

Artificial Photosynthesis for Sustainable Fuel and Chemical Production

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The apparent incongruity between the increasing consumption of fuels and chemicals and 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 CO₂ reduction. Advances in catalysis, concerning the use of renewable hydrogen as a feedstock for 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 on 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 by 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 efficient and sustainable production of fuels and chemicals, the method to be developed has to utilize energy and resources that are naturally abundant and easily renewable. Artificial photosynthesis uses solar power, which can provide up to 10⁵ TW of energy, to convert raw materials like water and CO₂ to useful chemicals, e.g., H₂, CO, and hydrocarbons.^[3] Therefore, the success of this approach relies on two aspects; the efficient utilization of solar power and the enhancement of the catalytic conversion of water and carbon dioxide to fuels and chemicals. These two main challenges were 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 the desire to mimic nature’s unique arsenal of photosynthetic processes to store energy from sunlight in high-energy chemical bonds. Ever since its first demonstration,^[4] there have been numerous efforts to split water to H₂ and O₂ with high conversion efficiency.^[3] Hydrogen is a great energy carrier and easily convertible to electrical power without generating byproducts that are harmful to the environment.^[5] More recently, due to the hope of renewably generating carbon fuels, efforts to reduce CO₂ have gained much attention. The production of carbon-based fuels from CO₂ can help to alleviate the shortage of fossil fuels and reduce our

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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 to modify our current energy infrastructure, alleviating some of the financial and logistical impediments to a fully renewable energy economy.

Furthermore, when coupled with other areas of catalysis, renewable H_2 produced from artificial photosynthesis can enable the synthesis of even more complex products that can be used in a wide range of applications currently dominated by petrochemical feedstocks. Carbon dioxide hydrogenation with renewable H_2 can produce methanol for use as a fuel or a basic synthetic component for hundreds of chemicals.^[7] Additionally, the application of H_2 in the selective hydrogenation of carbon–carbon double and triple bonds is the basis for the industrial synthesis of many fine 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

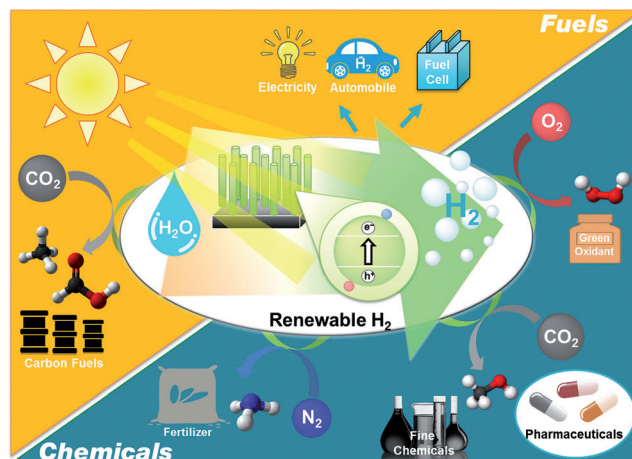
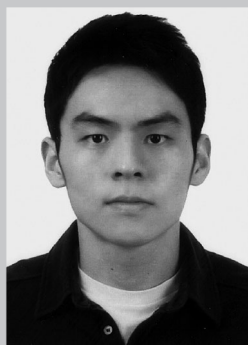
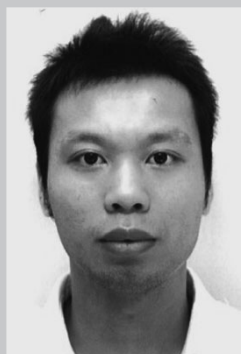


Figure 1. The role of artificial photosynthesis in green chemistry.

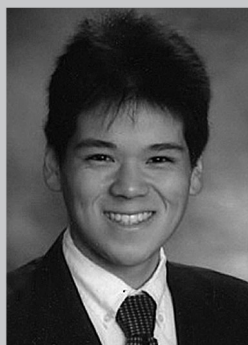
efficiency, based on a thorough understanding of each component and the interactions between them. Here, we describe the status and challenges in the field of photo-electrochemical water splitting. There has been much progress in its constituent parts such as light harvesting, charge transport, and catalytic conversion to H_2 and O_2 , and its design as a whole. Also, we discuss 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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2. Photoelectrochemical Water Splitting

Fundamental to the production of solar-based fuels is the transduction of energy from sunlight to chemical bonds. In artificial photosynthesis, this energy transduction can be achieved by means of the ability 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 the 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 needs 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 higher than 1 V, not accounting for the nontrivial kinetic overpotential required to drive these chemical reactions. Whereas 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, which ultimately results in a low photocurrent and low solar-to-fuel efficiency.^[3]

To solve this issue, artificial photosynthesis has taken its inspiration from nature, in which 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, a majority of the recent work has concentrated on improving 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 fabrication costs and advanced their transition toward 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] Whereas 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 ($\alpha\text{-Fe}_2\text{O}_3$), 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 the current density of hematite 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 stand-alone 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).

