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### A REVIEW ON ARTIFICIAL PHOTOSYNTHESIS

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#### ABSTRACT

Sunlight is the most abundant renewable energy source and yet it accounts for 1% of the global energy supply. The ever increasing demand for energy combined with the increasing awareness of climate change has driven the demand for cleaner energy sources. Today, intensive research, both fundamental and applied, is directed at establishing new and better ways to harness solar energy. One research area is photo electrochemical solar fuel generation, generally referred to as artificial photosynthesis (AP). Unlike solar cells, which capture and convert sunlight directly to electrical potential, AP converts sunlight to chemical bonds, for example, splitting water into hydrogen and oxygen. My research is focused on establishing methodologies, technologies, and analytical tools for realizing and analyzing AP prototypes. In this presentation I will focus the talk around the development of monolithically integrated AP systems, which are stable, efficient, safe, and scalable. The monolithically integrated AP prototypes consists of off the shelf triple-junction III-V compound semiconductor

Solar cell coated with a protective layer in conjunction with a platinum hydrogen evolving catalyst, Nafion membrane, sulfuric acid electrolyte, and iridium oxide oxygen evolving catalyst, all integrated into a chassis. The significant impact of this work has been the demonstration of a safe, stable, and efficient AP system. This would not of possible without the development of protective layers we have developed at JCAP which have significantly improved, lifetime (>7days), and solar-to-hydrogen conversion efficiency >10%. Ongoing research aims to enable large-scale implementation by improving efficiency, increasing lifetime, establishing manufacturing processes and systems, and decreasing life cycle environmental impacts, which support reduced prospective costs.

**KEYWORD:** Photosynthesis, solar, solar cell, AP converter.

#### **ARTIFICIAL PHOTOSYNTHESIS**

We have discussed why we are in desperate need of renewable energy sources to be able to sustain ourselves in the future. We have also demonstrated the quantity of energy the sun gives us for "free" and the way in which the plants collect this energy and store it. So what is the next logical step we should take? Artificial photosynthesis.

1. Introduction to Artificial Photosynthesis

By replicating the natural photosynthesis system(s) we could convert the energy from the sun into fuel. This would open up a whole new world of renewable energy opportunities for us. However, we soon run into a few challenges. The natural photosynthesis system is, as explained in the previous chapter, very complicated at a molecular level. This chapter is about how these challenges can be overcome and what our options might be at building an artificial photosynthesis system.

2. The process of Artificial Photosynthesis

Artificial photosynthesis consists of four steps and is aimed at mimicking natural photosynthesis:

1. Light harvesting: Trapping light particles or photons and concentrating their energy in the reaction Centre (RC).

2. Separation of charge: In the reaction centre, sunlight is used to separate the different electrical charges: positive 'holes' and electrons.

3. Splitting water: The positive charges obtained from the charge separation are used to split water into hydrogen ions (protons) and oxygen.

4. Fuel production: With the energy from new photons, the negative charges from step 2 are used together with the hydrogen ions from step 3 to produce hydrogen or might in the future be used together with carbon-dioxide to produce a carbon-based fuel.

Given the purpose of our research, we will look at the functionality of a water oxidation electrocatalyst in a prototype "artificial leaf" that splits water into hydrogen gas and oxygen, we will now mainly focus on the production of hydrogen. This is also because the production of carbon-based fuel is much more complicated.

### **International Journal of Engineering Technology Research & Management**

Only four hydrogen ions, four electrons and four photons are needed for the production of two hydrogen molecules:

 $4 \text{ H}++4 \text{ e}- \rightarrow 2 \text{ H}2 \text{ (4 hv needed)}$ 

Hydrogen is a very efficient fuel, but there are however some issues. For example, hydrogen is very flammable in combination with oxygen. This is why after the splitting of water into hydrogen ions and oxygen molecules, these two must be separated immediately from each other. Another issue is that hydrogen is a gas and the current fuel infrastructure is based on fluids, so this is something which would need to change in order for the transport and distribution of hydrogen to work.



