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Artificial Photosynthesis

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Nature is the source of all true knowledge.

*She has her own logic, her own laws, she has no effect
without cause nor invention without necessity.*

Leonardo da Vinci

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Abstract

There are currently lots of concerns about energy supply on earth and the environmental damages that energy obtained through fossil fuels create. Appreciation for nature also raises, and as technology advances, scientists are trying to mimic the process by which plants harvest energy from the sun and convert the second most abundant greenhouse gas, carbon dioxide (CO₂), into useful forms of energy: carbohydrates. This research project aims to understand the natural process of photosynthesis and gather enough information about it to study advances in this field of study. Using this information, the second goal of this research project is the elaboration of an undergraduate laboratory experiment that deals with artificial photosynthesis.

Keywords: photosynthesis, artificial photosynthesis, energy, photosystems, sunlight.

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Artificial Photosynthesis

1. Background

The energy dissipated from the sun is transformed into useful forms of energy through a process called natural photosynthesis. This process is carried out by the energy of the sun to convert CO₂ and water (H₂O) to produce carbohydrates that play a role in the plant's cellular respiration. Oxygen gas (O₂), which is vital to aerobic organisms, is also a product of this process.¹ Plants and bacteria use energy from the sun to produce two important molecules: nucleotide ATP and the coenzyme NADPH, the latter playing a critical role as an electron transporter, following CO₂ fixation during the Calvin Cycle. Artificial photosynthesis mimics the natural process of photosynthesis by capturing light, breaking bonds of H₂O, and fixing CO₂ with the goal to generate fuel.^{1,2}

2. Natural Photosynthesis

Essential to all biological processes, photosynthesis is the process through which green plants and other organisms such as bacteria use energy from the sun to convert water from the soil and CO₂ from the air into glucose. There are two phases to photosynthesis; light-dependent reactions and light-independent reactions. Light reactions occur when photons are absorbed to start a series of redox reactions. When light-independent reactions take place sugar monomers and electron carrier molecules are produced.^{1,2} One critical initial step in photosynthesis is the antenna pigments absorption of solar light. Present in a dimeric form, Photosystem II (PSII) is an integral membrane of chlorophyll protein complex in the light-dependent reaction. It provides all the electrons necessary for photosynthesis to happen. Each monomeric complex within Photosystem

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II is a dimeric protein that is made of several parts that consist of 19 subunits, including the reaction center, each carrying an internal antenna subunit, and the cytochrome.¹ On the other hand, Photosystem I (PSI) resembles PSII and is also found within the thylakoid membrane in algae and higher plants. It also exists in a trimeric form in cyanobacteria. Photosystem I is an integral membrane complex protein that consists of several parts.¹

2.1. Photons: The Link to Chemistry and Physics

In the 1900s, the work of German physicists, Planck and Einstein, provided us with the knowledge of energy in light. Mr. Planck derived what is called Planck's constant, (h), to prove his theory of the “quantization of energy.” Planck found that light energy is dependent on the vibrating atoms and the frequency of the atoms. From this he derived the formula $E = nvh$, where $n = 1, 2, 3$, etc. This formula states that “the energy, (E), of a vibrating atom, will vary according to the product of its frequency of vibration (ν), of which assume only specific values, that are whole integers multiplied by Planck’s constant.”¹ These values in the formula then compute what are known as quantum numbers. For the energy of atoms to be quantized, they must follow the quantum numbers. A quantum of energy provides researchers with a measurable value for a minuscule part of energy. This value relates to the transfer of energy, which researchers are still trying to understand.¹

There is a correlation between particles of energy and the frequency of light traveling, the correlation shows direct proportionality. The photoelectric effect, a wall of electrons, rebounds any photons that come with adequate force and aim to strike the metal.³ Quantum physics describes how the energy of a photon is absorbed. It can be absorbed through a specific type of

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receptor and losing electrons to start a process of photosynthesis. Photosynthetic energy can result by turning the potential energy of the lost electron and its void space, or hole, into usable energy. However, a thermodynamically unstable byproduct is a result of using photons to generate electrons and get it in the void space that was previously occupied. Moreover, there exists a high likelihood for the electron recently created to fit back in its original hole.^{1,2} The energy produced from the photons can be determined by how easily a valence electron gets displaced. Even though it can be determined, the energy and light produced weigh heavily on the wavelength frequency. The photon is then absorbed and does not allow itself to become a particle. A certain frequency range of photons from the sunlight is then absorbed through plants and help assist electrons to synthesize carbohydrates and oxygen.²

2.2. Photosystem II (PSII) and Photosystem I (PSI)

In organisms that carry photosynthesis, the first protein complex found on the inner surface of the thylakoid membrane is PSII. PSII carries out several of electron-transfer reactions that start from the excitement of electrons due to light energy. This process produces water to split into protons, electrons, and molecular oxygen. The water splitting occurs in a Mn_4Ca cluster that is located in the center of PSII, where the electron pathway depends on the reaction center protein's redox potential. The pigments in PSII absorb the shorter wavelength of light at the primary oxidant and other intermediate electron carriers. In addition to these redox potentials, the distances between cofactors such as chlorophyll, betacarotene, heme B, and plastoquinone are also measures in controlling the electrons flow.^{1,3}

