LATEST ADVANCES IN ARTIFICIAL PHOTOSYNTHESIS: A HIDDEN GEM IN THE REALM OF ALTERNATIVE ENERGY TECHNOLOGIES

To sustain lives on Earth, photosynthesis is the most important biochemical reaction. During this process, sunlight is used to split water which is later stored as $NADPH/H^+$ and translated to ATP through ATP synthase. However, even the most efficient plant is unable to store more than 1% of solar energy. Hence, many researchers have been trying to mimic this reaction artificially to increase efficiency and absorb more light [1]. Since most of the existent sources of energy (e.g., coal, gas, etc.) are considered to be unsustainable in the long run and have negative impacts on the environment, it is more important now than ever to find sustainable, cost-effective sources of energy [2].

During the 1900s, Italian Scientist Giacomo Ciamician first developed the idea of artificial photosynthesis to capture solar energy using photochemistry devices and convert it to solar fuel, which can be stored for later. This process intended to utilize catalysts and conductors to capture sunlight and mimic the photosynthesis process; however, this idea did not gain much attention [3]. Another early breakthrough was when Honda and Fujishima reported the possibility of splitting water in the presence of Titanium oxide using UV excitation [4]. Later, during the 1980s, a group of researchers developed an artificial leaf using a thin-film amorphous silicon multijunction sheet in the presence of a catalyst (titanium oxide) and split water into hydrogen and oxygen-later a polymer membrane was used to transport the protons. It was one of the first attempts in developing a device that was able to utilize low cost silicon multijunction cells and work as an "artificial leaf" for the artificial photosynthesis process [5].

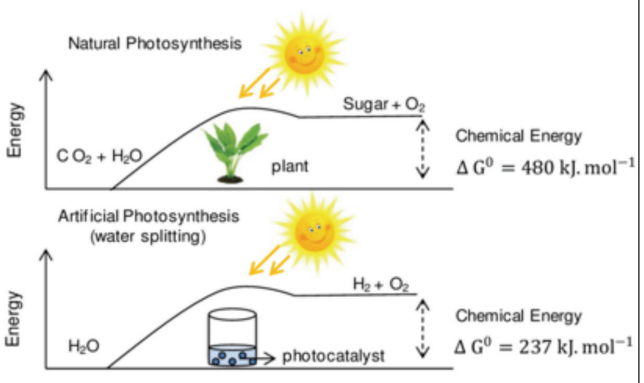

Figure 1: Natural vs. Artificial Photosynthesis [6]

In recent years, due to the increased demand for renewable energy sources, artificial photosynthesis has been investigated by researchers throughout the world. This paper reports some significant advancements in this field and how these advancements will affect the future of the renewable energy field.

Artificial photosynthesis uses solar cells instead of chlorophyll II to absorb sunlight and artificial or organic catalysts to split water into hydrogen and oxygen (Figure 1). This process is capable of producing electricity and hydrogen fuel [7]. Although current photovoltaic cells (PV) used in solar panels utilize similar technology, the main difference lies in the storage system. The PVs used in solar panels directly convert the energy into electricity and heavily depend on the weather, whereas the PV cells used in artificial photosynthesis, the semiconductors, can store solar energy for later use [8].

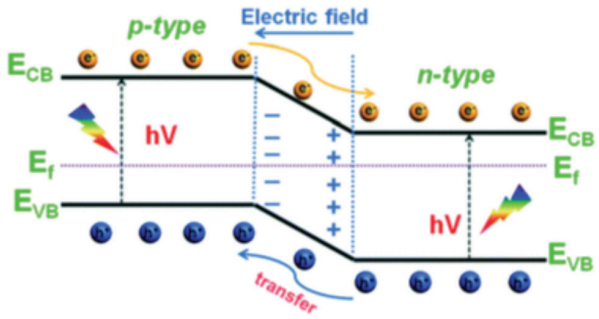

Figure 2: Charge separation in p-n heterojunctions [11]