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 materials development for high photocurrents and

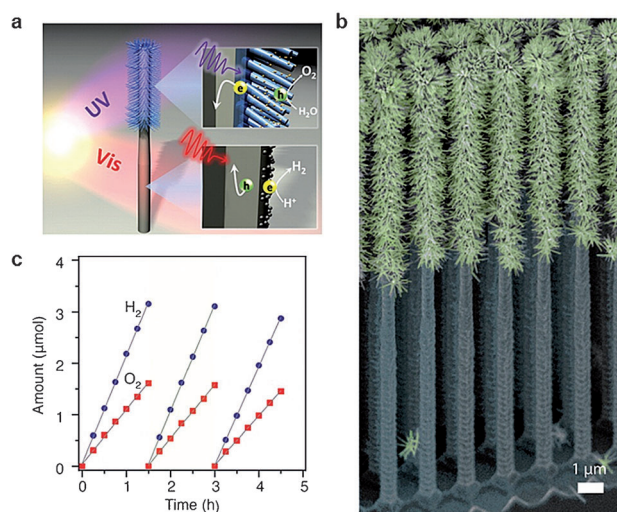


Figure 2. Fully integrated nanosystem for direct solar water splitting. a) Structural schematic of the integrated system, in which the TiO_2 nanowires are grown as branches on the upper half of a Si nanowire, resembling a tree shape. The two semiconductors absorb different regions of light and the excited electron–hole pairs separated at the semiconductor–electrolyte interface drive each half reaction 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.

photovoltages, methods establishment for the 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 the protection of compound semiconductors against photoanodic instability, ALD-based techniques can provide ways to ensure stability under oxidative environments, whereas at the same time providing highly active sites for O₂ 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 maximize its output. Charge transfer characteristics 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

Whereas 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 CO₂ 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, CO₂ 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.

Due to 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 CO₂ reduction products such as carbon monoxide, formate, methane, ethylene, ethanol, etc. However, most transition metal catalysts favor the production of H₂^[29a] and only a few transition metal catalysts, such as Cu,^[29b,30] Au,^[31] Ag,^[32] and Sn,^[33] show pronounced activities for CO₂ reduction. Because CO₂ 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 CO₂ to CO conversion with minimal overpotential,^[31] whereas 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 CO₂ 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 CO₂ reduction, carbon binding to the metal is the most important characteristic of a catalyst and governs the overall reaction rate. Most transition metals that are poor in electrochemical CO₂ reduction exhibit a too high binding strength to the carbon, whereas at the same time having an optimum binding strength to hydrogen, leading to low selectivity for CO₂-reduced products over hydrogen.^[31,35] The metals proven to be good for CO₂ 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 in which 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 CO₂-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 has been explained through varying densities of sites, which are able to strongly stabilize the intermediates, thereby 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 CO₂ 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 CO₂ 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 CO₂ reduction has simplified the overall process by identifying the governing parameters and providing some clues to the design of high-performance CO₂ reduction catalysts.

Active sites not commonly observed on traditional bulk catalysts have been devised and tested for CO₂ reduction.^[41] Especially, the active sites located at the boundaries between nanocrystallites have shown enhanced activity and high

