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Artificial Photosynthesis for Sustainable Fuel and Chemical Production

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Abstract: The apparent incongruity between the trend of our increasing consumption of fuels and chemicals with the finite amount of resources has led us to seek means to maintain the sustainability of our society. Artificial photosynthesis, which utilizes sunlight to create high value chemicals from abundant resources, is considered as the most promising and viable method. This minireview describes the progress and challenges in the field of artificial photosynthesis in terms of its key components: developments in photoelectrochemical water splitting and recent progress in electrochemical CO_2 reduction. Advances in catalysis, where renewable hydrogen can be used as feedstock in major chemical production, are outlined to shed light on the ultimate role of artificial photosynthesis in achieving sustainable chemistry.

1. Introduction

In every aspect of our lives, we rely upon fuels and chemicals, whose usefulness is typically exhausted once consumed. With the growing population and technological advances, this unidirectional flow of energy and matter has grown significantly to the extent that we face the threat of a dearth of supply and rising costs. For instance, energy consumption is expected to rise 56% worldwide by 2040 with close to 80% provided by fossil fuels.[1] The growing demand for fertilizers caused by the increased rate of food consumption of our rising population has necessitated the development of alternative routes to produce ammonia.[2] Considering that our average standard of living is likely to rise continuously, we must seek a drastic change in this consumption-oriented trend to maintain the sustainability of our society. The challenges we face require an efficient method to convert raw materials into useful fuels and chemicals, to make the flow of energy and matter bidirectional and help maintain a balance between production and consumption.

For the production of fuels and chemicals to be efficient and sustainable, the method to be developed has to utilize energy and resources that are naturally abundant and easily renewable. Artificial photosynthesis, which uses sunlight to convert raw materials (i.e. water) into useful chemicals, will be

the prime approach for humanity. It utilizes solar power, which can provide up to 10^5 TW of energy, to convert water and CO_2 into H_2, CO, hydrocarbons, etc.[3] Therefore, the success of this approach relies on two aspects; efficient utilization of solar power and enhancement of the catalytic conversion of water and carbon dioxide to fuels and chemicals. These two main challenges have formed the focus of many ongoing scientific efforts and will have to be solved in the near future for the practical application of artificial photosynthesis. If successful, the technology of artificial photosynthesis will be able to fundamentally transform the current economy of fossil fuels into a sustainable economy of "photons".

Artificial photosynthesis, as its name suggests, originated from humanity`s desire to mimic nature`s unique arsenal of photosynthetic processes to store the energy from sunlight into high energy chemical bonds. Ever since its first demonstration,[4] there have been numerous efforts to split water to H_2 and O_2 with high conversion efficiency.[3] Hydrogen is a great energy carrier and easily convertable to electrical power without generating byproducts that are harmful to the environment.[5] More recently, efforts to reduce CO_2 has gained much attention with the hope of renewably generating carbon fuels. Production of carbon-based fuels from CO_2 can help to alleviate the shortage of fossil fuels and reduce our overall contribution to atmospheric CO_2.[6] Furthermore, the development of carbon-based fuels, or so called "drop-in fuels", allows us to use renewable sources of energy without the need for modification of our current energy infrastructure, alleviating some of the financial and logistical impediments to a fully renewable energy economy.
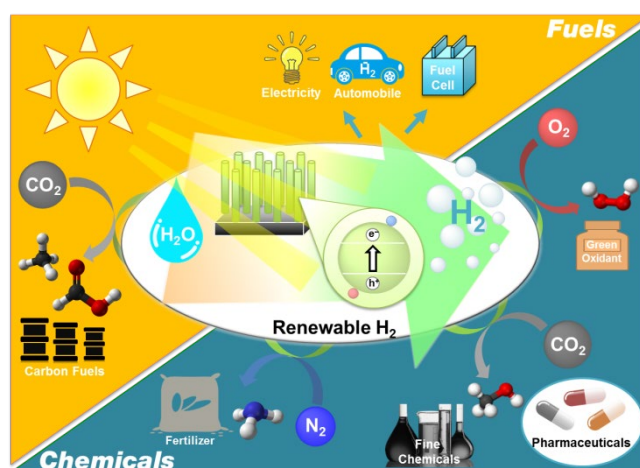
The role of artificial photosynthesis in green chemistry.

