SUNLIGHT TO SOLUTIONS: THE PROMISE OF ARTIFICIAL PHOTOSYNTHESIS

Artificial photosynthesis is a clean alternative energy source that mimics natural photosynthesis to turn sunlight into necessary fuels. Because of issues associated with alternative energy sources such as low efficiency, low durability, high cost, and scalability concerns, artificial photosynthesis struggles with mainstream integration. This article details recent research and advancements that aim to specifically address these setbacks, providing potential solutions. Recent research done with this process includes mechanisms that target low efficiencies in central processes within artificial photosynthesis as well as specific catalyst designs and selections that yield C2 hydrocarbons and extend operational lifetime. Another discovery in the ability to store four charges and facilitate multiple electron transfer, addresses recombination, another primary obstacle. Although artificial photosynthesis is currently not prepared for industrial applications, the advancements made within recent years indicate promising environmental reformation.

1.Introduction

Humanity's increasing demand for electricity, heat, and other sources of energy places great dependence on harmful energy processes to meet these needs. As much of the societal infrastructure is built on fossil fuel combustion, it continues to serve as the mainstream source of energy making up roughly 80% of the supply worldwide [1]. The issue with continued reliance on this burning process is due to greenhouse gas emissions, its resulting environmental change, and the unsustainability of the resource itself. Irreversible damage is continually noted as it has been observed that the average surface temperature has increased by approximately 1.1 °C compared to before the introduction of these industrial processes [2]. As this environmental change caused by these harmful processes damages the health of the earth, society is negatively affected in numerous ways. The very supplies that sustain livelihood deplete, extreme natural disasters increase, and the usual patterns of infectious disease can change [3]. Evidently, the adverse effects of fossil fuel combustion necessitate the introduction of alternative pathways to alleviate the steep decline in environmental health. One such form of alternative energy that is being extensively researched currently is artificial photosynthesis, the plant-mimicking clean energy process. By resolving critical issues faced in solar conversion engineering such as efficiency and industry level scalability, recent advancements in artificial photosynthesis provide a realistic pathway toward environmental reform.

2. Components of Artificial Photosynthesis

In natural photosynthesis, the leaf is often described as being the main driving force that converts solar energy into chemical energy. In the case of artificial photosynthesis, the process can be facilitated by various systems, one example of a common mechanism being photoelectrochemical cells. Generally, the system consists of the necessary materials to carry out the process: materials that capture photons, and catalysts that aid in water oxidation and carbon dioxide reduction [4]. The capturing of light is typically carried out through semiconductors or light absorbing dyes. The chosen material absorbs light and triggers electron excitation, creating holes. This charge separation then drives the subsequent reactions which are water splitting and most often the reduction of carbon dioxide [5]. As detailed in Figure 1, the overall splitting of water occurs through two half reactions: the oxidation of water and the reduction of protons.

$$\text{Water oxidation reaction: } 2H_2O \rightarrow 4H^+ + 4e^- + O_2,\ E^\Theta = 1.23\ V_{RHE}$$

$$\text{Proton reduction reaction: } 4H^+ + 4e^- \rightarrow 2H_2,\ E^\Theta = 0\ V_{RHE}$$

$$\text{Overall water splitting reaction: } 2H_2O \rightarrow 2H_2 + O_2$$

Figure 1. The two half reactions for water splitting. Source: [6]

The theoretical energy minimum required for the reaction to occur according to Figure 1 is indicated as 1.23 eV and is energetically unfavorable. Because of overpotential associated with reactions that do not follow theoretical standard state conditions, water oxidation catalysts are necessary. With the introduction of water oxidation catalysts, the creation of the oxygen-oxygen covalent bond is facilitated and the overpotential is lowered [6]. Simultaneously, the electrons and protons provided drive the reduction of carbon dioxide into valuable fuels typically carbon monoxide, formic acid, methane, or methanol [7].

