

# Artificial Photosynthesis: A Review of the Technology, Application, Opportunities, and Challenges

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## ABSTRACT

Artificial photosynthesis (AP) is a biomimetic approach to contemporary energy problems in which principles of natural photosynthesis are applied to synthesizing chemical fuels from solar power and CO<sub>2</sub>. Artificial photosynthesis is potentially more advantageous than solar panels as it provides stable and portable chemical fuels while also minimizing human carbon footprint in the environment. Although multiple artificial photosynthesis techniques have been developed, none of them have been successfully applied into scalable devices. This paper reviews the current progress and outlook of artificial photosynthesis technology. The mechanism and performance of available methods are presented with experimental data, and technical breakthroughs and challenges in scaling up the technology are reported. A wide range of projects worldwide is inspected to show the status of cost and performance. Finally, an outlook is provided on future trends and challenges in technical as well as socio-economic aspects.

## Introduction

As natural resources are depleted and environmental pollution continues to grow, our energy demand presents the need for renewable and carbon neutral alternative energy sources. Currently available and applicable alternative sources include solar, wind, and tidal power, all of which produce electricity, requiring certain infrastructure for storage and distributions. These features might not be feasibly implemented to certain nations or regions due to their socio-economic backgrounds or the characteristics of the natural environment. Moreover, generating sustainable energy from these resources can also lead to local environmental damage. For example, hydroelectric power facilities can cause flooding and create changes in temperature and streamflow in water sources, affecting habitats; wind power systems have been shown to kill wildlife. On the other hand, traditional chemical fuels, used for centuries, are still considered the more practical option for many reasons: they are extremely energy dense, are stable, are portable, and use already-existing infrastructure. Thus, storing energy in the form of chemical bonds is the ideal approach to energy storage and distribution.

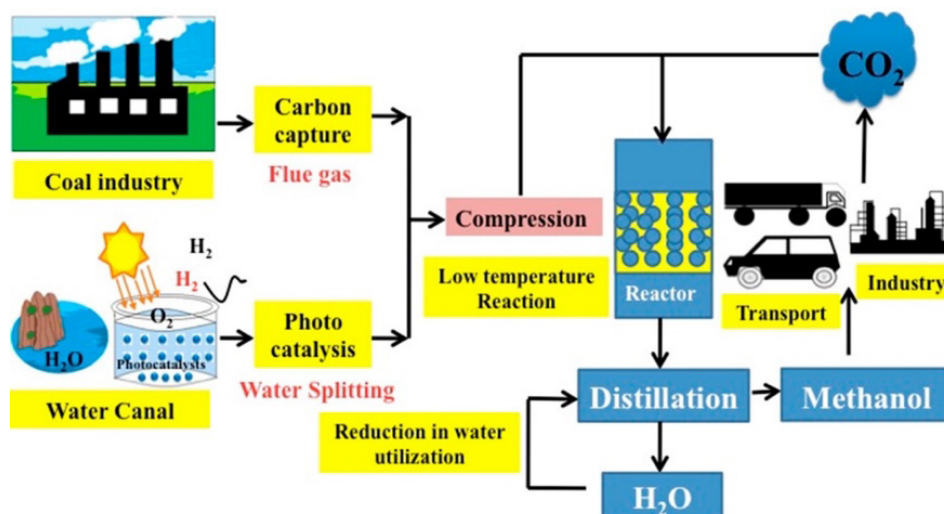


Figure 1. Schematic representation of how CO<sub>2</sub> exhaustion can be recycled into fuel<sup>15</sup>

Using principles of natural photosynthesis, researchers had simultaneously accomplished two goals: harvesting energy from a renewable source and storing said energy in chemical bonds. In natural photosynthesis, the energy from the sun would activate a series of oxidation and reduction reactions to ultimately produce oxygen and glucose from water and carbon dioxide. Artificial photosynthesis mimics this natural process to harvest solar power (arguably the most abundant and geographically dispersed source of renewable energy on Earth), and directly transform carbon dioxide into stable and portable chemical fuels. Aside from impressive storability, artificial photosynthesis is also environmentally beneficial. The technology can recycle CO<sub>2</sub> exhaustion in the atmosphere to make carbon-based fuel, minimizing the carbon footprint of fuel usage, while releasing oxygen into the ecosystem (Figure 1). Artificial photosynthesis indeed holds the key to a clean energy future. Although solar energy conversion was not new, and the feasibility of artificial photosynthesis technology has been demonstrated on a laboratory scale, more technical challenges must be overcome if researchers hope to establish inexpensive, industrially compatible approaches to make fuel out of sunlight.

