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Berkeley Scientific Journal

Title

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Permalink

<https://escholarship.org/uc/item/7x70b85p>

Journal

Berkeley Scientific Journal, 27(1)

ISSN

1097-0967

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Publication Date

2022

DOI

10.5070/BS327161283

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Undergraduate

PHOTOCATALYSIS: A REFLECTION OF NATURE

BY MELODY LI

The mystical rays of the sun illuminate the Earth, revealing a world of boundless beauty. From the fields of flowers that stretch across green hills to the hard-shelled chrysalises hanging upon the rigid branches of a plant—the very essence of all life originates from light. Although not apparent to the naked eye, light-induced chemical reactions can be commonly found integrated into the natural world. A well-known example is photosynthesis, a complex system of biological and chemical processes found within particular bacteria and in the chloroplasts of every plant species. In the light-dependent portion of photosynthesis, photons from the sun are first absorbed by the chlorophyll in photosystem two (PSII). Upon absorption, electrons in the chlorophyll are taken to a higher energy level. The excited electrons travel to photosystem I (PSI) where electrons are once again struck by a photon of light, allowing for a series of reactions to produce oxygen, and the primary energy source, glucose. This fascinating natural phenomenon depends solely on light, both a reliable and sustainable source of energy. Inspired by photosynthesis, scientists have synthetically created a new form of chemical reaction known as photocatalysis.¹

HISTORY OF PHOTOCATALYSIS

The term photocatalysis refers to any endergonic or thermodynamically uphill reaction driven by light and accelerated in the presence of a substance that itself does not undergo a chemical change known as the catalyst. The development of this field of study took place over an extensive period of time, stretching over half a century, and was championed by various individuals who felt inspired to alleviate environmental dilemmas regarding pollution and global

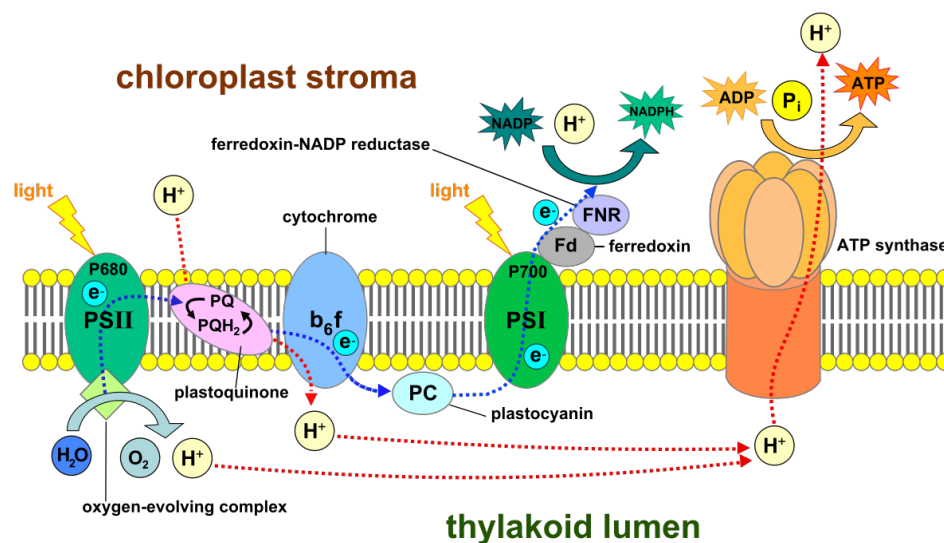


Figure 1: Light-dependent mechanisms of photosynthesis.

energy use.² In the 1900s, Giacomo Ciamician was one of the first scientists to test the boundaries of light-induced reactions. As a pioneer, his research inspired the later discovery of different photocatalysts such as TiO_2 and ZnO . During the early stages of exploration, the field of photocatalysis was primarily viewed as a study of personal interest due to its lack of applicability in the real world at the time. This all changed in the 1970s when modern revolutions brought attention to a new and rising concern for the environment. This shift was propelled by two factors: the large-scale industrialization of production and the oil crisis. Scientists during this period felt compelled to make developments in green chemistry, particularly in renewable resource.³ Chemists, Honda and Fujishima, have made incredible strides, utilizing UV light irradiation and TiO_2 electrodes to split water for the production of hydrogen. Under irradiation, H_2 was produced on a platinum black electrode and O_2

was produced on the TiO_2 electrode.⁴ This experiment in photocatalytic water splitting is vital to modern-day applications of photocatalysis, as hydrogen is an ideal candidate for clean fuel.⁵

