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Review Article

New Developments and Future Prospects in the Solar Water Splitting

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Abstract

Hydrogen is the material with the highest energy density. Therefore, we can consider it the fuel of the future. Methods of obtaining hydrogen in recent years have become the most important area of scientific research. Hydrogen production using solar energy is very important due to the absence of atmospheric pollution and environmental protection. In this article, we consider methods of obtaining hydrogen by water splitting on components using solar energy. With this goal, we consider a hydrogen fuel cell principle of operation and various methods for hydrogen production. The main attention is offered to the solar-powered water splitting driven by a photoelectrode reaction. We consider such methods as photoelectrochemical water splitting, photovoltaic electrolysis, and application plasmon-enhanced solar cells for the water splitting. The paper highlights advantages and disadvantages of different methods. According to our analysis, the further progress in the hydrogen production is based on application of nanotechnologies and plasmonic effects, which promise increasing of the water splitting efficiency. Advances in nanotechnology, including plasmon-enhanced materials and multi-junction photovoltaic cells, offer novel routes to higher efficiency and lower costs.

Keywords

Photoelectrochemical Water Splitting, Hydrogen Fuel Cells, Plasmonics

1. Introduction

Solar energy is becoming increasingly crucial as the world seeks sustainable and renewable solutions to meet rising energy demands. Solar energy is an inexhaustible natural resource, and its direct conversion into electricity is becoming a crucial necessity for daily use worldwide. With global concerns surrounding greenhouse gas emissions, climate change, and environmental degradation, the need for clean energy sources has never been greater. Hydrogen stands out as a promising fuel due to its high energy density and zero emissions, making it ideal for applications ranging from transportation to energy storage. This paper explores the various technologies being developed to produce hydrogen efficiently using solar energy, including water splitting, fuel cells, and innovative materials such as quantum dots and plasmonic nanoparticles. Water splitting is regarded as an attractive and promising method to provide clean and renewable energy, which over time will help humanity address and minimize global warming, greenhouse gas emissions, glacier melting, and air pollution. Additionally, clean and renewable energy reduces fuel consumption and provides many solutions to these problems [1]. These advancements aim to reduce reliance on fossil fuels, cut greenhouse gas emissions, and foster a cleaner, greener future.

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1.1. Hydrogen and Water as Energy Source

Hydrogen is the fuel of the future; it constitutes 90% of the elements in the universe and 30% of the sun's mass. Hydrogen excels with a very high energy density of 143 kJ/g, and its use does not emit carbon. Therefore, it serves as clean and sustainable energy, emphasizing high efficiency and clean energy production with low pollutant emissions [2, 3]. Hydrogen separation from water through the photoelectrochemical process (PEC) is one of the most promising methods for producing clean hydrogen. This process involves the absorption of sunlight by semiconductor materials leading to the creation of electron-hole pairs, enabling the decomposition of water into hydrogen and oxygen [1, 4].

Processes of creating electron-hole pairs occur in low-dimensional systems, such as quantum systems, which can lead to more efficient hydrogen production [5]. These structures are considered particularly promising for improving efficiency, and their energy gap can be tuned according to the size of the quantum dots. Quantum dots operate by absorbing low-energy photons, through up-conversion processes, or by generating multiple excitons, where each photon can produce several pairs of charges (electron and hole) instead of just one pair. Additionally, they can also function in a thin-layer structure, allowing cells to operate with photoelectric electrons, thus converting low-energy photons into electric current [6].

1.2. Energy Shortage

The world today is facing an energy shortage. One of the promising solutions to this is the use of fuel cells, especially hydrogen fuel cells. Fuel cells address energy problems by utilizing efficient and clean energy with minimal pollutant emissions, offering solutions for a wide range of applications, including transportation, electricity generation, and energy storage [7]. Therefore, there is a growing demand for resilient sources that can help meet the increasing demand for renewable energy [8].

2. Fuel Cells

2.1. Overview and Operating Principle of Fuel Cells

Fuel cells produce electricity and heat as long as fuel is supplied. A fuel cell consists of two electrodes: a negative electrode (or anode) and a positive electrode (or cathode), sandwiched around an electrolyte. Principle of operation is based on a chemical reaction between hydrogen gas and oxygen. The process occurs by passing a fuel (hydrogen) over the anode and air or oxygen over the cathode. This leads to the creation of positive ions H^+ (protons) and negative electrons e^-. The electrons move through an external circuit, creating an electricity flow and protons transfer through the electrolyte to the cathode, where they recombine within combination with oxygen [9]. A schematic view of a hydrogen fuel cell is presented in Figure 1.

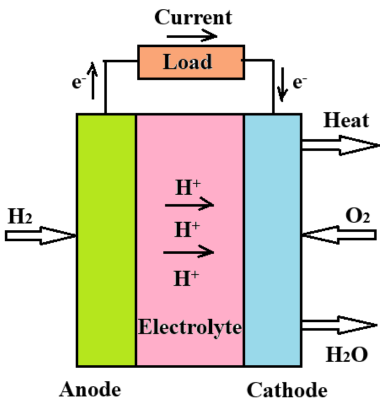

Figure 1. *A fuel cell is an electrochemical device that produces electricity through a chemical reaction between fuel and an oxidizing agent, usually oxygen or air.*

Anode reaction: Hydrogen gas (H_2) passes over the anode electrode, where it dissociates into positive ions (H^+) and negative electrons (e^-) according to the reaction $H_2 \rightarrow 2H^+ + 2e^-$.

