

Artificial Photosynthesis for Production of Hydrogen Gas for Fuel

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Abstract

Photolysis of water is one of the most reliable methods of producing hydrogen fuel to meet the global demand for clean and cheap energy. Over reliance on fossil fuels and hydro-electricity is unsustainable in the era of depleting resources and climate change. Artificial photosynthesis tries to mimic the natural process of photosynthesis that takes place in plants and some bacteria to produce oxygen gas and hydrogen protons. This review proposes the process of mimicking the plant photosynthesis to produce hydrogen gas for fuel. The extension to photosynthesis generates twice the amount of hydrogen gas compared to the amount of oxygen produced. Among the many advantages of using solar water splitting method, there is zero carbon dioxide emission, sufficient water resources in many parts of the world, plenty of sunlight energy, and renewability. This review paper provides detailed mechanisms of how the photolysis of water can be used to produce hydrogen fuel. The design of the photocatalysts and solar cell, as the photolysis device, has also been discussed in detail.

Keywords: Artificial Photosynthesis, Water Splitting, Photocatalyst, Hydrogen Fuel, Solar Cell

1. Introduction

The universe is largely powered by hydrogen gas as fuel. The Solar System gets its energy from hydrogen combustion in the Sun. This makes hydrogen a long term dependable source of energy that can meet any conceivable large scale demand. Currently the world population is increasing at a fast rate and so is the demand for energy. Indeed, it is predicated that the world population is expected to reach 11 billion people in the year 2100 [1]. The current population is just above 7.7 billion people. This will lead to high demand for energy among other resources. The developing countries are already facing enormous problems to produce enough energy due to climate change and rising environmental concern on the use of fossil fuels. Clean cheap energy sources are not easy to find. Any country's energy production has a direct impact on its economic development. The world is currently heavily reliant on fossil fuels such as coal, natural gas and oil. These fossil energy sources have been directly associated with global warming, air pollution and many respiratory diseases. Furthermore, oil and gas are localized energy sources; hence their availability is heavily dependent on local political situation.

The greatest challenge the whole world is facing is to produce cheap renewable energy that can be stored easily without causing any adverse environmental effects. Of course the most abundant cheap, clean, renewable energy source is sunlight. Plants, since time memorial have harvested this energy to produce their

own food and as well as food for animals. Mimicking the processes that plants use to produce food, it is possible to use the same sunlight energy to produce abundant environmentally friendly renewable energy that can easily be stored.

Photosynthesis is a photo-chemical process by which photons and charges in semiconductors such as chlorophyll *a* and chlorophyll *b* interact to split water to produce oxygen and hydrogen. The hydrogen will normally combine with carbon from carbon dioxide to form sugars. Photolysis is the splitting of water into hydrogen and hydrogen protons by light. Photosynthesis occurs in nature in green plants, algae and cyanobacteria. Artificial photosynthesis mimics the natural process of photosynthesis and also seeks to extend the natural process.

Sunlight is part of electromagnetic radiation, which is emitted by the sun. The amount of sunlight reaching the earth's surface can be calculated from the eccentricity of the Earth's elliptic orbit and the attenuation by the Earth's atmosphere. The carrier of sunlight energy is the photons. To efficiently utilize sunlight energy to produce renewable energy, it is very important that these high energy photons are directed to light absorbers that can then create a charge separation between excited electrons and holes. Separation of electrons and holes from excitons is used in photovoltaic cells to generate voltage and current, hence electricity. Although it is possible to generate electricity in this way, large scale storage and hence portability of this energy is a challenge. Because of this problem, people are still turning to fossil fuels. Instead of using the photons to directly produce electricity, the harvested solar energy can be converted to chemical energy, such as hydrogen. This stored chemical energy can later be used to produce electricity. This will help overcome the current challenge.

Many researchers have managed to split water into hydrogen and oxygen by electrolysis using high voltage electricity of the order of 3×10^{24} V/mole to break the bond energy (493 kJ/mole) of water molecules at very high cost, generally unsustainable for large scale production of hydrogen [2,3]. This study proposes the use of cheap mode of hydrogen gas production such as the use of cheap organic polymers such as Polyaniline (PANI) in the place of chlorophyll. Chlorophyll is generally unstable polymer when used in vitro hence the use of other polymers. PANI has high environmental stability, easy polymerization and low cost of monomers [4]. The advantages of using sunlight are that it is free and abundant. It is readily available in most parts of the world. Water is also abundant in oceans. One of the objectives of this study is to suggest affordable and effective photocatalysts. This will in turn lower the cost of harvesting hydrogen gas from water and hence be viable for large scale production.

In this paper a novel way of harvesting hydrogen gas by using sunlight to split water (H_2O) into hydrogen gas and oxygen gas with the help of two photocatalysts is proposed. Furthermore, the design of the model artificial photosynthesis device that can be used for large scale production has been described. The hydrogen gas can be used for many purposes including as fuel to power machines and drive economies of the world. The combustion of hydrogen in air as fuel is environmentally friendly as it produces water as a byproduct with no carbon dioxide. Currently there is a growing demand for hydrogen as a source of energy for automobiles such as cars, buses, scooters, aeroplane, trams, trains, ships, rockets, trucks, and others.

2. The Main Contributors to Global Warming

According to the report by the Intergovernmental Panel on Climate Change (IPCC) of the United Nations published in 2014, 65% of global warming is caused by the emission of carbon dioxide from the use of fossil fuels and industrial processes [5]. Forest and other land use contribute 11%. Thus carbon dioxide alone contributes 76% to global warming (Fig. 1). Other contributors include Nitrous Oxide at 6% of which the combustion of fossil fuels is part of the contributors. Fluorinated gases (F-gases), which can stay in the atmosphere for hundreds of years, contribute 2% to global warming. It is clear that fossil fuel use is the

primary source of CO₂ and major contributor to global warming. Fig. 1 summarizes the contributors to global warming.