Figure 9: The production of hydrogen by mimicking photosystem

II. Source: www.chembites.org

2.1 Light Harvesting

As e explained, nature has an excellent system for achieving light harvesting and charge separation. The lightharvesting pigment complexes in natural photosynthesis capture and focus the energy from sunlight and transfer this energy among themselves and then through to the reaction centre. This energy transfer is achieved due to Förster resonance energy transfer.

A task for researchers in the field of artificial photosynthesis is now to develop strategies similar to that found in nature. In such an artificial system multiple absorbers with complementary absorption profiles that are capable of efficient excitation energy transfer are used as light harvesters. These light harvesters must then transfer their excitation energy to an artificial reaction centre.

These light-harvesting systems could be made from organic molecules. Alternatively, semiconductors, like a solar cell, could be used. The most widely used solar cells are silicon solar cells. These cells absorb light with a wavelength of under 1100 nm. This means that they absorb even more light than the natural light-harvesting complex of plants. However, there is a problem. The maximum wavelength of the absorbed light defines the

## **International Journal of Engineering Technology Research & Management**

potential difference of the electrons produced during the charge separation. For the naturally harvested 700 nm wavelength the potential difference is 1.8 V, but for the silicon's harvested 1100 nm the potential difference is just 1.1 V. This is a problem as there simply is not enough energy for the water-oxidation to take place, at least 1.23 V is required to oxidize water. Although such materials can efficiently absorb sunlight, separate charges and are stable with extended exposure to sunlight, they have a limited flexibility and a work has to be done to give them the desired properties. As a last option organic light harvesting molecules could also be used in combination with semiconductor charge separators.



Figure 10: A tandem system for artificial photosynthesis and utilization of incoming photons. Green section is the visible light, from 400 nm to 700 nm. The purple section is the infrared light from 700 nm to 1100 nm. Resource: http://rsfs.royalsocietypublishing.org/content/5/3/20150014

Natural photosynthesis is a tandem system as it operates in two light-absorbing stages: photosystem I and photosystem II. A disadvantage of this system is the fact that both systems only absorb photons in the visible

## **International Journal of Engineering Technology Research & Management**

part electromagnetic spectrum, from 400 to 700 nanometers, without making any use of the infrared spectrum. This means plants only use half of the incoming photons, consequently half of the incoming energy, which reduces plant efficiency to turn energy from sunlight into chemical energy. In general artificial photosynthesis is aimed at mimicking nature. But why not improve on it? This led scientists to start researching an alternative system for artificial photosynthesis: a tandem system of two unique photosystems that each absorb different wavelengths from the electromagnetic spectrum (see: figure 10). With this technique all the incoming light is effectively used and we will be able to capture as much energy as possible in the most efficient way.

#### 2.2 Charge Separation

Photo induced charge separation is the process of an electron in an atom or molecule, being excited to a higher energy level by the absorption of a photon and then leaving the atom or molecule to a nearby electron acceptor. This process is very similar to the process in natural photosynthesis.

#### 2.3 Water Splitting

The positive charges obtained from the charge separation are used to oxidize water and split the hydrogen from the oxygen. This is done with the help of a water oxidation electrocatalyst. Without a catalyst, this reaction is very endothermic, requiring high temperatures (at least 2500 K) and high amount of energy to occur. [12] A catalyst reduces this amount of energy for the reaction to occur. In this research paper we will test three different water oxidation electro catalysts and we will see which proves to be the most efficient.

#### 2.4 Fuel production

The easiest way hydrogen gas (H2 gas) can be made is on the surface of noble metals such as platinum. However, scientists are busy looking for a substitute as noble metals are expensive and scarce, and therefore difficult to commercialize. As we said, at this point the production of H2 gas is the main focus. But maybe in the somewhat extended future we could try to reduce CO2 to these various products

 $\begin{array}{l} 2 \text{ H}++2 \text{ e}-\rightarrow \text{H2} \\ \text{CO2}+2 \text{ H}++2 \text{ e}-\rightarrow \text{CO} & +\text{H2O} \\ \text{CO2}+2 \text{ H}++2 \text{ e}-\rightarrow \text{HCOOH} \\ \text{CO2}+4 \text{ H}++4 \text{ e}-\rightarrow \text{HCHO}+\text{H2O} \\ \text{CO2}+6 \text{H}++6 \text{ e}-\rightarrow \text{CH3OH}+\text{H2O} \\ \text{CO2}+8 \text{ H}++8 \text{ e}-\rightarrow \text{CH4} & +2 \text{ H2O} \\ \text{This is practically an artificial reproduction of the Calvin Cycle.} \end{array}$ 