Electron Flow: The negative electrons travel through an external electrical circuit, creating an electrical current used for energy production, and then return through the cathode electrode.

Cathode reaction: The negative electrons meet the positive hydrogen ions and oxygen molecules to create water (H_2O) according to the following reaction $\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$.

Overall cell reaction: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O + 237.2\ kJ/mol$

2.2. Issues with Fuel Cells

Despite the high potential of hydrogen fuel cells, there are several significant problems and challenges that limit their widespread use:

High production costs of fuel cells, mainly due to the use of expensive materials like platinum as a catalyst [2].

Materials used in fuel cells require high temperatures for efficient operation, adding to the technical and economic difficulties of the system [2].

Most hydrogen today is produced from processes based on non-renewable energy sources like natural gas, which generate greenhouse gas emissions [2, 9].

Storage and transportation of hydrogen are problematic and expensive. Hydrogen is a very light gas, requiring high pressures or low temperatures for storage, making its use on a large-scale challenging [2].

Fuel cells may suffer from performance degradation over time due to catalyst wear and contaminant accumulation, necessitating regular maintenance and frequent component replacement [2, 9].

Fuel cells can operate at higher efficiency than internal combustion engines and can convert the chemical energy of the fuel directly into electrical energy with an efficiency that can exceed the efficiency of the Carnot engine between the same low and high temperatures and reach 80% or more [10]. In order to operate efficiently and smoothly, fuel cells require a continuous supply of hydrogen. It is obvious that a direct and fast way to obtain hydrogen is to split water into its components. However, this path is not simple and requires deep analysis and development. When using solar energy, water splitting in combination with a fuel cell promises to create a closed system that produces energy from the absorbed sunlight.

3. Water Splitting for Hydrogen Production

Hydrogen is the material with the highest specific energy compared to other materials, ~39 kWh/kg. Thus, hydrogen production is becoming an important area in the energy industry. There are many ways to produce hydrogen. One of them, very effective in our opinion, is solar-powered water splitting [1, 9]. Using this idea together with a hydrogen fuel cell leads to achieving a large amount of clean energy with minimal emissions of pollutants, offering solutions for a wide range of applications, including transportation, power generation and energy storage. Figure 2 presents two principal approaches to solar-powered water splitting.

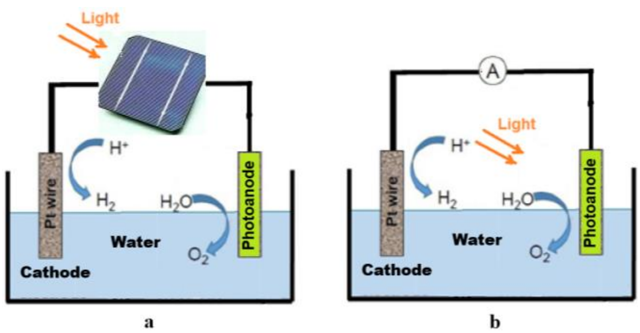

Figure 2. *Principal approach to solar-powered water splitting: (a) electrolysis of water driven by a solar cells application; (b) water splitting driven by a photoelectrode reaction.*

Figure 2a shows the use of a conventional solar cell to produce energy used to split water. Evidently, here we have two energy transfer processes. In the first process, the absorbed solar energy produces electricity, and in the second process, this electricity is used to split water. Each of these processes has energy losses, thereby reducing the efficiency of the system. Figure 2b represents the direct photoelectric splitting process using solar photon energy. In this case, our goal is to use photons with enough energy to split water and produce enough number of electrons at the photoanode to sustain the process.

The direct use of solar energy for water splitting into its components via photocatalysis may be cheaper and more efficient than using electricity obtained through the electrolysis process. This approach uses materials that react to sunlight to accelerate the decomposition of water [4, 11].

Water splitting using the photoelectrochemical process (PEC) is a method where water is split into hydrogen and oxygen using sunlight. This process includes several stages:

Light Absorption: The semiconductor electrode (anode) absorbs sunlight suitable for its bandgap. Semiconductors are the main choice for anodes as they get excited by sunlight to produce excitons [1, 2].

Charge Carrier Generation: The excitonic transition promotes an electron from the valence band to the conduction band, leaving behind a hole in the valence band and a photoelectron in the conduction band [3].

Charge Carrier Separation: Separation occurs when the semiconductor in contact with the electrolyte creates a built-in electric field at the interface. Eventually, the photoelectrons are transferred to the counter electrode, where a reduction reaction of protons to hydrogen occurs [1].

Charge Carrier Transport: The electrons generated at the anode reach the cathode through an external circuit, while the protons migrate to the cathode through the electrolyte and undergo reduction to form H_2 [1, 3].