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While PSI is located on the thylakoid membrane's outer surface, it is believed to be an important converter of bio-solar energy in catalyzing algae, cyanobacteria, and green plants. These organisms use it as one of the first photosynthetic steps. It consists of an antenna system that captures longer wavelengths and carries light energy to the reaction center (P700). Using light energy, PSI catalyzes the light-driven electron transfer across the thylakoid membrane from plastocyanin or cytochrome C6 (Cyt C6) on the lumen side to ferredoxin.¹ Its first initial step is trapping solar energy followed by the conversion of light-driven energy transfer to electron transfer between complexes. The redox potentials of cofactors involved in the charge separation reaction center are important for the electron flow within PSI, and PSII. Another important characteristic of PSI is the distance between cofactors in the system where the chlorophyll collects and absorbs the wavelength of light at P700, which is the primary electron donor and final electron acceptor FB.¹

2.3. Briefs on the Electron Transport Chain

The electron transport chain (ETC) is a string of molecules that accept or donate electrons. These electrons are transferred across the thylakoid membrane in a specific direction. The flow of hydrogen ions is moved across the membrane as electrons are moved. Two types of photosynthetic electron transport chains exist, the linear and the nonlinear (cyclic) electron transport chains. In the linear ETC, water is oxidized through energy created from photons.¹⁻³ This occurs in the light phase of PSII. As a byproduct, it creates electrons oxidize plastoquinone and then diffuse past the membrane.² In the nonlinear ETC, the electrons can return to the complex b_6 by transferring additional protons to the interior of the thylakoid membrane. As a

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result, the reduction potential is gradually increased so that the electrons can move in this direction.^{2,3}

Electrons are able to transfer through pheophytin and quinones within PSII and through plastoquinone and 4Fe₄S clusters in PSI. The goal is to reach plastoquinone and ferredoxin as a final destination of electron acceptors.² Solar energy is absorbed and transferred via chlorophylls and other pigments to reach the PSII and PSI reaction centers for charge separation and water splitting to take place. These reaction centers are activated independently by light, meanwhile, electrons flow from PSII to PSI. In PSI, the plastoquinol (QH₂) absorbs molecules that are oxidized by light. These molecules are what allow the continuous redox reactions to occur in oxygenic photosynthetic organisms.¹⁻³ The reducing equivalent in these organisms moves along the ETC. This is only able to happen due to the solar energy molecules exciting the reaction center and lifting it to a reducing potential value of -1.0V or more. Free electrons get excited in different electron carriers until reaching the final electron acceptors. This allows reducing equivalents to be transferred to NADPH¹. It is for this reason that PSII is seen as a water-plastoquinone-oxidoreductase that acts as a catalyst for water splitting as depicted in this formula :



Electrons transferred between PSII and the cytochrome b₆f (Cyt b₆f) are cycled within the lipid phase in the thylakoid membrane by plastoquinone. Consequently, the membrane forwards these electrons through a mobile electron carrier protein plastocyanin (Pc) or cytochrome c₆ (Cyt c₆) going to the luminal side of Cyt b₆f. These carriers interact with PSI across the thylakoid membrane and generate electrochemical transmembrane potential that is used by the ATP

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synthase to produce ATP from ADP and Pi.¹⁻⁵ During the light-independent reaction, NADPH and ATP are utilized in oxygenic photosynthetic organisms. The protein complexes consisting of PSII, Cytochrome b6f, and PSI are referred to as “the electron transport system,” where energy stored from the sun is used to facilitate the transfer of electrons to NADP⁺ from water. This process then produces oxygen, NADPH, protons, and energy in the form of ATP.¹

2.4. Function and Structure of the OEC

The OEC is the heart of PSII located at the lumen D1 subunit and connected to the CP43 protein by one direct ligand. It's a structure that resembles a distorted chair formed by a heterometallic Mn₃CaO₄ cuboidal unit.⁵ This distortion plays an interesting role in catalytic activity in water splitting. This unit is also supported by an Mn-O bond connected to manganese ions in several S states cycle of water oxidation by the manganese cluster, moving in a particular combination of Mn(II), Mn(III), Mn(IV) and Mn(V). Meanwhile, oxygen is produced by the dissociation of two molecules of water, to oxygen, four electrons and four protons, which is released into thylakoid lumen.^{2,3,5}

Four ligands bind to metal ions: two at Ca and two at Mn(IV). Only one N-donor, His 332 (DI-H332), coordinates the cluster at Mn(I), additionally mono coordinated by Glu 189 (DI-E189). Significant residues insert TyrZ - HisZ couple in the second coordination sphere, which is the electron transfer gate to form P680 (named after the wavelength at which its absorbance maximally decreases on photo-oxidation).¹⁻³

The Mn₄CaO₅ cluster and its course of substrate/product channels are part of the conditions of the specific spatial organization of the redox-active component involved in the excitation

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energy and electron transfer. The structural and folding adjustment of PSII must provide the necessity for the control of accessibility and water delivery at the OEC, release product, and proton transfer. A clear and concise comprehension of these process remain missing, moreover, crystallographic models, noble gas studies, pK_a calculations, and computer simulation methods are taking into consideration. The dynamic structure of the channels has determined a feasible path within PSII which involves water, O₂ transport, and proton transfer.⁶ The shape of the Mn₄CaO₅ cluster was obtained from a polarized XAS model and the 1.95-angstrom high-resolution crystal structure. The OEC is a model catalyst system for water oxidation with turnover frequencies in excess of 100 mol of O₂ in the presence of abundant quantities of electrons acceptors.⁴⁻⁶

3. Artificial Photosynthesis

The science of chemistry has allowed scientists to create innumerable innovations that aid the world in many ways. Scientists around the globe are trying to use their knowledge about natural photosynthesis to create a synthetic system that can produce a renewable source of energy². Artificial Photosynthesis (AP) is defined as the use of technology to capture light, transport electrons, break down molecules of water, and capture CO₂ with the goal to obtain fuels. It has the intention of mimicking the natural process of photosynthesis with the implementation of semiconductors materials that have been developed to achieve the two principal simultaneous reactions: breaking down water molecules (oxidation) to generate oxygen and H⁺, and later hydrogen and the reduction of CO₂. The utilization of semiconductors materials

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along with light, to develop different oxidation reaction and reductions, are categorized as heterogeneous photocatalysis, and thus satisfy all the requirements to achieve AP.

