



Advances in Photocatalytic Hydrogen Harvesting: An overview

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Abstract

Over the last few decades, the global energy demand has grown manifold creating a lot of pressure on our already depleting fossil fuel reserves. This looming energy crisis, coupled with growing concerns over climate change and pollution, has necessitated the search for sustainable supply of clean energy. Traditional fossil fuels not only contribute to environmental degradation but also pose economic and geopolitical challenges. In this context, the development of technologies for production of renewable energy is indispensable. Hydrogen, the most abundant element in the universe, holds immense potential as a clean energy carrier. It can be produced through various methods, and one promising approach is photocatalysis, a process that offers a unique opportunity to harvest hydrogen gas from water or biomasses using only sunlight as the driving force. This article aims to shed light on the principles of photocatalysis, its applications, recent advancements, challenges, and future prospects, ultimately highlighting the significance of hydrogen harvesting through photocatalysis in achieving a sustainable and clean energy landscape.

Keywords: photocatalysis, hydrogen harvesting, band gap, water splitting, photoreforming

1. Introduction

Hydrogen has emerged as a promising alternative fuel source in recent years, offering a clean and efficient energy solution for various sectors. With growing concerns over climate change, air pollution, and the depletion of fossil fuel reserves, the need for sustainable and renewable energy options has become paramount. Hydrogen, often referred to as the "fuel of the future," holds immense potential to address these challenges and reshape the energy landscape.[1]

Hydrogen is the most abundant element in the universe, but it is rarely found in its pure form on Earth. It is commonly extracted from water (H₂O) through a process called electrolysis,

which utilizes an electric current to split water molecules into hydrogen and oxygen. Additionally, hydrogen can be derived from various renewable sources, such as biomass, wind, and solar energy, through processes like steam reforming and biomass gasification. This makes hydrogen a versatile and sustainable energy carrier.

One of the key advantages of hydrogen is its clean combustion.[2], [3] When hydrogen is used as a fuel, it combines with oxygen from the air to produce energy, with water vapor being the only by-product. Unlike traditional fossil fuels, hydrogen combustion emits no greenhouse gases or harmful pollutants such as carbon dioxide (CO₂), nitrogen oxides (NO_x), or particulate matter. This makes hydrogen an attractive option for mitigating climate change and improving air quality.

Moreover, hydrogen offers high energy density for mobile applications,[4]–[6] meaning it contains a large amount of energy per unit of weight.[7] This characteristic makes hydrogen an excellent choice for applications where energy storage and transport are crucial. Hydrogen can be compressed, liquefied, or stored in materials like metal hydrides, allowing for efficient storage and distribution across long distances. It can be used as a fuel for transportation, powering fuel cell vehicles that produce electricity through an electrochemical reaction between hydrogen and oxygen, resulting in zero-emission transportation.[8]

In addition to its role as a fuel for transportation, hydrogen can be utilized in various sectors, including industry and power generation. Hydrogen can be directly combusted in gas turbines or used in fuel cells to generate electricity. It can also be employed as a feedstock in industrial processes, such as ammonia production, oil refining and the synthesis of various chemicals and materials.[9], [10]

However, despite its numerous advantages, the widespread adoption of hydrogen as a fuel faces several challenges. One significant hurdle is the cost of hydrogen production, storage, and distribution. Current production methods, such as steam methane reforming, can be energy-intensive and rely on fossil fuels. Developing more efficient and sustainable production methods is essential to overcome these challenges.

