Article

ENVIRONMENTALLY BENIGN ARTIFICIAL PHOTO-SYNTHESIS USING NANOMATERIALS

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Abstract

Direct solar-powered production of value-added chemicals from CO_2 and H_2O, a process that imitates natural photosynthesis, is of fundamental and practical interest. In natural photosynthesis, CO_2 is first reduced to common biochemical building blocks using solar energy, which are subsequently used for the synthesis of the complex mixture of molecular products that form biomass. For decades, researchers have been striving to develop an efficient, stable, and cost-effective photocatalyst that can decompose water into its constituents (i.e., hydrogen and oxygen) by employing solar energy. This process, known as artificial photosynthesis, promises to be one of the key sustainable energy technologies of the future, enabling clean, storable, and affordable energy (i.e., hydrogen and other fuels) from just sunlight and water. Matching the flux between electrocatalysts and light-absorbers, and between individual semiconducting light- absorbers, are two major issues to design economically viable devices for artificial photosynthesis. A hybrid semiconductor nanowire−bacteria system can reduce CO_2 at neutral pH to a wide array of chemical targets, such as fuels, polymers, and complex pharmaceutical precursors, using only solar energy input. With the knowledge that natural photosynthesis is an integrated nanosystem, individual building blocks of biomimetic artificial photosynthesis are discussed. Given the advantages of one-dimensional nanostructures, it is evident that semiconductor nanowires can function as essential building blocks and help to solve many of the issues in artificial photosynthesis.

Key words: nanomaterials, artificial photosynthesis, electrotrophs, Zsche

Introduction

The energy challenges facing humanity in the 21st century are of great importance. The human population has surpassed 7 billion, and technology is expected to provide 20−40 terawatts (TW) of power for a global population of 10 billion by 2050. Despite this dramatic growth in demand, the majority of primary energy sources utilized globally is derived from nonrenewable resources. Furthermore, the use of resources such as fossil fuels leads to pollution at the local and global level, affecting the health and quality of life on the whole planet. To address these challenges while maintaining an increasing standard of living will require a dramatic shift in the way that energy is harvested, converted, and stored. In particular, the large solar resource (105 TW) can provide a means to sustainably meet the energy needs of humanity. The cleanest by far would be renewable energy electrolysis: using renewable energy technologies such as wind, solar, geo and hydrothermal power to split water into hydrogen and oxygen.

Artificial photosynthesis, using solar energy to split water generating hydrogen and oxygen, can offer a clean and portable source of energy supply as durable as the sunlight. It takes about 2.5 volts to break a single water molecule down into oxygen along with negatively charged electrons and positively charged protons. It is the extraction and separation of these oppositely charged electrons and protons from water molecules that provide the electric power.

Natural photosynthesis uses chlorophyll to absorb visible light and many solar hydrogen cells are imitating this process by using light-sensitive organic dye molecules as light absorbers and then transfer the absorbed energy to a catalyst that reduces protons to hydrogen.

Working on the nanoscale, researchers have shown that an inexpensive and environmentally benign inorganic light harvesting nanocrystal array can be combined with a low-cost electro catalyst that contains abundant elements to fabricate an inexpensive and stable system for photo electrochemical hydrogen production.

Artificial Photosynthesis

Solar fuels are storable fuels produced using solar energy. Solar energy can indirectly generate usable fuels through biomass. Alternatively, the direct conversion of solar energy into fuels through a fully integrated system is known as artificial photosynthesis. Artificial photosynthesis applies the principles that govern natural photosynthesis to develop a man-made technology. It strives to be a viable fuel source based on the consumption of abundant resources: solar energy, water and carbon dioxide. Artificial photosynthesis takes advantage of the efficient primary solar energy conversion steps of photosynthesis, but does not use energy to sustain life as does the natural process, nor does it necessarily require the land usage associated with biomass production. Artificial photosynthesis produces fuel via two main pathways: carbon dioxide reduction to ultimately yield hydrocarbons and water oxidation to generate hydrogen. At pH = 0, water splitting can be described by the following overall equation:

$2H_2O \leftrightarrow 2H_2 + O_2 \quad E^\circ = 1.23\ V$ ------- (1)

In (artificial) photosynthesis, sunlight provides the required energy (kinetic and thermodynamic) to drive the reaction in the forward direction and split water into hydrogen and oxygen. Expansion of equation 1 demonstrates that it is the summation of two underlying half-reactions:

$2H_2O \leftrightarrow O_2 + 4H^+ + 4e^- \quad Eox = 1.23\ V$ ----- (2)

$2H^+ + 2e^- \leftrightarrow H_2 \quad Ered = 0.00\ V$ --------- (3)

These reactions show that converting water to hydrogen and oxygen is a multistep, multi electron process that not only needs energy to perform redox chemistry, but also requires different redox catalysts. One catalyst evolves molecular oxygen by oxidizing water (equation 2) and a second catalyst generates hydrogen (equation 3) by reducing protons. Similar to natural photosynthesis, artificial photosynthesis uses light absorbing molecules and/or materials to capture light and produce a charge separation. Then, through a series of inter-/intramolecular charge transfer reactions these charges are transported to catalytic sites to provide the requisite oxidizing/reducing energy to evolve oxygen or hydrogen. Depending on the architecture of the artificial photosynthetic device, the nature of the light capture, charge separation, charge transport and active catalytic sites vary greatly.

One way to make hydrogen using sunlight is to use a solar panel to make electricity and then use that electricity to power a commercial electrolyzer that splits water, forming hydrogen and oxygen. But combining the solar panel and the electrolyzer in one device might be cheaper and more efficient. The electrons produced when light hits a photovoltaic material could facilitate chemical reactions, and the capital costs of one machine would likely be lower than the cost of two. For some time now researchers have known that you could approach 15 to 25 percent efficiency if you combined two solar cell materials in such a system. One solar cell would power half of the water-splitting reaction forming hydrogen. The other could form oxygen. The most efficient solar cell materials for this reaction (silicon, for example) quickly corrode. The Stanford researchers discovered that they could make silicon last for days, rather than just a few hours, by coating it with a protective layer of nickel just two-billionths of a meter thick. Other materials, such as metal oxides, can last this long, but they split water very slowly.

b. Zscheme Process

“Zscheme” process imitates the natural photosynthetic process of two-photon absorption to drive the overall electrochemical reaction. Within such a process, one semiconductor acts as a photocathode for reduction, while the other acts as a photoanode for oxidation. In these electrodes, photo excited minority carriers move to the solution for a catalytic reaction, while majority carriers recombine at the interface connecting these light absorbers .The flexibility of material choices, along with the use of visible wavelengths for energy conversion, makes "Z-scheme" one of the most promising directions for solar-to-fuel conversion.

Due to the integrated nature of the components in artificial photosynthesis, an efficient solar-to-fuel device should operate in harmony such that there is no significant bottleneck hindering the charge flux. Under the "Z-scheme" approach, there are two major flux-matching issues that should be addressed: (1) between current-generating light absorbers and the current-consuming electrocatalysts, such that the electrocatalyst is capable of handling the chemical reactions efficiently and selectively under the flux of photoexcited carriers and (ii) between different light absorbers, such that both the photoanode and photocathode provide the necessary photocurrent flux for practical applications, while maintaining a desirable voltage output. These two issues are currently not fully answered, due to the inadequacy of catalyst and material development and the lack of structural design based on a device integration approach. The introduction of nanomaterials and nanostructures, particularly one-dimensional nanowire morphology, could contribute to tackling these issues in a variety of ways.

c. Role of Nanomaterials in Flux Matching

To address the issue of flux matching between the electrocatalyst and light-absorbers, nanowires array electrodes can provide a reduced over potential for solar-to-fuel conversion and are an ideal platform for a quantitative investigation of the interface between electrocatalysts and light-absorbing semiconductor junctions. It has been proposed that to be economically viable, a solar-to-fuel energy conversion efficiency of between 5-10% is desired. This corresponds roughly to a photo generated carrier flux of 10 mA/cm^2 under one-sun irradiation, which is equivalent to approximately 620 el/ ($nm^2 \bullet s$) (electrons per square nanometer per second).