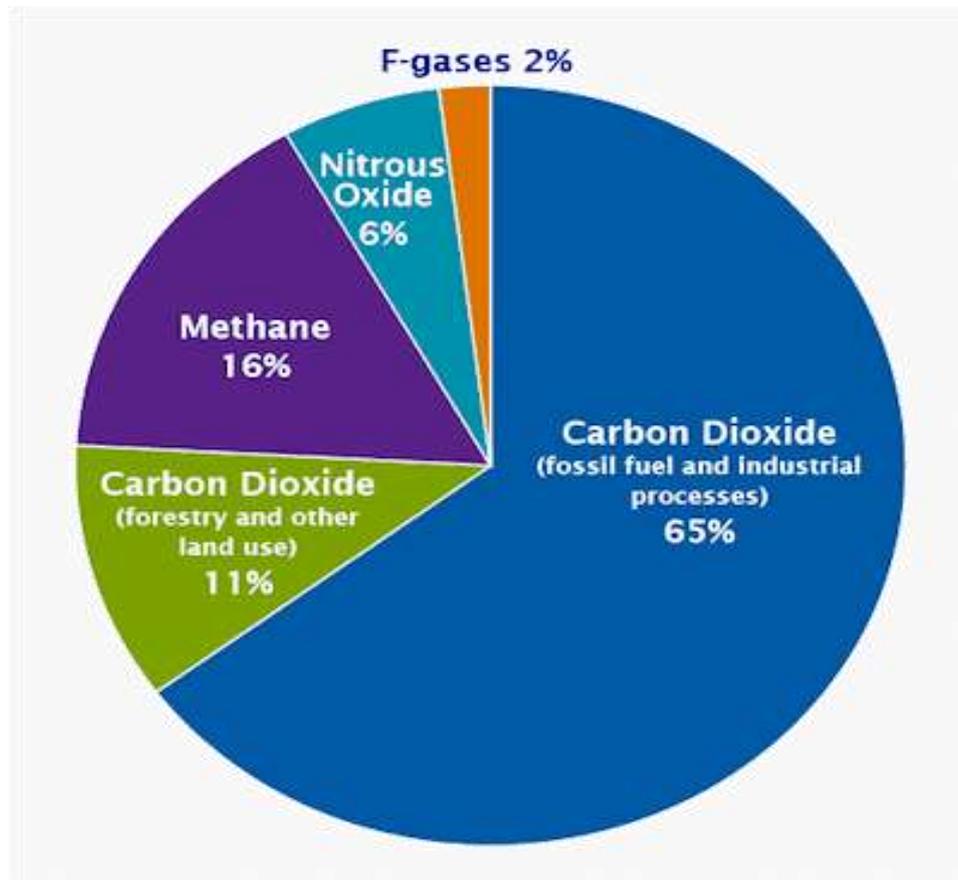


Figure 1 Main contributors to global warming [5].

3. Global Energy Needs

There is high demand for energy worldwide due to increasing population. There are too many controversies on how best to produce the energy without having adverse impacts on the environment. Due to the effects of global warming, it appears that the future energy production will mainly be driven by decarbonization policies. This will mainly be achieved by constructing energy efficient appliances, houses and focusing on renewable energy sources. Nuclear energy has many drawbacks especially in the management of the power plant and nuclear waste [6]. The main renewable sources at the moment are wind and solar power. Other renewable energies include wind, wave or tidal, ocean thermal energy, geothermal energy, biomass and hydraulic energy.

Majority of renewable energy sources are very unpredictable since they rely heavily on meteorological parameters. Wind and solar power varies depending on the year, season, day or even hour. And sometimes even hydro-electricity can be affected by rainfall in a given season, case in point southern African countries are enforcing load shedding due to low water levels in the dams along the Zambezi River in 2019. On the other hand, hydrogen produced by photolysis of water or gas reforming has massive energy storage potential. Hydrogen can be stored in solids (metal hydrates), liquid and gas state (tanks), which can later be used in the production of electricity. The combustion of hydrogen in air as fuel is environmentally friendly as it produces water as a byproduct.

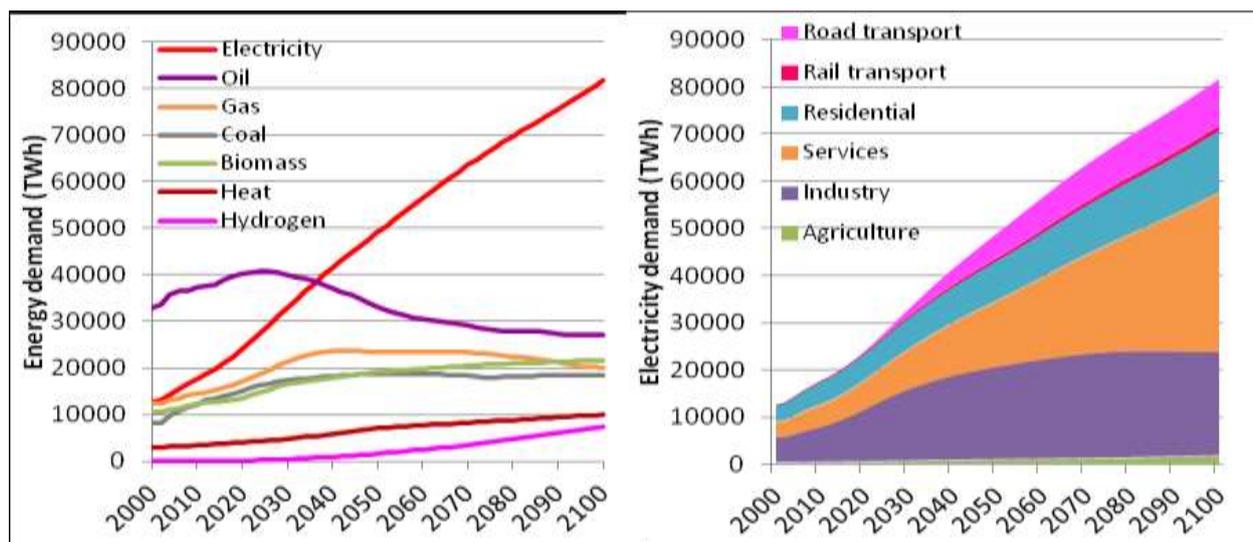


Figure 2 Global energy needs in the baseline scenario; decomposition by end-use fuel (left) and decomposition of electricity needs by sector (right) (Adapted from Després, J., 2015 [7]).