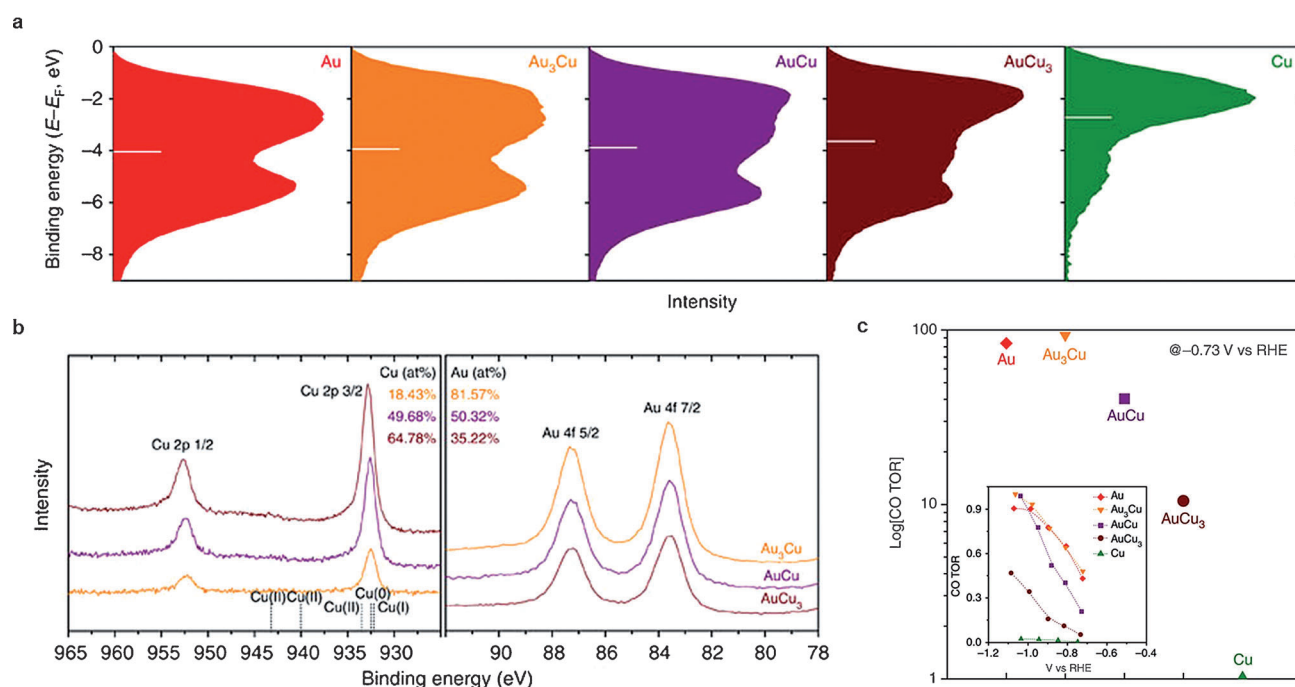


Figure 3. Understanding the structural parameters for electrochemical CO₂ reduction in Au–Cu bimetallic systems. a) Valence band spectra of Au–Cu bimetallic nanoparticles showing the continuous change in their electronic structure along with the composition. The binding strength of intermediates weakens as the d-band shifts lower relative to the Fermi level. b) X-ray photoelectron spectroscopy at grazing angle to identify the surface composition of Au–Cu bimetallic nanoparticles. The surface composition follows closely with the bulk composition of each nanoparticle indicating the uniform distribution of its constituent elements. c) Relative CO turnover rate (TOR) due to the synergistic effect of the electronic structure and the geometric configuration at the active site. The CO activity for bimetallic nanoparticles lies above the trend line, which indicates there might be more than the relative shift in the electronic structure with a change in composition between neat Au and Cu. The geometric configuration of having Cu as an element distributed across the surface, allows further stabilization of COOH with Cu–O binding, which leads to an enhanced CO activity.

selectivity for CO₂-reduced products, whereas 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 CO₂ reduction catalysts.

Of paramount importance in the development of efficient catalysts for CO₂ reduction is the establishment of design principles based on a thorough understanding of its reaction pathway. While the standard challenge is the development of catalysts with minimal overpotential for high activity, CO₂ reduction also requires catalysts with high selectivity for certain products to actually utilize catalysts in areas that demand specific substances. Additionally, there is a need for the development of highly stable catalysts that can run for prolonged time without degradation in activity or selectivity. Nanomaterials, with their controllability in structure and functionality, will continue to shed light on the mechanism for CO₂ 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 a primary source of energy. One area of prime importance is the storage of H₂ due to its low volumetric energy density. To meet the demand for various applications, we need to find other ways of storing H₂ instead of in its pristine form. For this reason, many research efforts aim at finding suitable materials for H₂ storage.^[42]

One possible way to circumvent this issue is to provide an alternative form of the potential energy stored in H₂, e.g., in new chemical bonds such as in ammonia.^[43] Furthermore, the combination of renewable H₂ with abundant resources like N₂, CO₂, and O₂ not only provides methods of alternative storage, but also allows for the flexible use of energy in a wide range of applications.