Furthermore, when coupled with other areas of catalysis, renewable H_2 produced from artificial photosynthesis can enable

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the synthesis of even more complex products that can be used in a wide range of applications dominated by petrochemical feedstocks. Carbon dioxide hydrogenation with renewable H_2 can produce methanol for use as a fuel or a basic synthetic component of hundreds of chemicals.[7] Additionally, application of renewable H_2 to the selective hydrogenation of carbon-carbon double and triple bonds is the basis for the synthesis of many fine industrial chemicals.[8] Hydrogen peroxide, well known as an environmentally friendly oxidant in the chemical industry,[9] can be generated directly from H_2 and O_2 using transition metal catalysts.[10] Besides carbon-based chemicals, ammonia (NH_3), which is the primary ingredient in agricultural fertilizers[11] and has potential use as a H_2 storage material[12] or directly as fuel,[13] can be produced from renewable H_2 and N_2. As evidenced by the wide applicability of renewable H_2, artificial photosynthesis lies at the center of all chemical reactions implemented in our society (Figure 1) and its success will determine whether we can achieve green sustainable chemistry for future generations.

Since artificial photosynthesis is an integrated system which consists of a light harvesting part and a catalytic conversion part, it is important to maximize the performance of each unit and to design a combined system with optimum efficiency, based on a thorough understanding of each component and the interactions between them. Here, we describe the status and challenges in the field of photoelectrochemical water splitting where there has been much progress in its constituent parts; such as light harvesting, charge transport and catalytic conversion to H_2 and O_2, and its design as a whole. Also, we introduce recent progress in carbon dioxide reduction which is expected to become an essential component of artificial photosynthesis. Some efforts to further convert H_2 into other chemicals are described briefly to shed light on the ultimate role of artificial photosynthesis in the achievement of green chemistry.

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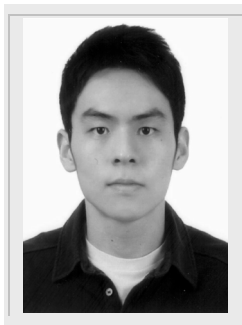
Kelsey K. Sakimoto received his B.S. in Chemical Engineering from Yale University, undertaking research with Professor André Taylor on carbon nanotube transparent conductive electrodes for photovoltaic applications. As a Ph.D. candidate and NSF Graduate Research Fellow in the Department of Chemistry at the University of California, Berkeley under the direction of professor Peidong Yang, his current work focuses on nano-bio hybrid systems for advanced solar fuel production.
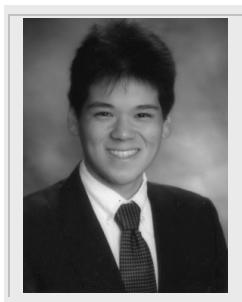
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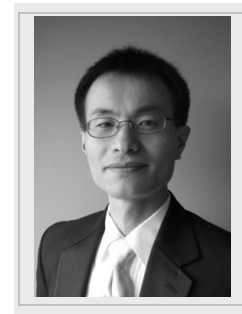
2. Photoelectrochemical Water Splitting

Fundamental to the production of solar-based fuels is the transduction of energy from sunlight into chemical bonds. Through artificial photosynthesis, this energy transduction can be accomplished through the means of semiconducting materials to absorb light and generate an electron-hole pair with sufficient potential energy difference to accomplish the electrochemical oxidation of water to O_2, and reduction of protons and CO_2 to chemical fuels. The potential of this electron-hole pair, or photovoltage, must be sufficiently large to drive the redox processes of interest. Thermodynamically, splitting water into H_2 and O_2 requires 1.23 V and reducing CO_2 to formate and methane with the anodic part of water oxidation need 1.4 and 1.06 V, respectively.[3] From this, it is clear that the photovoltage

of a single semiconductor electrode, whose upper limit is set by a material's band gap, would have to be in excess of 1 V, not accounting for the non-trivial kinetic overpotential required to drive these chemical reactions. While several materials, including TiO_2, possess a sufficiently large photovoltage, most often their optical band gaps are quite large, absorbing only in the UV region of the solar spectrum, giving ultimately a low photocurrent and low solar-to-fuel efficiency.[3]