The process of artificial photosynthesis by heterogeneous photocatalysis is similar to the conventional heterogeneous catalysis: i) absorption, ii) reaction, iii) desorption. One of the differences between heterogeneous photocatalysis and conventional catalysis is the catalyst activation because the thermal activation is replaced by UV light or visible. Instead, the activation process of the semiconductor (photocatalyst) occurs when the electrons located in the valence band (VB) absorb light, then jump up to the conduction band (BC). For this process to occur, energy is needed, which determines the wavelength of light that can be absorbed by the semiconductor as photocatalyst. When excited electrons are in (BC) left an empty space on (VC) leaving a positive charge (h^+). Thus, semiconductor lighting with a proper wavelength simultaneously produces electrons, and holes (h^+) able to do reduction, and oxidation reactions. Even though excited electrons participate in diverse reactions, they may also combine and can be deactivated releasing absorbed energy. This process of deactivation is responsible for low efficiency in photocatalytic reactions. To sum up, the efficiency of the photocatalyst process depends upon light absorption, charge separation, charge migration to the surface, and the recombination of it.⁵⁻⁷

Some photocatalyst utilized in the production of Hydrogen is described as heterogeneous photocatalysis, which means a large variety of reactions. To break down the water molecule to generate H_2 requires at least two catalytic steps: i) the oxidation of two molecules of water in O_2 and H_2 . ii) The reduction protons to H_2 molecular. To reach this reaction, a reduction potential ~

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1.23 eV is needed, it could be reached using photocatalyst with superior value to the energy band forbidden. Even though there are other thermodynamics requirements have to be satisfied.^{4,6}

One of the most common photocatalysts involved in breaking down molecules of water is TiO_2 . However, the photocatalytic efficiency of TiO_2 is low when it radiates with sunlight. Thus, only UV light has to be utilized to activate TiO_2 . Another photocatalyst of this type has been used for the same reaction for instead, $\text{M}_x\text{N}_y\text{O}_z$ ($\text{M} = \text{Na}, \text{K},$), and ($\text{N} = \text{Ta}, \text{Nb}, \text{Sr}, \text{La}$), Fe_2O_3 ZnS .^{6,7} This matter is important to develop photocatalytic materials that can work effectively.

3.1. Methods and Materials

To create models of photocatalytic reduction process of CO_2 and H_2O as an alternative to fossil fuels and put them to trial, it is necessary to have a broad knowledge of this potential source of sustainable energy. On the other hand, commercial systems are dependent on not just the pricing but also the difficulty of construction. Prices that are too high will not allow the success of a commercial system.¹ Multiples approaches have been developed including the ability to create a gate of which its size can directly select and allow only specific molecules to enter and thus employ certain molecules with electrochemical potentials that can be easily controlled. This can occur by using electric field gradients to their advantage allowing them to send electrons in a specific direction and thus creating the gate.¹

3.1.1. Covalently linked molecular systems

Scientists have already found and designed multi-component molecules with a donor and acceptor system covalently joined to a light absorbent material, an assembly that doesn't fit the

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Z-scheme. However, the system doesn't return enough energy as expected, as a result of the temporal order of the reactions. In the solution, the energy-rich molecules lose the stored energy by intermolecular or intramolecular back-electron transfer.¹⁻³ In nature, the various prosthetic groups of photosynthetic apparatus of plants can be arranged in the Z-scheme. The movement of the carriers away from one another is crucial to high efficiency. As in other electron-transfer systems, electrons flow from low to high reduction potentials. The unidirectional movement of electron in the Z-scheme is a result of the components of the ETC and its geometrical and energetical arrangement.^{1,2,4}

One important type of naturally occurring molecules are Porphyrins. Porphyrins have many characteristics that have long been studied by scientists so that they can try to reproduce the work these molecules do. Some of the important characteristics include excellent absorption in wavelength that are within the human eye's visible region, high response to solar light, and ability to intervene in the conversion of a photon to electrons.^{1,2}

3.1.2. Molecular Assemblies of Some Systems in AP

Frameworks that consist of covalently bonded donors and acceptors display amazing ground and energized properties with calculable lifetimes of states that have a separation of charge. They significantly contrast from normal frameworks, particularly within the way that donor and acceptor units bind. The reaction center of bacteria, for instance, photo and reduction-oxidation active components are organized into a protein complex via interactions that aren't covalent.