The global energy requirement is expected to rise from 79 000 TWh (in 2000) to 152 000 TWh in 2050 (respectively 186 000 TWh in 2100) (Fig. 2) [7]. It is clear from the graph that electricity will have the fastest growth almost fourfold between the year 2000 to 2050 (Fig. 2). Even though there is a slight increase in hydrogen consumption, it shows that the technologies to produce enough hydrogen as a source of fuel are far lagging behind than any other energy sources. Ideally, with the right mind set, hydrogen being renewable and cleanest energy source should exceed fossil fuels and hydroelectricity. The biggest consumers of electricity by 2100 will be services, industries, transport and residential areas (Fig. 2).

4. The Role of Photons in Photolysis

Electron promotion from HOMO levels to LUMO levels is achieved through the supply of energy from photons of the appropriate wavelengths. The energy of the photons must match the energy of the band gap of the semiconductor. This means that the kinetic energy gained by the electron must equal the band gap energy. This analysis can be explained by the photoelectric effect governed by the photoelectric equation below.

$$hf = \phi + K_{\max} \quad \text{----- (1)}$$

Where hf is photon energy, ϕ is work function and K_{\max} is maximum kinetic energy of the most energetic electron.

In this case

$\phi = 0$, since promoted electrons are initially on the surface of valence band (HOMO level). Hence we have

$$hf = K_{\max} \quad \text{or} \quad h \frac{c}{\lambda} = \frac{mv^2}{2} \quad \text{----- (1a)}$$

leading to
$$v^2 = \left(\frac{2hc}{m}\right) \frac{1}{\lambda}$$

$$v^2 = 4.36102 \times 10^5 \frac{1}{\lambda} \quad \text{giving} \quad v = \frac{660.38}{\sqrt{\lambda}} \quad \text{----- (1b)}$$

If we express equation (1a) in terms of momentum,

$$\frac{h}{\lambda} = mv \left(\frac{v}{2c} \right) \quad \text{or} \quad P_{phot} = P_{elec} \frac{v}{2c} \quad \text{giving} \quad P_{elec} = P_{phot} \frac{2c}{v}$$

Where P_{phot} is momentum of photon, P_{elec} is momentum of electron and v is velocity of the electron.

Energy of photon must equal the band gap of the semiconductor for electron to jump from HOMO to LUMO levels.

$$h \frac{c}{\lambda} = E_g \quad \text{----- (2)}$$

$$\lambda = \frac{1.23998 \times 10^{-6}}{E_g (eV)} \quad \text{----- (2a)}$$

The graph of wavelength of incident photon against band gap is depicted in Figure. 3.

Further, relating equations 1a and 2 we get

$$E_g = \frac{mv^2}{2} \quad \text{----- (3)}$$

$$v^2 = \left(\frac{2}{m} \right) E_g$$

$$v = 5.93044 \times 10^5 \sqrt{E_g (eV)} \quad \text{----- (3a)}$$

The graph of the velocity of promoted electron against band gap is depicted in Fig. 4 and 5.

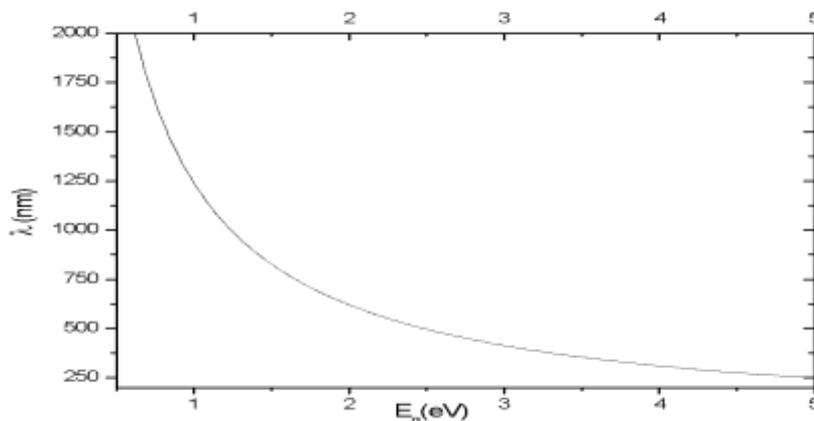


Figure 3 Wavelength of incident photon plotted against the matching band gap of semi-conductor

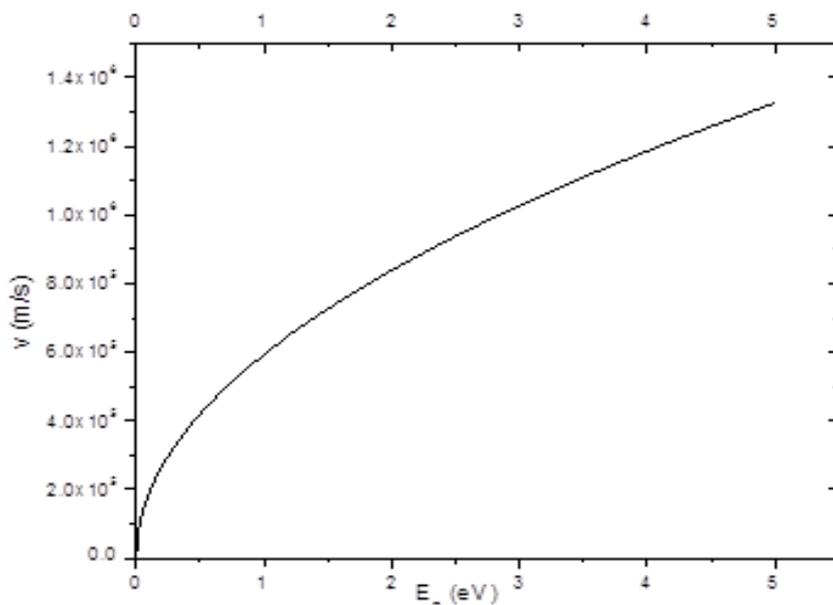


Figure 4 Velocity of promoted electrons plotted against the band gap they can cross