To solve this issue, artificial photosynthesis has taken its inspiration from nature, where two light absorbing components are employed. In this so called Z-scheme approach, two smaller band gap materials can be utilized to absorb a greater portion of the solar spectrum, and through careful alignment of their conduction and valence band energy positions, they can maintain a sufficiently large photovoltage.[14] As such, majority of the recent work has been to improve the performance of the major units; photoanodes and photocathodes, which comprise the overall photosynthetic device.

Of the most promising photocathode materials, Si[15] and InP[16] have emerged as potential candidates due to the reported high photocurrent densities and photovoltages in excess of 500 mV, suitable for several solar-to-fuel reaction pathways. Advances in nanostructuring and solution phase synthesis of these materials have also reduced the raw material requirements and the fabrication costs and advanced their transition towards commercial implementation.[17]

In contrast, despite continued efforts, a suitable photoanode material to match the high current densities of the top photocathodes, remains elusive.[18] While many III-V nitrides and phosphides, and II-VI chalcogenides have shown promise, ultimately their implementation is limited by poor stability under oxidative conditions, though many passivation schemes, such as the deposition of a thin protective shell by atomic layer deposition (ALD), have been investigated.[19] TiO_2 has been the most extensively studied photoanode material due to its stability, low material cost, ease of fabrication, and significant photovoltage.[20] However, intrinsically low hole mobilities and short wavelength absorption have limited its photocurrent output,[3] far short of the often cited 10 mA/cm^2 desired for solar-to-fuel efficiency of 5-10% for economic viability.[21] Likewise, hematite (α-Fe_2O_3), despite its stability and chemical abundance, shows limited performance due to the incongruity between the low hole mobility (meaning only holes generated within a few nanometers will make it to the catalytically active site) and the long absorption depth required.[22] Nonetheless, nanostructuring has provided a solution by enhancing its current density for water oxidation from its increased surface area producing photocurrents close to our targeted values.[22-23]

The ultimate goal of artificial photosynthesis is to create a standalone unassisted device that can spontaneously convert solar energy into chemical bonds. With the improvements in the performance of individual components, it has become critical to evaluate the performance in an integrated system to identify the aspects that impede the overall performance and to understand key factors to be considered in the design of the actual system to be employed. For this purpose, a fully integrated system composed of nanowire building blocks for direct solar water splitting was demonstrated.[24] Using catalyst loaded Si and TiO_2 nanowires as individual components, an integrated system, in a shape that mimics a tree, was able to split water with 0.12% solar-to-fuel efficiency, comparable to the conversion efficiency

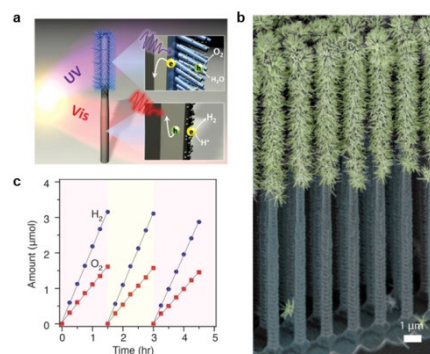for accessible energy produced by natural photosynthesis globally (Figure 2).

Figure 2. The A fully integrated nanosystem for direct solar water splitting. a) Structural schematic of the integrated system, where the TiO_2 nanowires are grown as branches on the upper half of a Si nanowire, resembling a tree-shape. The two semiconductors absorb different regions of light and the excited electron-hole pairs separated at the semiconductor-electrolyte interface drive each half-reactions with the help of cocatalysts. b) Large-scale SEM image of the nanotree arrays. The large surface area of TiO_2 nanowires provide high rates of water oxidation to match with the other half-reaction c) Unassisted water splitting shown by the evolution of H_2 and O_2 under simulated sunlight of 1.5 suns. The 2:1 stoichiometry confirms unassisted water-splitting and the stable performance of the device is shown by the linear increase in gas production.