#### 2.5 The energy budget for artificial photosynthesis

The potential difference of the electrons is a measurement for the amount of energy they carry. In an artificial tandem system, where both photosystems are sensitive for different wavelengths, the total potential difference of the produced electrons is 1.1 V + 1.8 V = 2.9 V. This is called the energy budget: the amount of energy that can be spent on breaking the bonds in water, creating bonds in oxygen and creating bonds in the fuel (hydrogen or carbon-based compounds). If the system is aimed at producing hydrogen, the following criteria for its budget to suffice:

•The standard redox potential for splitting water is 1.23 V, but in practice a higher amount will be required. For thermodynamic reasons, an extra 0.25 V is required to produce heat, bringing the total potential difference to 1.48 V.

• At least 0.5 V is necessary to prevent the reaction from going in the opposite direction.

• Catalysts need an over potential as they rarely succeed at getting the reactions to take place at the minimal potential. As the splitting of water is a complex four stage reaction, the needed over potential (with today's technology) is 0.4 V.

•The over potential for the production of hydrogen is 0.2 V.

•It costs 0.2 V to transport the hydrogen ions.

•In a stand-alone system, the energy needed to compress the hydrogen gas for storage must come from its own energy budget and this is at least 0.2 V.

### **International Journal of Engineering Technology Research & Management**

These are computer estimates, but the figures demonstrate the difficulty of achieving a total of 2.98 V while we only have an available energy budget of 2.9 V. In practice the amount of energy needed to perform the whole artificial photosynthetic reaction is still too high to fit in the energy-budged. Moreover, just 1.23 V is actually stored in the hydrogen molecules. This difference of 1.75 V is needed to stabilize and compress the fuel and to prevent the tandem system from working in the opposite way; emitting instead of absorbing photons. For carbon-based compounds this is even more difficult as they require an over potential of 0.5 V to reduce the CO2. We need to improve the efficacy of the different steps of the process to make the overall process of artificial photosynthesis more efficient and to meet the demands of the energy budget. This is why it is essential to find the most efficient catalyst possible: to facilitate the water oxidation and to help us minimize the catalytic over potential.

#### 3. Artificial photosynthesis in the future: challenges and possibilities

By now you might understand how an artificial photosynthetic system could work. In some areas the system is still in its infancy, but on various other aspects progress has been made. Still a lot of research needs to be done but according to Huub de Groot artificial photosynthesis will be fully operational in 2050; by that time it will be the backbone of energy supply. [14] In November 2015 a first prototype of an "artificial leaf" was made in de Bio Solar Cells program. This prototype of course still has many deficiencies. One of the many challenges in the coming decades is to improve on this first prototype system, which is the focus of chapter 8 'Third part of our research: investigating the deficiencies of the prototype "artificial leaf" and possible solutions' Generally speaking, for an artificial photosynthetic system to be a viable source of renewable energy, it must be efficient, robust and cost-effective.

#### 3.1 Efficiency

Probably the greatest challenge of them all is solving the issue of efficiency. The efficiency of an artificial photosynthetic system is important because the more efficient the system, the less land is required to capture the light energy from the sun. Any proposed solar energy conversion system must be socially acceptable. If the land area requirements are too large then this becomes a problem. At the moment, we have not yet managed to make artificial photosynthesis more efficient than other alternative fuel production methods. However, artificial photosynthesis has the theoretical possibility of reaching an efficiency of 40%. In practice, this figure would probably be 18-20%, while plants have a net efficiency of only 0.1-1%. This is partially due to the fact that the maintenance of the organism itself requires around 30% of the incoming energy. An artificial photosynthetic system does not have this issue. A tandem-system would result in absorption of light with broader range of wavelengths, thereby improving on the natural system. This would result in a greater efficiency. A part of the system at which natural systems surpass artificial ones, is quantum efficiency. The quantum efficiency is the percentage of absorbed photons that give rise to stable photoproducts. Photosynthetic organisms typically can operate at nearly 100% quantum efficiency under optimum conditions. Plants have embedded various photosynthetic components into a so called responsive matrix that uses molecular-scale

