworks (MOFs), have been designed, synthesized, and refined.

For instance, Rungtaweevoranit and colleagues developed a catalyst where Cu nanocrystals were encapsulated within a metal-organic framework called UiO-66 ($Zr_6O_4(OH)_4(BDC)_6$, where BDC = 1,4-benzenedicarboxylate). This catalyst, known as Cu⊂UiO-66, proved effective in catalyzing the production of methanol through the hydrogenation of CO2. The synthetic process involved creating an ordered UiO-66 crystal structure by reacting Zr oxide secondary building units (SBUs) with BDC, followed by encapsulating Cu nanocrystals within UiO-66.

The resulting Cu⊂UiO-66 catalyst ensured high interfacial contact between the Cu nanocrystals and Zr oxide SBUs, facilitating efficient reactant access to active sites. Comparative analysis of methanol turnover frequency (TOF) between Cu⊂UiO-66 and traditional $Cu/ZnO/Al_2O_3$ catalysts at different reaction temperatures revealed superior performance of Cu⊂UiO-66, particularly at lower temperatures (<250°C). This catalyst demonstrated a remarkable eight-fold increase in conversion rate and maintained 100% methanol selectivity under these conditions.( Rungtaweevoranit, B.; Baek, J.; Araujo, J.R.,2016)


a
$Zr_6O_4(OH)_4(-CO_2)_{12}$
BDC
UiO-66
$Zr_6O_4(OH)_4(BDC)_6$
b
100 nm
c
$CO_2 + 3H_2$
$CH_3OH + H_2O$
d
$CH_3OH$ (Cu⊂UiO-66)
$CH_3OH$ (Cu/ZnO/$Al_2O_3$)
CO (Cu/ZnO/$Al_2O_3$)
TOF of $CH_3OH$ formation x $10^3$ ($s^{-1}$)
0
5
10
15
20
25
30
175
200
225
250
Reaction temperature (°C)

## Photocatalyst:

Solar energy presents an ideal alternative to traditional fossil fuels due to its abundance, affordability, cleanliness, and sustainability. Harnessing solar energy through photocatalysts for the conversion of CO2 into fuels or chemicals is an appealing strategy. Similar to natural photosynthesis, photocatalysts generate electron-hole pairs upon exposure to solar light. These photoinduced electrons initiate a redox reaction with CO2, leading to the formation of hydrocarbons. The photocatalytic conversion of CO2 involves three crucial steps: sunlight absorption, charge separation and transfer, and catalytic reduction of CO2 coupled with oxidation of H2O. Each step heavily relies on the characteristics of the photocatalysts.

To date, most photocatalysts have been derived from semiconductor materials, which are readily available and abundant on Earth. Common reaction products include CO, methane, formic acid, and other single or dual-carbon-containing chemicals. Extensive efforts have focused on optimizing the structure and composition of photocatalysts or integrating them with other functional units to create multifunctional catalysts. For example, integrating photocatalysts with metal-organic frameworks (MOFs) has proven effective, offering more adsorptive sites for CO2 uptake due to their large surface area and microporous structure, leading to significant enhancements in CO2 conversion.

Despite progress, there remains a substantial gap between the photocatalytic performance of these complexes and practical application requirements. Strategies such as constructing multi-junctions distributed on the surface of photocatalysts have been explored to improve interfacial electron-hole separation and migration. For instance, Meng et al. deposited MnOx nanosheets and Pt nanoparticles on different facets of anatase TiO2, forming surface heterojunctions, which enhanced the CO2 conversion efficiency.

Two-dimensional nanosheets show promise in enhancing charge separation due to shorter distances for photogenerated electrons and holes to move to the interface. For example, Wei et al. synthesized heterostructured CdS/BiVO4 composites, which exhibited higher photocatalytic activity in CO2 reduction compared to pure BiVO4 and CdS. Computational approaches, including density functional theory (DFT), have been instrumental in understanding the catalytic effects of 2D photocatalysts and other catalysts, aiding in exploring materials' characteristics and the role of different components in the catalytic mechanism.