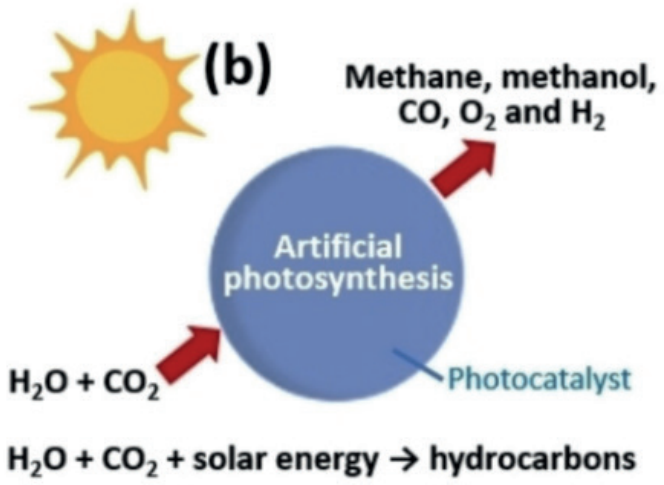

Figure 2. Carbon Dioxide Reduction Visual. Adapted from: [7].

3. Current Drawbacks

Unfortunately, many alternative sources of energy like artificial photosynthesis struggle with industrial integration because of economic and scientific hurdles. At large, the high costs associated with taking lab results to the industrial scale and the materials necessary serve as a significant barrier toward integration. Material degradation because of operating the reactions and the use of rare, noble metal catalysts for water splitting and carbon dioxide reduction will evidently accelerate costs for industrial scale applications despite possible lab level successes. Another significant hurdle for artificial photosynthesis is the low efficiency, with artificial systems struggling to achieve even the 3-6% solar-to-biomass conversion efficiency associated with natural photosynthesis [4]. Recombination, which occurs when the electrons and the holes caused by the absorption of light recombine, is one of the central challenges in artificial photosynthesis that leads to this efficiency loss [8]. Despite these setbacks, as this form of energy and other forms are continually being researched, these setbacks are constantly addressed. Promising results and advancements as will be mentioned in this paper can serve as potential hope for the possibility of mainstream integration.

4. Recent Developments

4.1 Mechanisms for Improved Efficiency

4.1.1 $Pb_2Ti_2O_{5.4}F_{1.2}$

A team of Japanese researchers led by Professor Kazuhiko Maeda, have shown that nanosized $Pb_2Ti_2O_{5.4}F_{1.2}$ or PTOF, yielded improved efficiency in activity for water splitting and carbon dioxide reactions compared to previous photocatalyst models [9]. One form, cit-PTOF, displayed roughly a 60-fold increase in performance from previous PTOF forms in hydrogen gas production and carbon dioxide conversion and a quantum yield of roughly 10%. Figure 3 provides a comparison of the hydrogen gas evolution and carbon dioxide reduction to formic acid based on the Ti-complex selection indicating important significance in precursor selection.

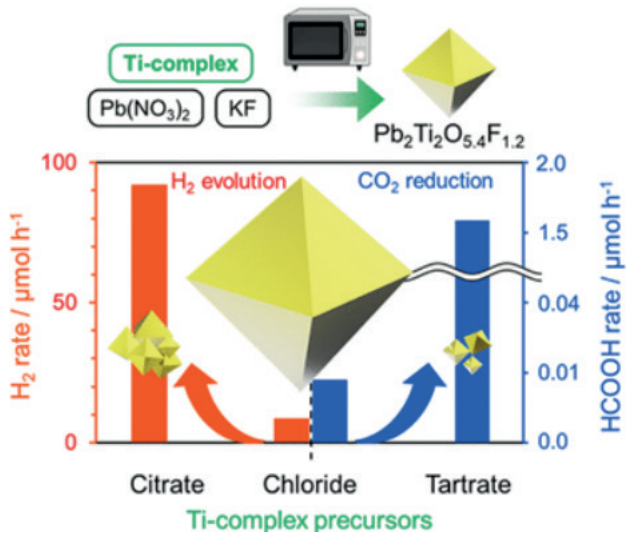

Figure 3. Respective performances of PTOF based on Ti-complex selection. Source: [9]