The advantages of the catalytic conversion of renewable H₂ to other chemicals are not only limited to the fuel sector, but H₂ can also be considered as a key component for many synthetic materials. Chemicals synthesized from H₂ are exploited in a wide range of applications and are the basic ingredients for more commonly used, complex products.^[7] Therefore, H₂ lies at the center of all industrial chemistry practices and the stable and sufficient supply of H₂, which can be accomplished through artificial photosynthesis, is critical for sustainability.

CO₂ hydrogenation with renewable H₂ can produce 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 CO₂ has been extensively studied to identify the catalytically active sites and to further improve the transformation of CO₂ to useful products. The best-known catalysts are 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 CeO₂^[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 the assembly of nanostructures, has proven to be useful in the selective formation of propanal from methanol and ethylene in a sequence of reaction steps (Figure 4).^[49] This shows that artificial photosynthesis, when coupled with unique catalytic system design, has the potential to convert protons, beyond hydrogen, to useful chemicals.

When renewable H₂ reacts with N₂, 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 H₂ storage.^[43] Since the common method of ammonia synthesis by Haber–Bosch is conducted at extreme conditions with high energy consumption, the development of 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 H₂, are transported through the solid electrolyte to the cathode at which the other half reaction of ammonia synthesis takes place with N₂. The cathode functions as a catalyst and needs to be electrically conductive and active for ammonia synthesis. To date, several transition metal and conductive oxide catalysts have been tested.^[11,50–51] Furthermore, the ionic conductivity of the proton-conducting media, especially at low temperatures, is critical to the success of the SSAS.^[11]

Another option for the use of renewable H₂ is the reaction with O₂ 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 in which H₂ is indirectly oxidized to H₂O₂ via hydroquinone.^[54]

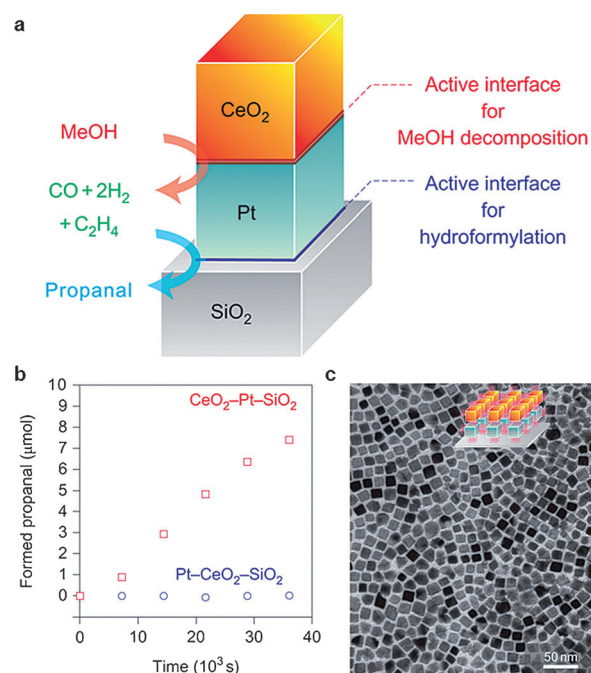


Figure 4. Design of tandem catalysis using nanocrystal bilayers.

a) Tandem catalysis. The two sequential reactions allow the hydroformylation of ethylene without the need to supply CO and H₂. This shows the potential of a systematic design approach in the creation of catalytic centers, at which 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 CeO₂–Pt–SiO₂ and Pt–CeO₂–SiO₂ 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–CeO₂–SiO₂ bilayer with no propanal production. c) Assembly of a bilayer film with CeO₂ on top of Pt.

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 H₂ and O₂ into H₂O₂ using Au, Pd, and Au–Pd alloy catalysts on various supports.^[10,54] Recently, coupling of a microreactor (more favorable in terms of safe operation) with a water electrolyzer has been shown to greatly enhance the H₂O₂ productivity by the in situ feeding of H₂ and O₂.^[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.

Some challenges still 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 a thorough understanding of the CO₂ 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 H₂ to various species, the 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 these fields, we will find ourselves in a society in which artificial photosynthesis lies at the heart of all chemistry.

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