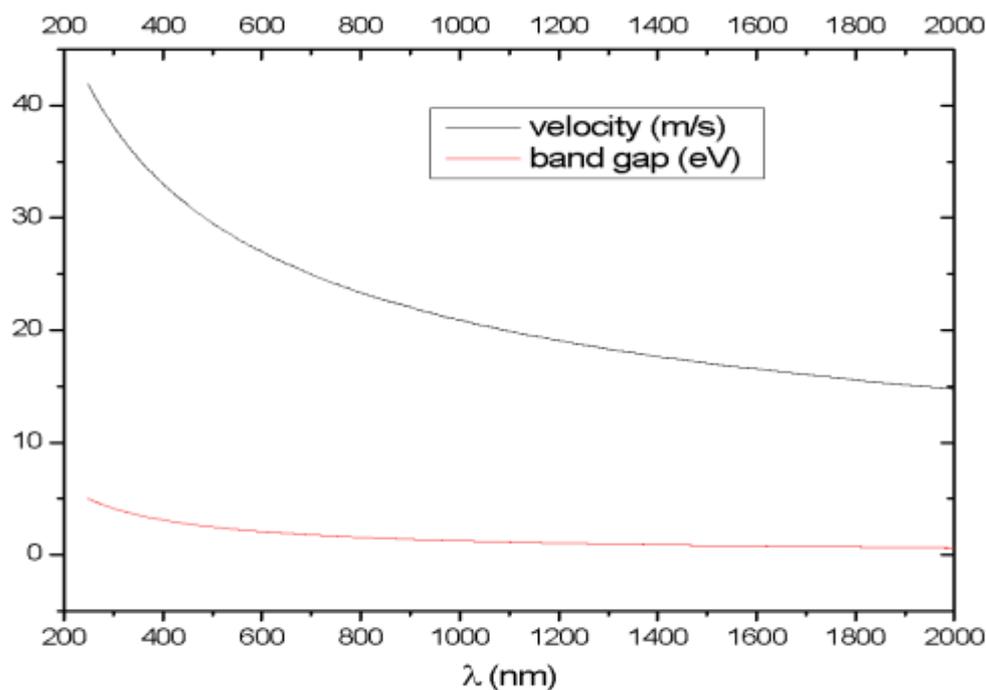


Figure 5 Wavelength of photons plotted against velocity of electrons (m/s) and band gap (eV) of energy.

5. The Role of Chlorophyll *a* and *b*

In general, Chlorophyll is divided into two main types namely Chlorophyll *a* (CA) and Chlorophyll *b* (CB). Both chlorophylls are characterized by a Porphyrin head that is largely hydrophilic and a tail that is hydrophobic. In the process of photosynthesis CB complements CA.

However, they both absorb approximately the same amount of energy, however, at different wavelengths. CB is the donor molecule while CA is the acceptor molecule (Fig. 6 and 7). The role of CB is to inject electrons into the conduction band of CA at longer wavelengths, though CA can also generate its own electrons at shorter wavelengths. CB absorbs light at 454 nm and 644 nm whilst CA absorbs light at 419 nm and 662.5 nm.

The energy absorbed in the blue region (450–485 nm, 2.64–2.75 eV) is largely for promotion of electrons from HOMO levels to LUMO levels, whilst the energy absorbed in the red region (625–740 nm, 1.65–2.00 eV) is for electron promotion and largely for thermal excitation of water molecules, which plays a crucial role in water splitting in the presence of the photocatalyst and excited electrons. Both energies are important for photosynthesis to take place. CA passes the excited electrons to the first photocatalyst which splits the water as an anode electrode.