The overall synthesis for PTOF was done using Ti-complexes formed using lactic acid, citric acid, and tartaric acid. Using microwave-assisted hydrothermal synthesis to form the PTOF, it was found that the Ti-complex precursor that was selected was what allowed for size control. The researchers discovered that despite the high structural disorder and low bulk crystallinity of cit-PTOF and tart-PTOF, their nanostructured form improved photocatalytic performance. The reduced particle size significantly shortens the distance that the electrons need to reach the active surface sites. This factor combined with the high surface area increasing overall reaction site availability, the material can overcome these bulk defects. Controlling the structural form of oxyhalides therefore has the potential to improve their roles in activity within artificial photosynthesis. Most importantly, the temperature that the microwave-assisted hydrothermal synthesis operated at was 200°C, which is a considerably low temperature for synthesis reactions. This process is therefore considerably energy efficient and environmentally friendly. Ti-complexes are also an abundant resource, which is a crucial consideration for industrial scale applications.

4.1.2 Ruthenium Complex

Nakada and other researchers delve into a typically disregarded photochemical ligand exchange reaction that accounts for and explains the low performance displayed by previous complex/semiconductor systems [10]. Photochemical ligand exchange occurs because the complexes themselves absorb light causing detachment of the CO ligand which is then replaced by a solvent molecule. This destruction of the internal structure is what the researchers accounted for through experimentation. Using RuP and RuCP loaded individually onto Ag/meso-PCN it was found that the tight packaging of RuCP catalysts on the semiconductor and reduced light intensity increased the previous low efficiency of CO_2 reduction to 27.7% apparent quantum yield for CO_2 reduction to formate. This arrangement was found to suppress the self-destruction of the catalyst, which was what caused the low efficiency from before. This record high efficiency bears important results since previous results were found with conversion rates of carbon dioxide to formate of a stark less than 6% [11].

4.2 Charge Recombination

To produce desirable fuels using artificial photosynthesis, multi-electron transfer is needed. Sacrificial redox reagents have typically been used but as they are consumed throughout the reaction process, they are not viable [12]. To address this concern, a team led by Oliver S. Wenger created a D_2-D_1-PS-A_1-A_2 (donor-photosensitizer-acceptor) model. With the unit's ability to store four charges - two positive and two negative - simultaneously, multiple electron transfer can occur to drive the reactions [13].

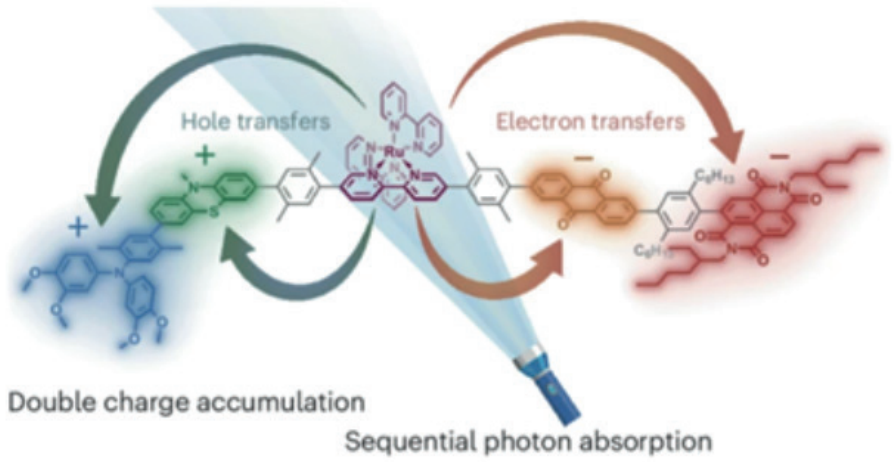

Figure 4. Simplified depiction of the D_2-D_1-PS-A_1-A_2 and photon absorption. Source: [12]

Previous models like D-PS-A, have been found to face the issue of recombination with the absorption of a second photon, however in this case it was found that absorption of a second photon was possible by making the absorption process sequential instead of simultaneous. The first excitation created a distance between the redox equivalents D2 and A2, allowing D1 and A2 to be charged with the second excitation. After the second cycle of electron transfer, the four charges accumulate. This model was also found to be able to work under dim light conditions considerably lower than other comparable systems. This discovery is important since sunlight is a variable energy source and likely a heavy contributor to the degradation of the materials.