Therefore, photoelectrochemical water splitting reaction is endothermic and requires at room temperature the Gibbs free energy change ΔG = 237 kJ/mol that corresponds with ΔE = 1.23 eV energy required for electron transfer [12]. Water splitting consists of two half-reactions: oxidation of water with production of oxygen, four protons and electrons and reduction half-reaction producing hydrogen. In pure water, these reactions may be presented as follows:

$$4OH^- + 4h^+ \rightleftharpoons O_2 + 2H_2O \; E_{ox} = -0.404\; eV$$

$$4H_2O + 4e^- \rightleftharpoons 2H_2 + 4OH^- \; E_{red} = -0.826\; eV$$

Which together brings ΔE = 1.23 eV. Figure 3 illustrate the process of photoelectrochemical water splitting

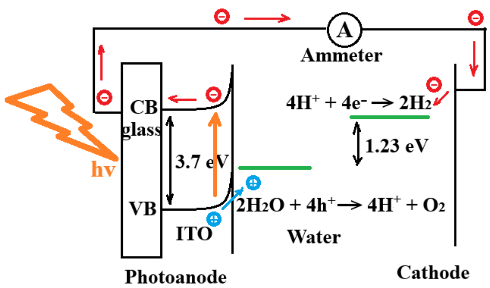

Figure 3. *Schematic illustration of the photoelectrochemical water splitting.*

When illuminated with light, the photon energy is absorbed by the semiconductor photoanode and excites electrons into the conduction band, creating holes in the valence band. The photogenerated holes participate in the oxidation of water, producing oxygen and hydrogen ions, i.e. protons. Photoelectrons are transported to the cathode through an external circuit and there they are used to reduce protons, producing hydrogen [13].

3.1. Water Splitting Using Electrolysis Process

An electrolysis process involves using electricity to drive non-spontaneous chemical reactions, such as water splitting. There are several types of electrolysis:

Basic Electrolysis: The electrodes are immersed in a liquid electrolyte containing NaOH or KOH salts, and gases are produced when an electric current passes through the electrodes [2].

Polymer Membrane Electrolysis (PEM): Porous electrodes are attached to a polymer membrane (usually Nafion). This process offers a better hydrogen production rate due to the suppression of the recombination rate and a lower resistance path [2].

Solid Oxide Electrolysis (HTE): At high temperatures, industrial waste heat is used to produce hydrogen on a large scale. The high production cost arises from the use of expensive metals like platinum (for hydrogen production) and IrO_2 (for oxygen oxidation) [2, 9].

Advantages

Lower Costs: The direct use of solar energy reduces the need for expensive external electricity sources.

Technological Simplicity: The approach requires fewer complex technological components, simplifying production and maintenance of the system.

Renewable Energy Utilization: The direct use of solar energy allows for the exploitation of an inexhaustible and environmentally friendly resource [3, 14].

Challenges

Efficient Light Utilization: Despite the advantages, the challenges include the need for materials capable of efficiently utilizing sunlight to produce the required chemical reactions.

Chemical Stability: The photocatalytic materials must be stable in an aqueous environment and not degrade or lose their chemical activity over time [1, 3].

So, the direct use of solar energy for water splitting is a promising approach for producing hydrogen and oxygen efficiently and cheaply, reducing the need for complex and expensive external electrical systems. However, to ensure the long-term success of the process, stable and efficient materials are required. Particular attention should be paid here to the design of the photoanode and the correct choice of semiconductor materials that allow the production of the maximum number of electrons.

3.2. Efficiency of Solar Energy Conversion to Hydrogen

The efficiency of solar energy conversion to hydrogen (STH) is defined as the ratio between the chemical energy of the produced hydrogen and the solar energy entering the system. Currently, the average efficiency in the laboratory for PEC (photoelectrochemical) systems is 12.4%, while photovoltaic-electrolysis (PV-electrolysis) systems have achieved a maximum efficiency of 30% [9]. Figure 4 represents the solar radiation spectrum showing the distribution of emitted photons by wavelengths or by energies of photons.

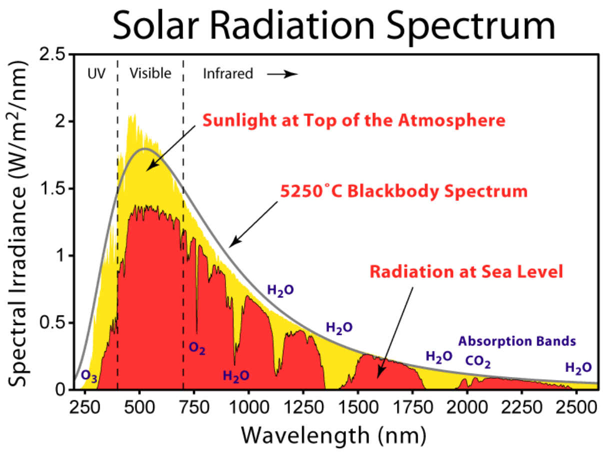

Figure 4. *Irradiance spectrum on different levels in the atmosphere (Wikipedia).*