In addition to inorganic photocatalysts, certain organic photocatalysts like porphyrin-based ones have been investigated for CO2 reduction. Porphyrins, planar macrocyclic molecules widely distributed in nature, possess strong absorption in the visible light region and unique electronic redox characteristics. Incorporating porphyrin into MOFs can further enhance photocatalytic performance, as demonstrated by Wang et al. with an indium-porphyrin MOF framework. However, challenges such as low conversion efficiency, poor product selectivity, and rapid charge recombination persist in CO2 photocatalytic conversion, necessitating further research and development of new materials and systems. Electric fields have shown promise in inhibiting charge recombination, prompting extensive study of electrocatalytic CO2 reduction as an alternative approach.

## Photoelectrocatalysis:

Given the abundant and renewable nature of solar energy, it's crucial to exploit it through various means. Photoelectrocatalysis, a technique combining the benefits of photocatalysis and electrocatalysis, has emerged as a promising strategy for selectively converting CO2 into both gaseous (e.g., CO, methane) and liquid products (e.g., formic acid, methanol, ethanol) under sunlight. This approach has garnered significant interest due to its potential to harness solar energy efficiently.

Photoelectrocatalysis maximizes solar energy utilization by generating photoelectrons. These electrons, generated through sunlight-driven processes, are then transferred to the electrode surface under an applied electric field and eventually utilized for the catalytic reduction of CO2. The applied electric field plays a crucial role in facilitating charge separation, promoting electron migration, and enhancing the intrinsic activity and energy efficiency of CO2 molecules. This process offers a solution to the high energy consumption typically associated with electrocatalytic CO2 conversion.

To enhance the performance of photoelectrocatalysis, efforts have been made to facilitate rapid charge transfer. For instance, Ding and colleagues employed photolithography to pattern a photocathode, exposing a Si-Bi interface formed by Bi3+-assisted chemical etching of Si wafers. This method effectively increased current density and facilitated CO2 reduction with high product selectivity.

Among semiconductors used in photo-assisted processes, TiO2 is particularly popular. Castro et al. loaded different amounts of TiO2 on the photoanode, utilizing a Cu plate as the photocathode to construct a photoelectric chemical device. This device, combined with an electrochemical filter-press cell, continuously converted CO2 into alcohol while consuming less external energy. The TiO2 photoanode system, when irradiated with ultraviolet light, exhibited enhanced alcohol production and reduced energy consumption compared to other conditions.

The performance of different photoelectrochemical systems for CO2 reduction varies depending on the characteristics of the photocathodes, which rely on the optical properties of the semiconductor. ( Yang Xiu, Fangyuan Liu, 2020),

## Enzyme:

The catalyst plays a pivotal role in CO2 reduction systems, spanning thermal catalysis, electrocatalysis, photocatalysis, and photoelectrocatalysis. However, a common challenge faced by most catalytic systems is low product selectivity, often yielding multiple products such as CO, formate, methane, ethylene, among others, in a single catalytic reaction. In contrast, biocatalytic processes for CO2 reduction have garnered attention due to their unique substrate and product selectivity, coupled with high conversion efficiency.

Enzymes stand out as biocatalysts renowned for their efficiency and selectivity. In living cells, different enzymes often collaborate in specific sequences to catalyze multi-step biochemical reactions, crucial for natural product synthesis and metabolism. Inspired by these biocatalytic reactions, researchers have explored enzymes, including enzyme cascades, in vitro, to achieve CO2 conversion into specific chemicals through one-step or multi-step processes. The rising trend in research focusing on the biocatalytic conversion of CO2 is evident in the increasing number of publications over the past two decades, especially in the last decade.

## Enzyme Coupled to Photocatalysis

Combining photocatalysis and electrocatalysis to create a photoelectric cooperative catalysis, and then integrating biocatalysis results in a sophisticated setup known as a photoelectrochemical (PEC) cell. This approach optimizes enzymatic conditions and enhances conversion efficiency. In this system, a conducting wire facilitates the directed transfer of reducing equivalents (primarily electrons and H+) from the photoelectrode to the biocatalyst.