MECHANISMS OF A PHOTOCATALYST

To better understand photocatalysis, it is vital to know how a photocatalyst functions. Similar to catalysts, photocatalysts can open alternative routes for a reaction to proceed, introducing a low activation energy pathway. However, they differ by way of mechanism as photocatalysts only work in the presence of light. In heterogeneous photocatalysis using semiconductors, there are three main components that are necessary for a photocatalytic reaction: a sufficient amount of energy absorbed, the creation of electron-hole pairs, and a consequential surface redox reaction. Initially, the photocatalyst itself is a semiconductor

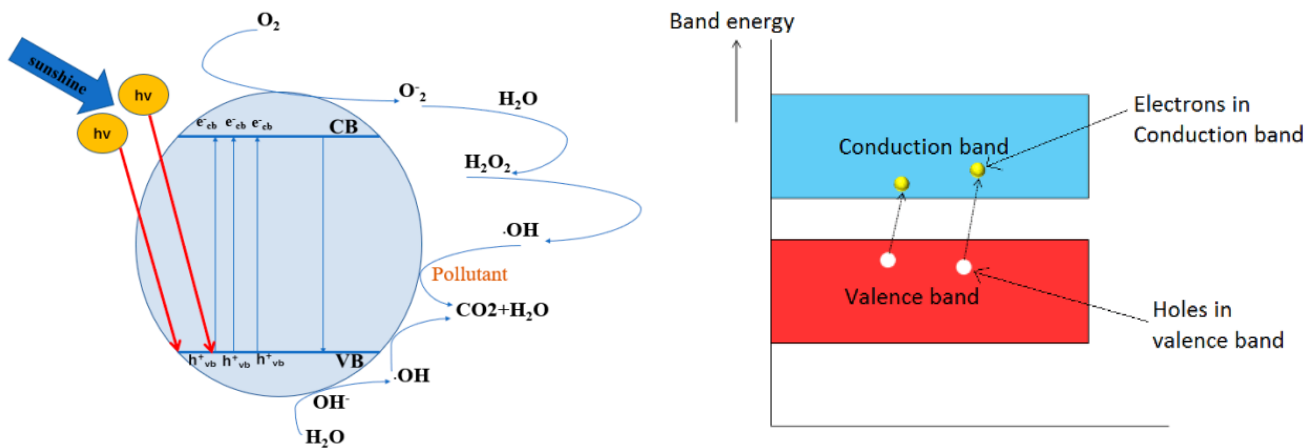


Figure 3: a (left) and b (right). 3a illustrates the reduction-oxidation reactions that occur on the surface of the semiconductor. 3b presents a diagram of electron-hole pairs across the different band energies.

comprised of various energy bands. There is the low energy valence band (VB) and the high energy conduction band (CB) connected by the forbidden band. When the energy of the photon exceeds the gap between the VB and CB, electrons in the VB become excited and move to the CB, where they exist as free electrons. The excitement and movement of electrons will leave vacancies or holes in the VB. The electrons in the CB then migrate to the surface of the photocatalyst and participate in a reduction reaction. The holes left in the VB, armed with oxidizing properties, disperse into the very surface of the catalyst and engage in an oxidation reaction.⁶ These reactions that occur on the surface of the semiconductor can be integral to many

necessary modern-day chemical processes.