In the visible wavelength range of the solar radiation spectrum (400–700 nm), the Sun emits most of its energy. Within this range, shorter wavelengths correspond to higher photon energy. Using the wavelength-energy relationship, it is possible to calculate the maximum wavelength of photons capable of providing an energy of 1.23 eV, which is the minimum energy required to split water in a photoelectrochemical reaction.

$$\lambda_{max} = \frac{hc}{\varepsilon} = \frac{1.24}{1.23} = 1.008[\mu m]$$

3.3. Improvements and Adjustments

Use of Multi-Junction Cells: Systems based on multi-junction photovoltaic cells show potential to achieve conversion efficiencies of up to 57-62% under concentrated light.

Matching Current-Voltage Characteristics: Matching the maximum power point voltage (VMPP) of multi-junction solar cells to the voltage required for electrolysis will allow optimal utilization of solar energy [9].

The gap between theoretical and actual efficiency is mainly due to the mismatch between the characteristics of multi-junction photovoltaic cells and electrolyzers. The maximum power point voltage of a commercial multi-junction solar cell is in the range of 2.0-3.5 volts under concentrated light, while the minimum voltage required for water electrolysis is only 1.23 volts. These voltage differences result in energy waste as heat instead of being stored in H_2 chemical bonds [1, 9].

Therefore, matching the current-voltage characteristics of the cells and electrolyzers is critical to improving the efficiency of solar-to-hydrogen conversion. Multi-junction photovoltaic systems offer significant potential for efficiency improvement, but further efforts are needed to overcome existing challenges and make the technology economically viable.

4. Existing Technologies Today

4.1. Research and Development in Water Splitting

Research in this field focuses on the synthesis and evaluation of various semiconductor heterostructures enabling produce maximum quantity of electrons in the photoanode under solar irradiation. One such research was synthesis of a ZnO/ZnS heterostructure with a controllable energy gap to improve visible-light-driven photocatalysis. The heterogeneous structure allows for increased light absorption and improved photoelectrochemical reaction efficiency, leading to increased hydrogen output under visible light. ZnO is a wide band gap oxide that allows for the creation of charge carriers (electrons and holes) in response to light. Research conducted on the addition of ZnO with dissolved nitrogen shows reducing the energy gap and enables better absorption of light in the visible range, thereby improving overall efficiency [15]. It was shown that the results significantly depend on the technological parameters of the semiconductor system growth.

Additionally, ZnO nanowires protected by a ZnS layer for use in photoanodes focus on improving the efficiency of solar cells by using nanomaterials to enhance light absorption and its conversion to electrical energy [16].

4.1.1. Effects of Anions and pH on the Stability of Nanostructures

Application the ZnO nanostructures as photoanodes requires understanding their chemical and physical properties in different environments. Here, the effects of anions and pH (concentration of hydrogen and hydroxyl ions in the solution) on the stability of semiconductor nanostructures becomes significant. Understanding the chemical conditions that affect the stability of ZnO nanorods is essential for improving their efficiency in energy applications [14, 17]. It was shown that stability of the nanostructure depends on the buffer solution and the pH degree. Increasing of the pH leads to the formation of passivating layer on the photoanode decreasing the working efficiency. Also, the lifetime of ZnO layer for the photoelectrochemical water splitting can be significantly increased using the complex electrolytes.

4.1.2. Utilization of Nanostructured Materials

Nanostructured materials, including metal and oxide nanoparticles, have the potential to significantly enhance the efficiency of electrolysis. They achieve this by increasing the reactive surface area and reducing the energy required for the reaction. One of the key benefits of these materials is their ability to catalyze electrochemical reactions, providing a larger surface area for electron absorption, which ultimately helps in reducing energy consumption.

4.1.3. Surface Engineering of Photoelectrochemical Electrodes

Today, studies are focused on surface engineering of photoelectrochemical electrodes to improve water splitting. Using advanced techniques for surface engineering allows for improved light absorption and the photoelectrochemical efficiency of the electrodes, leading to increased conversion efficiency and overall performance improvement [18]. Another study presents the use of spiked-nanosheet structures of ZnO as anodes for photoelectrochemical water splitting. The spiked structures improve the active surface area of the anode and its light absorption capacity. It was found that these structures have a larger active surface area but suffer from higher electron recombination [13].

4.1.4. Development of Thin Films and Heterojunctions Photoanodes

One study investigates the development of thin films of Cu_2O/InGaN heterojunctions for water splitting using sunlight. This combination of materials improves the separation of photoelectrochemical charge carriers and improves the efficiency of converting sunlight into chemical energy [19]. It should be noted that due to application of the heterojunction, the obtained photocurrent density was 4.2 and 3.2 times higher than that of pure InGaN and Cu_2O thin films photoanodes, respectively. In addition, another study explores the use of $BiVO_4$/ZnO nanodendrite-based anodes, which demonstrate high efficiency under low potential conditions, effectively reducing energy consumption during the process. The heterogeneous nanodendrite structure increases the surface area, contributing to greater stability and efficiency of the anode in photoelectrochemical applications [20]. Moreover, incorporation of metal nanoparticles into the semiconductor junction can improve efficiency of solar cells [6].