Nam et al. envisioned PEC cells as capable of inhibiting biocatalytic charge recombination and reverse reactions. This is achieved by spatially separating photocatalytic and biocatalytic reactions into distinct anode and cathode compartments, respectively. For instance, an anode compartment might utilize cobalt phosphate (Co-Pi) deposited hematite (Fe2O3) photoanode for photocatalytic water oxidation, while a cathode compartment employs formate dehydrogenase for NADH regeneration and CO2 reduction.

The inclusion of co-catalysts like Co-Pi in the photoelectrode serves several purposes. It reduces activation energy, enhances quantum efficiency by facilitating charge separation, and

ensures timely consumption of photogenerated charges, thereby improving the stability of the photoelectrode.

The division of the PEC system into two compartments, enabling efficient separation of the oxidation reaction of water from the enzymatic reaction. This separation ensures that the two compartments do not interfere with each other, allowing the formate dehydrogenase to operate under its optimal pH conditions. This setup can be considered as a  system, where each reaction occurs in its own optimized environment without adversely affecting the other.

In a separate investigation, researchers applied a voltage to a PEC cell comprising a Co-Pi/Fe2O3 photoanode and a BiFeO3 photocathode. This polarization treatment induced surface charge accumulation, expediting electron transfer to the electrolyte and thereby enhancing CO2 conversion efficiency.

The tandem PEC cell with an integrated enzyme cascade (TPIEC) system emulates the natural photosynthetic Z-scheme for the biocatalytic reduction of CO2 to methanol. The rate of methanol production per unit reaction volume and per unit mass of photocatalyst can reach impressive levels, at 220 μM h−1 and 220 μM gcat−1 h−1, respectively. This system demonstrates significantly higher methanol production rates compared to other studies. To address the high cost associated with metal rhodium complex, researchers modified the structure of the photoelectrochemical cell to reduce costs. They replaced the metal rhodium complex with neutral red, an alternative electron mediator conducive to electron recycling between the electrode and NAD+.

Sokol et al. adopted a semi-artificial design, connecting the cathode containing formate dehydrogenase to the photoanode containing photosynthetic water oxidase (photosystem II) to achieve the metabolic pathway of formic acid formation from the light fixation of CO2. This approach demonstrated the feasibility of nonmetal catalysts for CO2 conversion to formic acid, offering a novel method for CO2 photoelectrochemical reduction.

Figure 9 illustrates the schematic representation of the semi-artificial photosynthetic tandem PEC cell coupling CO2 reduction to water oxidation. Table 3 provides a performance comparison of different coupled photoelectrocatalytic/enzymatic CO2 reduction systems, highlighting various photoanodes, photocathodes, and their respective efficiencies.

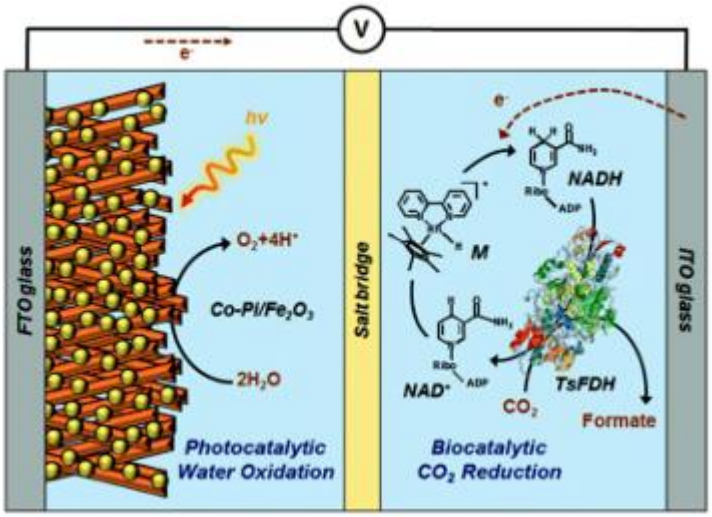
This diverse range of approaches underscores the ongoing exploration and innovation in the field of photoelectrochemical and enzymatic systems for CO2 reduction, aiming to address both efficiency and cost considerations.

noble metal mediators but have also delved into the regeneration of the coenzyme NADH, crucial in most biocatalytic CO2 reductions for providing electrons to dehydrogenase. However, NADH is expensive and prone to forming enzymatically inactive dimers (NAD2), leading to reduced enzyme activity. Therefore, developing cost-effective methods for NADH cofactor regeneration is imperative. Over the past few decades, chemical, photochemical, and electrochemical methods for NADH regeneration have been explored.