As demonstrated in the integrated nanosystem for solar water splitting,[24] the major bottleneck in the performance for solar-to-fuel conversion is the low photoanodic performance for driving solar water oxidation. Areas that need improvement are the materials development for high photocurrents and photovoltages, methods establishment for protection of photoanodes against corrosion, and catalyst discovery for efficient water oxidation. In terms of augmenting well-studied photoanodes, engineering interfaces in the form of heterojunctions and surface modifications may be the potential method to overcome intrinsically limited photoelectrochemical performance in well studied photoanode materials, such as hematite.[25] For protection of compound semiconductors against photoanodic instability, ALD-based techniques can provide ways to ensure stability under oxidative environments, while at the same time providing highly active sites for O_2 evolution.[26] Furthermore, the performance requirements imposed on photoanode materials can be supplemented by the development of efficient water oxidation catalysts that can drive the reaction with minimal overpotential.[27]

However, improvement of the individual components does not guarantee performance enhancements of the combined solar-to-fuel conversion system. Careful understanding of the whole system in terms of not only the performance of individual units but the interactions between them and their operational harmony is needed to maxmize its output. Charge transfer characterstics across the interface of the light-absorbing unit and catalyst, and systems design for physical separation of products to prevent undesirable back-reactions, or the need for further separation and purification, are some of the areas that need to be considered.

3. Electrochemical Reduction of Carbon Dioxide

While many shortcomings of water oxidation at the photoanode have been highlighted, the overall process becomes more difficult when the other half reaction is carbon dioxide reduction. Then, there is the added issue of facilitating the catalytic conversion of CO_2 to useful products. Carbon dioxide reduction is a much more complex and difficult process compared to its relevant competitor, the hydrogen evolution reaction (HER). First of all, though thermodynamically more favorable compared to HER, CO_2 reduction requires a large overpotential to drive the reaction at a sufficient rate.[28] In addition, its wide range of products and large number of different intermediate species makes the analysis and development of efficient catalysts with high selectivity difficult.[29] Since the first demonstrations of using transition metals as electrocatalysts, the progress in this field has been quite limited compared to other comparable areas.

Because of its inherent complexity, it has been imperative to understand the reaction by studying electrocatalysts with high activity/selectivity and identifying parameters that govern the reaction pathway. There have been many research efforts, so far, using transition metals as catalysts.[29a] Transition metal catalysts have been shown to produce CO_2 reduction products such as carbon monoxide, formate, methane, ethylene, ethanol, etc. However, most transition metal catalysts favor the production of H_2[29a] and only a few transition metal catalysts, such as Cu,[29b, 30] Au,[31] Ag[32] and Sn,[33] show pronounced activities for CO_2 reduction. Since CO_2 reduction leads to many products, each catalyst bears different selectivity for each product. Among them, Au and Ag have been widely considered as highly selective and active catalysts for CO_2 to CO conversion with minimal overpotential,[31] while Sn is well known for high efficiencies in formate production.[29a, 33] Though active, these catalysts lack the capability to generate products with multiple proton and electron transfers. Copper is the only known transition metal catalyst capable of reducing CO_2 with multiple reducing steps to generate products such as methane, ethylene, etc.[29b]

The reasons behind the trends found in transition metal catalysts have been attributed to different intermediate binding characteristics. Catalysis, in general, is governed by the interaction of the reactant (or an intermediate) with the active site. The well-known Sabatier principle is a clear demonstration of this trait in the field of catalysis.[34] With respect to CO_2 reduction, carbon binding to the metal is the most important characteristic of a catalyst which governs the overall reaction rate. Most transition metals poor in electrochemical CO_2 reduction possess too strong of a binding strength to the carbon, while at the same time having optimum binding strength to hydrogen, leading to low selectivity for CO_2 reduced products over hydrogen.[31, 35] The metals proven to be good for CO_2 reduction have the characteristic of optimum binding strength to the carbon for the desired reaction pathway, relative to other transition metals. The same volcano relationship, as in the case of HER, can be shown for CO production where the descriptor is the metal-to-carbon binding strength, for which Au seems to be at the optimum position.[31]

Recently, nanostructures of the same CO_2-active transition metals have been investigated. Nanostructures are not only advantageous for high surface-to-mass (volume) ratio, but these structures can provide active sites not available in the bulk form which possess different characteristics in terms of intermediate binding. Nanoparticles of Au,[36] Ag,[37] Cu[38] and Sn[39] have been studied and their varying activity in terms of size have been explained through varying densities of sites which are able to stabilize the intermediates strongly, reducing the potential barrier.