4.1.5. Designing Catalysts for Water Splitting

There are advanced methods for designing catalysts for photoelectrochemical water splitting that combine experimental and engineering aspects. The research emphasizes the importance of integrated approaches to improve the efficiency and stability of the catalysts, which leads to enhanced performance of photoelectrochemical systems [7].

Synthesis and characterization of thin films of ZnO nanostructures for PEC water splitting show that films annealed at high temperatures exhibit improved photoelectrochemical properties and higher light absorption capacity [21]. Precise control over the morphology and size of ZnO nanostructures is essential for optimizing their performance in energy devices. While thin films may offer advantages in terms of transparency and activity, they may also face challenges such as stability and durability [22, 23].

ZnO is considered a promising material for PEC processes due to its good electronic mobility, excellent optical properties, high availability, and low toxicity. Designing the nanostructure of ZnO can enhance photocurrent output due to a high surface-to-volume ratio [8].

The semiconductor used in the PEC process must meet certain requirements:

1. The band gap must be greater than 1.23 eV to overcome kinetic barriers.
2. The conduction band must be positioned above the hydrogen conversion potential (H^+/H_2).
3. The valence band must lie below the oxygen conversion potential (O_2/H_2O).

Additionally, stability in the PEC process and resistance to photo dissolution in aqueous environments must be ensured [8].

4.1.6. Application of Metallic Nanoparticles

Metallic nanoparticles, such as silver, gold, or platinum nanoparticles, can enhance electrical conductivity by providing a better pathway for electron conduction. Incorporating these particles into materials such as silicon or metal oxides can lead to a significant increase in conductivity, allowing the electrochemical process to occur more efficiently [24]. Another significant effect that occurs when using metal nanoparticles with dimensions smaller than the wavelength of the incident light is the emergence of a strong alternating electromagnetic field at the boundary between these particles and the dielectric or semiconductor medium [25, 26], the plasmon effect.

4.2. Plasmon-Assisted Photoelectrochemical Water Splitting

New developments include plasmon-assisted photoelectrochemical water splitting to improve the efficiency of water splitting processes. The use of metallic nanoparticles like silver and gold allows for enhanced light absorption and reduced charge carrier recombination [12]. The use of metallic nanoparticles creates plasmonic effects that enhance light absorption and improve the efficiency of the process [3]. Another study focused on improving photoelectrochemical water splitting using gold plasmonic nanoparticles. These nanoparticles improve light absorption and the efficiency of solar energy conversion to hydrogen [11].

4.2.1. Plasmonic Phenomenon

Plasmons are collective oscillations of free electrons in metals in response to a time-varying electric field, such as the light field hitting them. When light with the wavelength larger than dimensions of the metal particles hits a metallic surface, it can excite the plasmons, creating a surface plasmon resonance (SPR) or localized surface plasmon resonance (LSPR). These effects play a crucial role in enhancing the kinetics of chemical reactions and lowering the energy demands for electrolysis [24].

Surface Plasmon Resonance (SPR): This involves oscillations of free electrons on a metallic surface, creating a strong response to light hitting them at a certain frequency. This phenomenon is called Surface Plasmon Resonance (SPR).

Localized Surface Plasmon Resonance (LSPR): This phenomenon occurs when the dimensions of the metallic nanoparticles are smaller than the incident light wavelength, causing local oscillations of the free electrons at the metal-dielectric interface. LSPR depends on the size, shape, and dielectric properties of the surrounding medium [11].

Wide-bandgap semiconductors are materials that have a large energy gap between the valence band and the conduction band. These materials exhibit better chemical and physical stability under harsh conditions, making them ideal for applications such as photoelectrochemistry and fuel cells. Examples of wide-bandgap semiconductors include TiO_2, In_2O_3, ZnO, and $SrTiO_3$.

When plasmons are excited on a metallic surface, they can significantly influence the photoelectrochemical current in wide-bandgap semiconductors [24]. Plasma-related processes can lead to improvements in the properties of semiconductors. For instance, exposure to plasma can alter the electronic structure of materials, resulting in enhanced conductivity and electrical flow capabilities of the semiconductors. These effects arise from the interaction between free electrons and atoms within the semiconductor [8, 27].

4.2.2. Mechanisms of Action and Impact on Current

During the photoelectrochemical water splitting, plasmons can enhance the solar energy conversion process into hydrogen in several ways:

Light Absorption and Scattering: Plasmonic metallic nanoparticles can absorb and scatter light efficiently, increasing light utilization by semiconductors.

Hot Electron Injection: At the metal-semiconductor interface, plasmons can generate hot electrons that can cross the boundary into the semiconductor and enhance the photoelectrochemical current and improve the efficiency of light-to-chemical energy conversion. This process improves the photoelectrochemical current by adding electrons with higher energy levels than regular conductors. The use of hot electrons in wide-bandgap semiconductors like TiO_2 and ZnO significantly enhances the conversion of solar energy into chemical energy [14, 18].