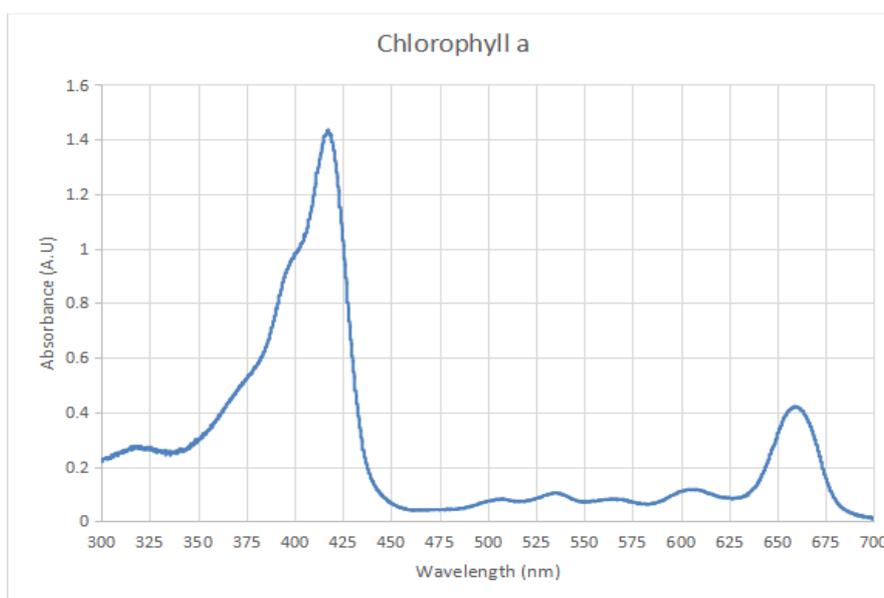


Figure 6 Spectral absorbance of chlorophyll *a*

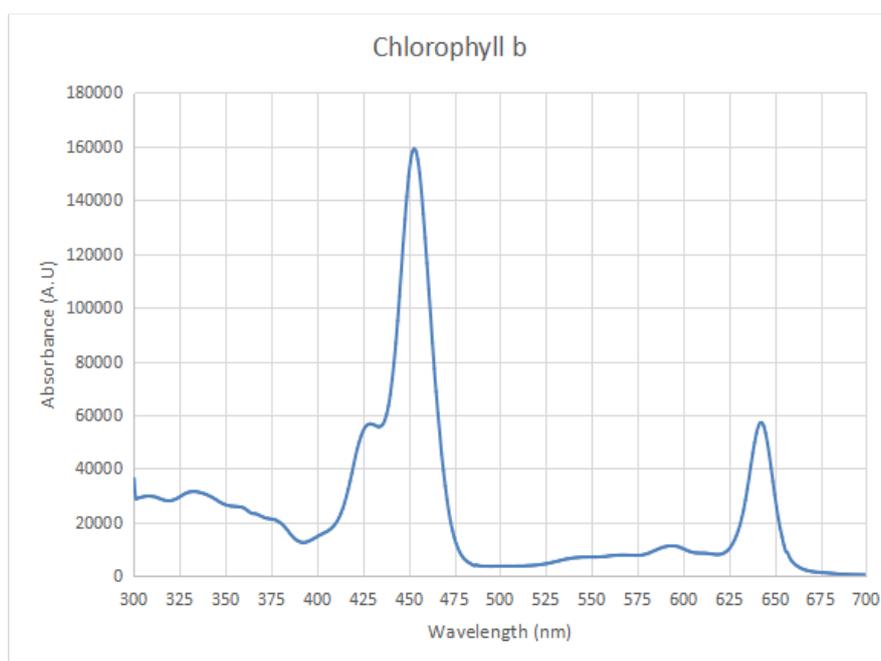


Figure 7 Spectral absorbance of chlorophyll *b*

5.1. Chemical Structures of Selected Semiconducting Polymers

The chemical structures of selected semiconductors that include Chlorophyll a, Chlorophyll b are shown in Figures 8.

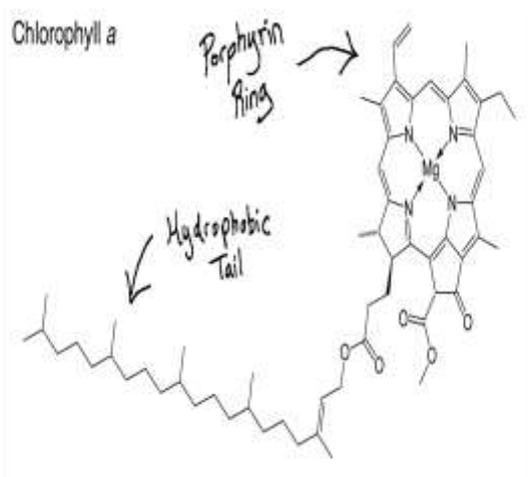
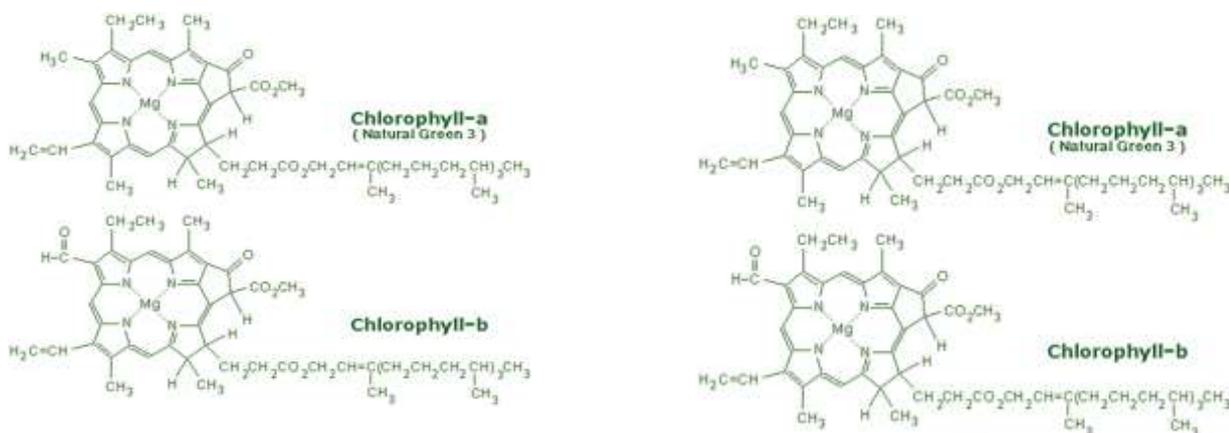


Figure 8 Chemical structures of chlorophyll *a* and chlorophyll *b*

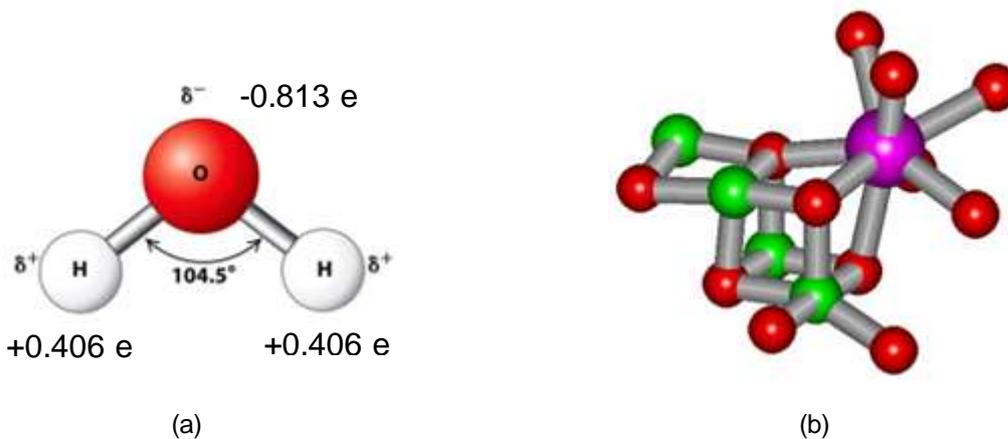


Figure 9 Chemical structure of (a) water molecule showing partial charges and bond angle, and (b) Manganese - Calcium -Oxide [8].