Electrochemically mediated electron injection into enzymes offers a promising avenue, bypassing the need for NADH and simplifying product separation. Amao and Shuto demonstrated the use of viologen-modified FDH immobilized on an ITO electrode to electrochemically convert CO2 to formic acid, showcasing direct electron transfer to FDH active sites from electrodes as a novel strategy for CO2 reduction without NADH.

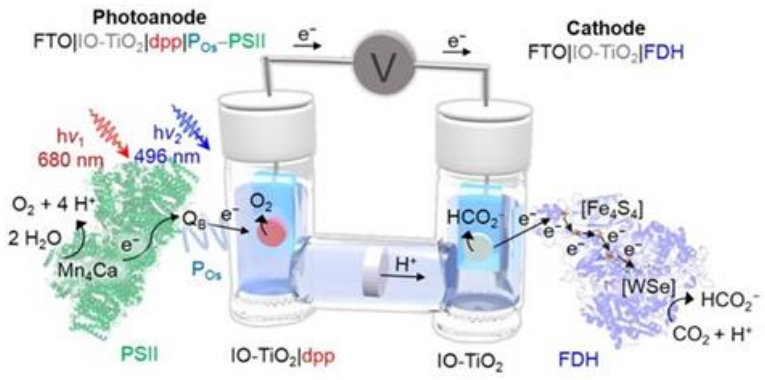
In the quest for alternative compounds to replace NADH, researchers have explored cheaper electron mediators like methyl viologen (MV2+). Miyatani et al. developed a system combining formic acid synthesis from CO2 (bicarbonate ion) with FDH and MV2+, along with photoreduction using ZnTMPyP as a photosensor and TEOA as an electron donor. This system successfully produced formic acid from bicarbonate ions and FDH in the absence of NADH. Furthermore, studies have shown that MV2+ inhibits the oxidation of formate to carbon dioxide, preserving the overall formate yield without losses from reoxidation.

In another approach, Ishibashi et al. utilized methyl viologen (MV2+) instead of NADH in a photoelectrochemical system comprising TiO2 nanoparticles as photocatalyst, MV2+ as an electron carrier, and FDH as a biocatalyst. This system achieved CO2 reduction to formic acid without requiring sacrificial reagents, external bias, or NADH, marking a significant advancement in CO2 reduction strategies. These endeavors represent a shift towards more sustainable and cost-effective methods for CO2 reduction, illustrating the ongoing exploration of alternative pathways in catalysis research.( Nam, D.H.; Kuk, S.K,2016)




Schematic illustration of the biocatalytic PEC platformTop

Enzymes in enzyme electrodes can be influenced by the reaction conditions, leading to instability. For instance, their activity may decrease significantly at pH levels that are not optimal. Eun-Gyu Choi and colleagues investigated how pH affects a combined photoelectric-enzyme system, finding that CO2 reduction was most efficient at an acidic pH, while formate oxidation was favored in basic conditions. They determined that a pH of 6.5 was optimal for CO2 reduction to formic acid in their system. To enhance enzyme stability and reusability, suitable fixation methods are crucial. Lee and co-workers developed a biophotocathode with a polydopamine (PDA) film, incorporating formate dehydrogenase (FDH) and nicotinamide adenine dinucleotide (NADH), allowing CO2 reduction to formic acid with high selectivity. The choice of PDA for enzyme immobilization was due to its excellent biocompatibility and charge transfer properties. This setup facilitated electron transfer and enzyme stabilization, prolonging the enzyme's lifespan. Similar photoelectrochemical cells were constructed using PDAs, CoPi/BiVO4 photoanodes, and different cathode materials, demonstrating efficient CO2 reduction without external bias. In another study, a voltage applied to a photoelectrochemical cell improved CO2 conversion efficiency by enhancing electron transfer. The tandem photoelectrochemical cell with an integrated enzyme cascade system mimicked natural photosynthesis, achieving high rates of methanol production. To reduce costs, researchers explored alternative electron mediators, such as neutral red, and semi-artificial designs combining enzymes with non-metal catalysts. These developments provide novel approaches for CO2 photoelectrochemical reduction, showing promise for sustainable energy production.( Sokol, K.P.; Robinson, W.E.; Oliveira,2018)