## Characteristics of artificial photosynthesis technology

Photosynthesis is characterized by four processes: light harvesting, charge separation, water splitting, and fuel productions. In natural photosynthesis, the task of capturing sunlight is assigned to antenna molecules like chlorophyll, carotene, and other pigments. This energy is then transferred to the plants' (or algae's, or cyanobacteria's) photosystem II, where it excites an electron in the antenna molecule, igniting an electron transfer sequence and ultimately separating positive and negative charges from each other. The positive charges are utilized to start the water splitting (water oxidation) process, producing hydrogen ions and oxygen; the electrons, coupled with the hydrogen ions and other electrons released by previous water oxidation phase, are used to convert carbon dioxide into carbohydrates.

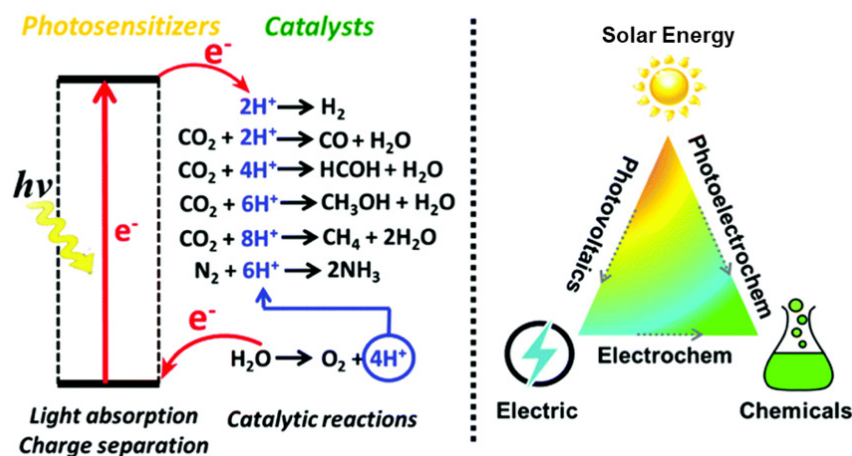


Figure 2. The general concept of artificial photosynthesis<sup>5</sup>

In an artificial photosynthesis system, researchers utilize a photosensitizer to capture solar energy, which would be transferred to a reaction center to trigger the charge separation process. Positive charges then initiate water oxidation in the catalytic center, producing hydrogen ions and oxygen molecules. At this step, the produced hydrogen gas is readily collected. Although hydrogen is an attractive energy carrier, research can be taken one step further to create carbon-based fuels. These fuels would be more advantageous than the highly explosive hydrogen gas, not only due to the ease of storage and transportation, but also because their production recycles excess CO<sub>2</sub> in the atmosphere. Potential fuel products that could be produced include carbon monoxide (CO), methane (CH<sub>4</sub>), methanol (CH<sub>3</sub>OH), and formic acid (HCOOH) (Figure 2). To turn artificial photosynthesis into reality, scientists and engineers have created a system containing a light harvesting device and a reaction center for water oxidation and CO<sub>2</sub> conversion to take place under catalytic processes. It will be important for these components to be integrated in such a way that optimizes energy efficiency.

In natural photosynthesis, solar energy can be lost through: wave-length degradation, saturation processes, and most importantly, fueling a series of reactions in the photosynthetic organism to maintain the plants' survival. The maximum efficiency of photosynthesis is estimated to be 4.5%; however, this maximum efficiency is rarely reached, and most of the time the efficiency is less than 1%. Seasonal changes and the existence of nonagricultural land and ocean significantly lower the efficiency of photosynthetic activity. Although the engineering of plants and other photosynthetic organisms is possible, an efficiency of over 1% is rarely achieved in these attempts. A man-made solar energy converting technology promises a much higher efficiency if properly developed. And although only an efficiency of at least 10% is required for artificial photosynthesis systems to become feasible industrially, BioSolar Cells, a Dutch research program, has estimated a theoretical efficiency of up to 40%<sup>1</sup> for their system.

