Solar to Fuel: Recent developments in conversion of sunlight into high value chemicals

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INTRODUCTION

By 2030, the agenda of the Sustainable Development Goals of the United Nations calls for an increase in the share of renewable energy in the global energy mix.[1] The way to achieve this goal is by a combination of different available technologies that can convert natural sources into reusable sources of energy.[2] Artificial photosynthesis is the conversion of sunlight, water, and carbon dioxide into chemicals, where energy is stored in chemical bonds of molecules such as hydrogen or hydrocarbons. This energy can then be released upon need. The most important constituents in an artificial photosynthetic system are semiconductor materials and catalysts. Through the absorption of light, semiconductors provide the charges that are required to reduce or oxidize the target reactants (i.e. water and/or CO_2). The introduction of materials interfaces leads to additional challenges. Semiconductors often need to be integrated with catalysts that can lower the kinetic barriers of the reaction and enable the actual charge transfer to the reaction site. In order to prevent losses in the critical charge transfer processes, charge extraction layers, and carefully engineered interfaces are utilized to facilitate and improve the charge extraction and transfer.

While artificial photosynthesis is obviously inspired by natural photosynthesis, the first demonstration of this approach is being attributed to Fujishima and Honda. In the 70', these two researchers demonstrated for the first time that through the band gap excitation of a semiconductor, in that case, rutile titanium dioxide, it is possible to split water into hydrogen and oxygen.[3] After this pioneering work, the international research community has exerted efforts with the goal of making efficient and durable photosynthetic systems. Since then, the research has focused on a variety of novel semiconductor materials, catalysts, interfaces, membranes, device architectures, testing conditions as well as modeling and theory to shed light on reaction mechanism and optimization of the reaction conditions. In this special collection, we report the latest advances of the broader international community in the field, with specific attention to the splitting of water and reduction of carbon dioxide to solar fuels. We collect both photoelectrocatalysis and photocatalysis advancements in the field. While sometimes these two words are used as synonyms as they can both refer to photosynthetic systems, it is important to keep in mind the differences between the two approaches. In photoelectrochemical

(PEC) devices at least one of the electrodes (cathode or anode) is a light absorbing semiconductor, where photon absorption leads to the generation of charge carriers. Minority carriers are used in oxidation (anode) or reduction (cathode) reactions at the photoelectrode surface, whilst majority carriers are transported to the partner electrode. In contrast during semiconductor photocatalysis charge transfer to an external electrode does not occur and reactions typically occur on the surface of a semiconductor material in an aqueous suspension.[4, 5]

SUMMARY OF THE SOLAR TO FUEL COLLECTION

1. **H_2 production: old and new materials**

In this special collection, a review of more common light absorbers for water splitting is accompanied by the optimization of existing systems through nanostructuring, interface engineering, and doping. For example, Vayssieres and colleagues provide a perspective on the recent progress utilized in photoelectrochemistry to improve the photoresponse of hematite-based photoanodes (α-Fe_2O_3).[6] While this material has attracted the interest of the community for decades, there are still many limitations that prevent its use to realize highly efficient and durable photoelectrochemical systems. Hematite is characterized by poor conductivity and charge carrier diffusion, high charge recombination rates, and slow reaction kinetics. Among different approaches, the authors emphasize the use of heterojunctions as an effective way to overcome some of the limitations of this material, together with nanostructuring to specifically improve the short charge diffusion length. These approaches are similar to the optimization of many materials in the field. Similarly suffering from short charge carrier diffusion length is another photoanode material, which has been gathering more recent attention, bismuth vanadate ($BiVO_4$). In this context, Zhang and collaborators have reported an elegant synthetic approach to fabricate $BiVO_4$ photoanodes by spray pyrolysis from a modified vanadium precursor solution. The ultraviolet and ultrasonic treatment of the vanadium solution stabilizes the V^{5+} oxidation state in the final material, and promote the fabrication of nanostructured photoelectrodes with a controlled amount of oxygen vacancies.[7] In addition to a good photoelectrochemical performance, this treatment allows for excellent charge separation. Alternatively, the careful design of heterostructures by first-principles calculations can be useful in predicting novel functional heterostructures, as proposed by Zhang and collaborators. It is now possible to study 2D/2D heterostructures and obtain information about interlayer distance, charge carrier migration, and optical absorption that can help materials selection for photocatalytic water splitting application, as the authors did for III-N/ZnO heterostructures.[8]

Doping is another interesting strategy to modify and improve materials properties in photosynthetic systems. In this collection, Yang and colleagues show how doping is a viable approach to boost catalytic activity of metal-free hydrogen evolution catalysts based on polymeric carbon nitride. They report that phosphorus-doped carbon nitride can evolve hydrogen about seven times faster than undoped carbon nitride when exposed to direct sunlight. The authors ascribe this behavior to a more efficient photoinduced electron–hole pair transfer and separation of the P-doped carbon nitride with respect to the undoped material.[9] Doping was also utilized by Tabata et al. to improve the conductivity of α-Fe_2O_3. These authors synthesized $InFeO_3$ by pulse laser deposition and provided density functional theory (DFT) calculations to provide further understanding of the electronic structure of the doped material.[10]