Plasmon-Induced Resonance Energy Transfer (PIRET): This mechanism allows energy transfer from plasmons to the semiconductor in the form of near-surface resonance, improving light absorption and conversion efficiency. This mechanism is especially suitable for wide-bandgap semiconductors, as they can efficiently utilize the transferred light [11]. Through PIRET, energy from the plasmon is transferred non-radiatively to the semiconductor, enabling the creation of additional charge carriers in response to light [3].

4.2.3. Advantages of Using Plasmonic Layers

Enhanced Light Absorption Efficiency: Increasing the active surface area and improving light absorption using metallic nanoparticles, leading to increased photoelectrochemical process efficiency [3, 11].

Improved Charge Carrier Separation: Metallic nanoparticles can act as antennas focusing light and transferring energy to the semiconductor, reducing electron-hole recombination rates and improving water-splitting efficiency [3].

Low Charge Carrier Recombination: The presence of plasmonic particles on the semiconductor surface can reduce the recombination rate of electrons and holes, leading to increased photoelectrochemical efficiency and overall performance improvement in the fuel cell.

In studies on water splitting and plasmon utilization, several effective semiconductor materials have been found, such as TiO_2, ZnO, $SrTiO_3$, and $BiVO_4$. Plasmonic particles integrated into these semiconductors can enhance light absorption and the overall efficiency of the photoelectrochemical splitting process [11].

4.2.4. Plasmonic Effect and its Impact on Current in a Semiconductor

In one study, the process of hot electron injection from gold (Au) nanoparticles to TiO_2 showed a significant improvement in photoelectrochemical current density. The plasmonic phenomenon allows TiO_2, a wide-bandgap semiconductor, to better utilize the visible spectrum of light, primarily due to the plasmonic interaction between the gold nanoparticles and the semiconductor [11].

ZnO with Silver Nanoparticles: Combining silver nanoparticles with ZnO allows for improved light absorption and energy transfer, leading to increased photoelectrochemical current and improved performance in the fuel cell. The plasmonic particles enhance visible light utilization and charge carrier separation [11].

Gold Nanoparticles on p-GaN: Creating a Schottky junction with gold nanoparticles on p-GaN showed that hot holes generated from plasmon decay could be used for efficient water oxidation reactions, improving cathode performance in water splitting [3, 6].

4.2.5. Impact of Plasmons on Current in a Semiconductor Photoanode

CdS–Au/MoS_2: In this system, gold nanoparticles are integrated into the CdS semiconductor with MoS_2, and the system shows a significant improvement in photoelectrochemical current due to hot electron injection from gold to the semiconductor [11].

Ag/$BiVO_4$: Combining silver nanoparticles with $BiVO_4$ improves visible light absorption, charge carrier separation, and transport, leading to improved photoelectrochemical splitting performance [20].

TiO_2/Bi nanoparticles/Sb_2S_3: Here it was shown that the efficiency of photocurrent generation and photoelectrochemical hydrogen evolution by a heterojunction semiconductor anode increases by an order of magnitude when it is incorporating plasmonic bismuth nanoparticles, which are common on Earth [28].

Therefore, the process of water splitting by improving light absorption and charge carrier separation is achieved using metallic nanoparticles in various configurations like LSPR. These nanoparticles allow optimal utilization of sunlight to produce clean and efficient hydrogen. Plasmonic phenomena significantly contribute to current in a semiconductor in a fuel cell, enhancing the efficiency of solar energy conversion to chemical energy. Mechanisms such as hot electron injection and plasmon-induced resonance energy transfer improve light absorption, charge carrier separation, and transport, leading to improved overall fuel cell performance. Metallic nanoparticles like gold and silver, in various configurations, maximize light absorption and charge carrier separation, leading to increased photoelectrochemical current and improved fuel cell performance.

Various study focuses on improving the efficiency of dye-sensitized solar cells (DSSC) using a TiO_2-based anode with silver nanoparticles. The efficiency improvement is due to the plasmonic effect of the silver nanoparticles, which enhances light absorption [11]. The synthesis of TiO_2/Cu_2O core/shell nanowire arrays using a chemical bath deposition method offers improved photoelectrochemical water splitting for hydrogen production and photostability [17]. The use of gold nanoparticles combined with zinc oxide (ZnO) nanorods improves the efficiency of photoelectrochemical water splitting [29, 30]. The optical properties of plasmonic nanoparticles enhance charge transfer and reduce recombination, thereby increasing the photoelectrochemical current density [31]. Overall, the use of metal nanoparticles exhibiting plasmonic effect plays an important role in the development of more efficient photoanodes. Researchers have studied how technological process conditions affect the growth of the plasmonic layer, such properties of these films as the size and shape of plasmonic particles, how the interface and roughness of the substrate, as well as the film thickness affect the stability and efficient operation of the layers. In this regard, the role of metals such as Ag and Au remains important, as their well-known properties make them suitable for proof-of-concept studies and encourage the search for new materials with plasmonic properties [11].

