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POINT OF VIEW

Artificial Photosynthesis Technology: Is it Possible?

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How to artificially mimic a natural process as important and complex as photosynthesis in plants? Apart from being essential for life on our planet, the phenomenon of photosynthesis is intriguing because it provides an incredible ability to capture light and energy, subsequently converting it into chemical energy with high-quantum efficiency. As a consequence of increasing economic and environmental interest, research on artificial photosynthesis has increased; an exponential growth has been seen from the 21st century onwards, with mastery of the phenomenon's mechanisms being a major challenge to stimulate further development of the subject. Since the 20th century, there have been great expectations regarding further advancing the process of artificial photosynthesis due to the clear recognition of its importance for humanity. With increasing problems in the context of climate change and energy shortages, the possibility of using the core concepts of photosynthesis to contribute to advancing our knowledge on the generation of clean energy from water splitting and hydrogen production, and the recycling of CO_2 into hydrocarbon compounds and/or fuels with ample added value has become increasingly important.

But the lingering question is how to use visible light irradiation to mimic the intricate multistep mechanism of photoexcitation produced by sunlight. The photosynthesis process involves the photooxidation of water to release oxygen and protons, concomitant to a light-independent second phase with complex chemical reactions able to convert carbon dioxide into glucose (fuel) for plants. In the last century, the use of p-type semiconductors, n-p heterojunctions, the doping process, and the combination of multiple semiconductor materials has increased our ability to design photocatalysts, contributing to the efficiency of water splitting, as well as to the reduction of carbon dioxide using solar irradiation alone. However, the materials used in this process are very different from those occurring during the natural process. The most efficient artificial photosynthesis process requires the construction of a system idealized by semiconductors and/or complex light-collecting organisms, which must be capable of capturing photons and transforming them into electrons and protons, which are then transferred to the photosynthetic chain through efficient local and spatial charge separation. In these systems, the search for semiconductors with low charge recombination and a sufficient lifetime to conduct the steps with intricate multiple electron transfer systems, formation of radical species, and surface adsorption can lead to low conversion efficiency or low selectivity regarding the formation of products.

The possibility of producing photochemical devices capable of capturing and promoting the conversion of water and CO_2 into carbohydrates from radiant energy provided by the sun was predicted in 1912. However, although photocatalytic arrays have been tested with relative success through the construction of "artificial leaves", and there have been remarkable improvements in the understanding of these reactions, there remain many controversies around the efficiency of the process.

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The great challenge is to find ideal semiconductor materials that can be photoexcited when exposed to sunlight, generate electron/hole charge pairs with a low recombination rate, and still present the ability to catalyze water reduction and/or conversion of CO_2 into hydrogen and hydrocarbons of economic interest, respectively. During the last 15 years, the use of photoelectrocatalysis has been proposed, to improve charge separation and consequently increase the efficiency of the photocatalytic process. This process consists of applying an external potential or current density to a semiconductor, immobilized on a conductive material, which can improve the adsorption of water/CO_2 in an aqueous medium, as well as improving the band bending of the semiconductor, subsequently increasing charge separation. Considering the latter, our research group has tested new functional semiconductor materials with the potential to be applied in both the promotion of water splitting and CO_2 reduction using solar irradiation and ultraviolet/visible irradiation.

To date, the most interesting results have been obtained using n-type and p-type semiconductors modified with thin films stemming from metallic nanoparticles, phosphorene, graphene, metal-organic frameworks (MOFs), porphyrins, copper complexes, ionic liquids, doping semiconductors, and/or coupled in heterojunctions. The use of nanostructures of semiconductors has increased the adsorption processes and surface area through the platform of nanotubes, nanospheres, nanoparticles, nanowires, bioinspired forms, and other nanoporous forms. Among all the arrangements, structures with multiple semiconductors in the form of heterojunctions of semiconductors and the modification of MOFs still deserve greater attention to achieve a higher CO_2 conversion efficiency.

Furthermore, since most of the photocatalyst can promote the formation of carbon monoxide, formic acid, methane, methanol, ethanol, formaldehyde, acetaldehyde, acetone, and other hydrocarbons as products during CO_2 reduction, another challenge concerns the selectivity of the process. This selectivity also depends on the pH, the supporting electrolyte type, the concentration, and the photocatalysis/photoelectrocatalysis time. The semiconductor material plays the most important role in the photo(electro)lytic reaction, and those based on copper oxides with different oxidation states have demonstrated very promising results. However, the low stability of the photocatalyst against self-corrosion, low efficiency to absorb solar radiant energy, low selectivity in product formation, competitiveness of parallel reactions, low solubility of CO_2 in aqueous medium, and high complexity of photocatalytic reactions has generally extended the dream of developing an efficient technological system that is economically viable for wide application in industrial systems or productive markets, with low cost. In the past year, we have been investigating new options for developing hybrid semiconductor materials modified with primitive photosynthetic bacteria or chloroplasts. The chloroplast is a promising photosynthetic material. When deposited on semiconductors, it has contributed to the construction of efficient biohybrid devices for solar energy conversion based on the thylakoid membranes (PSI, and PSII) with remarkably quantum efficiency, with potential applications in photo(bio)electrochemical sensors, as well as in solar energy conversion. However, to be practically applied at a large scale for practical application, there is still a lot to learn about the development of artificial photosynthetic systems and about water splitting, CO_2 reduction, and hydrogen production by light irradiation, which is still a dream and part of the ultimate goal: a sustainable world.

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