There are three important steps of every artificial photosynthesis device: light-harvesting/electron transportation, water splitting, and carbon dioxide reduction. In the first step, photons with a wavelength of 400-700 nm are absorbed, which is used as energy to carry out the next steps. During water splitting, the absorbed light by semiconductors' photoexcited electrons migrates to the surface of the catalyst and completes the hydrogen (oxygen) evolution half-reaction. In the last step, carbon dioxide is reduced to enhance the fuel quality [9, 10]. To enhance the efficiency of the artificial synthesis process, it is essential to use materials that have superior mechanical properties and economic viability. Photosensitive molecules and inorganic semiconductors are usually used to harvest light.

In recent years, semiconductor nanowires have gained significant interest because of their unique geometrical and electronic properties. In these semiconductors, the nanowires reduce the electrochemical over-potential, and the heterostructured junction increases light absorption and enhances the charge separation process [11]. A 1D semiconductor nanowire arrays (NWAs) coupled with another semiconductor create p-n junctions on which, if photons with higher energy are projected, the built-in electric field separates the charged particles [12]. These types of semiconductors not only effectively separate the charge but also separates the incompatible oxidation and reduction reactions [13]. In figure 2, the built-in electrical potential is seen to drive negative and positive charges in different directions, which will be used in the water splitting, and carbon reduction steps [11].

Many studies propose the use of silicon nanowires (SiNWs) to enhance the performance of photovoltaic cells. However, there is a debate between the efficiency of vertically aligned SiNWs and tilted SiNWs. A study conducted by Hong et al. designed a conductor using tilted SiNWs and reported efficiency of 33.45%, which is 15% more than the highest efficiency reported by vertically aligned nanowires [14]. This study investigated the difference between vertical and tilted SiNWs, the height and thickness of the SiNWs was reported to be 1 μm, and the slanted angle was 40°. The wavelength of light varied from 300 nm to 1100 nm [14]. The result shows that shorter wavelengths

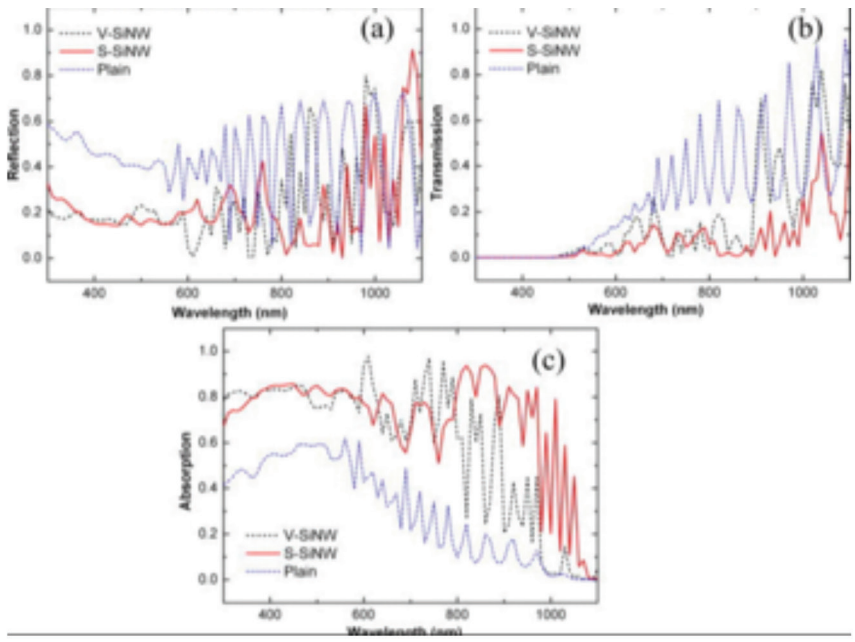

Figure 3: Reflection, transmission, and absorption spectra of the SiNW structures [hong]