5.2. The Process of Artificial Photosynthesis

Artificial photosynthesis starts with the process of absorption of photons that excite electrons in the semiconductor. The anode photocatalyst receives the excited electrons then interacts with the adsorbed water molecules. Two water molecules are split by the extraction of oxygen atoms by the anode as four hydrogen protons and four electrons are set free. The hydrogen protons are attracted to the cathode photocatalyst. The process involves redox reactions.

5.2.1. Reducing Agents

A reducing agent is also known as a donor molecule. The reducing molecule donates electrons to the acceptor molecule. A donor molecule generally has a low affinity for electrons. The majority charge carriers in donor molecules are holes [9]. A table of semiconducting organic and inorganic reducing agents is given in Table 1.

5.2.2. Oxidizing Agents

An oxidizing agent is also known as an acceptor molecule. The molecule accepts electrons from the donor. An acceptor molecule generally has a high affinity for electrons. The majority charge carriers in acceptor molecules are electrons. A table of semiconducting organic and inorganic reducing and oxidizing agents are given in Table 1.

Table 1: Some reducing and oxidizing agent semiconductors and their band gaps with a comparison with Chlorophyll a (CA) and Chlorophyll b (CB) HOMO and LUMO levels.

Donor Semiconductor (Oxidizing agent)	Band Gap (eV)	Difference with CB at (1.93 or 2.73)	Acceptor Semiconductor (Reducing agent)	Band Gap (eV)	Difference with CA at (1.87 or 2.96)
P3HT	2.1	0.17 lower	TiO ₂	3.2	0.24 upper
PANI	2.5	-0.23 upper	ZnO	3.2	0.24 upper
MBIS	1.5	-0.43 lower	SnO ₂	3.8	0.84 upper
PCPDTBT	1.4	-0.53 lower	PCBM	2.5	-0.46 upper
MDMO-PPV	2.2	0.27 lower	CdSe (at 300K)	1.74	-0.13 lower
P(NDI2OD-2T)	1.5	-0.43 lower	PbSe	0.8	-1.07 lower
PDBPyTT	1.6	-0.33 lower	CuInSe ₈ (300K)	1.13	-0.74 lower
CdTe	2.4	-0.33 upper	CuInSe ₈ (at 10K)	1.23	-0.64 lower
CuInS ₂	1.5	-0.43 lower	ZnTPP	2.9	-0.06 upper
Squarylium dye III	2.0	0.07 lower	ZnPc	1.84	-0.03 lower

From Table 1, we can combine some molecules to achieve dual band gap to match CA and CB.

6. Mimicking Chlorophyll a (CA) and Chlorophyll b (CB)

It is important to note the key characteristics of acceptor molecule (Chlorophyll a) and donor molecule (Chlorophyll b): (i) acceptor molecule should have dual band gap at both short and long wavelengths, ideally 2.96 eV and 1.87 eV, (ii) the donor molecule should have dual band gap at both short and long wavelengths, ideally 2.73 eV and 1.93 eV, (iii) good hydrophobicity for increased environmental stability, (iv) High charge (electron) mobility, and (v) the acceptor and donor molecules must be semiconductors having LUMO levels that match or have only a small difference whilst the difference of their HOMO levels must be large to allow dissociation of excitons. Table 2 is an extract from Table 1 of possible combinations that can mimic CA and CB.

Table 2: Chlorophyll *a* and Chlorophyll *b* Mimic Molecules

Chlorophyll <i>a</i> Mimic	Chlorophyll <i>b</i> Mimic
TiO ₂ and ZnPc	Squarylium dye III and CdTe
ZnO and CdSe	P3HT and PANI
TiO ₂ and CdSe	MDMO-PPV and PANI
ZnO and ZnPc	Squarylium dye III and PANI

6.1. Water Redox in Light-dependent Reaction

From the general point of view, water reduction is the loss of oxygen by the water molecule. It is also referred to as water oxidation due to the loss of electrons by the water molecules. Overall, two water molecules lose oxygen to the manganese complex which cause the manganese complex to change from lower oxidation state to higher states. The shifts to higher states by the manganese complex cause the complex to become unstable and hence decompose to the lower original state which is more stable. The decomposition evolves out an oxygen gas molecule. The main reason for decomposition is the poor participation of Manganese in the shared bonding electrons with the many number of oxygen atoms. The electrons rather spend more time on the two oxygen side thereby strengthening the oxygen-to-oxygen bond than on the manganese side. The manganese complex has been identified as Manganese (IV) Calcium Oxide (Mn₄CaO) and other closely related species of manganese (Fig. 9). The manganese complex in this case becomes the catalyst as it remains unchanged after the reaction.

The calcium in the manganese complex has a high affinity for electrons and receives electrons from the hydrophobic tail of Chlorophyll *a*. Chlorophyll *a* receives electrons from Chlorophyll *b* through donor – acceptor relationship. It is important to note that, generally, porphyrin compounds tend to form face-to-face aggregates [10], resulting in porphyrin rings facing each other and the hydrophobic tails facing outwards. This implies that both chlorophyll *a* and *b* do not make contact with water and are therefore not directly involved in water splitting. When the calcium in the manganese complex receives an electron, it develops a net negative charge which causes the nearby manganese atom to develop a partial positive charge. Manganese has a high affinity for oxygen. Hence the partial positive charge on manganese enhances its bonding with the partial negative charge of oxygen from water.

6.2. The Anode Photocatalyst Design

A photocatalyst is a material that accelerates a light dependent chemical or physical reaction without itself being altered in the process. An anode photocatalyst attracts and interacts with negative charged particles

that include partially negatively charged oxygen atoms in water molecules. The natural photocatalyst for oxygen evolution (OE) has been identified as Manganese Calcium Oxide complex or sometimes referred to as Calcium Manganese Oxide complex. The complex includes different oxidation states of the complex. Some common complexes are Mn_2CaO_4 , $Mn_3Ca_2O_8$, Mn_4CaO , Mn_4CaO_2 , Mn_4CaO_3 , Mn_4CaO_8 , $Mn_4Ca_2O_8$, and Mn_5CaO_8 [11]. The presence of the Manganese Calcium Oxide complex has been confirmed by X-ray diffraction spectroscopy [12]. The Manganese Calcium Oxide complex is capable of playing the dual role of being a reducing and oxidizing agent. It oxidizes CA by gaining electrons and reduces water by gaining oxygen. As the water loses oxygen (reduction) it also loses electrons (oxidation), hence the process may be described as redox reaction.