4.3. Hydrogen Production in the PEC Process Using Perovskites

Perovskites are materials with a unique crystalline structure, in general ABX_3, when A represents an organic or inorganic cation (Li+, Cs+, or methylammonium CH3NH3+ etc.), B is a divalent metal ion (Pb2+, Cu2+, Sn2+, etc.) and X is a halide (Cl-, Br-, or I-). Approximately 90% of metal ions can combine and form a perovskite structure [32]. These materials have advanced optical and electronic properties, making them a promising alternative to traditional semiconductors due to their high efficiency in light absorption. The use of photoelectrochemical cells based on metal halide perovskites and oxide based perovskites [33] attracts attention of many researchers due to unique properties of perovskites.

A photoelectrochemical cell can have only an n-type photoanode or only a p-type photocathode, or a tandem structure containing both a photoactive anode and a cathode [32]. Inside a photoelectrochemical cell, perovskite electrodes absorb sunlight, resulting in the formation of electron-hole pairs. The electrons move to the negative electrode where they participate in the reduction of water to produce hydrogen, while the holes remain at the positive electrode, promoting the oxidation of water to release oxygen. The perovskite structure increases the rate of generation of electrons and holes, thereby increasing the overall efficiency of the water splitting process. Unfortunately, perovskite layers cannot function directly as a photoanode or photocathode. These materials require electron and hole transport layers, such as ZnO and NiO, respectively, to extract charge carriers. This leads to more complex manufacturing processes for the efficient fabrication of water splitting cells. In addition, perovskite layers containing organic components suffer from a short lifetime, which is a pressing issue at present.

4.4. Enhancing Solar Energy Utilization with Multi-Junction Photovoltaic Cells

The efficiency of a photovoltaic cell can be significantly increased by combining several semiconductor junctions with different band gaps due to the expansion of the absorption of sunlight. The arrangement of several individual junctions in order of decreasing band gaps from top to bottom ensures the absorption of a larger spectrum and leads to an increase in the efficiency of the cell. It has been theoretically proven that a sequential combination of 36 junctions can achieve an efficiency of 72% in the ideal case [34, 35].

The essence of this technology is not only to enhance efficiency but also to reduce costs, making it more accessible for use and installation in the industry. In each layer of a multi-junction cell, the energy gap is tailored to a specific type of radiation, so the top layer can absorb shorter wavelengths (such as UV), while the lower layers work with longer wavelengths.

The use of a multi-junction semiconductor structure is a very effective way to increase the efficiency of solar cells. Such systems achieve very high efficiency. For example, a three-junction GaInP/GaInAs/Ge cell showed an efficiency of 39% under irradiation of 236 suns (23.6 W/cm2) [6]. Unfortunately, these systems are only laboratory samples. The main problem in the manufacture of multi-junction cells is their complexity, in the coordination of adjacent layers, in the manufacture of all included thin films with a very precise thickness, which together leads to a high final cost.

4.5. Use of CdS Nanowires in Photocatalytic Processes

An example of a promising approach in photocatalytic processes is the use of CdS (cadmium sulfide) nanowires as a catalyst. When a photocatalytic cell structured as a core-shell of CdS/TiN is exposed to light, it generates electron-hole pairs. The electrons move to the cathode, while the holes react with water at the anode to produce hydrogen and oxygen, effectively splitting water molecules using solar energy.

Although this method is a potential sustainable alternative to fossil fuels, its efficiency is limited by high recombination rates of electrons and holes, as well as stability concerns. Incorporating a TiN (titanium nitride) layer into the nanowires can reduce recombination and improve material stability, thereby enhancing hydrogen production.

To assess the efficiency of hydrogen production, various tests have been conducted, including gas chromatography (CG) measurements of hydrogen deposition during the photocatalytic process. Stability tests were performed under continuous solar light exposure, and quantum efficiency was measured under simulated sunlight conditions. Additionally, simulations analyzed the impact of generated plasmons on the electric field, contributing to increased charge carrier concentration and improved hydrogen production efficiency [36, 37].

5. Summary

In this article we reviewed current technologies and research applied in converting solar energy to hydrogen production, focusing on sustainable and high efficiency methods such as photoelectrochemical water splitting and photovoltaic electrolysis destined for application in fuel cells. Hydrogen, with its high energy density and non-polluting properties, is positioned as the "fuel of the future", which can successfully compete with other renewable energy sources such as solar cells for example. Key technological advances, such as quantum dots, multi-junction cells and plasmon-enhanced reactions, increase hydrogen production by improving light absorption, charge separation, and additional electrons generation. Challenges such as material costs, stability and energy storage are highlighted, along with potential solutions, including the use of nanostructures and new materials that can exhibit new properties and synergy of different materials with new phenomena to increase the efficiency of hydrogen fuel cells. The following tables provide a general comparison of various technologies, their advantages, and disadvantages, aimed at improving the use of green energy.

Table 1. Comparison of the various technologies discussed in this article for the production of hydrogen fuel cell.