Photocatalysis, a process that utilizes light to drive chemical reactions, offers a potential solution to overcome these barriers and unlock the full potential of hydrogen as a clean energy source. Since the first report on photolytic water splitting by Honda and Fujishima in 1972,[11] which demonstrated the photoassisted electrochemical splitting of water into H₂ and O₂, various techniques and photocatalysts have been employed to achieve solar-driven catalytic H₂ production. Among these methods, the photocatalytic production of H₂ from water under ambient conditions (pressure and temperature) has garnered significant

interest. This approach represents a self-sufficient process that effectively captures and stores solar energy in the form of chemical energy. As an alternative to pure water splitting, photoreforming utilizes oxygenated organic compounds in conjunction with solar energy. When bio-available oxygenated compounds are used as sacrificial agents, this method is considered to be close to a carbon-neutral process, as the resulting CO₂ can be converted back into biomass through plant photosynthesis.[12]

2. The Principles of Photocatalysis

Photocatalysis is a process that utilizes light energy to drive chemical reactions. Its principles involve the interaction between a photocatalyst material, light, and a target substrate. When a photon with sufficient energy is absorbed by the photocatalyst material, electrons are excited from the valence band to the conduction band, creating electron-hole pairs. Efficient charge separation is crucial to prevent recombination of these pairs, typically achieved through internal electric fields or co-catalysts. The separated electrons and holes participate in redox reactions with the target substrate or surrounding molecules. The electrons act as reducing agents, while the holes act as oxidizing agents. This leads to the conversion of the target substrate into desired products, such as hydrogen generation from water splitting or pollutant degradation. To sustain photocatalytic activity, the regenerated electrons and holes must return to their original state. This can be accomplished through sacrificial agents, co-catalysts, or surface recombination processes.

The key components involved in photocatalysis are as follows:

Photocatalyst: The photocatalyst is a material that initiates the photocatalytic reaction by absorbing photons from light and generating electron-hole pairs. Common photocatalysts include semiconductor materials such as titanium dioxide (TiO₂), zinc oxide (ZnO), and tungsten trioxide (WO₃), as well as organic compounds like graphitic carbon nitride (g-C₃N₄).[13]

Light Source: A light source is required to provide the necessary photons for the photocatalytic reaction to occur.[14] Typically, sunlight or artificial light sources such as lamps or LEDs are used. The energy and wavelength of the light source should match the absorption properties of the photocatalyst for efficient excitation.

Reactants: The reactants are the substances that participate in the photocatalytic reaction. In photocatalytic water splitting, for example, water is the reactant that is split into hydrogen and oxygen. Other photocatalytic reactions may involve organic compounds or pollutants as reactants.

Electron Donor or Sacrificial Agent: In some photocatalytic reactions, an electron donor or sacrificial agent is used to facilitate the transfer of electrons to the reactants. This sacrificial agent helps scavenge the photogenerated holes, allowing the photocatalyst to continue generating reactive species.[15] Common sacrificial agents include alcohols, organic acids, or other easily oxidizable compounds.

3. Hydrogen Production through photocatalysis

Hydrogen gas can be produced through photocatalysis by any of the following two approaches:

3.1 Photocatalytic Water Splitting

Photocatalytic water splitting is a process that utilizes light energy to split water molecules into hydrogen and oxygen. It involves the use of a photocatalyst, typically a semiconductor material, which absorbs light and initiates the chemical reactions.

The mechanisms of photocatalytic water splitting can be described in four main steps:

1. *Light Absorption:* The photocatalyst absorbs photons from a light source, typically solar radiation. The absorption of light creates electron-hole pairs within the semiconductor material.
2. *Charge Separation:* The absorbed photons excite electrons from the valence band (VB) to the conduction band (CB) of the semiconductor, leaving behind positively charged holes in the VB. This charge separation is essential for subsequent reactions.
3. *Water Oxidation:* The excited electrons in the conduction band (CB) of the photocatalyst can react with water molecules adsorbed on the catalyst surface. This process, known as water oxidation, results in the generation of oxygen gas (O₂) and positively charged hydrogen ions (H⁺).
4. *Hydrogen Evolution:* Simultaneously, the holes in the valence band (VB) can react with water molecules, leading to the release of electrons and generation of hydrogen gas (H₂). The liberated electrons from the VB can reduce protons (H⁺) to form H₂ molecules.