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Bonds that aren't covalent, such as intermolecular forces, ensure the control of modulation composition and hence give the chance to realize inflexible and nicely defined structures with high directionality and selectivity. In this way, investigation of these bonds shows them to be more promising to build imitates for common photosynthetic systems.^{1,3}

3.1.3. Oxidation of Water, Catalytic Pathways and Evolution of Hydrogen

In natural and artificial photosynthesis, oxidation of water, catalytic pathways, and evolution of hydrogen present a new perception of catalytic processes. It demonstrates the framework and function of the enzyme involving in water photo-oxidation. A heteronuclear Mn_4O_5Ca cluster that breaks down two water molecules to O_2 , four electrons, and four protons.⁵ Oxygen release occurs in the light-independent cycle between S_4 and S_0 , where two molecules of H_2O are bound. In the light-driven reaction, four electrons are removed one at a time, (S_0 through S_4), from two bound H_2O molecules.⁶ The complete reaction sequence allows a total of four water derived protons into the inner thylakoid space in series. These protons provide to the transmembrane proton gradient. The OEC abstracts electrons from H_2O , its five-stages must have high reduction potential since O_2/H_2O half-reaction has a standard potential of 0.815 V. The proximity of amino acids and cofactors to the cluster are compared to the photo electrocatalytic oxidation of water utilizing photoanodes and semiconducting photoanodes. Current studies of catalysts in the oxidation of water are based on transition metals such as manganese, cobalt, nickel, ruthenium, iron, and iridium.⁵

The application of electrolysis to create oxygen gas and hydrogen gas is utterly essential because pure hydrogen does not exist naturally in high concentrations in Earth. Pure hydrogen

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must be extracted from other sources, such as fossil fuels, biomass, and water. Currently, hydrogen production is based on steam reforming of fossil fuels, giving CO₂ as a byproduct. Hence, artificial photosynthesis and photoelectrolysis are a promising method of hydrogen production. The best part of all, this method would use solar energy to extract hydrogen from water.

3.1.4. Semiconductor Photochemistry and principles of photoelectrocatalysis

The design of a biomimetic system is relevant to the conversion of solar energy because there must be a process to retain and disperse energy while protecting the ecosystem. There also has to be an implementation to watch for surges in energy flux, as it needs to remain constant. Some major progress has been made in order to challenge the photoelectrolysis of water utilizing semiconductors. To solve the “holy grail” is in regards to artificial water splitting, there needs to be further research and insights on new materials required for the processes of anodic and cathodic. There must also exist a set configuration in regards to using the proper voltage of single or dual-bands in a photovoltaic cell junction. Ultimately, researchers are attempting to design a photoelectrolysis cell to its maximum competency by the linkage of natural water oxidation and hydrogen production. In order to complete this task, semiconductors which sustain an increased charge while in liquid, can sustain long term stability and retain an extraordinary amount of solar spectrum.

3.1.5. Photoelectrocatalysis for Solar Water-Splitting

The construction of competent equipment that uses sunlight for the oxidation of water depends upon the attachment of an active catalyst to the exterior part of the photocatalyst. Usually, these electrocatalysts are placed as nanoparticles or very thin layers in a form the extreme light absorption or reflection is deflected while conserving the interfacial energetics and surpassing the kinetics of the particular reaction.¹ Essentially, the connection of electrocatalysts particles impacts the properties of the electron transfer process at the outside part of the photocatalyst. When a metallic catalyst is placed on the exterior part of the photocatalyst for an n-type semiconductor, redox reactions are easily performed with the electrolyte emergence from the catalyst particle Fermi level (E_f) energy that is in equilibrium with the minority carrier quasi-Fermi level of the semiconductor as in the Schottky barrier contact. In consequence, placing metal catalysts on the uncover semiconductor exterior would lead to a reduction of power for the reaction as a result of a slower electrotransfer rate constant.

3.1.6. Electrocatalyst: Oxygen Evolution on Semiconductor Photo-electrodes

Electrolysis requires a potential of 1.23 V to exceed activation barriers between anode and cathode in order to generate water oxidation. The meaning of this overpotential is the voltage applied to the electrode determined to the reduction potential and the pertinent redox couple in the electrolyte of importance. It is necessary to apply an electrocatalyst to the surface of the semiconductor placed as a thin layer or as nanoparticles in order to enhance the performance of photoelectrochemical (PEC) devices. When submerged in an aqueous electrolyte, a semiconductor photo-electrode will create a significant amount of energy exposed to sunlight, a

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semiconductor photoelectrode, submerge to promote hydrogen and oxygen evolution reactions whilst the semiconductor is exposed to sunlight. These hydrogen evolution reactions release electrons into the electrolyte solution while the oxygen evolution reaction relay on free electrons. Developments in oxygen catalysis began in 1965, with H Beer's patent on the dimensionally stable anode (DSA). The RuO_2 and IrO_2 electrodes are highly active for electrocatalytic oxidation reaction, but due to the high cost of precious metals, the commercial alternative is nickel. The advancement of conductive metal oxides for OER focuses on RuO_2 and IrO_2 , Co_3O_4 and NiCo_2O_4 , NiLa_2O_4 and LaCoO_3 , and $\text{Pb}_2\text{Ru}(\text{Ir})_2\text{O}_7$. But water-splitting devices required more research and development because still isn't the design for material along with the correct combination of optical-electronic and chemical properties needed for them to perform properly and efficiently.

The complex for oxygen synthesis in PSII has motivated researches to empower efforts in a completely developed molecular catalyst for water oxidation to work in a homogeneous solution. Not only to understand better natural water oxidation but to come up with applications in AP. The advancement of molecular OER catalyst should be the primary focus, based upon those elements such as manganese, ruthenium and iridium are the best for homogeneous catalysis for OER. Interestingly, ruthenium "Blue Dimer" appears to be the first account of oxidation of water. Ruthenium complexes have synthetical and relatively slow ligand exchange rates permitting the presence of intermediates. Manganese compounds as water oxidation catalyst remain of high interest to elucidate the OER in the protein. Iridium was considered a very stable oxide catalyst, but the innovation of new compounds left it obsolete.