Furthermore, to deviate from the scaling relations of pure transition metals and to identify the activity parameters that govern the catalytic activity for CO_2 reduction, Au-Cu bimetallic nanoparticle catalysts have been well studied for their structure-activity correlation (Figure 3).[40] Understanding how the activity is determined, especially for CO_2 reduction which has a large number of products, from the properties of a catalyst is essential
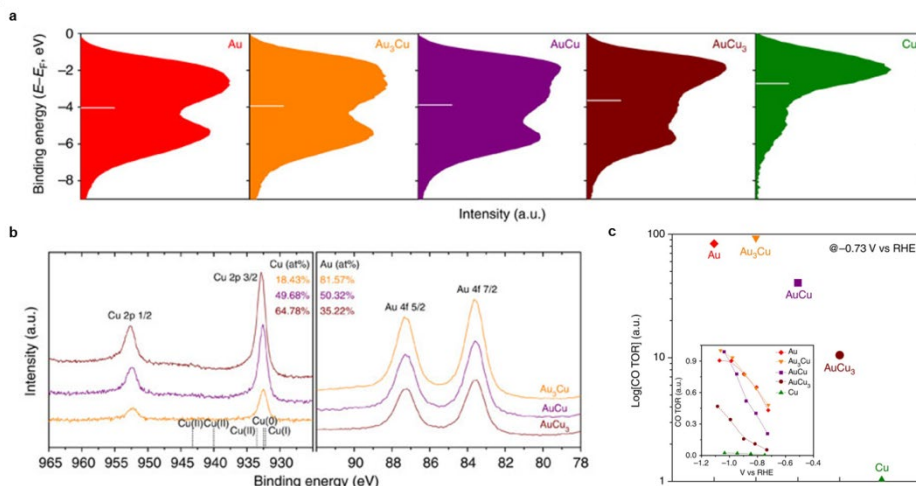
in the design of future catalysts with high activity/selectivity. Within the well defined platform of nanoparticles, their activity has been correlated with their electronic structure and the local geometric configuration and explained in terms of how these two effects determine the binding of various intermediates. The study of the link between catalyst structure and its activity for CO_2 reduction has simplified the overall process by identifing the governing parameters and providing some clues to the design of high performance CO_2 reduction catalysts.

Active sites not commonly observed on traditional bulk catalysts have been devised and tested for CO_2 reduction[41]. Especially, the active sites located at the boundaries between nanocrystallites have shown enhanced activity and high selectivity for CO_2 reduced products while effectively suppressing the HER. Though it still remains unclear as to how the boundaries act as active sites and what the requirements are to create these sites, the discovery of its activity has opened up a new pathway in the design of CO_2 reduction catalysts.

Of paramount importance in the development of efficient catalysts for CO_2 reduction is the establishment of design principles based on a thorough understanding of its reaction pathway. While the standard challenge to develop catalysts with minimal overpotential for high energetic efficiency exists, CO_2 reduction also requires catalysts with high selectivity for targeted products to compete with HER and to actually utilize catalysts in areas that demand specific substances for their operation. Additionally, there is the need for the development of highly stable catalysts that can run for prolonged hours without degradation in activity or selectivity. Nanomaterials, with their controllability in structure and functionality, will continue to shed light on the mechanism for CO_2 reduction and provide unique sites capable of achieving unprecedented activity/selectivity.