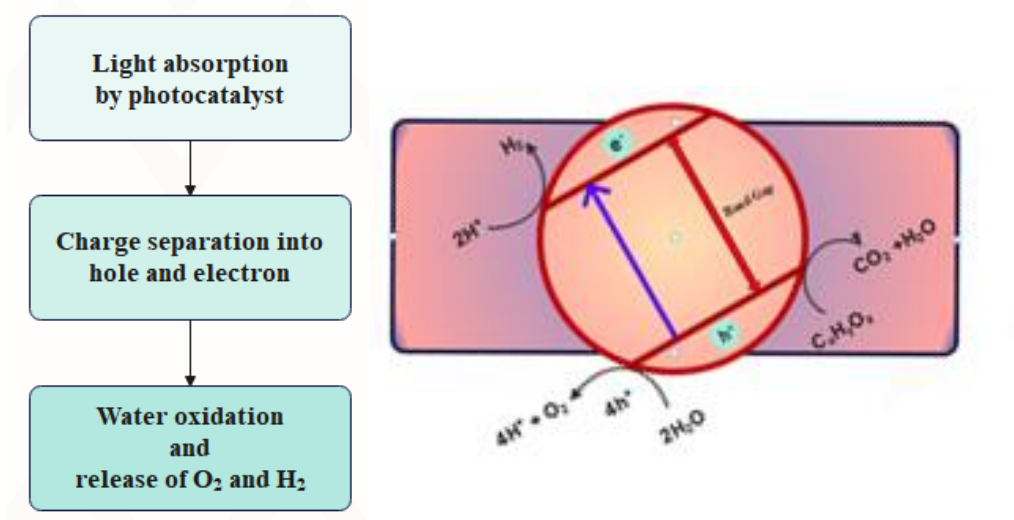


Figure 1. Steps involved in photocatalytic water splitting and its schematic illustration

Overall, the photocatalytic water splitting process involves the oxidation of water at the photocatalyst's CB and the reduction of protons at the VB, resulting in the simultaneous production of oxygen and hydrogen gases as shown in figure 1 above.



While photocatalytic water splitting has shown promise as a sustainable method for hydrogen production, several challenges still need to be addressed to make it a commercially viable and efficient process. Some of the key problems associated with photocatalytic water splitting are as follows:

Low Efficiency: The overall efficiency of photocatalytic water splitting is relatively low, mainly due to limited light absorption and inefficient charge separation and transfer processes. Photocatalysts often have narrow absorption spectra, which means they can only utilize a fraction of the solar spectrum. Additionally, the recombination of photogenerated electron-hole pairs reduces the efficiency of charge transfer to the reaction sites, resulting in lower hydrogen production rates.[16], [17]

Catalyst Stability: Many photocatalysts suffer from poor long-term stability under the harsh conditions of water splitting. The photocatalyst materials can degrade over time due to photocorrosion,[18], [19] oxidation, or chemical reactions with reactive intermediates. There are two factors contributing to the decline in stability of photocatalysts: the build-up of H_2 and the binding of the product H_2O_2 . Maintaining the stability and performance of the catalyst over extended periods of operation remains a significant challenge.

Kinetic Limitations: The kinetics of the hydrogen evolution reaction are often sluggish, requiring a large overpotential to drive the reaction.[20] This limits the efficiency and practicality of photocatalytic water splitting. Catalysts with higher catalytic activity and optimized reaction pathways are needed to improve the kinetics and reduce the energy requirements for hydrogen evolution reaction.

Quantum Efficiency and Charge Carrier Losses: Quantum efficiency refers to the percentage of photons absorbed by the photocatalyst that result in the desired chemical reaction. Losses can occur at various stages, such as incomplete light absorption, charge carrier recombination, or side reactions. Enhancing the quantum efficiency and minimizing charge carrier losses are crucial for improving the overall efficiency of photocatalytic water splitting.[21]

Limited Reaction Sites and Surface Area: The active reaction sites on the photocatalyst surface play a vital role in facilitating the water splitting reaction. However, many photocatalysts have limited active sites, leading to lower reaction rates. Increasing the surface area and optimizing the design of the photocatalyst to maximize the exposure of active sites to reactants can help enhance the reaction efficiency.