Schematicrepresentationofthesemi-artificialphotosynthetictandemPECcellcoupling CO2reductiontowateroxidation.AblendofPOsandPSIIadsorbedonadpp-sensitizedphotoanode (IO-TiO2|dpp|POs-PSII)iswiredtoanIO-TiO2|FDHcathode (M.M.; Ru , A.; Pereira, I.A.C,2018)

**Post-combustion capturing of CO2**

The extraction of CO2 from flue gas or from industrial chemical or food operations is accomplished using a variety of techniques. Common techniques for separating CO2 include cryogenic separation and the use of chemical and physical solvents, Adsorption on solids; membranes These techniques work well for industrial processes, however they appear to have issues when applied to the removal of CO2 from low concentration CO2 flue gas. A significant barrier to post-combustion CO2 collecting is the high cost of setting up a post-combustion system for processing large volumes of flue gas. In addition, after CO2 separation, there is a significant energy demand for removing CO2 from solvents or solids. Therefore, it's critical to get beyond these issues before post-combustion indicates a wise decision regarding CO2 separations

**Photochemical transformation of CO2**

Photocatalysis stands out as a promising avenue for transforming CO2 sustainably, leveraging light irradiation for reduction. Its appeal lies in its ability to operate under modest pressure and low temperatures, without demanding excessive energy inputs. In contrast, methods like electrochemical, chemical, and biological transformations often necessitate high temperatures, substantial energy, and operational costs. Thus, photocatalysis offers a compelling solution for current energy needs and environmental challenges.

However, despite its advantages, photocatalysis faces challenges such as low product selectivity and activity in CO2 reduction. Overcoming this requires two primary approaches: the development of novel catalysts and the design of efficient photo-reactors. Researchers are actively exploring methods to enhance CO2 reduction efficiency and selectivity. These efforts encompass strategies to improve charge separation and transfer, enhance CO2 adsorption kinetics, and address other factors affecting performance.

Various techniques have emerged, including pore texture modification, co-catalyst development, surface sensitization, band-gap engineering, and defect control. Engineering approaches play a crucial role in optimizing photocatalytic efficiency, allowing for the design of photo-reactors tailored to specific parameters like temperature, product yield, selectivity, and light intensity.

In understanding photocatalytic CO2 systems, three frameworks are essential: the type of phase (solid-gas, liquid-gas, etc.), catalyst bed type (fluidized or fixed), and operation type (continuous, batch, or semi-batch). To achieve efficient CO2 reduction, catalysts must lower the activation energy associated with the electrochemical process while exhibiting specificity to reduce CO2 without generating H2 from H2O.

Typically, a homogeneous photocatalytic CO2 reduction system comprises a catalyst, electron donor, and light absorber. Several factors influence the performance of the photo-reduction

system, including the properties of the catalyst, the nature of the electron donor, and the characteristics of the light absorber. Achieving optimal performance requires a holistic understanding of these factors and their interplay within the photocatalytic process.

The photochemical quantum yield (PQY) quantifies the efficiency of utilizing photons to drive the conversion of CO2 into products.

Catalytic selectivity measures the ratio of products resulting from CO2 reduction to that of hydrogen, offering insights into the preference of the catalyst in producing specific compounds.

The turnover number (TON) indicates the total number of reductions carried out by a catalyst throughout its operational lifespan.

A catalyst capable of transforming CO2 into CO and formate under thermodynamic conditions can also facilitate the reduction of protons to hydrogen. The extent of hydrogen formation can be assessed through catalytic selectivity, providing a numerical representation of CO2 reduction in relation to the hydrogen produced.

**Mechanism of photochemical transformation of CO2**

Utilizing solar energy for the photochemical conversion of CO2 into valuable products offers an environmentally friendly approach without the need for additional energy input. This process can be categorized into two main classes: homogeneous and heterogeneous photocatalysis. In homogeneous photocatalysis, both the reactants and the catalyst exist in the same phase, whereas in heterogeneous photocatalysis, they are in different phases.