4. Fuels and Chemicals from Renewable Hydrogen

Though using renewable hydrogen as a fuel seems promising, it requires advances in the relevant areas of hydrogen technology to be fully realized as the primary source of energy. One area of prime importance is the storage of H_2 due to its low volumetric energy density. To meet the demand for various applications, we need to find other ways of storing H_2 instead of in its pristine form. For this reason, there have been many research efforts to find suitable materials for H_2 storage.[42]

One possible way to circumvent this issue is to provide alternative transports of the potential energy stored in H_2 in the form of new chemical bonds, such as ammonia.[43] Furthermore, the combination of renewable H_2 with abundant resources like N_2, CO_2, and O_2 not only provides methods of alternative storage, but also allows for the flexible use of energy in wide range of applications.

The advantages of catalytic conversion of renewable H_2 to other chemicals is not limited to the fuel sector when it is considered that H_2 is a key component for many synthetic materials. Chemicals synthesized from H_2 are exploited in a wide range of applications and are the basic ingredients for more commonly used, complex products.[7] Therefore, H_2 lies at the center of all industrial chemistry practices and the stable and sufficient supply of H_2, which can be accomplished through artificial photosynthesis, is critical for sustainability.

CO_2 hydrogenation using renewable H_2 can lead to the production of methanol or long-chain hydrocarbons which can be used as fuels or chemicals. Direct methanol fuel cells can ideally provide 1.21 V,[44] which is comparable to a hydrogen fuel cell in its thermodynamic limit (1.23 V), and methanol can be converted to olefins[7] which are the basic building blocks for the production of plastics. Hydrogenation of CO_2 has been extensively studied to identify the catalytically active sites and to further improve the transformation of CO_2 to useful products. The most well-known catalysts are the metal-metal oxide composites bearing an interface with specific activity. Cobalt metal catalysts on various supports have been studied for hydrocarbon formation in relation to their structural aspects.[45] Specifically for methanol formation, Cu on ZnO[46] and CeO_2[47] have been identified as active catalysts and a descriptor-based approach for the discovery of Ni-Ga intermetallic has been reported[48] for its potential use in decentralized methanol production with solar-generated hydrogen.

Systematic design of catalysts can provide reaction pathways for efficient catalytic conversion or formation of complex products through multiple reaction steps. Olefins, which are produced with hydrogen, are often hydroformylated to aldehydes. However, the usual hydroformylation process is potentially hazardous and technologically difficult with high pressure and purification requirements. Development of tandem catalysis, using assembly of nanostructures, has proven to be useful in the selective formation of propanal using methanol and ethylene in a sequence of reaction steps (Figure 4).[49] This shows that artificial photosynthesis, when coupled with unique design of catalytic systems, has the potential to convert protons, beyond hydrogen, into useful chemicals.
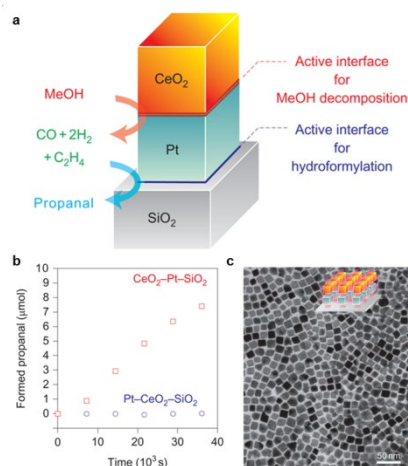

Figure 4. Design of tandem catalysis using nanocrystal bilayers. a) Scheme of tandem catalysis. The two sequential reactions allow the hydroformylation of ethylene without the need to supply CO and H_2. This shows the potential of a systematic design approach in the creation of catalytic centers, where product molecules or intermediates can go through a series of reactions by artificially extending the reaction pathway, to obtain complex products. b) Propanal produced as a function of time over CeO_2–Pt–SiO_2 and Pt–CeO_2-SiO_2 bilayers. Design of the system requires careful understanding of the role of each active center in the overall reaction pathway, as shown by the faulty design of Pt–CeO_2-SiO_2 bilayer with no propanal production. c) Assembly of a bilayer film with CeO_2 on top of Pt.