6.3. The Cathode Photocatalyst Design

A cathode photocatalyst is a material that attracts and interacts with positively charged particles such as partial positive hydrogen atoms from water molecules, or the free hydrogen protons during the photoexcitation and water splitting process. The cathode photocatalyst may play any one of the two roles vis a vis splitting water and then evolve out hydrogen gas or simply concentrate hydrogen protons coming from the anode and then evolve out hydrogen gas. A good cathode for hydrogen evolution should be non-reactive when in contact with hydrogen and should be a majority electron carrier. Candidate for this could include relatively cheap compounds such as TiO_2 , ZnO , and SnO [13]. The two photo-electrodes can be applied on one device or on isolated devices.

6.4. Designing Artificial Photosynthesis Solar Cell

The main aim of artificial photosynthesis is to mimic as much as possible the processes that take place in plants during photosynthesis. In order to achieve this there is a need to select donor and acceptor materials that should be able to interact with sunlight and release sufficient electrons at both short and long wavelengths. The electrons must interact with the two photocatalysts. The anode photocatalyst, interacts with water and splits it into protons and oxygen gas. The cathode photocatalyst interacts with protons to evolve hydrogen gas. The general properties of a photocatalyst include large surface area or rough surface for enhanced interaction with water and electrons, should be made of hydrophilic molecules, having matching or a small difference in conduction bands or LUMO levels with the acceptor molecules for easy transfer of electrons. The electrodes should be of infinitesimal areas and made to alternate for easy flow of protons from anode to the cathode (Fig. 10 and 11). This is important especially for stagnant water.

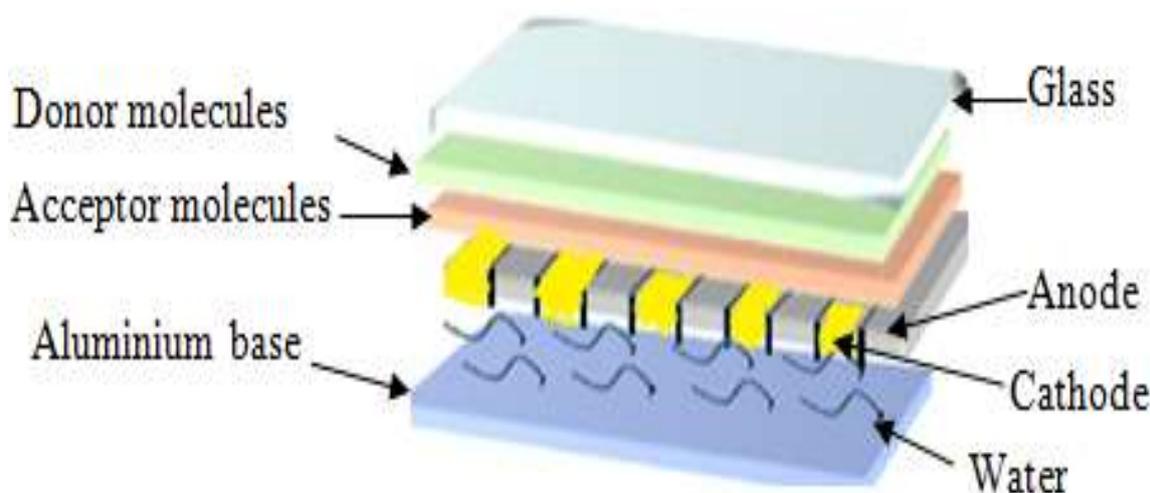
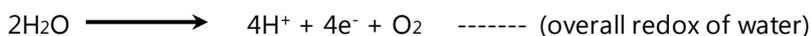


Figure 10 Structure of solar cell for water splitting and production of hydrogen and oxygen gasses.

6.5. Redox Reactions with the use of Mn_4CaO Anode as Catalyst



6.6. Cathode (Reduction) Equation [14]



6.7. Overall Reaction with the use of two Catalysts



It should be noted that the reaction produces double the amount of hydrogen gas to oxygen gas, which makes hydrogen gas harvesting more suitable for large scale production compared to oxygen.