Scalability and Cost: Scaling up photocatalytic water splitting from lab-scale to industrial-scale poses significant challenges. The development of cost-effective manufacturing processes, large-scale catalyst synthesis methods, and reactor designs that enable efficient mass transfer and light utilization are essential for the practical implementation of this technology.

3.2 Photoreforming process

In the photoreforming process, oxidation of the organic substrate takes place instead of water. The organic substrate serves also as a proton source. Therefore, it can be considered as the coupling of the oxidation of an organic substance and proton reduction. [7]

In contrast to the pure water splitting, organic substrates used in the photoreforming process present lower oxidation potentials (0.08 V vs. NHE for ethanol) scavenging h^+ more efficiently and therefore consuming faster h^+ preventing charge recombination, while, at the same time they can serve as proton source.[22] Therefore, from a thermodynamic point of view the photoreforming process is less demanding process compared with the pure water splitting reaction and diminishes in parallel the H_2 and O_2 backward reaction.[23] For such a process to be considered realistic, the sacrificial agents used must be abundant and continuously available, produced without competing for land used for food production, and of low cost if not renewable.

The early 1980s witnessed the initial demonstration of hydrogen (H_2) photoproduction from water and various organic compounds in the presence of a semiconductor.[24] A range of organic compounds, including methanol, ethanol, sugar, amino acids, proteins, raw biomass, aliphatic/aromatic compounds, fossil fuels, CO, ethylene, and lactic acid, were utilized as sacrificial agents over TiO_2 and CdS catalysts. This led to an increase in H_2 production compared to pure water splitting, attributed to the lower Gibbs free energy change and the generation of CO_2 as the oxidation product instead of O_2 . Since those pioneering reports, the field of photocatalytic H_2 production from water using carbon-containing compounds as sacrificial agents has garnered significant attention. Research has primarily focused on improving catalyst properties, understanding mechanistic aspects, and investigating the impact of sacrificial agents on efficiency. Various organic compounds have been investigated, with methanol being the most frequently employed due to its simple structure, contribution to reaction mechanism understanding, high H-content, and ability to capture h^+ . Ethanol, slightly more complex than methanol but non-toxic, has also been extensively studied. Bio-available compounds like ethanol, glycerol, and sugars derived from biological sources or waste materials are particularly attractive for the photoreforming process.[25] In the following section, some commonly used organic sacrificial agents in the photoreforming process for H_2 production will be outlined.

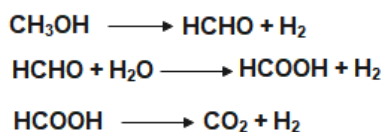
3.2.1 Photoreforming of alcohols

A possible mechanism for the photoreforming of alcohols on a photocatalyst surface involves the oxidation of water molecules by photoinduced holes. This produces hydroxyl radicals, which abstract an alpha-hydrogen to create a $\bullet RCH-OH$ radical. The radical gets oxidised to an aldehyde $RCHO$ which further oxidises to acid $RCOOH$. [26]–[28]

3.2.1.1 Methanol as sacrificial agent

Methanol, being the simplest alcohol with just one hydroxyl group and one carbon atom, serves as the prototypical molecule for photocatalytic H_2 production. Consequently, it has been extensively employed as the ideal feedstock in early investigations of the photoreforming mechanism. The pioneering work by Kawai and Sakata in 1980 reported H_2 production through methanol photoreforming.[24] They proposed a reaction mechanism involving the initial formation of formaldehyde, its subsequent oxidation to formic acid as intermediate, and finally its decomposition to CO_2 and H_2 . Further research conducted by Chiarello et al. utilized TiO_2 functionalized with noble metals (Ag, Au, Pt)[29] to establish a correlation between activity and the work function values of the cocatalyst. In situ studies using metalized TiO_2 at ambient or near-ambient temperatures suggested a stepwise oxidation