When renewable H_2 reacts with N_2, it can be converted to ammonia, largely used in the farming industry for fertilizers. In

addition, ammonia contains 17.6% of H by mass, which makes it as a promising candidate for H_2 storage.[43] Since the common method of ammonia synthesis by Haber-Bosch is conducted at extreme conditions with large excess energy consumption, developing ways to fixate nitrogen at ambient conditions is critical. With the development of solid state proton conductors, solid state ammonia synthesis (SSAS) has been devised[50] and improved over the past 15 years. Protons, converted at the anode from gaseous H_2, are transported through the solid electrolyte to the cathode where the other half reaction of ammonia synthesis takes place with the N_2. The cathode which functions as a catalyst needs to be electrically conductive and active for ammonia synthesis and several transition metal and conductive oxide catalysts have been tested.[11, 50-51] Furthermore, ionic conductivity of the proton conducting media, especially at low temperatures, is critical to the success of the SSAS.[11]

The other option for the use of renewable H_2 is to react with O_2 to produce hydrogen peroxide. Hydrogen peroxide is well known for its environmental friendliness as an oxidant and is used in the chemical industry for the manufacturing of numerous organic and inorganic compounds.[52] Also, it can be used in fuel cells with the theoretical output voltage being 1.09 V, comparable to other fuel cells.[53] Hydrogen peroxide is mainly produced by the anthraquinone (AQ) process where H_2 is indirectly oxidized to H_2O_2 via hydroquinone.[54] However, this process utilizes environmentally toxic solvents and is only economically viable for large-scale production, which limits the use of renewable hydrogen at on-site facilities. Therefore, there have been efforts to directly convert H_2 and O_2 into H_2O_2 using Au, Pd and Au-Pd alloy catalysts on various supports.[10, 54] Recently, coupling a microreactor (more favorable in terms of safe operation) with a water electrolyzer has shown to greatly enhance H_2O_2 productivity by the *in situ* feeding of H_2 and O_2.[55] This opens up the possibility for an artificial photosynthetic device to be modified to function as a spontaneous hydrogen peroxide generator.

5. Summary and Outlook

Since the very first aspiration to convert sunlight to chemical energy, the concept of artificial photosynthesis has made significant progress over the past few decades and now it does not seem like just mere hope. The deepening knowledge of solid state chemistry and advances in nanotechnology have made great strides in the development of efficient light absorbing semiconductors with high photoelectrochemical output. The establishment of fundamental concepts in catalysis, coupled with improvements in surface science, has allowed us to develop efficient catalysts to convert raw materials into a diversity of products. We have also been able to reach closer to our final objective of a sustainable society by constructing a system that mimics nature more closely.

Still, some challenges remain. Improvements in the components that perform the anodic half reaction are needed to match with the performance in the cathodic half reaction for economically viable solar-to-fuel efficiency. Production of carbon-fuels requires thorough understanding of the CO_2 conversion process and the establishment of design principles for achieving high activity/selectivity. A rational architecture for

the combined system which will maximize the overall performance is crucial for the success of artificial photosynthesis. Finally, together with the advances in the catalytic conversion of renewable H_2 to various species, development of means to efficiently couple the photosynthetic device with other fields in catalysis is crucial for the achievement of green chemistry. With combined progress in all of these fields, we will find ourselves in a society where artificial photosynthesis lies at the heart of all chemistry.

Acknowledgements

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MINIREVIEW

Artificial photosynthesis is considered as the prime approach for sustainable society. There have been significant progress to reach its full potential and the current status and challenges in water splitting and electrochemical CO_2 reduction are described in this minireview. Developments in catalysis, where renewable H_2 is converted to complex products, are outlined to clearly present its role in the achievement of green chemistry.
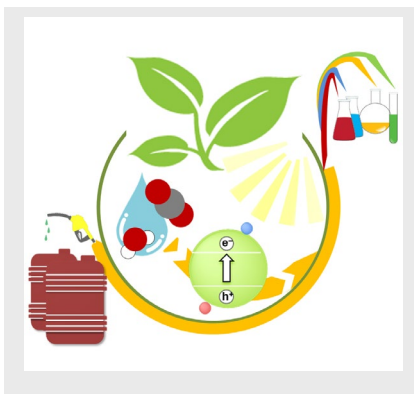
Dohyung Kim, Kelsey K. Sakimoto, Dachao Hong and Peidong Yang*

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MINIREVIEW

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