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Gersten et al. developed the first ruthenium-based water oxidation complex $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{py})\text{H}_2\text{O}]^{2+}$ and accentuated the role of proton-coupled electrotransfer (PCET) processes to activate water oxidation [35]. The oxidation of the metal center causes a pK_a shift of water ligands bound to the metal, contributing to the formation of hydroxy- and oxo-complexes, continuing the formation of the next oxidation state by stimulating the multi-electron oxidation necessary for water oxidation.

Iridium as a molecular catalyst for water oxidation was developed by Bernhard and coworkers. This group of researchers demonstrated that a specific iridium (III) complexes of substituted or unsubstituted 2-phenylpyridine (ppy) ligands were a suitable catalyst precursor. In searching for an efficient OER catalyst cobalt and copper-based complexes also were studied. Some developed the first Cu-base catalyst with a bipyridine-base system. Even though an overpotential of ~ 750 mV is required to achieve the catalytic reaction, the catalyst demonstrated a high turnover frequency of ~ 100 s^{-1} . Researchers have been collecting much information to develop synthetic, inorganic complexes for water oxidation to oxygen. Heterogeneous metal oxides based on ruthenium, iron, iridium, cobalt, and copper all of them demonstrated activity for water oxidation. However, in order to develop a stable and long performance catalyst beside electrocatalytic activity, it has to follow some criteria: (i) corrosion which has an important effect on the electrode throughout time; (ii) the poisoning of catalysis by solution impurities; and (iii) changes in electrode composition and morphology occurring on different time scales. Catalysts shouldn't absorb light itself or reflecting the incoming sunlight. The development of transparent catalysis such as transparent conductive oxide or the application of a system in which both, the absorber or the catalyst are micro or nanostructure to increase the outside area for both parts is

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the solution. Even though nature depends on its perfect water-splitting process which only “one element” is able to undergo multiple redox transitions.

3.1.7. Synthetic Mimics of the Mn_4CaO_5 cluster

The catalytic oxidation of water to molecular oxygen is accomplished by the Mn_4CaO_5 cluster in Photosystem II. This is the fundamental key for the production of solar fuels. For decades researches have tried to synthesize analog manganese complexes with the goal to demonstrate the natural water splitting mechanism and to create a model that mimics artificial photosynthesis. Although the geometry of nature's cuboidal Mn_4CaO_5 cluster and a high number of oxidation states they are very difficult to synthetically imitate, manganese complexes of different shapes have been synthesized and characterized. This insight into biomimetic model chemistry demonstrates that it is feasible to design prototypes of artificial photosynthetic systems, that utilize sunlight to create fuels by applying the tools of chemistry. Biochemistry, and principles of photosynthetic energy.

3.1.8. Nanostructured Photoelectrodes

Focus on the utilization of micro and nanostructure semiconductor electrodes that might work on photoelectrochemical water splitting are described as nanorods, nanotubes, and nanostructure of the semiconductor. The convince of a structured electrode is the decoupling of the direction of light absorption and charge -carrier collection. The light absorption in a traditional solar cell has the same direction as the charge carrier collection. To construct an efficient cell, the absorber needs to be thick sufficient to absorb all light, also it has to have

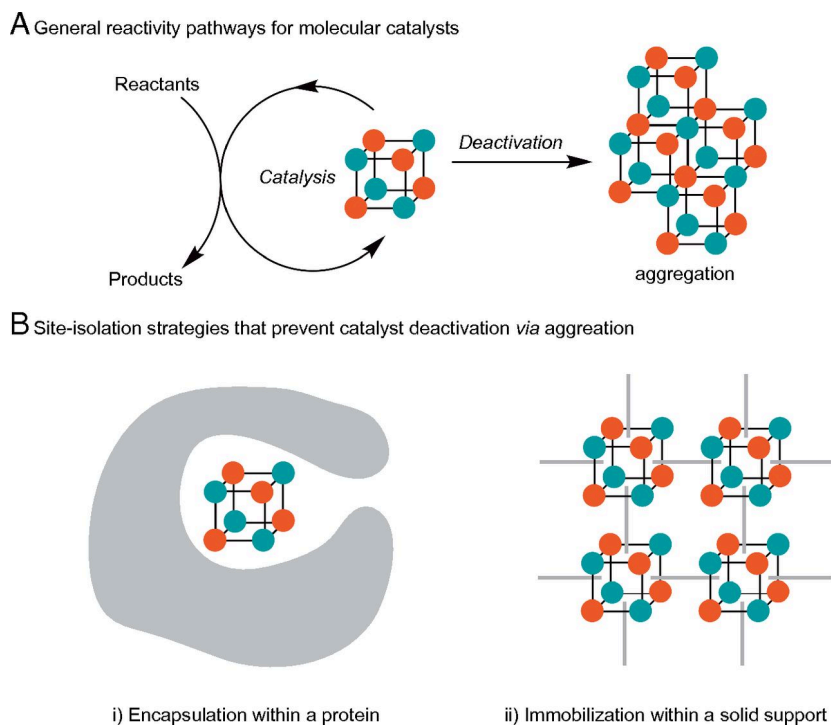
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enough electronic quality for the excited minority carriers which are photogenerated within the sample are capable to diffuse to the surface where they can be collected. High purity of semiconductors is required to achieve diffusion length in a planar geometry, and for the non-planar geometry, semiconductor rod arrays are used.