4.3 Catalytic Design

4.3.1 Copper Sunflower Electrocatalysts and Lead-halide Perovskite Photo Absorbers

Virgil Andrei, Peidong Yang, and Erwin Reisner and their team discovered that pairing copper sunflower electrocatalysts and lead-halide perovskite photo absorbers that generate 1 V photovoltage created an effective photocathode [14]. The copper nanoflower electrocatalysts were efficient in reducing the energy barrier and the high overpotential associated with hydrocarbon synthesis. Typical metal catalysts in the carbon dioxide reduction step generally reduce to single carbon compounds [15]. However, the structural make-up of the copper nanoflower catalysts within the study was found to optimize carbon-carbon coupling to favor C_2 hydrocarbons provided the geometric sizing is adequately tuned - roughly 4 mm^2 - to match the current of the light absorber. The lead halide perovskite created 1 V photovoltage to power the reduction of carbon dioxide into ethane and ethylene, which are energy intensive. The authors have also replaced water oxidation reaction with the less demanding glycerol oxidation reaction, to increase performance of the pair for practical applications, with the important caveat that this requires a continuous supply of glycerol.

4.3.2 $Bi@Fe_2O_3$

Traditional catalysts used for carbon dioxide reduction have been found to ineffectively absorb low-energy photons from sunlight. Researchers from Xi'an Jiaotong University in China have developed $Bi@Fe_2O_3$ (core@shell structure) introducing a structure that achieves broad-spectrum facilitated carbon dioxide reduction [16].

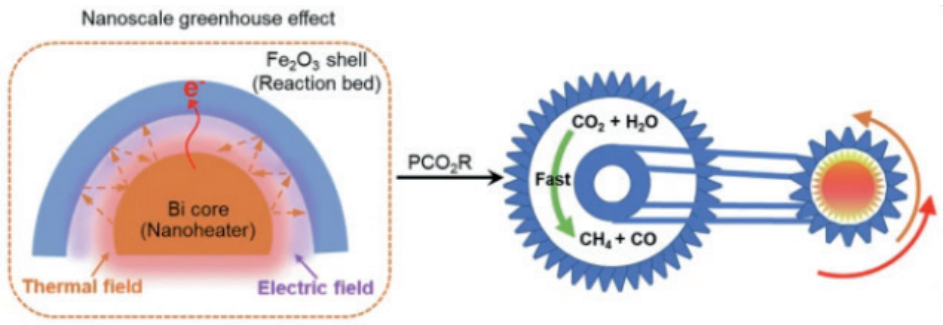

Figure 5. Visual Model $Bi@Fe_2O_3$. Adapted from: [16].

Effectively, high energy photons generate standard electron-hole pairs on the catalyst bed when photons hit the Fe_2O_3 shell. In addition, the bismuth core absorbs the incoming low-energy photons causing localized surface plasmon resonance (LSPR) and generating "hot electrons" and localized heat. Because of the interface between the two materials causing a built-in electric field, the hot electrons created inject into the Fe_2O_3 layer. In addition, as shown in Figure 5, the outer Fe_2O_3 shell acts as a thermal insulator, which raises the temperature within the shell. The "greenhouse" environment created, and electron accumulation facilitates CO_2 dissociation and subsequent methane formation. In addition to broad-spectrum utilization for carbon dioxide reduction, an important finding was the lack of the need for external heating and the extending electron lifetimes. The Fe_2O_3 shell also keeps the bismuth cores isolated, preventing past issues with melting and sintering allowing for prolonged operation.

5. Conclusion

Fossil fuel emissions and many harmful industrial processes produce carbon emissions that are of immense detriment to the environment. To reduce reliance on these processes, alternative energy sources are necessary. Artificial photosynthesis as one of the alternative energy solutions, has made many new advancements within the past few years gradually addressing common issues faced with the process. Recent advancement into PTOF semiconductors and Ruthenium complexes address low efficiency concerns, and newly discovered models like the D_2-D_1-PS-A_1-A_2 introduce solutions to central challenges like recombination. Specialized catalytic design and selection has also addressed energy challenges and introduced pathways into potential standalone operations. As with other alternative energy sources, there are still limitations with artificial photosynthesis
and its ability to become practical enough for large-scale industrial applications. However, relentless innovation and research into these alternative energy sources could help mitigate environmental damage.

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