It is interesting to study nanostructures such as nanowires, which can contain surface states with distinctive reaction activities. Precise co-catalyst loading and a well-controlled interface to link the semiconductor and electrocatalyst are crucial to optimize performance. With their well-defined structure and large surface area, nanowires are an ideal platform for such investigation, providing quantitative information. Furthermore, it will be intriguing to study these systems microscopically at the single nanowire or nanoparticle leve1. In the absence of statistical variations present in large ensembles, an improved understanding of the fundamentals of photoelectrodes and electrocatalysts can be unveiled by measuring individual structures.

d. **Nanomaterials as Semiconductor Light-Absorbers**

The second major issue facing present solar-to-fuel conversion devices is matching the flux between different light absorbers in the "Z-scheme". This requires a well-designed choice of material combinations with suitable band gaps and a low-resistance charge transfer pathway between the two light absorbers.

The introduction of nanowire morphology could help to improve the performance of existing photoanode materials. The nanowire morphology provides a large surface area for cocatalyst loading and electrochemical reaction sites, while at the same time leading to enhanced charge collection efficiency, especially for indirect band gap semiconductors with short minority carrier diffusion lengths. For example, TiO_2 nanowires photoanodes have been well studied, and the nanowire morphology has proven to be beneficial.

As an extension of the nanowire morphology, core-shell structures demonstrate unique advantages. Although single-composition nanowire electrodes improve charge separation within the band-bending region, charge transport through the electrode may still be restricted by a large resistivity of the bulk material in the core of nanowire. A core-shell configuration can alleviate this issue, by designing a photoactive shell for charge separation and a conductive core for charge collection. This could further benefit from light scattering and trapping in the shell material due to the nanowire geometry. Additionally, the heterojunction between two materials can provide extra photovoltage which is crucial for the successful application of a "Z-scheme" approach.

e. **Artificial Photosynthesis using Nanomaterials and Electrotrophic Bacteria**

The goal of highly efficient artificial photosynthesis is a long-standing one, and there are many approaches to the problem, all of which face scientific hurdles. One general approach is to rely on microorganisms called electrotrophs, which can be coaxed, through the application of electricity, to make certain chemical building blocks. The new system is the first one in which semiconductors, which are capable of both capturing solar energy and transmitting electricity to the microbes, have been directly combined with bacteria. Previous similar systems have relied on bulky solar panels to provide renewable electricity. In this case, semiconducting nanowires capture energy from sunlight and pass electrons to electrotrophic bacteria, which are nestled within the wires. The electrotrophs use the electrons to turn carbon dioxide and water into useful chemical building blocks. Those are then passed to genetically engineered E. coli, which in turn make a wide range of products. In natural photosynthesis, leaves harvest solar energy and carbon dioxide is reduced and combined with water for the synthesis of molecular products that form biomass. In this system, nanowires harvest solar energy and deliver electrons to bacteria, where carbon dioxide is reduced and combined with water for the synthesis of a variety of targeted, value added chemical products. This system is as efficient as natural photosynthesis at using the energy in sunlight.

Conclusions

Artificial photosynthesis, a renewable energy approach that stores solar energy in chemical bonds, is an interesting research field for both fundamental research and practical applications. While nature has evolved for millions of years to tackle the challenges of photosynthesis, we are just beginning our journey. Within this Perspective, we discussed current challenges in the research field. In particular, we discussed the benefits of the nanowire structure and possible future research directions, with an emphasis on design principles that are based on integrated artificial photosynthesis architecture.

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