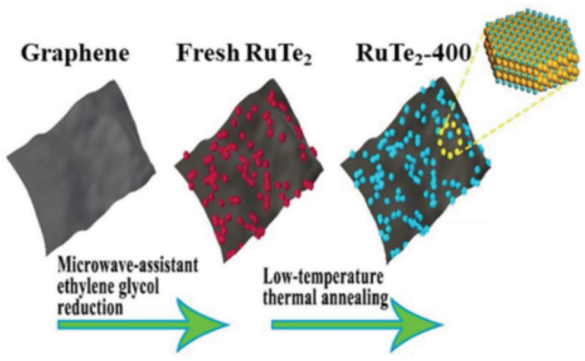

Figure 4: Fabrication Process of $RuTe_2$ [16]

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lead to greater absorption, which can be caused by stronger light scattering. Also, the periodicity of the SiNWs plays a significant role in the absorption. If the periodicity is significantly smaller than the wavelength, then it disrupts the interaction between slanted SiNWs and light-leading to poor light absorption. The study found that the optimal Diameter/Periodicity (D/P) ratio is 0.7 because the reflection and transmission drop significantly, increasing the light absorption capability of S-SiNWs [14]. In figure 3, compared to vertical nanowires, the SiNWs showed an 18% higher light absorbance, which is due to the structural difference, the presence of four mirror symmetries for the V-SiNWS, and for S-SiNWs is only one. This knowledge can be used to build similar structures using different solar cell materials; however, silicon solar cells have proven to be superior by far compared to others [14].

In recent years, researchers have been investigating biofunctional catalysts to make the artificial photosynthesis process more efficient and cost-effective. A biofunctional catalyst is capable of catalyzing both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER)-making it an attractive choice for water splitting during artificial synthesis [15]. A recent study conducted by Tang et al. found that crystallized $RuTe_2$ is an exceptional catalyst for water splitting because of its reliable catalytic stability and low cost. The crystallized $RuTe_2$ reports a current density of 10 mA/cm², resulting in a small over-potential of only 34 mV during HER and 275 mV for OER. In this catalyst, the Ru acts as the main active site, and Te is used to relocate different charges [16].

To synthesize crystalized $RuTe_2$ ($RuTe_2$-400), the nanoparticles are first supported over a thin graphene film through microwave irradiation (figure 4), and transmission electron microscopy revealed that the nanoparticles were anchored to graphene sheets, and $RuTe_2$-400 surface had visible lattice fringe. The low-temperature thermal annealing increased the surface area and porosity [16].

The design of $RuTe_2$-400 is superior to other existing catalysts because the increased surface area caused more active sites to be exposed in electrolyte and open channels for ion diffusion. The existing commercial Pt/C catalysts require 101 mV more to achieve a current density of 10 mA/cm² compared to $RuTe_2$-400. Moreover, the $RuTe_2$-400 reports the smallest charge transfer resistance of 15.14 Ω. The crystallized $RuTe_2$ showcased improved performance for OER, requiring no activation process and spending significantly less energy to carry out the reaction process. The stability test showcased steady performance at a fixed potential of 1.505 V in alkaline solution after 12 hours [16].

During the water splitting, the reported, the efficiency with which charge was transferred in a system (Faradaic yield) for collected hydrogen and oxygen gas was approximately 100%. At a cell voltage of 2V, the current density was reported to be 100 mA/cm², and the electrodes also didn't go through any significant changes after 20 hr cycle (figure 5), making $RuTe_2$-400 an exceptional bi-functional catalyst [16].

Another study proposes using a nitrogen-doped nanoarray over 3D porous Co foam (CoP–N/Co foam) as a bifunctional catalyst. For hydrogen evolution reaction (HER), it reports a current density of 50 mA/cm² when the overpotential is 100 mV, and for OER, the reported overpotential is 260 mV. This proposed design can maintain catalytic stability for more than 24 hours in a corrosive environment, which is more than most existing catalysts for artificial photosynthesis [15].

In figure 6, it can be seen that, the CoP–N/Co foam catalytic system significantly increased oxygen evolution reaction (OER) to 50 mA with only 260 mV overpotential. It also showcased superior catalysts kinetic by ensuring smallest Tafel slope, while the current density curve after 1000 cycles showcased a steady performance [15].