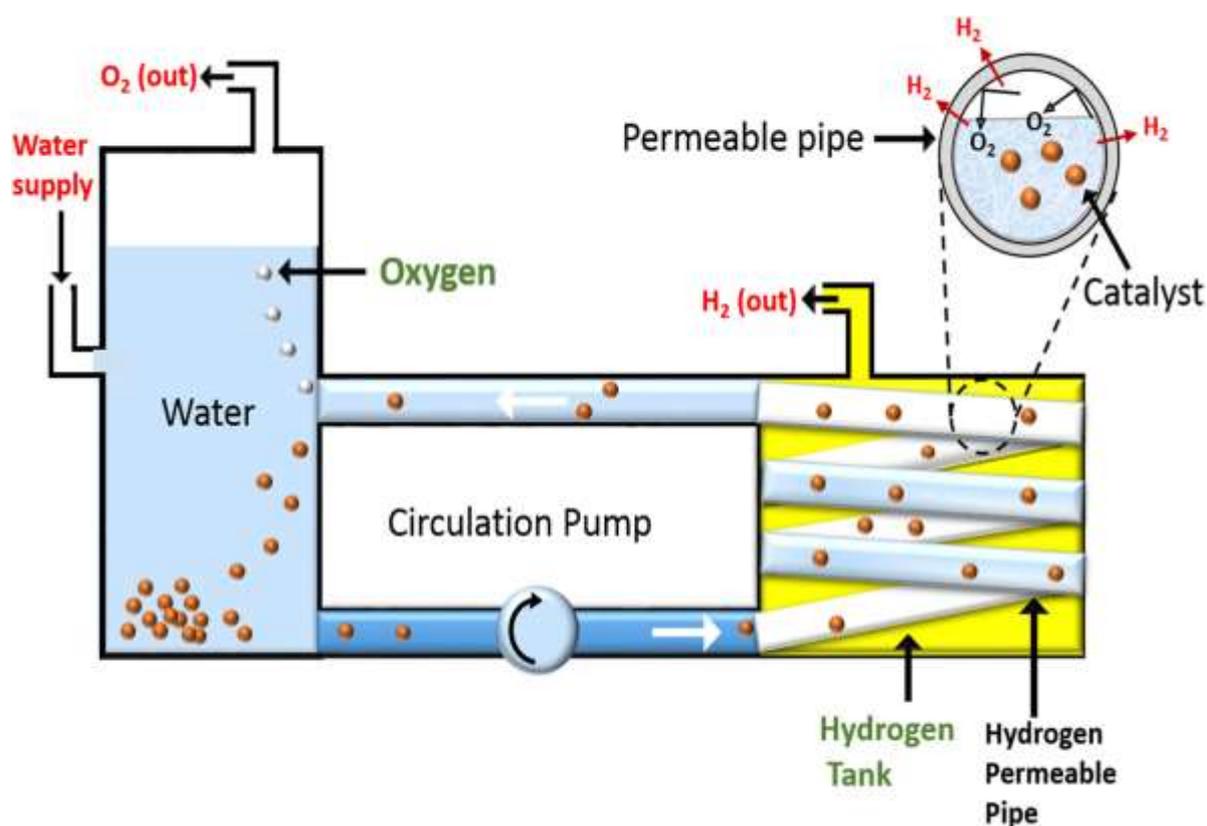


Fig. 11. Schematic diagram for solar hydrogen via photocatalytic water splitting system (PC). Adapted with permission from Osterloh, F. E. and Parkinson, B. A., 2011 [15]. Copyright 2011 Materials Research Society

7. Conclusion and Outlook

There is no doubt that the high human global population will demand high energy. The current unsustainable energy production is having an adverse impact on the climate and environment and is not meeting the energy

demands. This review has presented the fundamental methods of producing hydrogen as a clean and sustainable energy source. Comparisons have been made between natural photosynthesis and artificial photosynthesis in the process of water splitting.

Solar driven photoelectrolysis is the only ideal way of producing hydrogen cleanly. The process currently is facing many challenges due to the high cost of catalysis. There is an urgent need, through computer modelling, to design new cheap catalyst for production of hydrogen [16]. Further, there is need to develop a cathode catalyst that can split water (as opposed to depending on the anode to do the splitting) as this would more than double the production of oxygen and hydrogen gasses.

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Competing interests

All authors declare no conflict of interest.

References

1. Cilluffo, N. G. Ruiz. World's population is projected to nearly stop growing by the end of the century. *Pew Research Center*. 1615 L St. NW, Suite 800, Washington, DC 20036, USA (2019).
2. S. Saraireh, M. Altarawneh. Density functional theory periodic slab calculations of adsorption and dissociation of H₂O on the Cu₂O(110):CuO surface. *Canadian Journal of Physics*, **91**, 12, 1101-1106 (2013).
3. Y. B. Alfaifi, H. Ullah, S. Alfaifi, A. A. Tahir, T. K. Mallick. Photoelectrochemical solar water splitting: From basic principles to advanced devices. *Veruscript Functional Nanomaterials*. (2018).
4. R. Ansari, M. B. Keivani. Polyaniline Conducting Electroactive Polymers: Thermal and Environmental Stability Studies. *E-Journal of Chemistry*, **3**, 4, 202-217 (2006).
5. IPCC. "Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change", Geneva, Switzerland, 151 pp. (2014).
6. Q. Schiermeier. Energy Alternatives: Electricity without Carbon. *Nature*, **454**, 816–823 (2019).
7. J. Després. Modelling the long-term deployment of electricity storage in the global energy system. PhD Thesis, Université Grenoble Alpes, France (2015).
8. M. M. Najafpour. Calcium manganese oxides as structural and functional models for active site in oxygen evolving complex in photosystem II: Lessons from simple models. *Journal of Photochemistry and Photobiology B: Biology*, **104**, 111-117 (2010).
9. Kendrick, M. J. Kendrick, O. Ostroverkhova. Charge carrier dynamics in organic semiconductors and their donor-acceptor composites: Numerical modeling of time-resolved photocurrent. *J. Appl. Phys.* **114**, 094508 (2013). Doi: 10.1063/1.4820259
10. J. Matsumoto, T. Shiragami, K. Hirakawa, M. Yasuda. Water-Solubilization of P(V) and Sb(V) Porphyrins and Their Photobiological Application. *International Journal of Photoenergy*, 1-12, (2015). 10.1155/2015/148964.

11. Gagrani, T. Tsuzuki. Calcium manganese oxides as biomimetic catalysts in energy applications: A short review. *Chemical Engineering Science*, **194**, 116-126 (2019). doi: 10.1016/j.ces.2018.06.059
12. K. N. Ferreir, T. M. Iverson, K. Maghlaoui, J. Barber, S. Iwata. Architecture of the photosynthetic oxygen-evolving center. *Science*, **303**:1831–1838 (2004). doi:10.1126/science.1093087
13. L. Krasteva, K. Papazova, N. V. Kaneva, A. Apostolov. Synthesis and characterization of ZnO and TiO₂ powders, nanowire ZnO and TiO₂/ZnO thin films for photocatalytic applications. *Bulgarian Chemical Communications*, **45**, 4, 625-630 (2013).
14. M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis. Solar Water Splitting Cells. *Chem. Rev.* **110**: 6446–6473 (2010).
15. F. E. Osterloh, B. A. Parkinson. Recent developments in solar water-splitting photocatalysis. *MRS Bulletin*. **36**, 1, 17–22 (2011).
16. Zhang, L. Sun. Artificial photosynthesis: opportunities and challenges of molecular catalysts. *Chem. Soc. Rev.*, **48**: 2216-2264 (2019).