Artificial photosynthesis systems not only need to achieve the desired efficiency, but they also need to be durable enough to withstand extreme weather conditions and cost-effective enough to be commercially viable. There are two possible solutions to the former challenge: the materials used to build the system have to be extremely robust, or the system itself must be capable of self-repairing when damaged. To make artificial photosynthesis widely applicable, rare and expensive materials should be avoided to optimize cost-efficiency. Countless standalone prototypes of artificial photosynthesis systems have been developed, and efforts are being made to improve them so that they achieve the desirable durability, as well as energy and cost efficiency.

## Review on current approaches, breakthroughs, and challenges

### A. Approaches to light harvesting

Instead of the antenna molecules that plants have, an artificial system harvests solar energy with photosensitizers or light absorbers, such as semiconductors, molecular dyes, or quantum dots. The pioneering invention involved using titanium oxide ( $\text{TiO}_2$ ) as a light absorber and a catalyst for solar water splitting. However,  $\text{TiO}_2$  cannot absorb anything except for ultraviolet light, and is thus unable to optimally harvest all energy provided by the wide spectrum of wavelength. One way researchers have overcome this weakness has been to sensitize the  $\text{TiO}_2$  electrode with a dye sensitizer. Made from ruthenium tris(bipyridine), the dye can facilitate excellent interaction with the conduction band of the semiconductor substrate (in this case  $\text{TiO}_2$ ), enhancing electron-transferring and thus improving charge separation<sup>2</sup>.

Since titanium oxide demonstrated weakness in light-absorbing efficiency, researchers have also investigated other materials as light-harvesting semiconductors. One particularly attractive alternative is silicon for its abundance and affordability, as well as its ability to absorb and store energy<sup>3</sup>. Other semiconductors, both oxide and non-oxide, have been studied extensively. These materials include metal oxides such as  $\text{ZnO}$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{BiVO}_4$ , metal nitrides such as  $\text{Ta}_3\text{N}_5$ , metal oxynitrides such as  $\text{TaON}$ , etc<sup>4</sup>.  $\text{Fe}_2\text{O}_3$  photoelectrodes have received significant attention for their narrow band gaps, high stability, and low price.

### B. Approaches to catalytic reactions

In natural photosynthesis, chlorophyll (or other antenna molecules) and bacteria act as catalysts to produce oxygen and carbohydrates from water and carbon dioxide. The functions of these natural components are often replicated with man-made catalysts. Scaling up artificial photosynthesis techniques necessitates developing and improving said catalysts – simultaneously optimizing activity, stability, selectivity, cost, and energetic efficiency. Water splitting and fuel production processes are studied using three catalytic approaches: molecular, material, and biological. Molecular catalysts are discrete, synthetic molecules. Material catalysts refer to bulk or nanoparticulate solids, usually metals or semiconductors, which are heterogeneous and generally exhibit a distribution of active sites. Biological catalysts refer to enzymes or microorganisms (both natural and genetically modified forms)<sup>12</sup>.

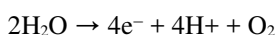
Molecular catalysts often consist of a metal center acting as an active site, with organic ligands creating an environment to regulate the active site<sup>5</sup>. These features give molecular catalysts certain distinct advantages. Most molecular catalysts possess a clear structure and distinguishable active site as well as catalytic mechanism. The ligand design allows appropriate adjustment to be made on the molecular complexes (such as steric configuration and electronic structure). Further development of molecular catalysts can promote their intrinsic activity, which in turn enhances electrode activity by increasing the selectivity of the  $\text{CO}_2$  reduction reaction. Catalyzation at the molecular level can also take full advantage of the metal atoms activity, making molecular catalysts outperform material-based counterparts<sup>5</sup>.