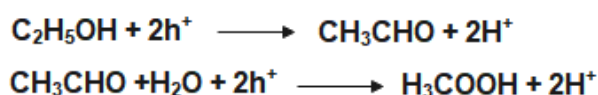
of methanol on the TiO₂ surface by photogenerated h⁺, resulting in proton release and the formation of HCOH and eventually HCOOH. The oxidation steps were also proposed to occur via an indirect path involving CHO attack. While methanol photoreforming occurs through VB h⁺ (either directly or indirectly), H₂ evolution takes place on the cocatalyst. It has been suggested that H⁺ from both H₂O and methanol contribute to H₂ generation in methanol photoreforming, and increasing the methanol concentration significantly enhances H₂ photoproduction. The sorption of methanol and the catalytic profile regarding the formation of by-products greatly depend on the conditions employed, such as the water/methanol ratio. However, HCOH and HCOOH are considered the primary oxidation intermediates. The suggested overall reaction over TiO₂ under irradiation is as follows:



The activity of the catalyst can also be influenced by the catalytic conditions. Bahruji et al[30] discovered that H₂ production using a Pd/rutile TiO₂ catalyst is ten times higher when the reaction takes place in the gas phase compared to the liquid phase. They proposed that the enhanced activity in the gas phase can be attributed to a higher relative concentration of methanol and reduced competition with water for adsorption.

3.2.1.2 Ethanol as sacrificial agent

Ethanol has been extensively studied as a sacrificial agent for H₂ production, primarily due to its ability to be produced in large quantities from renewable biomass sources such as cellulose or lingo-cellulose.[12] The photoreforming of ethanol involves the generation of acetaldehyde and acetic acid, as depicted in the following equations:



Concomitant H₂ production occurs through H⁺ reduction during the photoreforming process, accompanied by the formation of acetic acid and acetaldehyde.[31] These intermediates may undergo parallel oxidation reactions. Apart from the direct reaction between ethanol and h⁺, the formation of acetaldehyde can also be initiated by the spontaneous generation of ethoxide on the TiO₂ surface, followed by h⁺ oxidation, or through ethanol oxidation by CHO. Acetaldehyde is typically the predominant by-product, although other products such as CH₄, CO₂, CO, C₂H₄, and C₂H₆ have been detected in varying proportions. Complete ethanol photoreforming has been achieved over Pt/TiO₂ catalysts, leading to the production of CO₂ and H₂, with a reported apparent quantum yield of 50% for H₂ evolution at 365 nm. Recently,

a 65% quantum yield for H₂ production was achieved using 1D brookite nanorods.[32] Dehydrogenation resulted in the production of acetaldehyde and 1,1-diethoxyethane, while no CO₂ was observed, suggesting that ethanol oxidation occurs more readily than acetaldehyde.