Homogeneous photocatalysis faces limitations due to side reactions and catalyst degradation, which can lead to the premature termination of photocatalytic cycles. Heterogeneous photocatalysis, on the other hand, typically employs semiconductors to harness solar energy for driving thermodynamically favorable reactions that yield high-energy chemical fuels. The solar energy captured in this process can be stored in molecular bonds, akin to natural photosynthesis. Photoreactors are employed for this purpose, facilitating the transformation process along with heat and mass transfer.

In heterogeneous photocatalysis, it's crucial to mitigate recombination stages to prevent energy loss. Electrons and holes reaching the semiconductor's surface are captured by active sites on the catalyst, where they participate in the oxidation or reduction of reactants, including CO2. Once electrons and holes are generated, the feasibility of product production increases significantly.

# Photochemical transformation of CO2 using metal complexes

Metal complexes play a significant role in efficient CO2 reduction processes, with various complexes reported for this purpose. Several notable examples include nickel S2N2-type tetradendate, rhodium bis(bipyridyl), rhenium mono(bipyridyl) tricarbonyl, ruthenium mono(bipyridyl), ruthenium bis(bipyridyl) dicarbonyl, nickel cyclam, manganese monon(bipyridyl) tricarbonyl, cobalt tris(bipyridyl), nickel N-heterocyclic carbene-isoquinoline, osmium mono(bipyridyl) dicarbonyl, among others. These metal complex catalysts are primarily employed in heterogeneous systems.

The reduction reactions commence by reducing the catalyst to generate a low-valent metal complex, which subsequently interacts with CO2. This reduction of the catalyst occurs by acquiring an electron from the photosensitizer. Re(I) complexes and Ru(II) complexes are commonly utilized metal complexes in photochemical CO2 reduction processes.

**Photoreactors**

Designing photoreactors is a burgeoning strategy aimed at enhancing the efficiency of CO2 reduction. The design process hinges upon scrutinizing parameters that influence the effectiveness and performance of the reactor, such as heat exchange, construction materials, and light source .

The intensity and wavelength range of light in the photocatalytic system are dictated by the light source. A crucial aspect of photoreactor design is the capacity to effectively harness photons, making the choice of light source pivotal in determining efficiency. Common materials used for constructing photoreactors include Pyrex, stainless steel, and quartz. Quartz and silica are favored for their transparency in the UV region, essential for efficient light transmission.

Since light serves as the primary driver in photoreactors, there's a risk of adding excess energy in the form of heat, necessitating efficient heat exchange mechanisms critical for temperature control. To ensure proper contact between the catalyst and reactants, the design must account for flow and mixing characteristics. Other important design parameters include the type of light source, membrane, bed type, and mode of operation.

Photoreactors can be classified based on the phases involved, either as two-phase or three-phase systems. In two-phase systems, the catalyst may exist in gas or liquid form, while in three-phase systems, the catalyst is solid, and the reactants may be either gas or liquid. Depending on operation mode, photoreactors can be batch or continuous.

Various types of photoreactors exist, including fixed-bed, membrane, and slurry-based reactors. Slurry photoreactors, further classified as internally or externally illuminated, are prominent. Optical fiber and monolith photoreactors are common in fixed-bed designs.

Membrane reactors serve the dual purpose of water splitting and CO2 reduction, advantageous for fuel production. When sunlight is utilized as the light source, these reactors are termed solar photoreactors.

**Factors influencing photochemical reduction of CO2**

In the context of electron transfer in photocatalytic CO2 reduction, two methods are commonly employed: oxidative and reductive quenching. Oxidative quenching involves the addition of a photosensitizer (PS) with an electron acceptor (such as an electron mediator or a catalyst) to form PS+, while reductive quenching involves the reduction of PS+ using an electron donor to form PS−. Research indicates that the majority of photochemical CO2 reduction processes primarily follow the reductive quenching pathway.

The concentration of the electron donor can be feasibly increased, whereas the loading of the catalyst is often limited. This limitation in catalyst loading may render oxidative quenching less favorable for application.