Vibrations to control energy exchange with the environment and to guide reactions. Think about the Förster resonance energy transfer. Through such a responsive matrix nature has enabled itself to construct a self-assembling, self-repairing system from a limited set of materials that operates with a high efficiency. Scientist now believe it is possible to create an artificial system with its own 'responsive matrix' that is capable of mimicking nature's tricks. If scientist would succeed this would result in a much more efficient artificial photosynthetic system, and less materials would be required because of the self-repairing aspects of the 'responsive matrix'.

#### 3.2 Robustness

An artificial photosynthesis system must be robust enough to resist the test of time. An "artificial leaf" will take a lot of use and wear as a consumer product. Added to that, the system has to be resistant to possible extreme weather conditions. Furthermore, there must be an easy way of renewing the catalyst and other components of the artificial photosynthetic system, when needed. The self-repairing aspects of the earlier described 'responsive matrix' could be beneficial for the durability of an "artificial leaf". The system could simply repair itself when damaged.

## **International Journal of Engineering Technology Research & Management**

3.3 Cost

An "artificial leaf" as a product needs to be financially affordable, thus also easy and cheap to produce. This means that rare and expensive materials, such as platinum for example, should be avoided. The costs must be minimal if we want this system to be able to compete with other technologies. An advantage of artificial photosynthesis over other alternative fuel production methods, such as bio-ethanol production, is that it does not compete with food production, and thus does not have any harmful effects on nature or human society.

In order to make these fantastic dreams come true, we must first upscale the technology from its embryonic laboratory stage to a usable and viable product. We aim, through our research, to take the first steps in the up scaling of artificial photosynthesis by testing different catalyst on the prototype "artificial leaf" (or hydrogen generator as this is what the "artificial leaf" does: generate hydrogen gas). These are still small steps in this research field, but in the very far future we might one day be able to produce a diverse array of complex organic compounds as photosynthesis has a lot more to offer than a system for the production of hydrogen gas.

#### CONCLUSION

Technology for converting solar energy into fuel can help to close cycles and is suitable for large-scale or small-scale use. Developments in the field of conventional solar panels have shown that commercial renewable energy activities can develop quickly once they become economically viable. The Netherlands and the European Union have the scientific and industrial infrastructure needed to take the lead in the field of artificial photosynthesis.

Around the world, scientists and engineers are working on ways of making hydrogen and carbon-based fuels using water, carbon dioxide and sunlight. Such fuels offer the attractive prospect of enabling solar energy to be stored and transported, so that energy from the sun is available anywhere in the world whenever it is needed. Artificial photosynthesis can not only meet our need for sustainable transport fuel, but also serve as an alternative to the fossil raw materials used in industry.

Within the Bio Solar Cells programme, work is being done to unravel the fundamental principles of photosynthesis and then apply this knowledge not only in improving natural photosynthesis, but also to mimic it in a device. The aim is, amongst others, to develop two prototype artificial leaves, which will be able to split water into hydrogen and oxygen. After this, the research results will be translated into commercially viable systems. The active involvement of thirty-eight partners from industry is expected to lead to the results of the Bio Solar Cells programme finding rapid application and playing a major role in the Biobased Economy, first and foremost in Europe, but also beyond. A sustainable supply of resources by capturing solar energy is the single most important enabling factor for any form of a biobased economy coming into existence. It is surprising that biobased economy programs invest in research on downstream conversion technology but provide very limited funds for the resource side, where the competition will be between land use and efficiency. One of the key challenges is the creation of sufficient critical mass within industry to enable further development of the technology and to attract the funding needed to continue building on the results of the first five years of research. Molecular structures are now available, which can capture light and split water, and there is a semiconductor system capable of storing energy from sunlight in hydrogen with an efficiency of roughly 5 %. In addition, systems for converting CO2 are under development. In a number of countries, the next stage of the innovation process has begun: researchers and their industrial partners are developing concrete applications on a scale of about 100 m2, as precursors to the more general application of artificial photosynthesis.

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# **JETRM**

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