A myriad of research on molecular catalysts has been conducted over the last 30 years, and the synthesis of effective molecular catalysts has been made possible, including ligand designs, the synthesis and characterization of the ligands and the final metal complex, catalytic analysis, and revelation of mechanism<sup>5</sup>. Fruitful results have been obtained from a wide range of materials: from the rare noble Ru and Ir, to the Earth-abundant Mn, Co, Cu, and Fe. Researchers have determined that the next step to synthesizing the right molecular catalysts for artificial photosynthesis entails heterogenizing the molecular catalysts. If we can deposit the molecular catalysts onto a solid support without aggregation, while also retaining the molecular catalysts' advantages in structure and activity, we might be one step closer to an applicable artificial photosynthesis device.

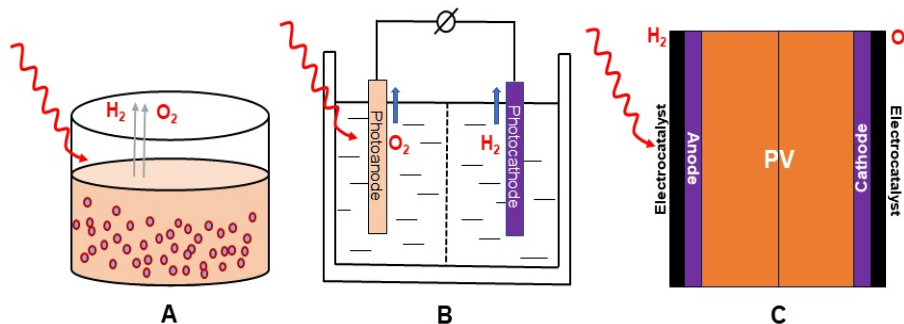
Bacteria and enzymes can act as great catalysts due to their self-sustainability and renewability. Recent biotechnology research has utilized halotolerant bacteria as an electrocatalyst for a bio-electrochemical system operating undersea. However, the current output obtained from such system is relatively low because this series of bacteria uses up energy to sustain its metabolism and to operate in the extreme saline conditions. Energy loss from self-sustainment in bacteria might need to be taken into consideration if living organisms were to be incorporated into artificial photosynthesis. Another series of enzymes that has been inspected for artificial photosynthesis system design is hydrogenases for their ability to activate hydrogen evolution<sup>6</sup>. Unfortunately, scaling up hydrogenases has been proven impractical due to its oxygen sensitivity and lack of robustness for long term operation. Difficulties in large-scale cultivation of necessary organisms also hinder techniques concerning biological catalysis.

## 1) Catalytic approaches to water oxidation

Water oxidation, or the water-splitting process, proceeds via the reaction:



Transferring 4 protons and 4 electrons requires a high thermodynamic potential and a high overpotential to overcome the high kinetic barrier. In nature, this reaction is catalyzed by the oxygen-evolving complex in photosystem II, the design of which influences researchers' partial understanding of the water oxidation mechanism, thus enabling them to develop a substitution for the natural oxygen-evolving complex. Uncovering the secret to nature's water oxidation might provide a blueprint for efficient catalysts in artificial photosynthesis. Figure 3 illustrates the water oxidation process in 3 common artificial photosynthesis devices.



**Figure 3.** Illustration of 3 water-splitting system: (A) Photocatalytic (PC) system, (B) photoelectrochemical (PEC) system, (C) photovoltaic-photoelectrochemical hybrid (PV-PEC) system<sup>16</sup>