Although these catalysts showcase a promising performance, however, the research is still elementary, and further investigation is needed to project these findings in commercial settings. The current catalyst involving Pt is very expensive, and catalysts using Ru-based catalysts cost only ¼ of the Pt-based catalysts [16]. Hence, considering these benefits, it is worth investing resources in this research.

One of the biggest challenges to commercializing artificial photosynthesis is the absence of efficient technology to reduce carbon dioxide. Various studies claim that metalloporphyrin catalysts are the solution to this challenge [17,18,19]. A study led by Sinha et al. proposes a design where metal groups are connected to one hydroxyphenyl group and three other phenyl groups where the hydroxyphenyl group works as a local proton donator (Figure 7). This study emphasized metal-substituted 5-(2-hydroxyphenyl)-10,15,20-triphenylporphyrin (MTPOH, M=Mn, Fe, Co, Ni, Cu), ClFeTPOH, which are active homogeneous catalysts in organic solvents, and reduce carbon dioxide to carbon monoxide [19].

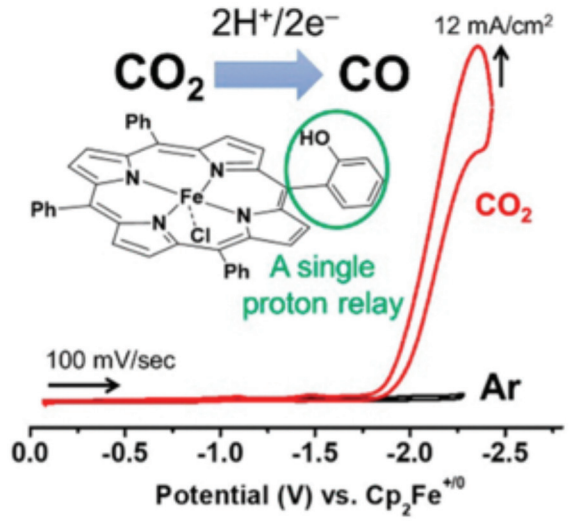

Figure 7: Proposed Catalyst and mechanism [19]

The result showcases a promising future, and the ClFeTPOH proved to be an efficient catalyst in CO2-saturated MeCN + 1 M H2O, yielding 96% of Faradaic efficiency and reducing all carbon dioxide to carbon monoxide. However, the result differs when a DMF solution is used; therefore, it can be concluded that the solution matters in carbon dioxide reduction. Asymmetric porphyrins ensure optimal proton delivery and H-bonding properties [19].

Conclusion

Considering the recent advancements in the artificial photosynthesis field, the future looks expansive and promising. In recent years, the $122 investment of the US government also proves the validity of this field [20]. The obstacles (e.g., absence of efficient catalysts, commercial settings, high production cost, etc.) still remain to make future advancements more challenging. However, the recent research related to enhancing the performance of semiconductors to increase light absorbance and the use of different cost-effective catalysts might help to address these pressing issues. Therefore, the positive advancements outweigh the obstacles and re-emphasize a reliable future for artificial photosynthesis technology.