SOME MODERN-DAY APPLICATIONS

This photocatalytic redox reaction can facilitate or speed up the process of desired chemical reactions, such as the degradation of air pollutants. For instance, fossil fuels produced from modern-day industrial methods have been a growing concern. Harmful quantities of CO₂ are released into the atmosphere daily, negatively affecting both humans and ecosystems. Yet, through collective research efforts, developments in the photocatalytic reduction of CO₂ can allow for a decrease in these harmful atmospheric pollutants.⁷ It is also interesting to note that this process mirrors

photosynthesis, where H₂O and CO₂ are converted to carbohydrates and oxygen. The CO₂ reduction can be modeled with the photocatalyst mechanism described earlier. Ideally, electrons that migrate to the CB will transfer to CO₂, effectively reducing it to a carbohydrate. In addition, the vacancies in the VB can oxidize H₂O to O₂. Normally, a CO₂ reduction via H₂O would be thermodynamically undesirable, but the energy from an incident photon allows for the procession of the reaction.⁸ Although highly desirable, this photocatalytic conversion of CO₂ to carbohydrates has yet to be achieved.

SCIENTIFIC CHALLENGES

On the surface level, it seems extraordinarily easy to decrease CO₂ concentrations through facilitated photocatalytic mechanisms; however, there are many complications that prevent this process from being completely industrialized. The reaction itself is highly complex and, oftentimes, a combination of various conditions must be considered. For instance, the activation of the catalyst itself requires a certain amount of energy since the excitation of the electrons depends solely on the photons striking the surface of the semiconductor. Therefore, only a specific range of light wavelengths can be used for the reaction. Other factors include the intensity of the light or even the attributes of the catalyst surface, such as the configuration or charge. Even the pH or the concentration of reactants and compounds in the surrounding environment can

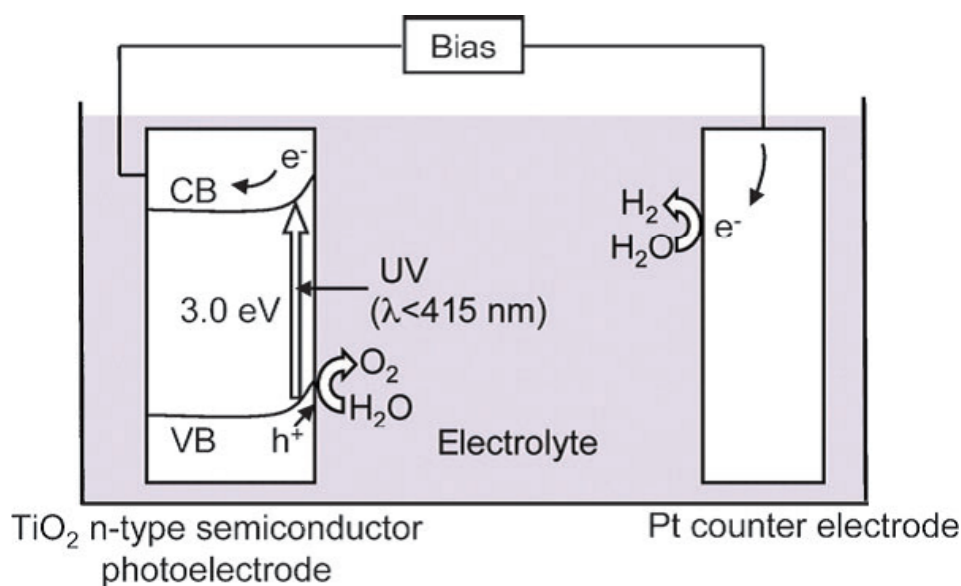


Figure 2: Honda & Fujishima's experiment with water-splitting.

make a significant impact.⁶ All these considerations make it quite difficult for the mechanism to be scaled up for industrial use. Another obstacle would be finding the most optimal photocatalyst for the reaction. Factors including “high photocatalytic efficiency, a large specific surface area, a full utilization of sunlight, and recyclability,” are all components utilized to determine the productivity and quality of a photocatalyst. A possible candidate for the photocatalytic reduction of CO₂ is BiOBr (Oxobismuthanylium; bromide), a semiconductor with intrinsic properties that allow for highly active catalytic sites. Although further research is still required for large-scale industrial use, the potential solution offered by photocatalysis is highly promising.⁹

ACKNOWLEDGEMENTS

Special thanks to Dr. Mina Narouz for reviewing the article and providing feedback and guidance.

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