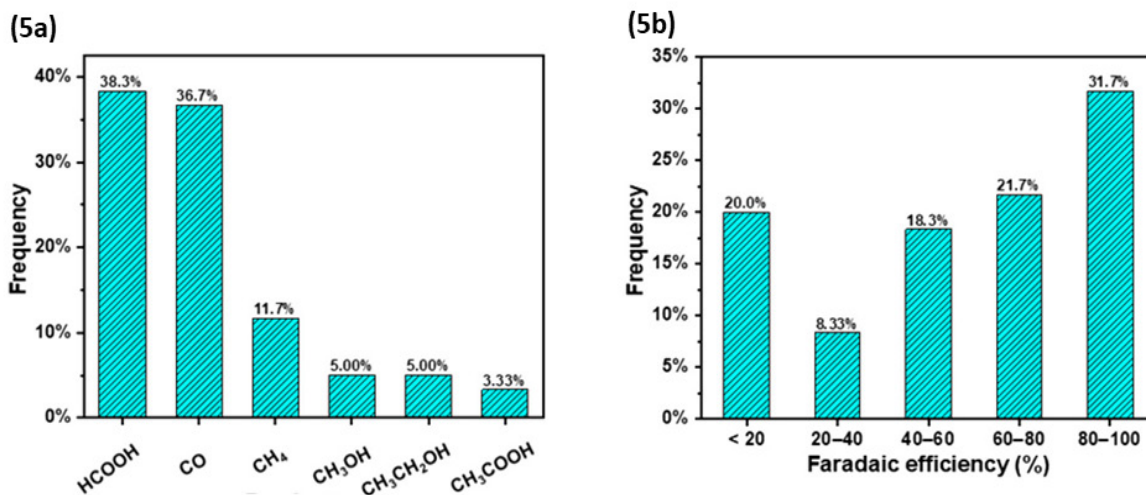
Water-oxidation catalysts (WOCs) currently under development are redox-active transition metal-based complexes, with unsaturated first coordination spheres functioning as catalytic active sites. WOCs derived from ruthenium are the earliest molecular WOCs being studied, with the first molecular WOC developed being the dinuclear ruthenium complex (the blue dimer). Since then, many binuclear Ru-based WOCs have been developed, until 2005 when the existence of a series of mononuclear Ru WOCs— introduced by the Thummel group— suggested that one metal active center is enough for water-oxidation catalysis<sup>7</sup>. This marked a significant advance in molecular WOCs studies.

Ir-based complexes represent another classic line of WOCs. Research on single-atom catalysts constitutes for a large portion of studies done on Ir-based catalysts, while catalysts featuring two or more atoms are poorly studied because synthesizing such structures poses a critical challenge. However, successful synthesis of iridium dinuclear heterogeneous catalysts (DHCs) was reported in 2018 — the results of which demonstrate outstanding stability against detachment and aggregation, as well as high activity toward water oxidation<sup>8</sup>.

Though well-developed over 30 years, both Ru-based and Ir-based WOCs are impractical for large scale application due to their high costs and scarcity. The solution to a cost-effective artificial photosynthesis device calls for earth-abundant transition-metal-based molecular WOCs. And ever since research on earth abundant molecular WOCs started in the 2010s, progress has been made toward the development of molecular WOCs from Mn, Co, Ni, Cu, and Fe. Unfortunately, the activity rate for these economical choices is still very low. Obtaining WOCs that are both effective and inexpensive for large-scale application is a tremendous challenge that requires more research<sup>6</sup>.

## 2) Catalytic approaches to CO<sub>2</sub> reduction

In contrast to the situation with WOCs, the development of earth-abundant molecular CO<sub>2</sub>-reduction catalysts (CO<sub>2</sub>RCs) has been fairly successful. Complexes synthesized from transition metals like Re, Ru, Ir, Co, Ni, Mn, Fe, and Cu have been studied extensively for catalyzing CO<sub>2</sub> reduction under electrochemical or photochemical conditions. Candidates for noble-metal-free CO<sub>2</sub>RCs include macrocycle ligand-based catalysts deriving from Co and Ni, Mn-bpy type catalysts, Fe porphyrin catalysts, binuclear copper catalysts, metal corroles, and even metal-free pyridinium ions<sup>6</sup>. In 2017, cobalt chlorin complex was successfully incorporated into a photoelectrochemical system as a CO<sub>2</sub> reduction catalyst, yielding CO with a high faradaic efficiency of 83%<sup>9</sup>. Yet the overall (or solar-to-fuel) efficiency and the quantum yield of such systems are still relatively low. Rarely are these systems capable of producing multielectron-reduced products like methanol or methane<sup>5</sup>.