**Photosensitizer**

A superior photosensitizer demonstrates superior adsorption ability at specific wavelengths compared to other species involved in the reaction, such as catalysts and electron donors. Its excited state should have a longer lifetime to facilitate efficient electron transfer to or from an electron acceptor or donor. Additionally, the photosensitizer should exhibit higher oxidative strength in its excited state compared to its ground state, enabling it to accept an electron from the donor.

One commonly used photosensitizer in photochemical CO2 reduction is [Ru(N^N)3]2+. However, a drawback of this type is the potential photo-dissociation of the N^N ligand during the reduction process. Although the dissociated product may act as a catalyst for CO2 reduction, its presence in the absence of the catalyst could interfere with product dispersal.

Currently, Os(II) trisdiimine ([Os(5dmb)3]2+) complexes are being utilized as photosensitizers. They offer advantages such as higher absorptive power at longer wavelengths near the visible region. Despite their short emission lifetimes, they serve as strong electron donors, effectively operating photochemical CO2 reduction.

Key properties that a photosensitizer used for CO2 reduction must possess include:

1. Stronger adsorption rate at a specific excited wavelength compared to other materials, particularly in the visible region.

2. Longer emission lifetime.

3. Strong oxidation power in the excited state for capturing electrons from the reductant.

4. High stability.

Other redox photosensitizers utilized in photocatalytic processes include Os(II) diimine complexes, Re(I) carbonyl diimine complexes, cyclometalated Ir(III) complexes, and Ru(II) diimine complexes. Each type offers unique advantages and may be selected based on factors

such as absorption characteristics, emission lifetime, stability, and oxidation power to suit specific CO2 reduction applications.

The mechanism of photochemical CO2 reduction involves both a catalytic cycle and an electron relay cycle. The rate-determining factor depends on the specific state of the reaction. When the rate-determining process occurs within the catalytic cycle, the concentration of the catalyst and the rate of CO2 reduction are proportional to each other. However, upon further increasing the catalyst concentration, the reaction rate saturates, and the catalyst concentration remains constant. At this point, the rate-determining phase shifts to the electron relay cycle. In such cases, the activity of the catalyst cannot be directly examined.

Hence, both the photosensitizer (PS) and the electron donor are considered important parameters in the photochemical CO2 reduction process. Their roles in facilitating electron transfer and driving the reduction reactions are critical for optimizing the efficiency and selectivity of the photocatalytic system.

**Limitations and enhancement techniques**

The kinetics of CO2 photocatalytic reduction are influenced by several parameters, including process temperature, CO2 activation, product desorption and reactant adsorption, photocatalyst properties, surface characteristics, light intensity, specific surface area of the photocatalyst, and incident light absorbed by the catalyst. Numerous techniques have been proposed to enhance the efficiency of CO2 photoreduction.

One approach involves selecting semiconductors with appropriate bandgap energies. CO2 adsorption onto the photocatalyst surface is a crucial step in photocatalytic CO2 reduction, often exhibiting pseudo-first-order kinetics due to the increase in photoreduction rate with initial CO2 concentration. Electron transfer or CO2 activation from the photocatalyst to CO2 is also considered a limiting step due to its complex nature. The structure of the photocatalyst can enhance product selectivity and yield, thus accelerating the reaction rate. Therefore, meticulous preparation of the photocatalyst is vital for optimizing the efficiency of the photocatalytic reduction system.

Semiconductors with broad bandgaps are preferred for CO2 photoreduction processes as they offer sufficient positive and negative redox potentials in their valence and conduction bands, respectively. However, utilizing broad bandgap semiconductors requires higher energy input.

## Conclusion

This review provides a brief overview of the photochemical conversion of $CO_2$ into valuable chemicals and bio-based products. While these technologies hold promise, practical applications face challenges, particularly in capturing and transforming atmospheric $CO_2$. Photochemical reduction shows potential, but overcoming limiting steps in the complex reduction mechanism is essential. Approaches such as selecting appropriate semiconductors, designing morphologies, and developing hybrid structures have been proposed to address these challenges. Government financial support is aiding the further development of $CO_2$ capture and transformation approaches, resulting in valuable products and greenhouse gas storage. Clearer understanding and simplified approaches to $CO_2$ utilization may improve productivity, eco-friendliness, stability, and cost-effectiveness in these processes.

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