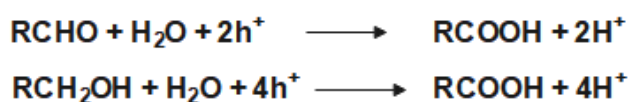
3.2.1.3 Glycerol as sacrificial agent

The utilization of glycerol as a sacrificial agent in the photoreforming process holds significant interest. Glycerol, which is abundantly generated as a by-product (roughly 10% by weight) in the biodiesel industry, currently has limited demand in the market. Consequently, it is commonly considered as waste material, and employing it for H₂ production serves as both a hydrogen source and an electron donor, thereby potentially reducing additional disposal costs.[33] Previous studies have examined various catalysts, with TiO₂-based nanostructures being the most extensively investigated. Although the specific catalyst used has led to the detection of different intermediate products, the majority of studies on glycerol photoreforming, both in the liquid phase and gas phase steam reforming, have observed the formation of ketones, alcohols, and acids. Notably, Montini et al.[34] observed the presence of 1,3-dihydroxypropanone and hydroxyacetaldehyde as the primary by-products in the liquid phase, along with CO₂ and H₂ in the gas phase, when employing Cu/TiO₂ nanocomposites under simulated solar light irradiation. The complete photoreforming of glycerol into H₂ and CO₂ occurs through the generation of 2,3-dihydroxypropanal, followed by the subsequent formation of alcohols, aldehydes, and carboxylic acids. The initial steps of glycerol oxidation involve glycerol chemisorption, direct oxidation by H⁺ ions leading to the breaking of C-H bonds, and the formation of acetyl radicals that transfer electrons to TiO₂, resulting in ketone release.

3.2.2 Photoreforming of carbohydrates

Due to the current inefficiency of the water splitting process, there is growing interest in utilizing biomass-derived substrates, particularly carbohydrates, as a plentiful, renewable, and environmentally friendly feedstock for hydrogen production. Additionally, the food industry generates substantial amounts of solid and liquid waste, classified as second-generation biomass, which needs to be utilized effectively. The wastewater from the food industry primarily contains water-soluble carbohydrates and is commonly treated using biological methods. However, utilizing these pollutants as electron donors presents an opportunity to combine waste decomposition with hydrogen production. The potential for hydrogen photoproduction from carbohydrates such as sugars, starches, and cellulose using RuO₂/TiO₂/Pt catalysts was first demonstrated by Kawai and Sakata.[31] The high abundance of hydroxyl groups in sugars facilitates substrate activation, although fully degrading their

complex structure is more challenging compared to simple alcohols, resulting in lower productivity. The reactivity order is typically starch < sucrose < glucose. Notably, the photoreforming of glucose and sucrose over B,N-codoped TiO₂ catalysts has been reported, even with visible light. A reaction mechanism has been proposed for Pt/TiO₂, where glucose adsorbs to an under-coordinated Ti(IV) surface site through one of its oxygens and dissociates, releasing a proton and an alkoxide anion.[35] The organic fragment is oxidized by a hole, forming a radical that reacts with another glucose molecule. Further oxidations lead to the formation of aldehyde and carboxylic acid derivatives, which are eventually converted to CO₂. Adsorbed H⁺ ions can be reduced to hydrogen on Pt sites using photogenerated electrons. Fu et al proposed a mechanism for glucose photoreforming process which is given below:[36]



4. Conclusion

The field of photocatalytic hydrogen harvesting has witnessed significant advancements that hold immense potential for the production of clean and sustainable energy. The development of efficient photocatalysts, coupled with innovations in solar energy harvesting, has opened up new avenues for harnessing the power of sunlight to drive chemical reactions and generate hydrogen gas. These breakthroughs have the potential to revolutionize the energy landscape and accelerate the global transition towards a greener and more sustainable future. Researchers have made notable progress in enhancing the photocatalytic activity of materials by designing novel photocatalysts, nanostructuring their surfaces, and introducing co-catalysts to improve light absorption and charge separation. Additionally, efforts to optimize solar energy harvesting systems, such as tandem photocatalysts and integration of light-conversion materials, have expanded the range of light absorption and facilitated efficient charge transfer processes.

In summary, the advances in photocatalytic hydrogen harvesting offer tremendous promise for clean and sustainable energy generation. By harnessing the power of sunlight and leveraging innovative photocatalysts and solar energy harvesting techniques, we can reduce our dependence on fossil fuels and mitigate the environmental impacts of conventional energy sources. With continued research and development, along with concerted efforts to bridge the gap between laboratory-scale achievements and commercial applications,

photocatalytic hydrogen harvesting can play a pivotal role in shaping a brighter, cleaner, and more sustainable energy future for generations to come.

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