Technology	Advantages	Disadvantages
Photoelectrochemical Process	Direct hydrogen production from solar energy and water. Zero greenhouse gas emissions. Relatively low operational costs	Relatively low efficiency in laboratories (~12.4%). Requires stable materials in aqueous environments. Material stability issues under light.
Photovoltaic Electrolysis	High efficiency (up to 30%). Allows large-scale production. Established and widely used technology.	Requires expensive electrolysis systems. Dependency on costly metals (platinum). Durability and long-term reliability issues with equipment.
Plasmons – Metallic Nanoparticles	Significant improvement in light absorption. Reduction in electron-hole recombination rate. Enables utilization of a wide range of light wavelengths.	Requires advanced technologies for stable particle production. Dependency on costly materials like gold and silver.
Multi-Junction PV Cells	Broad absorption spectrum with multiple layers. Theoretical efficiency potential up to 72%. Improves energy conversion efficiency.	Very high production costs. Complex manufacturing processes requiring advanced materials.
Quantum Processes – Quantum Dots	Generates multiple charge pairs per photon. Enhances overall efficiency by producing more electrons.	Complex and expensive materials to produce. Requires improvements in stability under light and chemical reactions.
Integrated PV-PEC Systems	Combines photovoltaic and electrolysis systems. Provides sustainable hydrogen production with high efficiency.	Voltage matching between solar cells and electrolysis requires optimization. Efficiency gaps between solar cells and electrolysis systems.

Table 2. Advantages and disadvantages of green energy application.

Category	Points
General Advantages of Green Energy	Reduction in carbon and greenhouse gas emissions. Decreased dependence on fossil fuels. Utilization of inexhaustible energy sources (e.g., solar and wind). Creation of jobs in green energy industries. Reduction in air pollution and improvement in public health.
General Disadvantages of Green Energy	Dependency on weather conditions and geographical location. High initial installation costs. Energy storage challenges during low sunlight or wind conditions. Requires upgrading existing infrastructure (e.g., power grids).

6. Conclusions

Hydrogen is the most sustainable and widespread energy source, along with solar energy, to replace fossil fuels and mitigate their impact on the environment. Therefore, methods for producing hydrogen and using it to produce energy for human needs are becoming very important. In this review, we have considered photoelectrochemical and photovoltaic methods for producing hydrogen by splitting water using solar energy. In our opinion, the combination of solar water splitting cells with hydrogen fuel cells can help solve the problem of energy shortage.

Research and development in solar-based hydrogen production technologies show great promise in addressing global energy and environmental challenges. Methods such as PEC and PV electrolysis have achieved significant efficiency, but still face challenges in cost, material durability, and scalability.

Recently, more and more researchers have turned their attention to nanotechnology, in particular multilayer thin-film systems, plasmonic materials, new semiconductor materials and heterojunction compounds. These studies are devoted to clarifying the physical mechanisms of water splitting processes using new methods based on nanotechnology. The right methods should apply several different approaches together. Thus, the combination of new semiconductor structures together with the plasmonic effect in the design of photoelectrodes will exhibit synergistic effects, allowing the production of a large number of charge carriers under the same irradiation.

Advances in nanotechnology, including plasmonic-enhanced materials and multi-junction photovoltaics, offer pathways to higher efficiency and lower costs. In addition, a global transition to solar and hydrogen energy could significantly reduce carbon emissions, reduce dependence on fossil fuels, and pave the way for a sustainable energy future.

Abbreviations

PEC	Photoelectrochemical Process
PEM	Polymer Membrane Electrolysis
THE	High Temperature Electrolysis
STH	Solar Energy Conversion to Hydrogen
VMPP	Maximum Power Point Voltage
SPR	Surface Plasmon Resonance
LSPR	Localized Surface Plasmon Resonance
DSSC	Dye-sensitized Solar Cells
PV	Photovoltaic

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Author Contributions

Alexander Axelevitch: Conceptualization, Writing – review & editing, Supervision.

Sivan Marianna Tal-Mor: Conceptualization, Writing – original draft

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Data Availability Statement

Not applicable.

Conflicts of Interest

The authors declare no conflicts of interest.

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Biography

Alexander Axelevitch has completed his PhD at 2002 in physical electronics from Tel-Aviv University, Israel. Since 1995, he has been with Holon Institute of Technology (HIT). He is currently leading the Nanotechnology and Microelectronics Branch of the Engineering Faculty, the Laboratory of Microelectronics and Thin Films and works as the Senior Lecturer in faculty of Engineering in HIT. His main research interest includes thin films deposition methods, semiconductor thin films, transition metal oxides, alternative energy sources, solar cells, plasmonic effects. Dr. Axelevitch has 8 patents, 2 published books, more 70 referred articles and more 150 papers presented on scientific meetings. Also Dr. Axelevitch is the recognized Expert Evaluator for evaluations of projects submitted to the Program Horizon 2020.

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Research Field

Alexander Axelevitch: thin films deposition methods, semiconductor thin films, transition metal oxides, alternative energy sources, solar cells, plasmonic effects.

Sivan Marianna Tal-Mor: green energy, hydrogen fuel cells, water splitting.