3.2. Stabilization of reactive Co_4O_4 Cubane oxygen-evolution catalysts within porous frameworks

The advance of powerful X-ray spectrometry techniques and super-fast calculations has uncovered cobalt oxide, one of the most promising catalysts for artificial photosynthesis. One of the obstacles to obtaining a proper conversion of sunlight into chemical fuels is the lack of a stable molecularly designed catalyst. In nature, this process is accomplished with the Mn_4CaO_5 cluster, which rapidly produces water splitting. Despite the progress in mimicking the structure of the natural OER catalyst, synthetic molecular catalysts remain unusual due to the instability of many molecular complexes under OER conditions. Significantly cobalt (III) oxo “cubane” cluster $\text{Co}_4\text{O}_4(\text{OAc})_4(\text{py})_4$ is the exception because it imitates the oxo-bridged arrangement of four metals centers of the OEC, and it is the only one among tetra-metallic groups that have been exhibited as a functional OER catalyst. The short-term stability and the cluster adjustable favorably make the Co(III) an interesting initial position for mechanistic and structure-function. A goal for the carboxylate is to stabilize the catalytic Co_4O_4 core but due to its deactivation and aggregation of cluster units, there is a need for more intricate studies of its reactivity. The instability of the catalytic Co_4O_4 has impeded observations of reactive intermediates during the OER catalytic cycle. Meanwhile, nature stabilizes this issue through OER catalytic along with

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Source: pnas.org

the protective protein environment in PSII. This protein encloses the OEC protecting it against aggregation and degradation while providing an electronic environment able to do multiple redox steps of the OER. provides a design for a new generation of catalysts. This molecular cluster and protein enclose the OEC provides a prototype for a new generation of catalysis that meets the interest of practical artificial photosynthesis.

These new concepts have been applied in the incorporation of a Co_4O_4 cluster into a mutated pocket of a metalloprotein. This pocket allows for the stabilizing and prevention of condensation and secondary sphere interactions between multi-electron and multi-proton reactivity. At this point, greatly improved stability of a Co_4O_4 molecular cluster was found. This cluster was immobilized by a porous metal-organic. This procedure allowed for improved stability for the OER catalyst and a reactive within the mechanism. Co_4O_4 units were further

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optimized through the use of organic linkers for the protection against aggregation and to enhance the reactivity through electronic and structural tuning. Through experiments conducted regarding reactivity showed that these previous procedures preserve the Co_4O_4 core through catalysis while undergoing rough OER conditions.

3.3. The photo electrochemical Device: Utilizing Solar Energy

To imitate photosynthetic conversion mechanisms, many paths were attempted. The ultimate goal is to create a piece of equipment that utilizes solar energy to split water, known as an “artificial leaf.” A basic photo electrochemical equipment can be built by using semiconductors of n-type or p-type as a single band device or as a dual-band gap device which is connected in series. In the creation of a biomimetic artificial leaf as a renewable alternative to fossil fuels, scientists have begun intensive research. The PEC cell design is complex and involves multiple processes related to the following; illumination, charge separation, molecular transport, electrical conduction, catalytic chemistry, and the limitation of current materials.

3.3.1. Can We Create an Artificial Leaf?

For the realization of an artificial leaf, a good PEC equipment for a solar water-splitting couple to H_2 and CO_2 reduction needs plenty of light absorbers to generate enough electrochemical potential. Upon light absorption to conduce the catalytic reaction of water splitting and H_2 production and CO_2 reduction at a low overpotential with liked catalyst.

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Scientists from Berkeley National Laboratory have developed a synthetic system made on Nano sided tubes that can do all the key steps of the fuel generating reaction. This synthetic version is one of the more sophisticated and effective leaves in nature. Protons can easily flow from the interior space of the tube to the outside. In the interior space, they are formed from molecules that allow for the splitting of water while in the outer space, they combine with electrons and carbon dioxide to form fuel-energy. Protons transfer rates across solid-to-solid interfaces by inserting an ultra-thin amorphous silica layer into metal oxide nanolayers. Measurements done using FT-IRRAS, demonstrate that this extraordinary improvement is to emerge from the sandwich silica layer forming interfacial SiOTi and SiOCob linkages to TiO₂ and Co₃O₄ nanolayers. Here, bridges of oxygen provide fast H⁺ hopping pathways across the solid-to-solid interfaces. Furthermore, taking into account the impermeability of oxygen and the high flux of proton transport across multi-stack metal oxide layers allows the integration catalytic environments that would otherwise be incompatible to create nanoscale assemblies that indeed work, such as artificial photosystems for reduction of carbon dioxide by water.

This system consists of small squares called “solar fuel tiles” containing billions of nanoscale tubes in between flexible silicate. In the silica layer, inside silica-titanium dioxide, hydrocarbons attach to cobalt oxides. The hydrocarbons act like molecular wires which conduct charges generated by light absorption. The absorbing molecules are located at the boundary and span across the membrane to the cobalt oxide which enables water oxidation. The development of ultrathin oxide has been an important discovery in catalysis for energy that empowers systems integration on the nanoscale. One example is the ultrathin transition metal oxide co-catalytic layers such as cobalt oxide on semiconductor photoelectrodes. They offer an enhanced transfer

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of charge along the light absorber and the catalyst, as well as oxidation of water. For the first time, ultrathin oxide layers empower the challenge of integration of incompatible catalytic environments that are nanoscale, through separation by a membrane. Cyclic voltammetry (CV) measurements have allowed the report of proton transport and gas permeability for these single oxide nanolayers. Moreover, the process of functional nanoscale system needs incorporation of ultrathin structures that have a pretty high complexity level. For instance, artificial photosynthetic systems in the nanoscale need the incorporation of certain catalytic function and chemical separation methods. Upon raised challenges across multiple layers and interfaces, regarding delivering charges and protons as well as preventing cross over of chemical species. Within this process, H^+ conductivity and O_2 impermeability of multi oxide stacked nanolayers are investigated. Here, interfacial properties promote the transport of protons but at the same time, uses silica membranes that enable the complete blocking of oxygen.