**Figure 4.** Statistical analysis of CO<sub>2</sub> conversion in studies of photoelectrochemical devices: (a) product distribution, (b) Faradaic efficiency distribution<sup>14</sup>

The photoelectrochemical cell (PEC) is one of the two distinct classes of devices utilized in solar energy conversion. Researcher have conducted a statistical analysis on several current PEC CO<sub>2</sub> conversion studies<sup>14</sup>. Figure 4 demonstrates the distribution of carbon-based fuel products and Faradaic efficiency (FE) across 60 cases. While 38.3% of the cases produced HCOOH and another 36.7% yielded CO, productions of multielectron-reduced chemicals (namely CH<sub>4</sub>, CH<sub>3</sub>OH, etc.) only occurred in a minority of the cases. Most of these studies achieved high Faradaic efficiency (above 60%), and 32% reported a FE higher than 80%. The statistical analysis is consistent as "Zhang and

Sun's review paper<sup>5</sup> suggested that many researchers have made significant progress improving the Faradaic efficiency but not as many have been able to produce multielectron-reduced chemicals. A lack of understanding on CO<sub>2</sub> transformation mechanisms at the cobalt center constituted a major drawback to contemporary research. Hence, system designs may still benefit from more research being done on the mechanism of CO<sub>2</sub>-reduction at the catalyst center. CO<sub>2</sub>RCs are also required to work under organic conditions, and so currently available molecular CO<sub>2</sub>RCs need to be made adaptable to water-oxidation conditions before they can be applied to future device design and production<sup>6</sup>.

Gold and silver nanoclusters have been shown to be another candidate for the ideal CO<sub>2</sub>RCs. Their molecular purity and crystallographically-solved atomic structures allow scientists to better understand the mechanism underlying electrocatalytic CO<sub>2</sub> reduction, while their size and structures enable a high thermodynamic stability, suitable for practical application<sup>11</sup>. One successful example is the Au<sub>25</sub>(SR)<sub>18</sub> nanocluster (SR=SCH<sub>2</sub>CH<sub>2</sub>Ph). Under aqueous conditions, this catalyst can yield CO with a faradaic efficiency of approximately 100% and a formation rate 7-700 times higher than what can be achieved with traditional gold-based bulk<sup>11</sup>. However, gold-based clusters have only been able to produce CO so far. Further works on Au-based bimetal clusters are expected if researchers aim to yield hydrogenated products. Introducing cheap metals into gold nanoclusters also warrants additional research since this is a promising method to maximize metal economy while preserving catalytic activity.

Hybrid catalysts that merge approaches from all three disciplines (molecular, material, biological) are also under investigation for catalyzing CO<sub>2</sub> reduction. Enzymes have been shown to catalyze sustainable energy conversion reactions with highly effective and selective active sites, using Earth-abundant materials. However, enzymes are enforced with protective protein surrounding their active site, without which researchers encounter great difficulties in recreating the same level of catalytic activity. Even though direct mimicry could not be achieved, enzymes still provide a blueprint for hybrid catalyst design and synthesis.

In hybrid catalysts, elements from biological and material designs (like high surface area and porosity) can be incorporated into molecular catalysts to optimize active site, enhancing rates of CO<sub>2</sub> reduction and selectivity. For example, researchers have assembled supramolecular cages of tetrapodal porphyrins on copper electrodes, with amides in porphyrin-copper surface linkers. These amides can potentially interact with the surface-bound intermediate via hydrogen bonding like an enzyme. Under optimized conditions, the porphyrin cages demonstrated a high selectivity for high-value C<sub>2</sub> products: 57% ethanol, 24% acetate, and 2% ethylene<sup>12</sup>. This design exemplifies how bioinspired elements can be integrated into molecular and material designs to promote selective CO<sub>2</sub> reduction and improve fuel production.