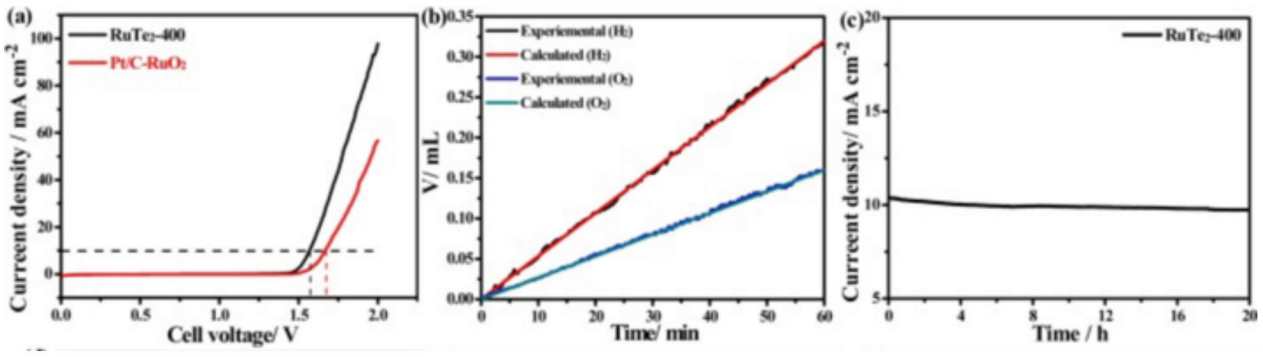

Figure 5: (a) and the amount of H2 gas and O2 gas experimentally measured and theoretically calculated versus time (b) for RuTe2-400 in an overall water electrolysis system (c) The long-term durability tests at 1.57 V [16]

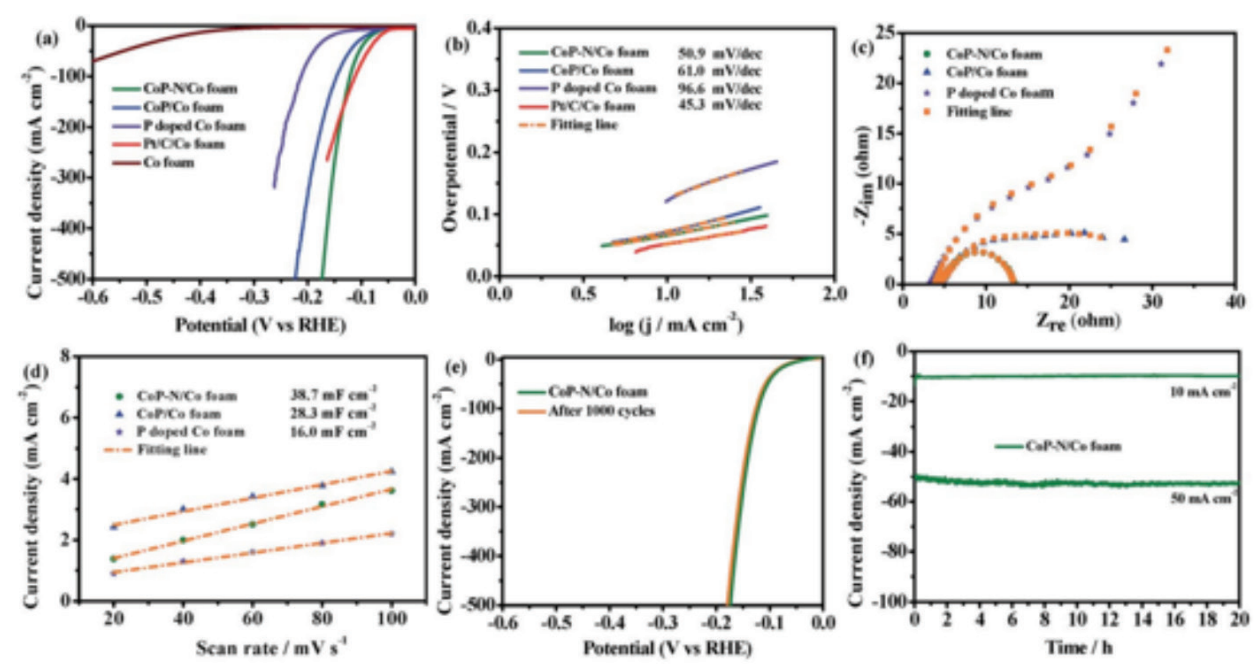

Figure 6: (a) Polarization curves (b) Tafel plots (c) Nyquist plots and fitting at the potential of 0.090 V vs. RHE (d) Linear plot of capacitive current density vs. scan rate (e) Polarization curves for CoP–N/Co foam before and after 1000 cycles (f) Chronoamperometry curves of the CoP–N/Co foam [15]

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