On the verge of investigations of novel materials with improved photoelectrocatalytic properties, a collaborative work between the Research Center for Advanced Science and Technology and the University of Tokyo led by Tsutomu Minegishi presents the modification of zinc telluride (ZnTe) photocathodes to enhance hydrogen evolution from water. Interestingly, this multi-layered ZnTe-based photocathode shows an enhanced photoresponse due to the synergy between an effective morphology with large grains and an intermediate-band energy level in ZnTe, which allows for multi-photon excitation with an incident-photon-to-current conversion efficiencies extending >710 nm.[11] The morphology and quality of thin film photoelectrodes are fundamental to determine the materials properties of light absorbers. Another case where morphology and materials quality are key to improve the materials property is the work proposed by Abdi and colleagues. In this case, copper bismuth oxide ($CuBi_2O_4$) photocathodes are synthesized by pulsed laser deposition and modificated through a post-deposition annealing under oxygen partial pressure. Specifically, this post-annealing treatment affects the absorption properties and reduces bulk recombination in the material.[12] Nitrides materials have also received increasing interest from the community. Haussener and co-workers proposed the use of $In_xGa_{1-x}N$/Si tandem as a water splitting photoanode.[13]

One of the main challenges of PEC systems still remains the need for improved stability. Agbo and Kistler propose a novel analysis of the device photocurrent, which is often utilized as a measure of degradation of PEC systems. Through modeling, the authors isolate the photovoltaic and electrocatalytic component in the overall device performance losses. This approach shed light on the understanding of performance degradation of PEC systems to provide targeted compensation.[14]

2. A community shift: towards hydrocarbons production

As the production of hydrogen seems to climb to higher levels of technology readiness, the scientific community has witnessed a recent shift of interest towards the production of hydrocarbons as fuels and high value chemicals. Specifically, the reduction of CO_2 conversion has the alluring, two-fold benefit to make fuels, while removing CO_2 from the atmosphere. This field is moving towards two main directions. On the one hand, there is a lot of effort in the discovery of selective electrocatalysts. On the other hand, research groups are trying to understand how to possibly utilize sunlight in a process that is otherwise run under dark conditions by natural systems.

In this vein, Zhang and colleagues reviewed recent discoveries on p-block post-transition metal (e.g., Sn, In, Pb, and Bi) based electrocatalysts. One of the main challenges in CO_2 reduction, where multiple products can form depending on the material and on the potential applied, is to find effective ways to address product selectivity. Specifically, p-block post-transition metal exhibit selectivity for formate production. Formate is receiving interest as a target product as a fuel cell feedstock. To provide design principles for optimization of existing catalysts and design of novel ones, the authors focus on different aspects including surface chemistry, active sites, reaction mechanism, and structure–activity relationships.[15] Pivotal role in the design of new electrocatalysts for CO_2 reduction plays theory. Wang and Zheng have introduced a new method to compute reaction barriers in CO_2 reduction. Since non-adiabatic processes play a significant role in this reaction, the authors used adiabatic Born–Oppenheimer molecular dynamics and non-adiabatic real-time time-dependent density functional theory as a more suitable methodology to predict the energy barriers at play in the reaction.[16]

Developments in the field of light driven CO_2 reduction are described by Sun and co-workers and by Du and colleagues. Sun et al. looked at the role of TiO_2 photocatalysts.[17] While TiO_2 is characterized by limited absorption in the visible light range and fast charge recombination, nanostructuring appears as a viable option to overcome these issues. Specifically, different nanostructured heterojunctions based on TiO_2 photocatalysts have been reported to be active for carbon monoxide, methane, and methanol production.[18] Careful design of heterostructures to promote effective charge carrier separation has been proven useful also in photocatalytic methanol oxidation, as suggested by Ombaka, Bahnemann, and collaborators. They specifically design a carbon dots/$NiFe_2O_4$ photocatalyst where the carbon dots are utilized as electron acceptors that can enhance the photocatalytic activity of $NiFe_2O_4$.[19]

However, the search of novel materials for light-driven CO_2 reduction is still wide open. Du et al. survey a variety of photocatalytic materials and propose that the existing major challenges in the field revolve around the efficiency and stability of the existing materials.

CONCLUSIONS

All these different efforts highlight how the fields of light-driven H_2 and hydrocarbons production are both still open and at the same time clearly delineate what are the main open questions in the field. The need for high efficiency is well understood and the field is now also working to meet the need for long term stability of operation. While efficiency improvements can be achieved through a synthetic approach that leads to high-quality films and through careful nanostructuring, interface engineering still occupies a fundamental role in improving charge separation and extraction as well as protection of otherwise unstable materials. It also appears that the field of photoelectrochemical production of hydrogen is reaching a viable technological solution. In contrast, although the fast-developing field of photoelectrochemical CO_2 reduction has yet to demonstrate scalable systems that are both sufficiently stable and efficient, we envision that the next few years will be crucial to establish the technological viability of light-driven solar fuel production. At the same time, we will witness a more consistent shift of the scientific attention towards CO_2 reduction, accompanied by the nascent interest in N_2 reduction and utilization of light-driven approaches for the synthesis of commodity chemicals.

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