4. Research: Chemical Understanding of Artificial Photosynthesis Through the Lenses of an Undergraduate Student

4.1. Overview

Due to recent environmental impacts, the need for larger-scale clean energy constantly increases. Hence, the development for more energy renewable processes are necessary. This makes us think of the following question: Is it possible to overcome one of the greatest challenges of our generation and that of the future generation: the ability to sustainably produce energy that meets global demands without damaging the world we live in? One possible way to answer this question is *artificial photosynthesis*.

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Today, there is no efficient integral practical system that exists for artificial photosynthesis, but much progress has resulted due to the development of the essential components. Artificial photosynthesis fuel production requires a light-harvesting material (a photosensitizer), a catalyst for O₂ evolution (i.e. water oxidation), and a catalyst for proton reduction to make hydrogen. The oxygen evolution reaction, the half-reaction of water splitting, occurs at the anode and the proton reduction reaction to hydrogen occurs at the cathode.^{4,5} The oxygen evolution reaction is an endergonic reaction which requires $\Delta G = + 475 \text{ kJ/mol}$, and a thermodynamic potential of 1.23 V ($\Delta G = -nFE_{\text{cell}}$). The energy supplied can be provided from sunlight using a light absorber material (e.g. a semiconductor). The rate of the water-splitting redox reaction is governed by the slowness of the O₂ evolving step. This is because four electrons need to be removed from two water molecules and an oxygen-oxygen double bond needs to form. Hence, a catalyst is useful in this reaction to help maximize the rate of the reaction.⁶

4.2. Methodology

With great interest and curiosity about artificial photosynthesis, this research involves the start of an experiment in which the student will monitor the catalytic oxygen-evolution reaction. In order to do so, the student will use a dissolved oxygen optical probe which consists of luminescence that calculate concentrations within aqueous solutions. The laboratory experiment follows closely to an undergraduate laboratory presented by Renderos et al., which is made up of two different steps. The first being the identification and evaluation of an active molecular O₂-evolving catalyst. The next step results in the use of a kinetic based procedure on the initial rates method. Within this method, there is an empirical rate law expression for the turnover frequency and rate constant for a benchmark OEC, $[\text{FeII}(\text{tpy})(\text{bpy})(\text{H}_2\text{O})]^{2+}$ (tpy is 2,2':6',2''-terpyridine;

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bpy is 2,2'-bipyridine).⁶ The experiment differs in that Renderos et al. propose the use of a Ruthenium (Ru–II) complex while this project is replacing Ru(II) for Iron (Fe–II) due to (1) cost and (2) avoid exposure to any potentially hazardous transition metal.

4.3. Experimental Section

4.3.1. Equipment and Materials

Using the Vernier DOOP, the dissolved O₂ concentration (mg/L) measurements will be found. The Vernier Logger Pro software is used for data collection and analysis, which is connected to a probe that uses Vernier Lab Quest. Using a sidearm glass flask, the student is able to measure oxygen-evolution. The [FeII(tpy)(bpy)(H₂O)](Cl₂) catalyst will synthesize according to the literature. In order to use the Vernier DOOP, a range of procedures must be completed. These procedures include the preparation of the solutions and synthesizing by following the guideline given by Renderos et al. in the supporting materials section. Summary of equipment and materials as per Renderos et al. is as follows:

- Vernier Dissolved Oxygen Optical Probe
- LabQuest Interface and a Laptop
- 1 L Beaker filled with deionized water
- Deionized Water Wash bottle
- 1 L Water bath beaker fitted with an immersion heater purchased from Cole Palmer
- Thermometer
- Mini stir bar
- Side-arm round bottom tube flask with joint size with top 24/40 ground outer joint and 160mm

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long with 5/8mm OD tubing side arm x 55mm

- 20 mL scintillation vial
- Needles for purging, venting and a septum (19/22)
- 1000 mL Micropipettes and 10 mL volumetric flasks
- Gas-tight syringe (5 mL) fitted with a needle
- N₂ tank
- Stirrer plate and clamp

4.3.2. Procedures

Summary of procedures as per Renderos et al. is as follows:

4.3.2.1. Part A – Identification of an O₂ Evolving Catalyst

1. Rinse the tip of the probe with deionized water.
2. Place the probe in a beaker filled with about 100 mL of deionized water.
3. Connect the Dissolved Oxygen Probe to the LabQuest interface and laptop, and open the LoggerPro data-collection program.
4. Collect DO (mg/L) data by clicking the green Collect icon from the toolbar at the top of the screen. Successive, constant, near room temperature readings in the data table and graph should be seen; allow these readings to continue for 180 seconds to establish an accurate initial temperature baseline.
5. Take the mean value of the reading (DO value in pure water) by selecting a region of the graph and then display Statistics for that region. Make a note of the temperature of the water.