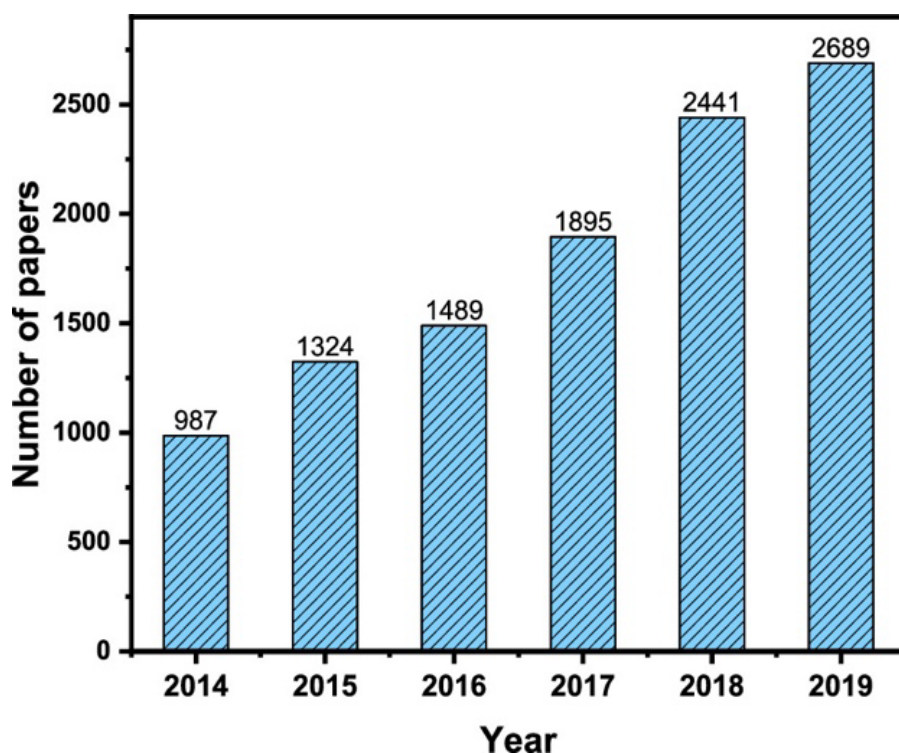
If we ever achieve the ideal CO<sub>2</sub>RCs in the future, the CO<sub>2</sub> source utilized for fuel production should also be taken into consideration. CO<sub>2</sub>'s concentration in the atmosphere or solubility in water is generally not high enough to comply for large-scale production. This might limit the scalability of CO<sub>2</sub> reduction reactions. In addition, CO<sub>2</sub>RCs often produce a mixture of products, and so product separation methods and their energy consumption are challenges that should be addressed.

## Notable projects and prospective research effort

The first working model of a noble-metal-free photoelectrochemical (PEC) device was only reported in 2020<sup>10</sup>. Before that, in an earlier model, researcher Shunichi Fukuzumi and his team utilized a two-compartment cell composed of a FeO(OH)/ BiVO<sub>4</sub> photoanode and a Co (II) chlorin-supported cathode to produce CO with a high faradaic efficiency of 83%. However, the photocurrent they achieved under simulated sunlight was insufficient (<20 μA at 1.3 V). This most recent PEC system contains a two-electrode composed of a Co<sub>4</sub>O<sub>4</sub> cubane complex-modified BiVO<sub>4</sub> photoanode and a cobalt phthalocyanine complex-modified carbon cloth (cc) cathode<sup>10</sup>. The device achieved a 4% increase in Faradaic efficiency for CO production compared to Fukuzumi's invention, and a solar-to-CO conversion efficiency of 0.44%<sup>10</sup>. More significantly, its electrode complexes designs have successfully facilitated long-term stability in aqueous condition; its molecular catalysts have established compatibility with CO<sub>2</sub>-reduction conditions and adapt to

a two-electrode configuration. Although the solar-to-CO conversion efficiency isn't ideal, this model provides a promising framework for the fabrication of low-cost artificial photosynthesis systems, a foundation to widely marketable artificial photosynthesis energy production.