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6. Construct the setup by first clamping the sidearm flask inside a temperature-regulated water bath placed on a magnetic stirrer.
7. Transfer 25 mL of the given 22 mM CAN oxidant solution prepared in 1.0 M HClO₄ to the reaction flask. Add a magnetic mini stir bar and adjust the stirring rate to between 1000-1200 rpm for mixing (no splashing). Make sure that the stirring rate is not changed during your experiments.
8. Insert the DOOP probe inside the solution and carefully suspend it in the solution. After stirring for one minute, start another data collection for 180 secs. The reading should be stable to the nearest 0.2 mg/L for this step. Record the temperature of the bath.
9. Once the dissolved oxygen (mg/L) baseline has been established, cut a Parafilm sheet and wrap it around the DOOP head and flask joint and place a septum on the side-arm joint to have a leak-free reaction vessel.
10. Carefully open the nitrogen as instructed in the lab and make sure you adjust the flow rate appropriately. Insert a venting needle in the side-arm septum, and place the needle connected to the gas hose line into the solution. Carefully purge the solution with nitrogen until the dissolved oxygen signal drops to ca. 1 mg/L (no splashing).
11. Pour ca. 10 mL of the metal complex [Fe(tpy)(bpy)(OH₂)]²⁺ solution (stock solution) into a 20 mL scintillation vial. Insert a septum (19/22 joint size) and sparge the solution with nitrogen gas for about 5 mins. Meantime, go to Data Collection and set your run to 1000 secs.
12. Using a gas-tight syringe fitted with a needle, remove 1.0 mL of the Fe catalyst, and inject the solution through the side-arm septum into the CAN solution. Begin collecting

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data using the green Collect icon immediately after the complete mixing of the reaction solution. An O₂ evolution reaction will occur by observing an increase in the concentration of dissolved oxygen (mg/L). Note: Do not worry about getting some air inside the reaction setup; this will introduce a very small change in the concentration of dissolved oxygen recorded.

13. When the run is complete, record the amount of dissolved oxygen (mg/L) measured. Save data on the computer. Rinse the probe with clean deionized water and keep in the water bath after completing the run. Gently blot dry the Optical Probe with a Kimwipe when ready to use for another reaction.
14. For the plot recorded, calculate the max [O₂] reached (mg/L) from $\Delta[\text{DO}] = [\text{DO}]_f - [\text{DO}]_i$.

4.3.2.2. Part B – Kinetic Studies of O₂ Evolution using the Fe(tpy)(bpy)(OH₂)²⁺ catalyst.

Important: Record the temperature of each reaction. You should make sure that the temperature of each reaction is $\pm 1^\circ\text{C}$. The reaction rate will depend on temperature, and any fluctuation in the temperature can skew your data.

1. Start by preparing three dilutions from your stock catalyst solution using 10 mL volumetric flasks and the volumetric pipets of choice. Solutions should range in concentration between ca. 1.86 mM – 0.2 mM. Make each dilution separately from the stock solution; do not make serial dilutions. Solutions can be prepared with the following volumes of stock solution:

dilution #1: 5 mL to 10 mL

dilution #2: 2.5 mL to 10 mL

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dilution #3: 1.25 mL to 10 mL

(1/2 dilution) (1/4 dilution) (1/8 dilution)

2. Perform O₂ evolution runs using the catalyst solutions prepared. Follow the same protocol described in Part A by repeating steps 7-14. Record a graph of dissolved oxygen (mg/L) vs. time (secs) using the Logger Pro software and set the duration of each run to 1000 secs.
3. Record the initial rate (v_{O_2}) for each DO plot collected. This can be calculated using Logger Pro by fitting the linear portion of the dissolved oxygen curve to a straight line (read the kinetics analysis section on the next page for more clarification).
4. Perform another trial with the same solution by repeating steps 7 -14 from Part A. Perform two trials per catalyst solution for a total of 8 runs. Perform more than one trial for each solution to improve the linearity and goodness-of-fit of your kinetic data.
5. Save all data runs and proceed to the kinetics data analysis section.
6. Use the 'Results and Tabulation' section on page 19 from your lab handout to help in recording the required data in the laboratory notebook.
7. If all runs are completed, unplug the Dissolved Oxygen Optical Probe from the LabQuest interface, rinse it well with water and keep it in a fresh deionized water bath. The DOOP sensor does not need a warm-up, so just plug it back again when needed.
8. Clean the flask setup and discard the waste acid solution in the designated acid waste container. Make sure to retrieve the mini stir bar with a magnetic stirring bar, wash it with water, and place it in a clean vial.
9. Dry the optical probe using a Kimwipe and place it back in the storage box.

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This laboratory experiment could be certainly be applied to upper-level chemistry courses such as inorganic chemistry or physical chemistry. Doing this, students can have a better understanding of the futuristic potential of artificial photosynthesis. It is time that scientists find a way to alleviate the Earth's effort to keep us all alive despite the high pollution concentration we all create.

5. Conclusion

Inspired by nature, scientists all over the world are attempting to mimic natural photosynthesis. This is not an easy task but if we compare it with the desire of Leonardo da Vinci from the 15th-century dream of flight, or with the hydrogen gas discovery that led to the invention of hydrogen balloons, the dream of artificial photosynthesis will one day be possible. Not only that, but it will be just as common as it is today to go for a hike in the mountains. However, the only way that this will become an accomplishment is by expanding our knowledge. This is the reason why I decided to work on this project. I have a deep appreciation for nature, and I would like to somehow compensate nature for the hard work conducted in keeping all of us alive. If I have just a little bit more knowledge, I can pass this on to other people. Hence, the reason behind pursuing a laboratory experiment that any student taking an upper-level chemistry course can carry on. One person at the time, one mind at the time, as long as knowledge is spread, we may one day become the new pillar of our existence.

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