Over ten years ago, the U.S. Department of Energy (DOE) established a program dedicated for artificial photosynthesis technology advancement—the Joint Center for Artificial Photosynthesis (JCAP). In 2020, JCAP research effort was rewarded with a highly efficient solar-driven CO<sub>2</sub> reducing device. By powering a gas diffusion electrode (GDE) with a photovoltaic (PV) cell, with nano silver particles-based catalyst, researchers have been able to reach a near-unity Faradaic efficiency for CO<sub>2</sub>-to-CO conversion, and a solar-to-CO conversion efficiency of up to 19.1%<sup>13</sup>. The unconventional way in which the device was assembled is attributed to this success. The GDE component is reverse assembled (meaning the catalytic coating of silver nanoparticles were facing the CO<sub>2</sub> gas supply instead of the electrolyte) and treated with polytetrafluoroethylene to prevent flooding. The configuration ensured that the catalysts remained in a wetted but not flooded condition, minimizing CO<sub>2</sub> loss, and extending the device's lifetime. Hence, the device exhibits stability for over 150 hours, roughly 6.25 of a day. Under outdoor sun conditions, the PV-GDE system demonstrates an average conversion efficiency of 18.7% during noontime, setting a record for energy efficiency in solar-driven CO<sub>2</sub> reduction.



**Figure 5.** Numbers of papers on artificial photosynthesis published from 2014 to 2019<sup>14</sup>

Over the past few years there has been a notable growth in research interest in solar energy conversion, as the number of publications on the topic tripled from 2014 to 2019 (Figure 5). Multiple research initiatives— such as SUN-ERGY and Solar-Driven Chemistry Initiative of the European Chemical Society— were established globally. In 2020, the U.S. DOE announced a 5-year funding plan with a budget of \$100 million for artificial photosynthesis development. These research efforts not only signify the potential of artificial photosynthesis as the solution for current energy crisis, but also promise significant progress in the field of solar energy conversion in the years to come.



## Limitations

Although the idea of mimicking nature to harvest the sun appeared in 1918, meaningful progress has only been made over the last 30 years. Projects funded by the U.S Department of Energy have reported a highly effective and stable PV-GDE system, which yields CO with an average energy conversion efficiency of 18.7% at noon time and a max of 19.1%, which is one of the highest, if not the highest, reported among inventions<sup>13</sup>. However, such victory is short-lived, as the overall performance still falls short of satisfying the targeted efficiency of a commercially viable energy-generating system. Questions on the device's performance in less sunny conditions and/or in a long (and discontinuous) run are also left unanswered. Another promising research provided a low-cost approach to producing CO using a photoelectrochemical cell with noble-metal-free catalysts<sup>10</sup>. While this system also achieved a high faradaic efficiency for the CO<sub>2</sub>-reduction module, the overall energy conversion is still inefficient, signaling more research effort in this area.

Researchers had already developed a thorough understanding of the water splitting/water oxidation process; the mechanism of catalyzing CO<sub>2</sub> reduction, on the other hand, is largely uncovered. Even though we have had extensive knowledge and development over water oxidation catalysts, energetically effective ones are still rather expensive and therefore need to be economized. What's left for future investigation might include: improving the solar-to-fuel conversion rate, which means ultimately improving the yield of artificial photosynthesis devices that have been already developed, discovering more methods to produce multielectron reduced products in place of CO, and addressing the challenge in finding CO<sub>2</sub> source and separating CO<sub>2</sub>-reduced products when designing our artificial photosynthesis device.

## Conclusion

Research on artificial photosynthesis as a renewable energy technology has been under investigation for decades. Countless artificial photosynthesis techniques have been developed, yet we are still far from the commercially viable technology. All currently available technology faces bottlenecks: a lack of energetic efficiency, long-term stability, and/or cost efficiency.

Although artificial photosynthesis faces many challenges, it is still considered a promising technology as it presents an appealing solution to our current global energy crisis. If such technology is successfully developed, human can largely eliminate the demand for fossil fuels, while retracting their carbon footprint as well. Fortunately, over the last three decades, researchers have made enormous progress in understanding the mechanism behind the technology, creating various kinds of catalysts, and assembling effective and stable models. The challenge now is to fill in the gap of knowledge and assemble the missing components for scalable production. Even if we have a long way to go, contemporary research progress has made it possible to envision scalable production of this renewable energy technology, and hopefully, we can see major installations in the upcoming years.

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